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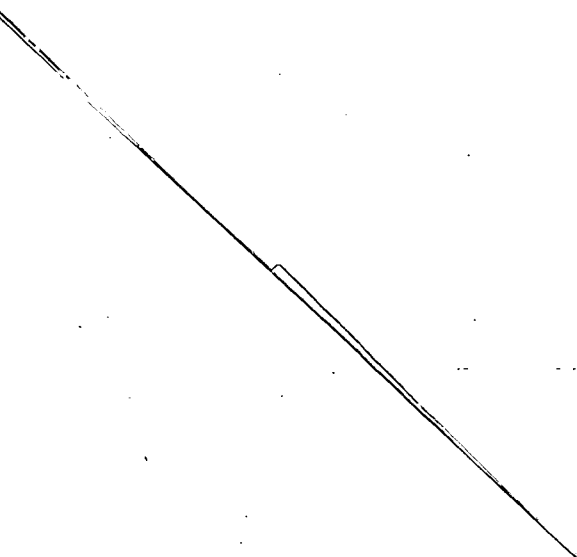
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of the

SYMPOSIUM ON ZEOLITES

SZEGED, HUNGARY

September 11—14, 1978

APPLICATION OF ZEOLITES
IN HETEROGENEOUS CATALYSIS
AND RELATED FIELDS

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REACTIONS OF ISOMERIZATION, HYDROGENATION AND DEHYDROGENATION OVER ZEOLITES CONTAINING NO TRANSITION METALS

By

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Hydrocarbon transformations such as isomerization, hydrogenation and dehydrogenation usually take place over the catalysts which include one of the VIII group metal. However, it was found recently that these reactions can be carried out over zeolites without transition elements. This paper describes new results of investigations of catalytic properties on various zeolites obtained in our laboratory. These include the reactions of saturated hydrocarbons, isomerization of unsaturated compounds, hydrogenation and dehydrogenation of cyclic hydrocarbons. The mechanisms of these reactions over zeolites without transition metals are discussed.

Introduction

Reactions of isomerization, hydrogenation and dehydrogenation of hydrocarbons play an important role in petroleum processing. As a rule, these reactions proceed over catalysts involving metals of group VIII on various supports, such as oxides, amorphous aluminosilicates and zeolites. It has been known for long that metals of group VIII can catalyze reactions of hydrogenation — dehydrogenation. The role of these metals in bifunctional catalysts for isomerization of saturated hydrocarbons is that of dehydrogenation of alkane to olefine which undergoes skeletal isomerization of the acidic centres of the catalyst followed by hydrogenation of the isomeric olefine into the corresponding isoparaffine.

Intensive studies of the catalytic properties of zeolites have demonstrated that most reactions effected earlier over catalysts involving metals of group VIII as an important component can proceed over zeolites without these metals. The studies by BENESI [1], VOORHIES [6, 7], KOUWENHOEVEN [8, 9] and in this laboratory [2—5] have demonstrated that *n*-pentane, cyclohexane, *n*-hexane isomerization proceeds at a high rate over the hydrogen form of mordenite. Introduction of palladium and platinum into this catalyst does not affect its activity in alkane isomerization. And this is an essential difference between H-mordenite, and bifunctional and metal-faujasite catalysts.

The catalytic activity of zeolites with no transition metals has been found by studying benzene [10] and ethylene [11] hydrogenation in our laboratory.

The catalytic studies with zeolites have developed intensively, and the catalytic properties of zeolites of type A, L, X, Y, erionite, mordenite, chabazite and omega

involving cations of group I, II, III in hydrogenation of aromatic hydrocarbons (benzene, toluene, xylols) [2, 4, 5, 12, 14], amylenes [12, 14—19], acetone [20, 21], aldehydes [22], alkylfuranes [23], propylene [24—27], 1,2-epoxyhexane [28] have been extensively studied.

Other reactions accelerated by zeolites without transition metals are dehydrogenation of hydrocarbons [29—31], isopropyl alcohol into acetone [32], cumene into α -methylstyrene [33], hydrocarbon oxidation [34—37]. Recently we have demonstrated high activity and selectivity of Na-forms of various zeolites in hydrocarbon oxidative dehydrogenation [38, 39]. Thus, zeolites without metals of group VIII can catalyze both the reactions effected earlier over bifunctional catalysts (alkane isomerization) and those of a redox type (hydrogenation, oxidation, oxidative dehydrogenation). The redox properties of zeolite catalysts as well as their activity in acid-base reactions are of great importance and should be thoroughly studied.

The objective of this paper is to discuss the data obtained in the author's laboratory by studying the catalytic properties of various zeolites containing no transition metals in the reactions of saturated and unsaturated hydrocarbons and of a number of oxygen containing compounds. Special attention is given to the reactions of skeletal isomerization of saturated hydrocarbons, hydrogenation of aromatic, olefinic and dienic hydrocarbons, a carbonyl group of aldehyde and ketones, furane compounds, dehydrogenation of cyclane, cyclene and cyclo diene hydrocarbons.

Reactions of isomerization, hydrogenation and dehydrogenation over cationic forms of zeolites

1. *n*-Pentane and cyclohexane isomerization

Isomerization of saturated hydrocarbons over decationized and cationic forms of faujasites (X, Y) without metals proceeds at a much lower rate than that over bifunctional metal containing catalysts. The studies made by RABO, in this laboratory, and lately by many other workers have demonstrated that for example, with CaY a 15.5% yield of *isohexanes* is obtained at 420 °C, and with CaY involving 0.5% of Pt or Pd the yield of *isohexane* is nearly equilibrium (70—74%) at 360 °C [5, 40, 41].

Specific catalytic properties have been shown by decationized and cationic forms of synthetic mordenite [2—5]. It can be seen from Table I that the hydrogen form of mordenite is an active catalyst in isomerization of saturated hydrocarbons: at 280 °C

Table I

The activity of mordenite catalysts in *n*-pentane and cyclohexane isomerization

$t = 280\text{ }^{\circ}\text{C}$; $P = 30\text{ atm}$; $P_{\text{H}_2}/P_{\text{CH}} = 3.2$; $V_{\text{CH}} = 1\text{ h}^{-1}$

Catalyst	Yield of isopentane, %	Yield of methylcyclopentane, %
HM	46.6	28.5
0.5% Pd/HM	45.4	44.3

and a pressure of 30 atm the yields of *isopentane* and *methylcyclopentane* amount to 46.6 and 28.5%, respectively.

An interesting specific feature of this zeolite is that in *n*-pentane isomerization, metal is not an important component of the catalyst as is the case for the bifunctional and metal — containing catalysts of the faujasite type [5, 40].

In *n*-pentane isomerization the activity of HM and Pd/HM is the same whereas in the case of cyclohexane Pd/HM is more active than H-mordenite. But the activity of H-mordenite is higher in isomerization of saturated hydrocarbons than that of the well-known bifunctional catalysts, including metal-zeolites.

The activity of mordenite depends on the degree of its decationization, and the extent of isomerization of cyclohexane, for example, is proportional to the degree of Na^+ exchange for H^+ (Fig. 1). This dependence shows uniformity of the active centres of the catalyst.

The catalytic properties of H-mordenite are greatly different from those of its cationic forms. Table II shows that the activity of di- and tri-valent mordenite cationic forms is inferior to that of H-mordenite. For instance, over Al-mordenite at 300 °C the yield of methylcyclopentane is twice as small as that over H-mordenite. The activity of Cd- and Zn-zeolites is higher than that of Mg- and Ca-modifications

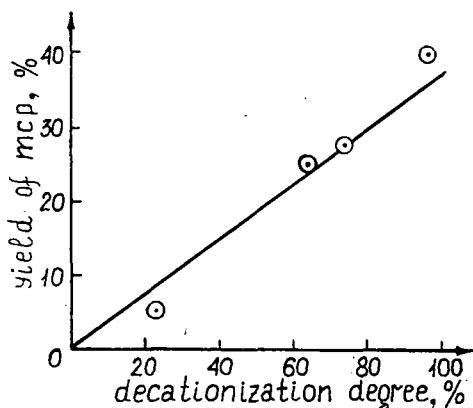


Figure 1. Isomerization rate of cyclohexane vs. mordenite decationization degree at $t = 300^\circ\text{C}$, $P = 30\text{ atm}$, $V = 1\text{ h}^{-1}$

Table II

Cyclohexane isomerization on the cationic forms of mordenite

$P = 30\text{ atm}$; $P_{\text{H}_2}/P_{\text{C}_6\text{H}_{12}} = 3.2$; $V_{\text{C}_6\text{H}_{12}} = 1\text{ h}^{-1}$

Catalyst	HM	LiM NaM KM	MgM	CaM	ZnM	CdM	AlM	Pd/CaM	
$t^\circ\text{C}$	300	300—450	360	420	374	374	300	300	350
Yield of Mcp*	39.2	no reaction	9.9	6.2	27.1	34.6	18.7	0.0	28.0

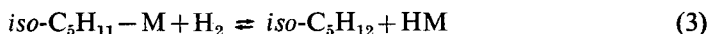
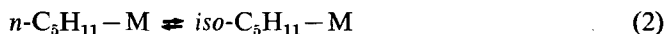
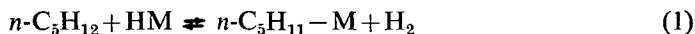
* Mcp — methylcyclopentane.

of mordenite, whereas over Li-, Na- and K-forms the reactions does not take place at all. The fact that univalent cationic forms of mordenite as well as faujasite do not show any activity can be accounted for by the absence of proton acidity in zeolites. On the other hand, the activities of decationized and cationic forms of mordenite are different, whereas for zeolites of type Y this is not the case.

Absence of catalytic activity in polyvalent cationic forms of mordenite in the reaction of isomerization may be explained by very low acidity of the samples. Therefore introduction of Pd, for example, into Ca-mordenite does not produce active isomerization catalysts. At 300 °C they are not active, and at 350 °C the yield of methylcyclopentane is 28%, *i. e.* much lower than that of Pd/CaY (60%), for example.

The ability of H-mordenite to effect isomerization of saturated hydrocarbons in the absence of metals may indicate to a specific mechanism of the reactions with this catalyst. The kinetic studies of *n*-pentane isomerization over H-mordenite provide evidence to support this supposition [3, 5]. It has been found that for the reaction to proceed, the presence of hydrogen is necessary, and an increase in the partial H_2 pressure decreases the rate of isomerization as is the case with bifunctional catalysts. Since H-mordenite is not a bifunctional catalyst (it does not contain metals of group VIII) the isomerization mechanism involving the stage of saturated hydrocarbon dehydrogenation into olefine (cycloolefine) should be excluded.

To account for the kinetic regularities observed it may be assumed that isomerization over this catalyst would proceed according to the following scheme:



where HM is H-form of mordenite; $n-C_5H_{11} - M$, $iso-C_5H_{11} - M$ are carbonium ions bound to the active centres of the catalyst.

Assuming that carbonium ion isomerization is slow (stage 2) whereas the other intermediate stages are fast and in equilibrium one can obtain the following kinetic equation:

$$r = \frac{K_2 a_1 \frac{P_{n-C_5}}{P_{H_2}} - \frac{K_{-2}}{a_3} \frac{P_{i-C_5}}{P_{H_2}}}{1 + a_1 \frac{P_{n-C_5}}{P_{H_2}} + \frac{1}{a_3} \frac{P_{i-C_5}}{P_{H_2}}}$$

where r is the reaction rate, K is the rate constant of the corresponding step, a is the equilibrium constant of the corresponding step; P is the partial pressure of the reagents.

According to this equation the rate of the direct reaction at a constant temperature depends on the ratios of *n*-pentane and hydrogen partial pressures only (P_{n-C_5}/P_{H_2}). At low P_{n-C_5}/P_{H_2} , with $a_1 P_{n-C_5}/P_{H_2} \ll 1$, $r = K_2 a_1 \frac{P_{n-C_5}}{P_{H_2}}$, whereas at high P_{n-C_5}/P_{H_2} , with $a_1 P_{n-C_5}/P_{H_2} \gg 1$, $r = K$.

Fig. 2 presents the experimental data in terms of $r \sim \frac{P_{n-C_5}}{P_{H_2}}$ which shows that they are in agreement with the kinetic equation for the direct reaction. It should be noted that at low partial hydrogen pressure the operation of the catalyst is unstable and therefore the experimental dots on the right-hand branch of the curves in Fig. 2 have been obtained taking into account the degree of catalyst poisoning [42]. From the temperature dependence of the equilibrium constant of the first stage of the pro-

cess the thermal effect and entropy of *n*-alkyl cation formation on the catalyst surface was calculated, which were found to be equal to 11 kcal/mol and 20 cal/mol. degr., respectively. Independent approximate estimation of these values from the energies of bond cleavage and reagent entropies gives 16 kcal/mol and $12 \frac{\text{kcal}}{\text{mol. degr.}}$

[42]. The agreement may be considered satisfactory, with insufficiently high accuracy of the experiment and approximate calculations. Thus, according to the mechanism suggested hydrocarbon isomerization proceeds via a carbonium ion resulting from splitting off a hydride-ion from a molecule of the initial hydrocarbon rather than by addition a proton of the catalyst to the intermediate olefine.

The ability of H-mordenite to split off a hydride ion is likely to be due to the presence of strong acidic centres [43], whereas the low activity of di-valent forms may be due to the absence of the Brönsted acidity (according to the i. r.-spectroscopic studies of the adsorbed pyridine [44]). The same conclusion can be made from the results of studying the hydrogen content in mordenites by isotopic exchange with deuterium performed in this laboratory. For example, the protium concentration in 0.8 CaNa-mordenite was found to be an order lower than that in H-mordenite [45]. As to a relatively high isomerization activity of Zn- and Cd-forms of mordenite it should be taken into consideration that these cations can be reduced to metals with simultaneous formation of H-form.

The acidic properties of Al-mordenite have not been studied yet. One may suggest, however, that it is a cation-decationated form of zeolite since in the process of ion-exchange together with substitution of Al^{3+} for Na^+ the exchange of Na^+ for H^+ is also possible (pH of the solution is 2.6). Besides, Al^{3+} cations are capable of decomposing water molecules to generate protons to a greater extent than divalent metal cations. Therefore the activity of AlM catalyst is only twice as low as that of H-mordenite.

To conclude, the chemical composition and structure of mordenite seem to be responsible for unusually high activity of its H-form in hydrocarbon isomerization. The acidity of this catalyst appears to be so high that metals of group VIII are not necessary in alkane isomerization, which distinguishes mordenite from other zeolites.

2. Hydrogenation of unsaturated compounds

High catalytic activity of zeolites in hydrogenation of various unsaturated compounds is illustrated in Table III. These data show that synthetic zeolites containing no ions or atoms of transition elements are active in hydrogenation of various unsaturated compounds [10, 12, 14]. It should be noted that hydrogenation of aroma-

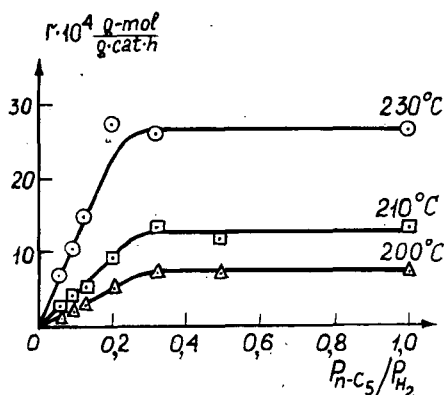


Figure 2. Reaction rate vs. ratio of *n*-pentane and hydrogen partial pressure (P_{n-C_5}/P_{H_2}) plots for *n*-pentane isomerization over HM



Table III
Hydrogenation reactions over zeolites without transition metals

Unsaturated compound (A)	Catalyst	Reaction conditions				Conversion, %
		t , °C	P , atm	V_A , h ⁻¹	$H_2:A$	
C_5H_{10}	NaY	300	30	1.0	3	96.5
$CH_3-CO-CH_3$	NaM	300	30	1.0	3	51.5
CH_3-CHO	Na, K—Ch	300	30	1.0	3	40.0
silvane	NaA	300	60	0.5	4	44.0
toluene	NaΩ	270	30	1.0	5	95.5

tic hydrocarbons and olefines proceeds selectively without formation of side products but in the case of acetone, aldehydes and silvan one can observe secondary reactions, dehydration of *isopropyl* alcohol and tetrahydrosilvan, and also hydrogenolysis of the latter. Selectivity of primary hydrogenation product formation varies from 20 to 100% with the catalyst and condition of the process.

In hydrocarbon hydrogenation zeolite catalysts are more active than sulphide and oxide catalysts (WS_2 , MoS_2 , MoO_3 , NiS and their combinations on supports). For instance, benzene hydrogenation over zeolites proceeds at 200–250 °C and a pressure of 30 atm whereas with the former at 300–450 °C and 50–250 atm [46]. Metals of group VIII (Pt, Pd, Ni) on Al_2O_3 , $Al_2O_3 \cdot SiO_2$ and other supports, *i. e.* the most active hydrogenation catalysts are superior to cationic forms of zeolites in their activity since the latter do not effect hydrogenation of aromatic hydrocarbons at atmospheric pressure. In spite of zeolite catalysts being of lower activity than metal containing catalysts it should be stressed, however, that practically important processes of hydrogenation, that of benzene, for example, are carried out at elevated hydrogen pressure even over metal containing catalysts to attain a high degree of transformation [47, 48]. Therefore, zeolites without transition metals may be promising in hydrogenation of unsaturated compounds under hydrogen pressure. The comparison of the zeolites studied and other hydrogenation catalysts containing metals of group VIII, such as chromium, zinc, metal oxides [49, 50] shows that they are comparable in conversion and selectivity of oxygen containing compounds although over metal containing contacts reactions proceed at lower temperatures.

The catalytic activity of zeolites without transition metals in hydrogenation of aromatic hydrocarbons, olefines, and oxygen containing compounds depends on their structure and composition [12, 14]. The concentration of cations in zeolites of various structure contributes most significantly to their hydrogenating activity. For instance, the rate of 2-methylbutene-2, benzene and acetone hydrogenation decreases with zeolite decationization and increases with introduction of sodium ions, exchange into their ammonium form (Fig. 3).

However, there are differences due to the structure of mordenite and faujasite (Y). Linear dependence is characteristic of Na-mordenite whereas for zeolite NaY one can observe hysteresis of the hydrogenating activity upon decationation-recationation (Fig. 3). This indicates that upon decationation-recationation Na^+ cations are first to be removed from the accessible places (occupy the accessible places) in the zeolite lattice, for example, in large cavities.

The hydrogenating activity of zeolites depends not only on the cation concentration but also on their nature. Consideration should be given to the dependence of zeolite activity on the value of the electrostatic potential of a cation e/r^2 . The validity of this dependence can be supported by the data obtained from the studies of cations in zeolites by X-ray photoelectron spectroscopy [51]. They indicate to a predominant

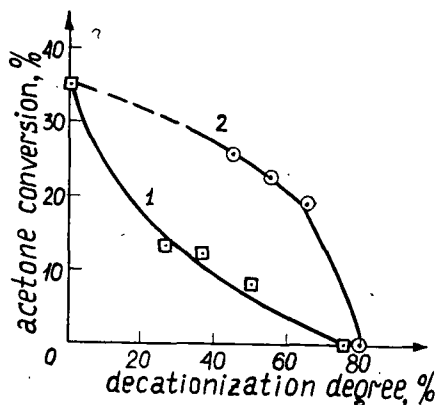


Figure 3. Activity of zeolite NaY vs. Na^+ concentration plots for acetone hydrogenation.
1 — decationization NaY
2 — decationization NH_4Y

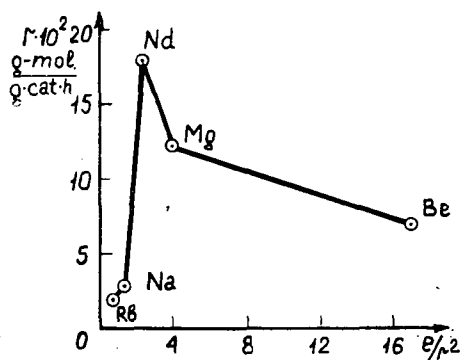


Figure 4. Activity of cationic forms of zeolite Y vs. value of cation electrostatic potential (e/r^2) plots for 2-methylbutene-2 hydrogenation

ionic character of the cation bond with the lattice of zeolites. It has been shown that in hydrogenation of 2-methylbutene-2 and acetone the dependence of the activity on the e/r^2 value passes through a maximum indicating optimal energy of the reagent molecular bonds with the active centres of the catalyst (Fig. 4).

Thus, the data on the dependence of the catalytic activity of zeolites in hydrogenation reactions on the concentration and nature of the exchange cations allow a conclusion that either zeolite cations themselves are the active centres of the catalysts or are involved with them.

In the studies of the activity of zeolite Y, with various degrees of decationization, in hydrogenation of 2-methylbutene-2 an attempt has been made to estimate the number of the Na^+ cations involved in the active centre of the zeolite [52]. A formula was derived to calculate the probable distribution of cations as a singlet or doublet *etc.* in zeolite large cavities. This formula is

$$P_k = \frac{m!}{m^K(m-K)!} \cdot \frac{v^K}{K!} \cdot e^{-v}$$

where P_k is the probability of multiplet formation of K -order, m is the number of localizing cation sites in zeolite large cavities, K is the multiplet order: v is the average number of cations in the large cavity of a zeolite sample (measured from the number of Na^+ cations going into solution upon treatment of the zeolite sample with an excess amount of NH_4Cl solution).

The formula allowed calculation of the number of large cavities containing a certain amount of Na^+ cations in zeolite Y samples with various degrees of decationization, that is, the number of cationic multiplets of different order is calculated followed by estimation of the specific activity of the multiplets. The results of these calculations are presented in Table IV.

Table IV

Specific activity of different multiplets (molecules/active site $\cdot \text{sec} \cdot 10^2$) in 2-methylbutene-2 hydrogenation over NaY with various decationization degrees at 200 °C, $P = 30$ atm, $\text{H}_2:\text{C}_5\text{H}_{10} = 3$

Multiplet order K	Decationization degree, %				Standard deviation of multiplet specific activity, %
	0	38	55	75	
1	0.71	0.93	0.68	0.47	23.8
2	1.88	2.51	1.89	1.53	18.0
3	3.95	6.67	5.43	6.67	39.4
4	3.95	28.90	26.30	50.00	59.8
5	3.95	328.0	342.0	1000.0	86.5
hydrogenation rate $\text{g}\cdot\text{mol}/\text{g}\cdot\text{cat}\cdot\text{h}\cdot 10^2$	9.0	5.9	4.1	1.8	

As seen from the table it is only in the case of the multiplets of the first and second order that the specific activity remains constant within the experimental error.

Hence, the active center involves one or two Na^+ cations.

A considerable contribution into the activity of hydrogenation zeolite catalysts is made by crystalline aluminosilicate lattice which is responsible for the concentration, distribution and accessibility of the cations for the reacting molecules.

Fig. 5 shows that the rate of 2-methylbutene-2 hydrogenation passes through a maximum with an increase of silica and alumina ratio in Na-zeolites. The studies of 2-methylbutene-2 molecule thermodesorption from various zeolites have demonstrated that a similar dependence is observed also for The coefficient of the initial hydrocarbon diffusion in the intracrystalline pores of zeolites [53]. The catalyst efficiency factor proved to be close to a unity in the case of zeolite Y only. In narrow porous zeolites of type A, chabazite, erionite, mordenite the efficiency factor is much lower than a unity, which indicates to inner diffusion area of the reaction and thereby the dependence of the hydrogenation rate on the zeolite composition becomes understandable.

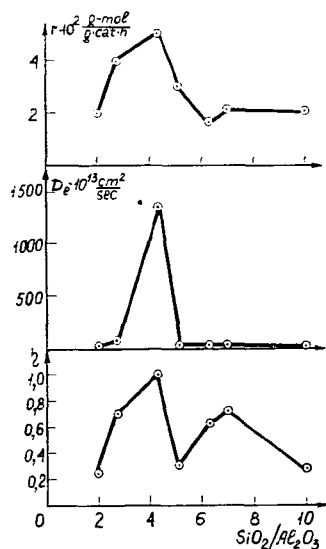


Figure 5. Activity, diffusion coefficient and effectiveness factor vs. zeolite composition plots for 2-methylbutene-2 hydrogenation

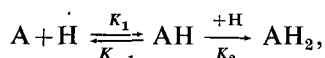
A different picture is observed in the case of acetone and toluene hydrogenation [12, 14]. During hydrogenation of these compounds the reaction rate first decreases when going from zeolite A to faujasites, and then it increases, mordenite showing the highest activity. To explain the differences of these dependences and those observed in hydrogenation of 2-methylbutene-2 it can be assumed that in this case we have inner kinetic region of the reaction over all the catalysts. The reason for it is a considerably lower activity of zeolites in acetone and toluene hydrogenation as compared with that of 2-methylbutene-2.

To elucidate the mechanism of the reaction kinetic studies were made of 2-methylbutene-2, acetone and toluene hydrogenation. The results obtained [13, 14, 18] are presented in Table V. To account for the kinetics observed it may be assumed

Table V
Kinetics of unsaturated compounds hydrogenation over zeolites

Catalyst	Unsaturated compound (A)	Reaction order		E_{app} kcal/mol	Kinetic equation
		H ₂	A		
RbY	2-methylbutene-2	1	1	15.0	$r = k \cdot P_A \cdot P_{H_2}$
NaM	acetone	1	0	10.0	$r = \frac{k \cdot P_A \cdot P_{H_2}}{(1 + a_A \cdot P_{H_2})^2}$
NaM	toluene	0.5	0	22.4	$r = \frac{k \cdot P_A \cdot P_{H_2}^{1/2}}{(1 + a_A \cdot P_A)^2}$

that a successive addition of hydrogen atoms takes place on the catalyst surface to the unsaturated bonds of the hydrogenated compound according to the scheme:



where A is the hydrogenated compound. Assuming the Langmuir character of the adsorption of the initial compounds one may obtain the following kinetic equation:

$$r = \frac{K_2 a_A a_{H_2} P_A P_{H_2}}{\left(1 + \frac{K_2}{K_1} a_{H_2}^{1/2} P_{H_2}^{1/2}\right) (1 + a_A P_A + a_{H_2}^{1/2} P_{H_2}^{1/2})^2} \quad (1)$$

If we are to assume small values of the adsorption coefficients of the initial components in 2-methylbutene-2 hydrogenation, then equation (1) is reduced to the dependence observed experimentally (Table V). In the case of acetone a zero order against the hydrogenated substance indicates more or less strong adsorption of this component, and, hence, equation (1) may give the kinetic equation observed (Table V) which describes well the experimental data (Fig. 6). To bring the above scheme of the reac-

tion in the case of toluene hydrogenation into agreement with the experimental data it is necessary to assume that the slow step is addition of the first hydrogen atom to the benzene ring. The resulting kinetic equation (Table V) is in good agreement with the experimental data (Fig. 7).

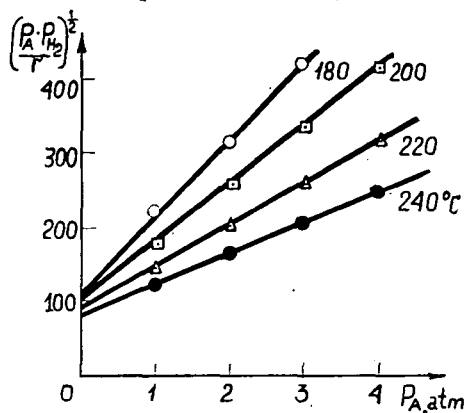


Figure 6. $\left(\frac{P_A P_{H_2}}{r}\right)^{1/2}$ vs. P_A plots for acetone hydrogenation over NaM.

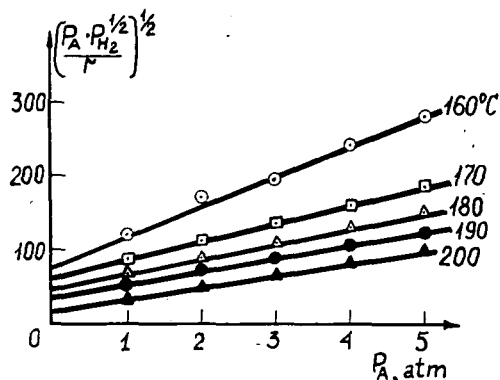
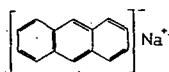


Figure 7. $\left(\frac{P_A P_{H_2}^{1/2}}{r}\right)^{1/2}$ vs. P_A plots for toluene hydrogenation over NaM.

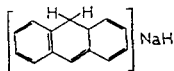
The nature of the activity of the new hydrogenation catalysts should be somehow dependent on activation of hydrogen and the unsaturated compound. The assumption about dissociative adsorption of hydrogen on zeolites without transition metals is in agreement with the kinetics of toluene, acetone and 2-methylbutene-2 hydrogenation. Moreover, hydrogen dissociative adsorption and successive addition of hydrogen atoms to the unsaturated bonds of the hydrogenated compound are indicated also by the results obtained from the reaction of piperylene hydrogenation over Na-forms of zeolites A, Y, chabasite, erionite and mordenite. It is possible to demonstrate that the ratio pentene-1: pentene-2 in the reaction products should be 0.5, with successive presence of hydrogen atoms, and 1.0 if molecular hydrogen is added to piperylene. The experimental value obtained is 0.5 which is indicative of dissociative adsorption. As to the ratio of *cis*-pentene-2: *trans*-pentene-2, it is not characteristic of the reaction mechanisms involved and is dependent on the ratio of syn/anti configurations of piperylene isomers under the reaction conditions.

The mechanism of the reaction involving hydrogen dissociative adsorption and successive addition of hydrogen atoms to unsaturated bonds of the hydrogenated compounds explains satisfactorily the experimental data obtained. Since zeolite cations are responsible for the reaction hydrogen adsorption with dissociation on atoms may proceed, for example, on the dipole formed by a cation and oxygen of zeolite lattice.

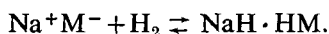
This mechanism is also supported by high catalytic activity of a dative complex of the type



found by TAMARU [54] in the reactions of unsaturated hydrocarbon hydrogenation. These reaction can be catalysed by such complexes in a temperature range of 50–120 °C. Molecular hydrogen is supposed to undergo chemisorption on the complex to give



involving sodium hydride and monohydroantracene, which is a hydrogen donor in hydrogenation of unsaturated compounds. With these ideas extended to the cationic forms of zeolites considered as dative complexes of the atoms of alkaline and alkaline-earth compounds with aluminosilicate zeolite framework, hydrogen chemisorption can be presented as follows (*e. g.* mordenite):

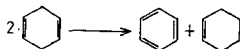


Upon heterolytic cleavage of the H—H bond the hydride-ion passes to the metal cation and the proton forms a hydroxyl group with the oxygen of the lattice. One may suggest also that the H—H bond would not break completely, and the extent of the cleavage would depend on the nature of the metal cation, which would affect the catalyst activity.

3. Cyclic hydrocarbon transformations on zeolites

High catalytic activity of various cationic forms of zeolites in hydrogenation of unsaturated hydrocarbons allowed us to suggest that these catalysts would be active also in the reactions of dehydrogenation. To verify this assumption we have studied transformation of cyclohexane, cyclohexene and cyclohexadiene-1,4 in an impulse microreactor over various cationic forms of zeolites.

Over Na-zeolites cyclohexane did not undergo any transformation up to 500 °C. In the case of cyclohexene the reaction products were methylcyclopentane and cyclohexane (Table VI). As seen from the table the most active catalyst is Na-mordenite. It is well-known that cyclohexene transformation into methylcyclopentane and cyclohexane proceeds over acidic catalysts [55]. In the case of Na-forms of zeolites the acidic centres may be due to deficient Na^+ cations in the zeolite structure. Cyclohexadiene-1,4 is converted over Na-zeolites into benzene, cyclohexene and cyclohexadiene-1,3 (Table VII). The most active catalyst in benzene formation is NaY. Small amounts of cyclohexene in the reaction products indicate that benzene is formed not only as a result of direct dehydrogenation of cyclohexadiene-1,4 but also from disproportionation reaction



Calculations show that 85–90% of benzene is formed by direct dehydrogenation.

Over H-forms of zeolites the major product of cyclohexane transformation is coke, cracking products, methylcyclopentane, and at a high degree of decationization benzene and toluene are also formed. The most active in this process is zeolite HY,

Table VI

Cyclohexene conversion in pulse reactor over Na-forms of zeolites at $V_{He}=20$ cm³/min, $t=450$ °C, catalyst weight 40 mg*

Zeolite ($\frac{SiO_2}{Al_2O_3}$)	Yield of reaction products**, %	
	Methylcyclopentane	Cyclohexane
A (2.0)	2.9	7.8
Y (4.3)	1.3	1.7
erionite (6.2)	1.7	4.4
mordenite (10.0)	11.6	32.6

* Zeolite types X, L and chabazite were inactive at these conditions.

** Conversion of the hydrocarbons to coke was not observed in the range of chromatographic method sensitivity.

Table VII

Cyclohexadiene conversion in pulse reactor over Na-zeolites at $t=400$ °C, $V_{He}=20$ cm³/min, catalyst weight 40 mg

Zeolite ($\frac{SiO_2}{Al_2O_3}$)	Yield of reaction products*, %		
	Cyclohexene	Cyclohexadiene-1,3	Benzene
A (2.0)	1.0	20.6	11.7
X (2.9)	0.7	8.8	<1.0
Y (4.3)	4.7	14.9	31.6
chabazite (5.1)	0	4.5	7.8
erionite (6.2)	2.2	14.3	5.6
L (7.1)	1.6	20.9	18.2
mordenite (10.0)	1.2	16.8	<1.0

* Conversion of the hydrocarbons to coke was not observed in the range of chromatographic method sensitivity.

Table VIII

*Cyclohexane conversion over HY (98%) at $t = 500^\circ\text{C}$,
 $V_{\text{He}} = 20\text{ cm}^3/\text{min}$, catalyst weight 0.2 g*

Slug number	Hydrocarbons quantity converted to the coke, %	The composition of gaseous products, %			
		$\text{C}_1 - \text{C}_3$	Cyclohexane	Benzene	Toluene
1	62	100.0	—	—	—
2	56	84.0	2.5	4.5	9.0
3	53	75.9	4.1	5.8	14.2
4	50	82.3	2.7	7.6	7.4

Table IX

*Cyclohexene conversion over HY (98%) at $t = 500^\circ\text{C}$,
 $V_{\text{He}} = 20\text{ cm}^3/\text{min}$, catalyst weight 0.2 g*

Slug number	Hydrocarbons quantity converted to coke, %	The composition of gaseous products, %		
		$\text{C}_1 - \text{C}_3$	Benzene	Toluene
1	71	76.0	10.1	13.9
2	66	59.0	17.8	23.2
3	60	57.9	14.9	25.2
4	56	55.9	17.4	26.7
5	58	58.9	16.0	25.1

with decationation equal to 98% (Table VIII). As seen from the table, cyclohexane is first converted into coke and cracking products followed by formation of benzene and toluene the latter resulting from benzene alkylation by the cracking products. Over H-zeolites cyclohexane gives benzene and toluene in addition to the cracking products. With an increased decationization of zeolite Y its activity in this process increases. Table IX presents the data obtained from the studies of cyclohexene transformations over zeolite HY (98%). Over this catalyst the initial cyclohexene is fully converted into coke, cracking products benzene and toluene. Over H-zeolites cyclohexadiene is converted into coke, methylcyclopentane, cyclohexane, cyclohexene, cyclohexadiene-1,3 and benzene the activity of the zeolite increasing with decationation (Fig. 8). This figure shows that benzene is the major product of cyclohexadiene-1,4 transformations over decationated zeolites.

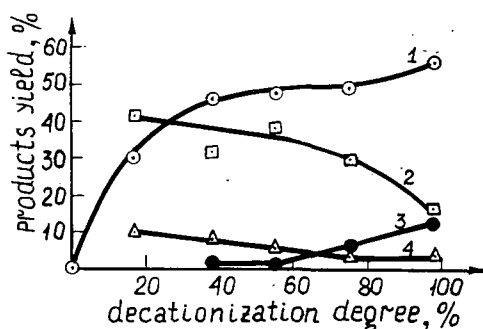


Figure 8. Yield of reaction products vs. decationization degree plots for cyclohexadiene-1,4 conversion over zeolite NaY. 1 — benzene, 2 — coke, 3 — cyclohexane, 4 — cyclohexene

Over Mg- and Nd-forms of zeolite Y cyclohexane undergoes cracking and isomerization into methylcyclopentane only. In the case of cyclohexene the products obtained over multivalent forms of zeolite Y are not only those of cracking, isomerization and disproportionation but also benzene and toluene (Table X). Thus, the

Table X

Cyclohexene conversion over cationic forms of zeolite Y at $t = 500^\circ\text{C}$,
 $V_{\text{He}} = 20 \text{ cm}^3/\text{min}$, catalyst weight 0.2 g*

Zeolite	Hydrocarbons quantity converted to coke, %	The composition of the gaseous products, %					
		$\text{C}_1 - \text{C}_3$	Methylcyclopentane	Cyclohexane	Cyclohexene	Benzene	Toluene
BeY**	65	45.9	49.9	4.2	—	—	—
MgY	58	55.3	30.0	1.7	—	3.0	10.0
NdY	67	73.6	11.8	—	—	3.7	10.9

*. The data of the first slug.

** Some amount of benzene and toluene in reaction products on BeY was observed in the second and third slugs.

composition of the products of cyclohexene transformation over H- and multivalent forms of zeolite Y is about the same, which indicates to their similar activity in this process. Cyclohexadiene-1,4 over multivalent forms of zeolite Y gives the same products as those of cyclohexene, but in this case benzene is formed with higher selectivity (Table XI).

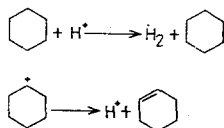
Table XI

*Cyclohexadiene-1,4 conversion over cationic forms of zeolite Y
at $t = 200^\circ\text{C}$, $V_{\text{He}} = 20 \text{ cm}^3/\text{min}$, catalyst weight 10 mg*

Zeolite	Hydrocarbons quantity converted to coke, %	The composition of the gaseous products, %				
		Methylcyclopentane	Cyclohexane	Cyclohexene	1,4-cyclohexadiene	Benzene
BeY	50	2.2	6.9	6.3	3.1	81.5
MgY	75	5.9	13.2	6.5	—	74.5
NdY	30	8.8	14.2	5.5	—	71.6

The results obtained allow certain conclusions to be made about hydrocarbon dehydrogenation over zeolites. First, the ease of benzene formation increases in the series: cyclohexane < cyclohexene < cyclohexadiene. Second, the activity of zeolites in dehydrogenation increases when going on from Na- to H- or multivalent forms. For instance, over zeolite HY, with a degree of decationation equal to 98%, even cyclohexane is partially converted into benzene, whereas with decationization of 75% and lower the reaction products indicate to the reactions of cracking and isomeriza-

tion only. It seems likely that in the reaction conditions studied the active centres of cyclic hydrocarbon dehydrogenation can be not only metal cations but also the Brönsted acidic centers, and the reaction may be presented as follows:



Conclusion

As is shown in this paper zeolites containing neither atoms nor ions of transition metals can be active and selective in isomerization of saturated hydrocarbons and hydrogenation of various unsaturated compounds. As to dehydrogenation of the cyclic hydrocarbons studied over Na-forms of various zeolites it is cyclohexadiene-1,4 only which can be converted into benzene to some extent. In the case of cyclohexene, cyclohexane and methylcyclopentane are formed, and cyclohexane, taken as an initial reactant, does not undergo any transformations over Na-zeolites. Introduction of multivalent cations into NaY zeolite or its decationization results in an increase of its dehydrogenating activity in cyclohexadiene transformation. It should be noted that over multivalent and decationated forms of zeolites cyclohexene is also partially converted into benzene, and over highly decationated zeolite Y even cyclohexane is partially dehydrogenated to benzene, although the principal direction is cracking. From the data obtained by studying transformations of cyclic hydrocarbons over various zeolites we may conclude that although the catalysts studied show some dehydrogenating activity it is much lower than that which could be expected on the basis of the catalytic activity in hydrogenation. What is responsible for it remains to be clarified.

As to hydrogenation over zeolites containing no transition elements we can conclude from the dependence of catalytic activity on zeolite composition, nature and concentration of cations that ion-exchange cations are involved into the active centre, with the number of sodium cations in the active centre of zeolite Y not exceeding two as in hydrogenation of 2-methylbutene-2. The mechanistic studies of hydrogenation reactions have shown that the problem of hydrogen activation over cationic forms of zeolites is of great importance. It seems likely that hydrogen molecule dissociation into atoms takes place on the active centers of catalysts. This assumption is in agreement with the kinetics of hydrogenation reactions, isomerization of the double bond upon hydrogenation of 2-methylbutene-2 over NaY and the ratio of pentene-1: pentene-2 in the reaction products of piperylene hydrogenation.

As is mentioned above there are many examples at present which illustrate that zeolites without transition elements show high activity in the reactions which were effected earlier over catalysts involving transition metals or their oxides as an indispensable component. This property of zeolites which is of great scientific and practical importance should be thoroughly studied.

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SPECTROSCOPY APPLIED TO ZEOLITE CATALYSIS

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Introduction

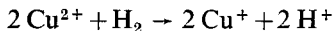
The remarkably broad and rapid development of works dealing with zeolite is obviously due to the diversity of the discipline. Because of the diversity of the problems existing in the zeolite science it appeared important to have effective and fruitful communication among the different branches. During the past years several workers from various origins have joined their efforts for a better understanding of the phenomena occurring in zeolites. It is not necessary to recall the important part taken in this field by the catalytic reaction. However it must be noticed that a better correlation between the catalytic activity and/or selectivity and the structure and the nature of active sites was obtained when the parameters interfering in the hydrocarbon transformation have been defined precisely. The numerous papers already published have shown that spectroscopic techniques are potentially of great value for the investigation of exchanged zeolites and almost indispensable for the unambiguous identification of the active sites of the localization, oxidation state and electronic structure of the exchanged cations and of the chemical changes occurring during the activation of the zeolites. Indeed much of the rapid progress in zeolite chemistry can be attributed partially to the increased works dealing with characterization of the material and also to the wide-spread availability of equipments. The usual chemical and spectroscopic techniques employed up to now were elemental analysis, infrared spectroscopy, X-ray crystallography, electron spin resonance, nuclear magnetic resonance, optical spectroscopy and more recently ESCA technique. Several well referenced reviews have already been published [1—6]. In the recent ACS monograph "Zeolite chemistry and catalysis" edited by RABO [7] the reader will find most of the spectroscopic data concerning zeolites. In view of the variety of outstanding reviews published we have the feeling that our contribution at this meeting will be more fruitful if we develop few examples where unusual chemical processes were found in the study of zeolites and where new applications for zeolites have been developed. The emphasis here will be on the way in which informations of chemical interest can be extracted from various spectroscopic techniques. No attempt will be made to give exhaustive data. Two major topics will be reviewed in the present report: redox behaviour of transition metal ions in zeolites along with the interaction of the metallic component with the carrier in zeolite-supported metal catalysts and solid solvent effect of the zeolite matrix for synthesizing or/and immobilizing metal complexes within the zeolite framework.

*Redox behaviour of metal ions**Chemical reduction of transition metal ions*

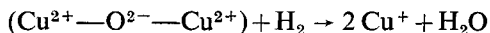
More than a decade ago RABO and COWORKERS [8] have shown that univalent nickel ions can be formed and stabilized within the zeolite framework by heating exchanged Ni^{2+}Y zeolite with sodium metal vapor. The presence of Ni^+ ions, which have a $3d^9$ electronic configuration was demonstrated by esr and optical spectroscopy. Since the esr parameters of Ni^+ ions depend strongly on the local crystal field, the analysis of the esr parameters of Ni^+ ions within the zeolite has led these authors to conclude that for a low nickel content Ni^+ ions were essentially localized in S_I sites while for a high nickel loading Ni^+ ions were present both in S_I and S_{II} sites. The interesting finding was that univalent nickel ions were chemically and thermally more stable toward further reduction or disproportionation into nickel metal when they are located at S_I sites. This stabilization effect was ascribed to lower mobility of both nickel ions or atoms in S_I than in S_{II} . Hence one should expect that, in general, hidden ions or atoms in S_I will be more stable toward reduction and/or aggregation than surface species in S_{II} . As it will be shown later, the influence of cation localization or their reducibility and aggregation, conclusively established for nickel, gave reasonable explanation for the various metal dispersions obtained when the metal ions exchanged zeolites were thermally treated at different temperatures before hydrogen reduction.

Further investigations on the formation of univalent nickel ions within Y zeolite have been performed. Generally esr, optical spectroscopy and infrared techniques were used to identify Ni^+ ions. It has been shown that Ni^{2+}Y zeolite contacted with NO at room temperature gave esr signals assigned to Ni^+ ions [9–10]. The formation of such species results from the transfer of the odd electron from NO to a d orbital of Ni^{2+} ion. The formation of $\text{Ni}^+ \text{NO}^+$ species was further proved by the presence of an ir band at 1892 cm^{-1} from the nitrosyl group [10]. It is known that the stretching frequency of the N—O bond reflects sensitively the change of electron density along the N—O bond. Since Ni^+ was formed by the removal of the odd electron of the antibonding π^* orbital of NO molecule followed by a π back-donation from the nickel to the π^* orbitals of NO one should expect a shift of ν_{NO} with respect to the free NO. Similarly NO_2 , known for its high oxidizing properties, is able to reduce Ni^{2+} within the zeolite framework, into Ni^+ as shown by esr and ir studies [10]. Furthermore NO or NO_2 adsorption has been used to reveal the presence of Cr^{2+} ions in H_2 -reduced Cr^{3+}Y zeolites. Indeed upon NO or NO_2 adsorption on these samples a strong esr signal, attributed to Cr^+ having a low spin d^5 electronic configuration, was observed. The ir spectra of $\text{Cr}^+ \text{NO}^+$ and $\text{Cr}^+ \text{NO}_2^+$ complexes presented bands at respectively $1895\text{--}1780 \text{ cm}^{-1}$ and $1580, 1410, 1370 \text{ cm}^{-1}$ due to the NO^+ and NO_2^+ groups [10]. The most interesting feature of these studies is that they reinforce the generally accepted fact that zeolites possess high polarizing and ionizing properties which could radically affect the electron affinity of the transition metal ions within the zeolite toward a substrate and/or the ionisation potential of the substrate. Thus the zeolite framework would facilitate electron transfer reactions. With respect to these properties the zeolites have been viewed as a "solid electrolytic solvent" [8–9]. This property is responsible for the ionization of water molecule into OH^- and H^+ by the zeolites as well for the occlusion of salts such as NaCl

in the form of $\text{Na}^+ \text{Cl}^-$ [9]. Other workers [11–12] have reported the formation of Ni^+ ions resulting from the reduction by hydrogen of NiCaY zeolite. Univalent nickel ions were identified mainly by means of uv, optical spectroscopy esr and infrared. It was shown that after dehydration of the zeolite both Ni^{2+} and Ca^{2+} compete for S_I sites, thus for a high nickel loading Ni^{2+} ions occupy S_I and S_II sites. CO could adsorb on Ni^{2+} in S_II sites to give a ν_{CO} infrared band at 2215 cm^{-1} . Upon hydrogen reduction at about 200°C Ni^+ ions were formed as revealed by the appearance in the uv spectrum of bands at $13\,500$ and $29\,500 \text{ cm}^{-1}$ assigned to $d \rightarrow s$ transitions from the ground state d^9 to the excited state $d^8 s^1$ and one band at 4500 cm^{-1} attributed to $d \rightarrow d$ transition of Ni^+ ions. With the use of esr it was confirmed that Ni^+ was formed. This ion forms readily a $\text{Ni}^+(\text{CO})_x$ adduct. The structure of the Ni (I)-carbonyl adduct was determined by ir and esr. The ir spectrum of this species showed two bands at 2140 and 1930 cm^{-1} which have been attributed respectively to the symmetric and antisymmetric ν_{CO} stretching vibrations for $\text{Ni}^+(\text{CO})_2$ species. Furthermore the esr signal of this species enriched with ^{13}C was interpreted as resulting from the interaction of the unpaired electron with two ^{13}C nuclei which confirms the structure $\text{Ni}^+(\text{CO})_2$ for the nickel carbonyl species. MINACHEV *et al.* [13] have also shown using ESCA technique the formation of Ni^+ ions in Ni^{2+}Y zeolite reduced by hydrogen. Transition ions exchanged zeolites have been used as catalysts for reactions such as oxidation, isomerization, oligomerization of olefins *etc.* Satisfactory correlations between the catalyst and the catalytic activity may be obtained if the structure of the active site is well understood. Thus it is necessary to investigate the properties of the material subjected to treatment with CO or hydrogen. Copper exchanged Y zeolites have been extensively investigated with regard to the reduction of Cu^{2+} ions. NACCACHE and BEN TAARIT [14] have shown that the esr signal intensity of Cu^{2+} in Cu^{2+}Y zeolite decreased upon treatment of the sample with hydrogen at 500°C . The kinetic data concerning the disappearance of Cu^{2+} follow a second order rate law with respect to Cu^{2+} concentration. Furthermore upon H_2 -reduction ir bands at 3650 and 3540 cm^{-1} appeared and they were removed by a subsequent adsorption of pyridine to give the characteristic pyridinium bands at 1630 , 1540 and 1488 cm^{-1} . Reoxidation of the reduced sample produced only CuO . It has been concluded that Cu^{2+} ions are easily reduced by hydrogen at high temperature with the subsequent formation of large copper crystallites which migrate outside the cavities. Simultaneously Brönsted acid sites were formed. The following scheme for reduction was suggested [14]



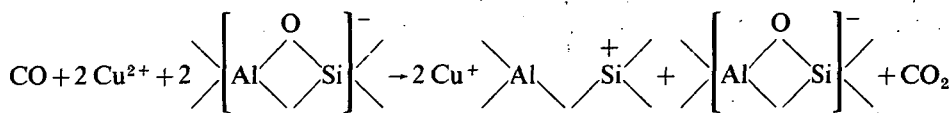
or



followed by $2 \text{Cu}^+ + \text{H}_2 \rightarrow \text{Cu metal} + 2 \text{H}^+$.

In contrast reduction by carbon monoxide generated cuprous ions Cu^+ as evidenced by the disappearance of Cu^{2+} esr signal and by chemical analysis. Furthermore in contrast with H_2 -reduction, CO-reduction produced Lewis acid sites evidenced by ir bands at 1620 , 1488 and 1451 cm^{-1} upon pyridine adsorption, attributed to pyridine coordinatively bonded to tricoordinated aluminium atoms, and by the formation

of positive radicals when anthracene is adsorbed on the CO-reduced sample. The reduction process may be [14]



A similar approach has been employed by MAXWELL and DRENT [15] to study the reduction of Cu^{2+} exchanged faujasite with butadiene and ammonia. It was shown that on reduction by butadiene at 100°C the color of the sample initially green-blue turned white. Simultaneously the esr Cu^{2+} signal decreased. Phosphorescence spectra in the excitation mode showed a band at 390 nm assigned to Cu^+ ions. Thus a direct proof of the formation of Cu^+ was obtained. Kinetic studies of Cu^{2+} disappearance again indicated a second order rate law for Cu^{2+} reduction. Furthermore it was shown that the second-order rate constant decreased when the copper exchanged zeolite was dehydrated at increasing temperature. Since it is known that Cu^{2+} ions migrate toward hidden S_I sites [16] as the dehydration temperature increases it was concluded that Cu^{2+} located in the supercages are the more reactive toward reduction. Same conclusions have been reached by JACOBS, UYTTERHOEVEN *et al.* [17]. Their kinetic results strongly support the general trend: the reducibility of metal ions within the zeolite framework is mainly determined by their location. Cations localized in hidden sites, S_I , S_{II} are less reducible than those in S_{II} sites.

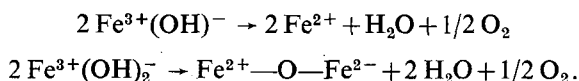
Zeolites have been used as carriers to prepare highly dispersed supported metal catalysts. Again it was observed that the location of the cations before the reduction plays an important role. For example it was shown [18] that in Pt^{2+} exchanged Y zeolites thermally treated at 350°C , almost all the Pt^{2+} ions were localized in the supercages, H_2 -reduction leads to the formation of metal particles of about 10 Å diameter. In contrast, if the sample was heated up to 650°C prior to reduction, X-ray analysis indicated that Pt^{2+} ions have migrated to the sodalite cages, and after H_2 -reduction about 75% of the platinum atomically dispersed within the sodalite cages, and only a relatively small amount of the platinum was found in the form of metal particles and available for reactions. The implication of all the results described herewithin is that both the mobility and the reducibility of cations in the sodalite cages or in the hexagonal prisms are low. Thus one should avoid to have the active precursor cations in these sites when high dispersion and accessible particles are desirable. A useful way to achieve this goal would be to exchange first the Na^+ by unreducible cations such as Ca^{2+} , Ba^{2+} , Mg^{2+} , La^{3+} *etc.* showing a strong preference for S_I and S_{II} sites and then to introduce the active component such that it will remain in the supercage.

Selfreduction of transition metal ions

It is now well accepted that the very strong electric fields present in zeolites are responsible for the ionization of water by multivalent exchanged cations. There are enough experimental evidences to state that the exchanged zeolites activated at moderate temperatures contain $\text{Me}^{n+}(\text{OH})_x$ groups and acidic OH. The thermal decomposition *in vacuo* of transition metal ion exchanged zeolites very often led to the

reduction of the cations. MINACHEV *et al.* [13] using X-ray photoelectron spectroscopy have unambiguously shown that cobalt, iron, nickel, silver and palladium cations in zeolites were partially reduced during the thermal treatment *in vacuo* at high temperature. In general the reduction has been attributed to the presence of undesirable hydrocarbons adsorbed on the zeolite surface. Although adsorbed hydrocarbons may effectively act as reducing agents it appears now that H_2O molecules were involved in the reduction process. In the present section we have selected a few studies because of their relevant contribution to the role of water in the reduction process.

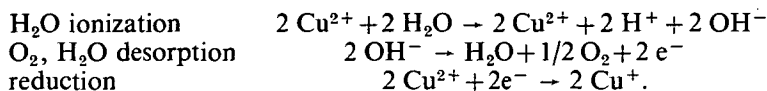
MORICE and REES [19] have many years ago shown that dehydration of Fe^{3+}Y zeolite produced ferrous ions. Later GARTEN *et al.* [20] used Mössbauer spectroscopy to investigate the reversible oxido-reduction of iron zeolite and the effect of water on the chemical states of iron. Starting from Fe^{2+}Y zeolites they showed that the Mössbauer spectrum of the Fe^{2+} ions present in the dehydrated sample changed drastically when the zeolite was calcined at 673 K in dry oxygen. The new spectrum was ascribed to $\text{Fe}^{3+}-\text{O}^{2-}-\text{Fe}^{3+}$ groups resulting from the oxidative insertion of one oxygen atom between two Fe^{2+} ions. This suggestion was further proved by quantitative measurements of adsorbed oxygen which gave O:Fe ratio 1:2. Water adsorption resulted in the hydrolysis of $\text{Fe}^{3+}-\text{O}^{2-}-\text{Fe}^{3+}$ into $2\text{Fe}^{3+}(\text{OH})^-$. Upon dehydroxylation at high temperature oxygen gas was produced. Mössbauer results indicated that ferric ions were reduced to ferrous ions according to the following equations



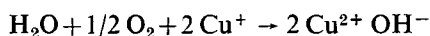
The formation of bridged species in Y zeolite has been suggested by several authors. This type of auto-reduction prevails for Cu^{2+} exchanged Y_1 zeolite. JACOBS *et al.* [21] have demonstrated that reduction occurred during the calcination of Cu^{2+}Y *in vacuo*. Several spectroscopic techniques have been used. Infrared spectra of CO and CO_2 adsorbed on copper ions are indicative of the oxidation state of the ions since CO adsorbed on cuprous ions gives a stretching vibration at 2180 cm^{-1} while CO_2 adsorbed by ion-dipole interaction on cupric ions gives an ir band at 1370 cm^{-1} . Thus the fact that upon dehydration at increasing temperature there is a decrease of the intensity of the 1370 cm^{-1} band and an increase of the 2180 cm^{-1} band one could conclude that Cu^{2+} ions were reduced to Cu^+ ions. Furthermore the ir spectra of pyridine and dimethylpyridine adsorbed on dehydrated samples were indicative of the formation of true Lewis acid sites. The formation of Cu^+ ions was proven by the appearance of a band near 400 nm in the phosphorescence spectra characteristic for Cu^+ ions, this band disappearing by reoxidation at 823 K. Finally these authors detected by mass-spectrometry analyses the presence of oxygen in the products evolved during the calcination at high temperature. All these results again indicate in agreement with the above statement that transition metal ions within the zeolite framework can be reduced during the dehydration *in vacuo*, oxygen is removed from the lattice with the subsequent formation of true Lewis sites.

Following the same experimental trend as those described above, KASAI and BISHOP reported that zeolites possess the remarkable property to decompose water into oxygen and hydrogen, when they are exchanged by suitable cations, in a two-way thermochemical cycle. Their studies started from the observation, by esr

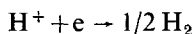
technique, that the *esr* signal intensity of Cu^{2+} in copper exchanged mordenite-type zeolite decreased by about one half when the sample was outgassed above 573 K. Mass spectroscopy analyses of the uncondensable gas desorbed during the thermal treatment revealed the presence of oxygen. On the basis of these results they suggested that Cu^{2+} ions were reduced to Cu^+ ions by water molecules as follows: [22]



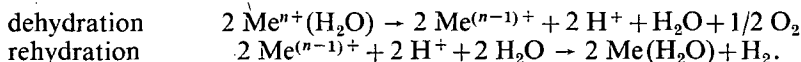
Since cuprous ions were reoxidized to cupric ions at room temperature only if oxygen and water are both contacted with the sample one could conclude that following the equation:



the reduction and oxidation by water form only oxygen. However, since the reduction potential for



is $E^\circ = -0.414 \text{ V}$, they concluded that multivalent cations in zeolites for which the reduction potential of the halfcell reaction $\text{Me}^{n+} + \text{e} \rightarrow \text{Me}^{(n-1)+}$ is more negative than -0.414 V will be reoxidized by water, hydrogen being generated. Indeed, they found that oxygen evolved during dehydration *in vacuo* of Cr^{3+} exchanged mordenite and hydrogen by rehydration of the dehydrated sample. Similar results were obtained on In^{3+} exchanged mordenite, the reduction potential for $\text{In}^{3+}/\text{In}^{2+}$ cell being -0.49 V . The following equations summarize the water decomposition

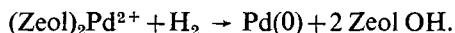


It is interesting to note that the two-step decomposition of water is associated with the polarization of adsorbed water molecules by the electric field. Since, in general, it is suggested that the unshielded cations in the zeolite are responsible for the intense electrical fields, one should expect a more pronounced effect with mordenite than with faujasite type zeolites. This general trend has been observed for palladium exchanged zeolites [23—24]. Unfortunately the products evolved during the dehydration process were not analyzed. $[\text{Pd}^{2+}(\text{NH}_3)_4]$ exchanged zeolite containing about 12.5 Pd^{2+} ions was deammoniated and subsequently dehydrated *in vacuo* at 773 K. Both *esr* measurements [23] and ESCA analysis [25] indicated that almost all the palladium ions were in the 2+ oxidation state. By *esr* a small signal attributed to Pd(III) ions was found. In contrast mordenite type zeolite exchanged with $[\text{Pd}^{2+}(\text{NH}_3)_4]$ showed after dehydration *in vacuo* at 773 K a very strong *esr* signal with 2-*g*-values at $g_{\parallel} = 2.97$, $g_{\perp} = 2.146$ unambiguously assigned to Pd(I) ions [24]. These findings imply that, as stated above, mordenite type zeolites are intrinsic favorable materials for auto-reduction of the exchanged cations. The mechanism suggested for copper exchanged zeolites should also prevail for Pd^{2+} -zeolites.

Metal zeolite interaction in metal supported zeolite catalysts

RABO *et al.* [25] have reported that atomically dispersed platinum catalysts may be obtained by hydrogen-reduction of Pt^{2+} exchanged Y zeolites. Since this work, several papers concerning the method of preparation, the metal dispersion and the catalytic properties of these materials appeared in the literature. These materials showed unusual catalytic behaviour [25–28] which was ascribed to the metal-zeolite interaction. One type of interaction which was frequently invoked was “electron transfer interaction” between the metal and the zeolite carrier [26, 29]. Recently it has been tempted to obtain, using spectroscopic techniques, direct proofs on the possible interaction between the metal and the zeolite. In the next paragraph the various phenomena occurring during the reduction process will be discussed.

The mechanism of reduction of palladium exchanged Y zeolite was investigated by ir spectroscopy [23]. $\text{Pd}^{2+}(\text{NH}_3)_4\text{Y}$ zeolite thermally treated at 773 K showed weak ir bands in the OH stretching region. At room temperature about 60% of the palladium was reduced into Pd(0) and Pd(I) by hydrogen. Monovalent palladium ions were revealed by *esr* since Pd(I) has a $4d^9$ electronic configuration and hence is paramagnetic. Infrared spectra of the H_2 -reduced samples showed two intense bands at 3635–40 and 3540–45 cm^{-1} , the intensity of which increased with the reduction temperature up to 473 K. Above 473 K and in a wide temperature range these bands remained unchanged [30]. It was concluded that Pd(II) ions were almost completely reduced by hydrogen at 200 °C with the subsequent formation of Brönsted acid sites following the reaction



Using infrared spectra of pyridine adsorbed on reduced samples PRIMET and BEN TAARIT [30] have determined the state of the zeolite surface. They stated that the 8a vibration mode of adsorbed pyridine would appear at 1620–30 cm^{-1} for pyridine adsorbed on Lewis sites and at 1595–1610 cm^{-1} for pyridine coordinated to palladium atoms. The presence of a band at 1605 cm^{-1} (8a) and 1452 (19b) upon pyridine adsorption on Pd Y samples reduced under mild conditions (298–473 K) led these authors to suggest that atomically dispersed palladium atoms were formed and may give a Pd(0)-pyridine complex. Since the band at 1605 cm^{-1} strongly decreased as the reduction temperature increased up to 773 K provides strong evidence that isolated palladium atoms aggregate to form palladium metal particles. MINACHEV *et al.* [31] have shown that heating $\text{Pt}^{2+}(\text{NH}_3)_4\text{—NaY}$ zeolite *in vacuo* at high temperature removed NH_3 ligands and simultaneously produced Brönsted acid sites as evidenced by the appearance of an infrared band at 3657 cm^{-1} . Furthermore a band at 2120 cm^{-1} assigned to Pt—H^- hydrido complex was formed. The hydrido platinum complex was destroyed *in vacuo* at about 523 K. They concluded that Pt^{2+} cations were reduced during the thermal treatment *in vacuo*. Complete reduction of the platinum was obtained in the presence of hydrogen at 673 K. DALLA BETTA and BOUDART [26], FIGUERAS *et al.* [29] have concluded that the enhancement of the catalytic activity of zeolite-supported platinum or palladium was probably due to electron transfer between the metal and the zeolite. RABO *et al.* [25] have observed an increased sulphur resistance in Pt—CaY catalyst which was related to the atomic dispersion of the metal in the zeolite. There is little doubt that zeolite-supported metal catalysts behave differently from conventional metal catalysts. The question is what is the nature of

the metal-zeolite interaction. Several spectroscopic techniques were recently used to try to answer this question.

In a previous publication [32] we have suggested that Pd(I) ions formed by hydrogen reduction at 297 K of $\text{Pd}^{2+}\text{NH}_4\text{Y}$ exchanged zeolite resulted from the formation of atomically dispersed Pd(0) which interact with Lewis acid sites, one electron being transferred to the carrier following $\text{Pd(0)} + \text{Lewis site} \rightarrow \text{Pd}^+ + e^-$ Lewis site. However further experiments carried out on these systems have shown [33] that:

i) Pd^+ esr signal disappears when the sample which has been reduced by hydrogen at 270 K is outgassed at 573 K and reappears by a subsequent adsorption of hydrogen. The cycle may be repeated several times.

ii) The type of zeolite used as carrier (NaX or NaY) and the number of Lewis sites present had no effect on the number of Pd^+ formed on samples with the same palladium loading.

iii) Reduction at high temperature removes completely the Pd^+ esr signal this phenomena was attributed to the aggregation of atomically dispersed palladium atoms. From these results we are now tempted to conclude that a better explanation for the formation of Pd^+ is that hydrogen reacts with Pd^{2+} ions to give atomically dispersed Pd(0) which in turn could interact with hydrogen to form palladium hydrido complex Pd H^+ similarly to Pt-H^+ [31]. However another explanation might be suggested from the results of CHUKIN *et al.* [34]. These authors used HY and dealuminated Y zeolite forms. These samples dehydrated at 673 K showed infrared bands in the OH stretching region respectively at 3650–3550 and 3640–3550 cm^{-1} . The small ν_{OH} shift (10 cm^{-1}) to lower frequencies observed, in the case of dealuminated zeolite was ascribed to a stronger proton donor or electron acceptor properties of the OH groups in deal-HY zeolite. When these samples were exchanged with $\text{Pd}^{2+}(\text{NH}_3)_4$ complex and then activated at 573 K, a strong decrease of the 3640 cm^{-1} band in deal-HY zeolite was observed while no change occurred with the original HY sample. They concluded that upon thermal treatment of the palladium exchanged zeolites $\text{Pd}^{2+}(\text{NH}_3)_4$ complexes were decomposed and that the evolved NH_3 acted as a reducing agent leading to the formation of palladium metal. Pd metal would interact with the strongest Brönsted sites present in dealuminated HY zeolite. It resulted a decrease in the number of these OH groups as evidenced by the decrease of the 3640 cm^{-1} *ir* band. It was suggested that an electron transfer from the metal to the more acidic OH groups has occurred with the formation of a charge transfer complex $\text{Pd}^{+\delta} \dots ^{-\delta}\text{HO-zeolite}$. These palladium atoms interacting with strong acidic OH groups would be electron deficient and thus less sensitive to sulphur poisoning [34]. Electron transfer between metal aggregates and the zeolite carrier has been evidenced by infrared spectroscopy and ESCA using CO as a probe and by esr of adsorbed hydrocarbons. It is well known that the ν_{CO} frequency of CO adsorbed on an atom is very sensitive to the charge density around the atom. CO adsorbed on zeolite supported palladium aggregates gave ν_{CO} infrared band around 2100 cm^{-1} , while this band appeared around 2085–2070 cm^{-1} for CO adsorbed on unsupported or supported conventional palladium catalysts. The shift of ν_{CO} to higher frequency in the case of zeolite carrier is due to a lower π -back-donation of *d*-electrons into the CO π -antibonding orbitals. This one could conclude that palladium supported on zeolite is electron deficient compared with Pd supported on conventional carrier. Similar conclusions were drawn by VEDRINE *et al.* [35] from their ESCA and esr

results. These authors found an XPS chemical shift of +1.3 eV and +1.4 eV respectively for Pt 4f and Pd 3f lines in the case of platinum or palladium aggregates supported on zeolite, with respect to bulk metals. Furthermore they studied the electron-donor and electron-acceptor properties of these materials with and without metal by following the formation of positive or negative radical ions upon adsorption of perylene or tetracyanoethylene. It was found that in general the introduction of a metal such as Pt produced a decrease of the number of electron acceptor sites and simultaneously an increase of the electron donor sites. They concluded that Pt aggregates act as electron donors thus poisoning the electron acceptor sites for perylene. This electron transfer from Pt atoms to the carrier would increase the electron density around the electron donor sites of the zeolite thus increasing its reducing properties.

*Immobilized metal complexes on zeolite. Zeolites as "solid solvents"
for synthesizing metal complexes*

Homogeneous catalysts are in many cases more efficient and more selective than heterogeneous catalysts. In general the reactions take place at much lower temperature but need higher pressure in homogeneous catalysis. One major disadvantage of soluble catalysts is the difficult separation of the products from the catalyst, and the self-aggregation of the active sites which decreases the efficiency of the catalyst. These disadvantages may be overcome by linking the active metal complex on a solid carrier through covalent bonds. The catalyst attached to a non-soluble phase thus would conserve the high activity and selectivity of its soluble counterpart and still maintain the advantage of heterogeneous catalysts. As stated above, generally the metal complex is anchored to a functionalized organic support, the metal complex being coordinatively bonded to the functionalized surface groups. An alternative means for converting homogeneous metal catalysts into heterogeneous catalysts is to introduce the active complex in the intercrystal space of a swelling layer lattice silicate. These materials are made up of silicate layers, the void space between two layers is occupied by exchangeable cations such as Na^+ and water. Thus if one exchanges Na^+ cations with cationic transition metal ion complexes it would be possible to anchor the homogeneous catalysts to the mica-like structure carrier by electrostatic binding. PINNAVAIA and WELTY [36] have introduced by ion exchange Rh_2^{4+} cations in the intercrystal space of the mineral hectorite. Triphenylphosphine reduced Rh_2^{4+} cations into a rhodium (I) triphenylphosphine complex are bound to the silicate lattice by electrostatic forces. As expected the silicate-anchored rhodium catalyst exhibits high catalytic activity for hydrogenation of 1-hexene and no activity for benzene hydrogenation. These findings demonstrate that the rhodium complex immobilized within the layer silicate by electrostatic forces is stable toward aggregation into rhodium metal, known for its high activity for reduction of aromatic hydrocarbons, and that it has preserved its molecular properties. Thus the use of zeolites for immobilizing metal complexes appears very promising since cationic species may be uniformly dispersed within the zeolite framework by ion exchange and furthermore strongly held to the solid by ionic forces. However one of the major disadvantages of zeolites is that in many cases the organometallic complexes are too large to enter the zeolite cavities through the small windows of the material but small enough to fit the di-

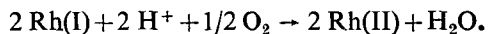
mensions of the cavities. Thus it appeared that this difficulty may be overcome if one synthesizes the metal complex directly within the zeolite cavities. In this section we will describe how spectroscopic techniques have been used to characterize such complexes. Examples showing the similitude of the chemistry of the zeolite entrapped species with their soluble analogues will be given. This chapter is intended to provide general and representative cases of the formation of transition metal complexes in zeolites.

Transition metal ion-oxygen adducts in zeolites

The ability of solutions of transition metal salts to adsorb molecular oxygen has been known for many years. It has been shown that a variety of oxygen adducts may form, with or without electron transfer from the metal atom to the dioxygen ligand.

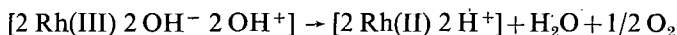
Cobalt-O₂ adducts have been extensively studied. It has been shown that tetraphenylporphyrin cobalt(II) adsorbs molecular oxygen. The electron configuration of the oxygen complex TPP Co(II)—O₂ approaches Co(III)—O₂⁻ [37]. Pentaammine Co(II) in ammonia solution was shown to react with molecular oxygen to form a μ -peroxodicobalt ammine complex [(NH₃)₅CoO₂Co(NH₃)₅]⁴⁺ the oxygen molecule bridging two cobalt ions. HOWE and LUNSFORD [38] have demonstrated that such oxygen adducts were formed when cobalt(II)ammine exchanged Y zeolite were contacted with molecular oxygen. *esr* spectra of L_xCo(II)—O₂ adducts, where L was ammonia, methylamine or propylamine, were interpreted as resulting from the formation of monomeric [Co^{III}(CH₃—CH₂—CH₂—NH₂)_xO₂]²⁺ or dimeric [Co(III)(NH₃)_xO₂Co(NH₃)_x]⁴⁺ oxygen adducts similar to those of analogous adducts in solution. Cobalt exchanged zeolites thus may serve as model systems for reversible oxygen carriers.

Rhodium(II)porphyrin in dimethylformamide was found to adsorb hydrogen at 293 K in a molecular H₂:Rh ratio of 0.5:1 [39]. Rh(II) was thus converted into Rh(I) following the reaction: 2 Rh(II) + H₂ → 2 Rh(I) + 2 H⁺. Rh(I) species was found very sensitive to oxygen and was reoxidized with the subsequent formation of water and Rh(II) following the reaction:

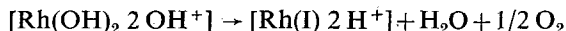


NACCACHE *et al.* [40] have investigated by *esr* technique the oxygen adsorption on rhodium exchanged zeolites. The sample was prepared by exchanging Na⁺ ions with an aqueous solution of [Rh(III)(NH₃)₅Cl]²⁺. The rhodium complex is completely decomposed *in vacuo* at 573 K as indicated by the absence of *ir* stretching vibration around 1300 cm⁻¹ of NH₃ molecules. *esr* technique revealed the presence of a small number of Rh(II) cations. Furthermore, oxygen was adsorbed reversibly at 77 K with the formation of a paramagnetic species with *g*_{||} = 2.015, *g*_⊥ = 1.913. The line broadening of the *esr* spectrum when ¹⁷O enriched molecular oxygen was used and the *g*-values led these authors to conclude to the formation of an Rh(II)—O₂ adduct. Furthermore, simultaneous adsorption of H₂O and O₂ developed an *esr* signal at *g*₁ = 2.11, *g*₂ = 2.016, *g*₃ = 1.98, similar to that of Rh(II)-porphyrin compound [39]. Thus it has been suggested that μ -peroxodirhodium(II) species were formed within the large cavities of the zeolite. From these results it can be suggested that upon thermal treatment *in vacuo* part of the Rh(III) cations undergoes the following

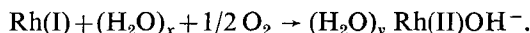
reactions:



and



O_2 molecule reacts with two close Rh(I) , one electron from each Rh(I) ion is transferred to the antibonding π^* orbitals of O_2 to form the μ -peroxo rhodium(II) complex $\text{Rh(II)}-\text{O}-\text{O}-\text{Rh(II)}$. Rh(I) is irreversibly reoxidized by H_2O and O_2 to form mononuclear Rh(II) species



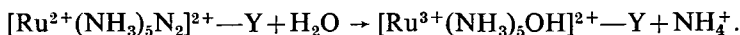
The conversion of rhodium(I) to Rh(II) and the reverse reaction observed in zeolites appeared similar and this emphasizes the "solid solvent" properties of these materials. The great interest of these materials is also based on the fact that the new type of oxygen-adduct, which has not been isolated in solution may be stabilized in zeolite framework. An example is given by palladium exchanged mordenite type zeolite. We have shown in the first paragraph that Pd(I) species were formed when a mordenite type zeolite exchanged with $[\text{Pd}(\text{NH}_3)_4]^{2+}$ is dehydrated at 773 K *in vacuo*. The *esr* spectrum of this species is characterized by two g -values at $g_{\parallel} = 2.97$ and $g_{\perp} = 2.146$. The adsorption of oxygen at room temperature on this sample [24] resulted in the disappearance of the *esr* signal attributed to Pd(I) and a new signal at $g_{\perp} = 2.05$, $g_{\parallel} = 1.99$ developed. The adsorption of oxygen enriched with ^{17}O ($I = 5/2$) led to a spectrum with two sets of 6 and 11 hyperfine lines attributed to the interaction of the unpaired electron with one ^{17}O nucleus ($^{17}\text{O}-^{16}\text{O}$) and two ^{17}O nuclei ($^{17}\text{O}_2$) respectively. From the hyperfine splitting $A_{\parallel} = 77$ gauss it was shown that the unpaired electron is almost completely localized in the π^* antibonding orbitals of O_2 . It has been suggested that $\text{Pd(II)}-\text{O}_2^-$ adduct was formed. This interpretation was not unique since the authors proposed an alternative interpretation of the *esr* spectrum and the possible formation of $[\text{Pd(II)}]_3-\text{O}_2^{3-}$ oxygen adduct. In this work the zeolite appeared again very suitable material for stabilizing unusual complexes which might have interesting catalytic properties.

Chemistry of transition metal ions in zeolites

A particular point of interest of transition metal ions exchanged zeolites is their catalytic property for reactions such as oligomerization of olefins, carbonylation of methanol, hydroformylation of olefins, *etc.*, generally catalyzed by soluble complexes. During the past years several spectroscopic techniques have been used to investigate the structure of various transition metal ion complexes stabilized within the zeolite framework. We intend to present here some of the recent results obtained in this field. Although extensive works on zeolites exchanged with transition metal ions have been reported in the literature less attention has been paid to zeolites exchanged with group VIII metal ions. Group VIII metal complexes are known for their catalytic properties for oxidation, oligomerization isomerization, hydrogenation, hydroformylation, carbonylation, *etc.* We are of the opinion that interesting materials might be obtained by exchanging zeolites with group VIII salts. Indeed, during the recent past years, works have been published which indicated that zeolites loaded with group VIII metal ions can be used as catalysts for the above reactions.

Although the amount of information so far published in this area is limited the results of these studies should stimulate new investigation on the properties and the specificities of group VIII exchanged zeolites. Our purpose is to describe several results showing the great similitude existing between ruthenium or rhodium exchanged zeolites and their homologous complexes in solution.

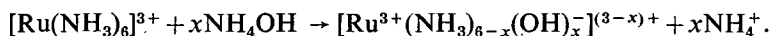
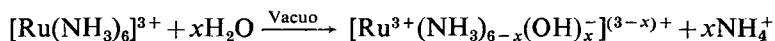
LUNS福德 *et al.* [41] studied by infrared spectroscopy the formation of dinitrogen ruthenium complexes in Y zeolites. $[\text{Ru}(\text{NH}_3)_5\text{NO}]^{3+}$ exchanged zeolite showed *ir* bands at 1927 cm^{-1} assigned to ν_{NO} and at 1365 cm^{-1} due to NH_3 bonded to ruthenium cations. Hydrazine treatment resulted in the formation of characteristic dinitrogen stretching band at 2132 cm^{-1} . Simultaneously *ir* bands at 1885 cm^{-1} due to nitric oxide and at 1460 cm^{-1} attributed to NH_4^+ appeared. These latter two bands were easily removed at 298 K *in vacuo*. It has been suggested the formation of $[\text{Ru}(\text{NH}_3)_5\text{N}_2]^{2+}$ complexes in a similar way to that proposed in solution [42]. $[\text{Ru}(\text{NH}_3)_5\text{N}_2]^{2+}$ exchanged zeolites showed the same *ir* feature as those of $[\text{Ru}(\text{NH}_3)_5\text{NO}]^{3+}$ reduced by hydrazine. However this complex was highly unstable since it decomposed in the infrared beam into $[\text{Ru}^{3+}(\text{NH}_3)_5\text{OH}]^{2+}$ following the reaction



The N_2 ligand may be removed by outgassing and was restored by adding N_2 to the sample, furthermore the formation of NH_3 has been observed. However, experiments performed with $^{15}\text{NO}_2$ ruled out that these ruthenium exchanged zeolites may achieve ammonia synthesis.

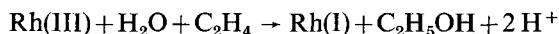
NACCACHE *et al.* [43] have investigated ruthenium(III) ammine exchanged zeolites by *esr* and infrared spectroscopy. An aqueous solution of hexaammine ruthenium(III) chloride was used for ion exchange. A white exchanged zeolite was thus obtained which turned wine-red or purple over a period which depended on the experimental conditions. The sample turned also rapidly wine-red in the infrared beam. The infrared spectrum of the sample degassed at room temperature was characterized by a strong band at 1335 cm^{-1} due to NH_3 ligands and bands at 1460 cm^{-1} and 1930 cm^{-1} attributed to NH_4^+ and NO respectively. These results indicated that $[\text{Ru}(\text{NH}_3)_6]^{3+}$ underwent significant change in the infrared beam. The *esr* spectrum of $[\text{Ru}(\text{NH}_3)_6]^{3+} - \text{Y}$ zeolite showed an anisotropic line shape with $g_{\perp} = 2.20$ and an undetectable $g_{\parallel}$ component. The *esr* spectrum was considerably broadened at 293 K . Ru(III) has a low spin configuration and in an octahedral field such as in $[\text{Ru}(\text{NH}_3)_6]^{3+}$ the ground state is $(t_{2g})^5$. The triply degenerate (t_{2g}) orbitals split into a non-degenerate d_{xy} and a doubly degenerate (d_{xz} , d_{yz}) orbital when the spin-orbit coupling is superimposed to the octahedral crystal field. This spectrum was assigned to $[\text{Ru}(\text{NH}_3)_6]^{3+}$. It was found that $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{3+}$ in zeolite did not show an *esr* spectrum even at 77 K as expected since it is known that the π interaction with chlorine ion is stronger than with ammonia and the d_{xz} , d_{yz} molecular orbitals become less stable than the xz orbital which leaves the unpaired electron in a degenerate d orbital. There was a drastic change in the *esr* spectrum when the sample was outgassed at about 353 K . The sample turned wine-red and it exhibited an *esr* spectrum with g -values at $g_1 = 2.70$, $g_2 = 2.24$, $g_3 = 1.60$. The same *esr* change occurred when $\text{Ru}(\text{NH}_3)_6 - \text{Y}$ sample was contacted at 298 K with NH_4OH . The fact that the *esr* spectrum has 3 g -components indicates that Ru(III) experienced an orthorhombic crystal field thus it was suggested that the former octahedral crystal field in $[\text{Ru}(\text{NH}_3)_6]^{3+}$ was

lowered by ligand change. Since the appearance of the 3 *g*-value *esr* spectrum was always accompanied by the formation of NH_4^+ ions as shown by the appearance of an *ir* band at 1460 cm^{-1} and that basic medium such as NH_4OH accelerated these modifications, it was suggested that NH_3 ligands may be easily replaced by OH^- groups following the reactions:



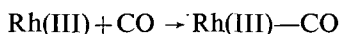
YASHIMA *et al.* [44] recently studied the dimerization of ethylene over nickel or rhodium exchanged Y zeolites. The products formed were mainly 1 and 2-butenes which distribution changes with the reaction time. *Trans*-2-butene formation was favoured with respect to *cis*-2-butene. The catalytic properties of rhodium and nickel exchanged zeolites were modified by changing the activation procedure. The highest activity was achieved when the samples were outgassed at about 673 K. Furthermore H_2 -reduction at moderate temperature ($\sim 573\text{ K}$) changes little the activity of the samples while more severe reduction ($\sim 773\text{ K}$) lowered the catalytic activities. The nature of active sites was studied by poisoning experiments and by *esr* and *ir* spectroscopy. It was found that CO poisoned drastically the active sites for ethylene dimerization. Carbon monoxide interacts with NiY and RhY to give *ir* bands at 2070 , 2030 , 1995 cm^{-1} (Ni) and 2110 , 2045 cm^{-1} (Rh) respectively. From these results they concluded that the active sites were highly dispersed zerovalent nickel and rhodium. Although the present results appear consistent, it is not clear how atomically dispersed rhodium or nickel were formed during thermal treatments *in vacuo* of the samples, and homogeneous analogues are not obvious since in general Rh(I) and Ni(I) are generally cited in the literature. Recent studies on rhodium exchanged zeolites may serve for a better understanding of the nature of active sites formed following various treatments of the samples.

Rh(III) salts are active catalysts for the oxidation of ethylene into acetaldehyde. The first step of this reaction involves the reduction of Rh(III) to Rh(I) following

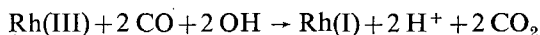


and C_2H_4 coordinates rapidly with Rh(I) to form $\text{Rh(I)}(\text{C}_2\text{H}_4)_2$ complex [45]. NACCACHE *et al.* [46] have investigated the formation of rhodium carbonyl complexes in zeolites. NaY type zeolite was exchanged with an aqueous solution of $[\text{Rh(III)}(\text{NH}_3)_5\text{Cl}]^{2+}$. The sample was examined by XPS. Samples degassed at room temperature showed the $3d_{3/2}$ and $3d_{5/2}$ peaks at 315.7 and 310.8 eV respectively. The binding energy of various Rh(III) salts are close to those found for Rh Y zeolite. Furthermore the Si/Rh atomic ratio derived from ESCA and chemical analysis are about the same. Then one can conclude that the surface composition is identical to the bulk composition. Thus the rhodium complex is homogeneously distributed within the zeolite as one should expect for samples prepared by ion exchange. Thermal treatment at increasing temperature produced a decrease of the Cl/Rh and N/Rh ratios and at about 773 K almost all the NH_3 and chlorine ligands were removed. The interesting feature was that the $3d$ binding energy of Rh in RhY degassed at 773 K was found also at 315.7 and 310.8 eV which suggests that almost all the loaded rhodium remains at $3+$ oxidation state. It was noticed that the Rh $3d_{5/2}$ peak was

broadened, this broadening being attributed to the presence of Rh(I). Nevertheless, these results indicate that evacuation at high temperature leaves almost all the rhodium ions at the 3+ oxidation state in contrast with the proposal of YASHIMA *et al.* [44]. The action of carbon monoxide on RhY was also examined [46]. It was found that partially hydrated RhY reacts at 298 K with CO and gives two sharp infrared bands at 2100 and 2030 cm^{-1} , each *ir* band is further splitted. Dicarboxyl rhodium(I) complexes have two infrared bands in the same region which are attributed to the antisymmetric and symmetric vibration modes of CO. Thus it was suggested that Rh(III) in zeolite is reduced to Rh(I) with the concomitant formation of Rh(I)(CO)₂ complex. This was further proved by ESCA measurements which showed that the new rhodium carbonyl complex formed within the zeolite presented the 3d5/2 binding energy at 308.1 eV which is very close to 308.3 eV found for zeolite supported [Rh(I)(CO)₂Cl]₂. RhY dehydrated *in vacuo* at 773 K showed the same feature, however it was found that water adsorption accelerated the reduction of Rh(III) by CO. Furthermore CO adsorption and *ir* measurements when performed at 77 K gave *ir* bands at 2172 and 2138 cm^{-1} which slowly decreased as the temperature increased and simultaneously the *ir* bands at 2100 and 2030 cm^{-1} developed. Thus it was concluded that the reduction of Rh(III) by CO is an activated process and at 77 K only Rh(III)—CO complex was formed. The mechanism suggested for the reduction of Rh(III) by CO is



Rh(III)—CO complex decomposed by water or hydroxyl groups following



and Rh(I) forms readily in the presence of an excess of CO the dicarbonyl Rh(I) complex entrapped in the zeolite. The evolved CO₂ was detected by an *ir* band near 2350 cm^{-1} . The action of carbon monoxide on hydrated Rh(III)Y zeolite appears similar to the reactions occurring in solution [47]. The reductive carbonylation reaction to give Rh(I)(CO)₂ may be an interesting precursor in several reactions. Indeed it has been shown by CHRISTENSEN and SCURRELL [48] that Rh(III) exchanged X zeolite is active and selective for the carbonylation of methanol, methyl iodide was used as promoter. The selectivity in acetic acid and methyl acetate was 90%. Ethanol carbonylation was also performed however the selectivity decreased at high temperature, this was associated with the conversion of ethanol into ethylene and diethylether. It appeared that rhodium exchanged 13 X zeolites are more active than other heterogenized rhodium catalysts. This work confirms the feasibility of using group VII metal ion exchanged zeolites as heterogenized homogeneous catalysts. However in the case of RhY, the structure of the embedded rhodium complex efficient for methanol carbonylation is not yet well defined. In general the methanol carbonylation is catalyzed by anionic rhodium complexes such as Rh(CO)₂I₂⁻ while in zeolite cationic complexes were found.

Rhodium carbonyl clusters entrapped in zeolites have also been studied recently. Infrared spectroscopy [49] has shown that when Rh(III) exchanged Y zeolite is treated at 403 K under a pressure of 80 atm of CO:H₂ mixture the sample turned red and showed CO stretching vibrations at 2095 (vs) 2080 (sh) 2060 (w) and 1765 (s) cm^{-1} . It was suggested the formation of Rh₄(CO)₁₂ or Rh₆(CO)₁₆ clusters within the zeolite

cavities. Similar conclusions were reached by GELIN *et al.* [50]. Zeolite supported $\text{Rh}_6(\text{CO})_{16}$ was prepared by sublimation *in vacuo* of $\text{Rh}_6(\text{CO})_{16}$ on dehydrated NaY zeolite. The sample has *ir* bands near 2090(s) 2074(sh) 2021(w) and 1830(w) which are slightly shifted to higher frequencies in comparison with those found for unsupported $\text{Rh}_6(\text{CO})_{16}$. CO ligand was removed by outgassing the sample at about 473 K or by reaction with oxygen at 373 K with the concomitant formation of CO_2 . The decarbonylated sample heated at 373 K under 100 torr of CO showed two strong *ir* bands at 2098 and 1761 cm^{-1} which were attributed to linear and bridged CO. It was suggested that $\text{Rh}_6(\text{CO})_{16}$ first was supported on the external surface of the zeolite since the cluster is too large to enter the cavities through the 8 Å pores. Upon decarbonylation fragmentation of the cluster occurred, and the Rh fragments migrate in the zeolite framework and are stabilized toward aggregation. These Rh fragments reacted with CO at 373 K to form $\text{Rh}_x(\text{CO})_y$ clusters containing a limited amount of rhodium atoms. In contrast rhodium metal supported on zeolite prepared by H_2 -reduction of Rh(III) exchanged Y zeolite behaves differently. Electron microscopy has shown that the particle size was in the 5–10 Å range [51]. CO adsorbed at 298 K on this sample gave two *ir* bands near 2100 and 2035 cm^{-1} which were assigned to dicarbonyl rhodium species $\text{Rh}^{+\delta}(\text{CO})_2$, a band near 2060 cm^{-1} attributed to linear by bonded CO on rhodium metal and bands at frequencies lower than 2000 cm^{-1} due to multibonded CO. The need of higher CO pressures in the case of rhodium exchanged zeolite to form rhodium cluster as shown in [49] as compared with $\text{Rh}_6(\text{CO})_{16}$ supported on zeolite [50] is probably due to the formation, by H_2 -reduction, of larger rhodium particles, which increases the cohesion of Rh–Rh bonds. The zeolite entrapped rhodium carbonyl clusters were found active and selective for hydroformylation of olefins [49]. 1-hexene was converted into 1-heptanol, 2-methylhexanal and 1-ethylpentanal.

In conclusion these few examples have shown clearly the possibility of conducting with transition metal ions exchanged zeolites, reactions which are generally performed with homogeneous catalysts.

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ZEOLITES IN INDUSTRIAL CATALYSIS

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A) Unifying Principles in Zeolite Catalysis

1. Introduction

The "zeolitic surface" within zeolite crystals is different from ordinary crystal surfaces. It is a real surface in a physical sense because adsorbed molecules are in direct contact with it. However, it is also part of a crystal fully surrounded by the crystal lattice. Consequently, both the "surface" atoms and the molecules adsorbed within the zeolite crystal are subject to the zeolite crystal field. Indeed, the zeolitic surface has properties of both the ordinary crystal surface and the crystal lattice. Accordingly, a substantial part of zeolite chemistry resembles phenomena found in the solid state. To emphasize the influence of the zeolite crystal lattice upon the "zeolitic surface" it has been suggested that zeolites are strong solid electrolytes.

In this discussion we shall attempt to relate the unusual chemistry of zeolites with their unusual catalytic behavior based on some unifying physical principles which control both phenomena. It is proposed that the strong polar environment of the zeolitic surface caused by both the zeolite cations and the crystal field of the surrounding anionic crystal lattice results in a strong polarizing interaction between the zeolite crystal and adsorbed molecules. The results of this electrolytic behavior are: 1. the stabilization of ionic species with the resulting ionizing influence upon adsorbed molecules and reaction intermediates, and 2. an unusually high concentration of the reactants in the zeolite crystal with a resulting enhancement of the rates of bimolecular reaction steps over unimolecular reaction steps.

2. Fundamentals

The principle features of zeolite catalysts are their molecular sieve property and their outstanding activity as acidic catalysts. The molecular sieve selectivity for size and shape of the reactant molecule results from the size and shape of the pores and cavities within the zeolite crystal. However, some question about the selectivity of the molecular sieve effect still remains in the cracking of large molecules such as occurs in the cracking of heavy feedstocks: the zeolite catalyst efficiently cracks mole-

cules both smaller and larger than the crystal aperture. Here the precise nature of the zeolite crystal surface as well as a more detailed knowledge about the kinetics of the cracking process for both small and large molecules will be necessary to define the limitations of shape selectivity.

The acidic character of zeolites containing OH groups attached to framework cations (Si, Al) has been characterized by numerous investigators. There is good agreement that these OH groups are very polar and possess strong proton donating ability. There are indications suggesting that the nature of the zeolite (Si/Al ratio and structure) has strong influence upon OH groups acidity. It has been suggested that the influence of the zeolite framework and overall structure is related to the crystal field of the crystal lattice [1, 2].

What physical principle is responsible for the unusually high acidity, exceeding that of all other known oxides? The search for such a principle is greatly facilitated by the large body of surface chemistry and catalytic properties reported for zeolites. With this information in hand, it is of interest to look for unifying principles which are consistent with catalytic as well as chemical behavior.

Since the intracrystalline zeolitic surface is surrounded by the crystal lattice, it seems reasonable to infer that the special behavior of zeolites is inherent in the zeolite structure itself. Among the various potential causes for the special behavior, it seems reasonable to examine whether the chemical and catalytic behavior of zeolites is mainly influenced by thermodynamics, namely by the tendency to minimize crystal lattice energy. Of course, here one must consider not only the crystal lattice but the occluded molecules, the reactants, as well.

Unfortunately, the lattice energies of zeolite crystals are not known. Their calculation with any degree of reliability is impossible without knowing the covalent and ionic character of the linkages between lattice atoms. Several observations, especially the preference of zeolite cations for water over framework oxygen indicate that the bond between framework cations and oxygen is strongly covalent. Nevertheless, a certain amount of ionic character must exist, and a corresponding crystal field must pervade the whole porous crystal. Adsorbed molecules, especially the polar or strongly polarizable ones, will be polarized by the zeolite and they will exert a similar effect on the zeolite crystal as well. The overall interaction between zeolite and adsorbate must tend to minimize the free energy of the zeolite-adsorbate system, and therefore, the simplest way to forecast thermodynamically favored reactions in zeolites is just to evaluate their effect on the energy of the zeolite lattice.

Inspection of the ionic lattice energy equation shows that with regular ionic crystals the lattice energy is enhanced by placing more ion pairs and ions of higher valence within the same crystal volume. According to this simple principle the *occlusion of added ionic matter* into the porous zeolite lattice *should generally lower the lattice energy and increase the thermodynamic stability of the overall system*. Of course, the occluded ionic matter may affect the zeolite structure and symmetry, ultimately affecting the Madelung constant or other parameters and thus rendering the interaction between zeolite and occluded ionic matter complicated and difficult to analyze. In spite of these limitations, the study of interactions between zeolites and occluded ionic matter is a convenient technique to assess the role of the zeolite lattice upon zeolite chemistry and catalysis, and generally as a solid electrolyte.

In order to evaluate this concept we shall review in the next two sections some relevant data in zeolite chemistry and catalysis.

3. Chemical Properties of Zeolites

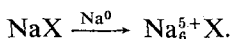
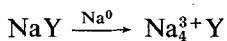
It was suggested in the previous section that the porous zeolite lattice must have high affinity for occluded ionic matter. This ionic matter may consist of regular ionic compounds such as salts, or it may consist of atoms or molecules which are not ionic outside the zeolite but which become ionized only upon occlusion into the zeolite crystal. There are many examples of both types of occlusion.

a) *The occlusion of salts* has been described in several publications [1]. The experimental evidence on zeolites A, X and Y clearly shows that ionic compounds such as salts readily penetrate the zeolite crystal, filling up the available space in the large cavities. Salts, especially salts of univalent anions, can even penetrate the sodalite cages in zeolites A and Y. This is surprising because the O_6 -ring port of the sodalite cage is only about $\sim 2.4 \text{ \AA}$ wide, much smaller than any anion. It was found that the occlusion of salts into sodalite cages requires high temperatures, presumably to provide the high activation energy needed for enlarging the O_6 -ring port, probably by the temporary cleavage of $O-Al$ or $O-Si$ bonds. Interestingly, halide salts as well as salts of large complex anions such as ClO_3^- and NO_3^- can be occluded in the sodalite cage.

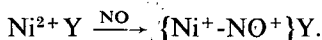
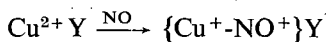
From the point of view of our discussion on fundamentals the most important aspect of salt occlusion is the stability of the zeolite-salt occlusion compound. It was reported that in every salt occlusion experiment both Y zeolite and the occluded salt were greatly stabilized, well beyond the decomposition temperatures of the zeolite and of guest salts. It was also found that the guest salt can not be removed from the host Y crystal even by steaming at 700°C [2]. Thus, the zeolite lattice is stabilized by the occluded salt and vice versa. Consequently, the salt occlusion phenomena are consistent with the principal discussed earlier.

b) *Ionization of occluded atoms and molecules.* The most frequently observed ionization phenomenon in zeolites is the ionization of water through cation hydrolysis. This is a particularly important reaction for zeolite catalysts because it generates acidic OH groups attached to framework cations which are directly responsible for the acid behavior of multivalent cation zeolites. While the hydrolysis has been well demonstrated by X-ray and IR spectroscopy as well as other techniques, no specific data are available which can be used for quantitative evaluation of the contribution of the zeolite lattice to cation hydrolysis.

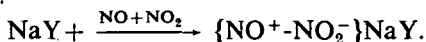
The most revealing information on ionization effects in the zeolite lattice comes from the occlusion of alkali metals and certain gas molecules. It was reported that alkali metals readily reduce both alkali X and alkali Y zeolites [1] and the sodium ions of the host crystal capture the electron from the occluded alkali atoms forming symmetrical Na_4^{3+} or Na_6^{5+} centers



It was also reported that certain transition metal zeolites readily ionize adsorbed NO radicals forming electron transfer complexes with the zeolite cation [1].



Another interesting ionization phenomenon is observed on the simultaneous interaction of both NO and NO₂ radicals in zeolites. Here, both radicals become ionized, presumably forming a salt-like complex in the zeolite [1].



From the point of view of our discussion the most important aspect of these redox reactions is that they are all highly endothermic in the gas phase without the stabilizing effect of the zeolite. For example, the formation of the NO⁺ and NO₂⁻ species from NO and NO₂ radicals is endothermic by about 5.5 eV (~126 kcal/mol), not considering coulombic interaction between the products. In spite of this, this reaction readily occurs on NaY at moderate temperatures. In the case of interaction between sodium metal and NaY zeolite the highly endothermic ionization of sodium metal (I. P. = 5.14 eV ~ 118 kcal/mol) is readily accomplished at 300°C, with a Na₄³⁺ center formed in each large cage.

These examples demonstrate the high affinity of zeolites for ionic matter, and they also provide semi-quantitative information on the size of the contribution of zeolites to the ionization of occluded species. It should be noted that in the cases described above the ionization processes readily occurred on Na-zeolite or cation exchanged zeolites, and thus, the ionization phenomena did not require the presence of acidic OH groups.

4. Catalytic behavior

In the context of the large chemical effects of zeolites upon occluded molecules as shown in the previous section, it is relevant to examine to what extent these effects are operative in catalysis. Since most of the chemistry discussed here was carried out on alkali-cation zeolites we shall first review the reactions of hydrocarbons over such zeolites.

a) *The influence of alkali zeolites (K-Y) on the cracking of hydrocarbons* was investigated [3] with hexanes as reactants. For all the hexanes the zeolite gave conversion levels 2 to 5 times as high as in the empty tube. The product composition obtained from *n*-hexane and its isomers over K-Y was markedly different both from that typical of acidic zeolites and that obtained at the same reaction conditions in an empty reactor (Table I).

An analysis of the reaction mechanism based on product distributions obtained from all the hexane isomers showed that the thermal, free radical mechanism still occurred but with specific changes in the relative rates of the chain steps. The K-Y does not change the selectivity of alkyl radicals either in the choice between competitive β-scission steps or among competitive H atom abstraction steps when positionally different choices are available. In contrast, the K-Y has a very large effect upon the ratio of rates of H atom abstraction to β-scission. Mechanistic analysis of the cracked products obtained from the hexane isomers shows that over K-Y the ratio $\frac{\text{rate of H-abstraction}}{\text{rate of } \beta\text{-scission}}$ is increased for alkyl free radicals by a factor of 6 to 9. This effect accounts for the large difference in product distribution between the non-catalysed and the K-Y "catalysed" reactions [3].

Table I

Products from pyrolysis and KY-catalyzed^a cracking at 500°
(mol/100 mol converted)

	n-hexane		2-methylpentane		3-methylpentane	
	thermal	KY	thermal	KY	thermal	KY
Hydrogen	2.8	3.1	24.4	4.3	5.6	3.9
Methane	50.3	23.5	27.9	21.7	63.5	57.3
Ethylene	56.5	26.0	11.5	6.5	23.7	23.0
Ethane	37.7	37.4	42.2	43.5	44.2	44.3
Propylene	55.7	58.5	57.8	44.2	20.5	15.7
Propane	10.7	38.2	19.2	36.4	—	0.5
1-butene	31.3	12.0	—	—	7.6	11.2
2-butene	—	19.6	—	—	34.2	34.8
Isobutene	—	—	40.5	40.1	—	—
Isobutane	—	—	0.2	1.6	—	—
1-pentene	7.3	1.9	1.0	2.3	—	<i>b</i>
2-pentene	—	4.7	8.5	8.4	13.3	6.4
2-methyl-1-butene	—	—	—	—	20.9	<i>b</i>
3-methyl-1-butene	—	—	4.5	1.6	—	1.0
2-methyl-2-butene	—	—	—	1.7	—	19.5

^a=rate enhancements ~ 5-fold

Speculating over the reason why zeolites enhanced the rate of H-abstraction over β -scission, it was considered that H-abstraction is a bimolecular process step whose rate is strongly influenced by the concentration of the reacting substrate whereas β -scission, being a unimolecular process, is unaffected by changes in reactant concentration. Accordingly, the effect of K-Y could be largely a matter of increasing the reactant concentration within the zeolite cavities relative to the surrounding gas phase [4].

The concentration, or adsorption, of hydrocarbons within the zeolite crystals is, of course, well documented in adsorption studies carried out at low temperatures. For the temperature range used in the hexane cracking study the hexane loading on K-Y at 500°C was estimated from the reported Arrhenius plot of loading on NaX at temperatures up to 300°C. The estimated hexane loading at 500°C is substantial and is consistent with the reactant concentration suggested by the mechanistic analysis [4]. Thus, it is concluded that zeolites concentrate hydrocarbon reactants to a large extent within the zeolite crystal, and that this concentration effect is responsible for a substantial shift in product formation, specifically by enhancing the rate of bimolecular reaction steps.

From the total absence of hexane skeletal isomerization during these cracking experiments over K-Y, the absence of ionic (carbenium ion) cracking intermediates can be inferred. Hence, OH group free K-Y is not capable of ionizing either hexane or the radicals formed upon its fragmentation. One has to recognize, however, that these ionization processes in the gas phase require very high energy. Thus, ionization of a *tert.*-C—H bond to form a *tert.* carbenium ion and hydride ion is endothermic by 240—250 kcal/mol while the ionization potential of a *tert.* radical is ~ 170 kcal/mol.

b) *Hydrocarbon cracking over H-zeolites* shows markedly different behavior from that obtained over alkali cation zeolites. Activity is further increased, skeletal

isomerization becomes dominant, and the product distribution is generally consistent with what occurring with other strong Brønsted acid catalysts, (Table II) for which a carbenium ion rather than free radical mechanism is generally accepted.

Catalysis with H zeolites does, however, show certain special, new features not found with other acid catalysts. Zeolites show greater selectivity to gasoline than

Table II

Products from cracking n-hexane

Catalyst — 93% exchanged NH_4Y activated at 550°

Cracking temperature — 350°

Conversion — 11% isomerization
7% cracking

Isomerized products, mole %

2-methylpentane	49.5
3-methylpentane	34.9
2,3-dimethylbutane	12.3
2,2-dimethylbutane	3.3

Cracked products, mole %

Methane	<0.1
Ethane	0.8
Ethylene	
Propane	28.7
Propylene	0.7
iso-butane	31.8
n-butane	11.4
Butenes	<0.2
iso-pentane	25.1
n-pentane	5.5
Pentenes	<0.2
Benzene	0.4
Toluene	2.0
Xylenes	1.6
$\text{C}_6\text{H}_5\text{C}_3\text{H}_7$	1.1

Tung and McInich (Continental oil)

does silica-alumina when cracking gas oil. Different gasoline compositions are also obtained on cracking gas oil over H-Y and amorphous silica-alumina (Table III). Mechanistic suggestions by WEISZ [6] regarding these inter-related differences in gasoline yield and composition have been made to the effect that there is a more efficient hydrogen redistribution between hydrocarbon molecules over the zeolite

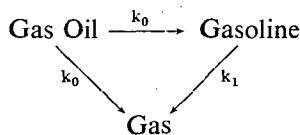
Table III

*Gasoline Composition as a Function of Catalyst**

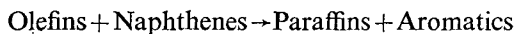
Catalyst	Composition (%)			
	P(araffin)	O(lefins)	N(aphthene)	A(romatic)
Silica-alumina	13	17	41	29
Zeolite	23	5	23	49
Difference	+10	-12	-18	+20

* Data from Ref. [6]

catalyst as shown below. According to the gasoline selectivity model of WEEKMAN and NACE [5] the primary cracking (k_0) produces gasoline and gas whereas while the secondary cracking (k_1) produces only gas and thus lowers gasoline yield. The differences in product



distribution between zeolite and silica-alumina (Table III) can be quantitatively explained by the greater occurrence of the following overall hydrogen redistribution reaction in the zeolite:



WEISZ, therefore, suggested [6] that this reaction effectively reduces k_1 in the gas oil cracking model by converting the initially produced olefins and naphthenes to more refractory paraffins and aromatics before they crack further to gas. The high efficiency of the conversion of olefins + naphthenes to paraffins and aromatics may be explained by the superior hydrogen redistribution *via* hydride ion shift between carbenium ions and neutral hydrocarbons over the zeolite catalyst.

Although distinctly different mechanisms are thus involved over K-Y and H-Y, the following parallelism can be drawn. During the free-radical mechanism, enhanced hydrogen atom abstraction compared with β -scission alters the product distribution over K-Y from that observed thermally. During the carbenium ion mechanism, enhanced hydride ion abstraction compared with β -scission alters the product distribution over H-Y from that observed over silica-alumina. *The common feature of both H-Y and K-Y is then that they favor bimolecular reaction (hydrogen transfer) steps over the unimolecular reaction (fragmentation) steps. This tendency in both cases may be interpreted on the same basis: zeolites concentrate hydrocarbon reactants to a larger extent than other catalysts.* This mechanistic conclusion is confirmed by adsorption measurements showing that toluene is desorbed at a significantly higher temperature from H-Y than from amorphous silica-alumina [7].

5. Conclusion

The unusual chemical environment of the zeolitic surface and especially the crystal field of the surrounding crystal lattice render it a strong solid electrolyte. Zeolites interact strongly with polar and polarizable atoms and molecules resulting in unusually strong adsorption, or even ionization of adsorbed species.

The adsorption properties of zeolites well demonstrate the strong electrostatic interaction between zeolites and occluded molecules. The redox chemistry of zeolites testifies that the interaction often goes beyond physical interaction and even to the extent of ionization of the adsorbed molecules. Reactions resulting in the ionization of adsorbed molecules which would otherwise be endothermic by as much as

~ 126 kcal/mol in the gas phase readily proceed at moderate temperatures because of the "solvation" effect of the zeolite on the ionic products.

Mechanistic studies show that ionization of hexanes or their reaction intermediates does not occur on *alkali zeolites*, and that the cracking of hydrocarbons proceeds by a radical mechanism. It is worth noting that the ionization energy of hexanes and their radical fragments is $\cong 170$ kcal/mol, significantly higher than the free energy change of redox reactions readily occurring in zeolites. The radical mechanism over alkali zeolites shows distinct differences in product distribution from the non-catalyzed thermal process. These differences are explained on the basis that zeolites concentrate the reactants in the zeolite, resulting in a strong enhancement of bimolecular reaction steps over unimolecular reactions steps. Thus, zeolites generate a substantially higher reactant concentration relative to the gas phase outside the zeolite crystal.

In the cracking of hydrocarbons over H-Y zeolite, an unusually strong Brønsted acid activity is observed. The product distribution indicates great enhancement of H redistribution, presumably through hydride ion shifts. Here again, as with K-Y, bimolecular reaction steps (H redistribution) are favored over unimolecular reaction steps (fragmentation). The cause of this phenomenon is that zeolites concentrate the reactants in the zeolite pore-and-cavity system. Enhanced concentration of reactants on catalyst surfaces is, of course, characteristic of any heterogeneous catalyst. However, from the mechanistic evidence reviewed here it appears that this concentration effect is greater with zeolites than with other, amorphous acidic catalysts. In respect to the strong acidity of H-zeolites the acidic nature of structural OH groups has been well established by IR spectroscopy and other techniques. In addition to their OH acidity we expect that zeolites exert a strong stabilizing influence on ionic hydrocarbon reaction intermediates (carbenium ions), similar to that shown in their redox reactions with other adsorbed atoms and molecules.

B) Applications in industrial catalysis

1. Established processes employing zeolite catalysts

At present, the large-scale, well-established industrial processes that utilize zeolite-based catalysts are catalytic cracking, certain hydrocracking processes, and paraffin isomerization. It is the purpose of this section to highlight the important aspects of these processes and to provide references to more detailed discussions of them.

a) *Catalytic cracking.* The addition of relatively small amounts of hydrothermally stable acidic zeolites to conventional cracking catalyst formulations has been found to result in significant increases in both the yield and quality of the products from fluidized bed and moving bed cracking reactors [8]. Since catalytic cracking is so extensively practiced in petroleum refining, it is at present the largest-scale industrial process employing zeolite catalysts [9]. A recent estimate indicated that about 22,000 tons of synthetic zeolite, principally zeolite Y but also some zeolite X, is produced annually to satisfy world-wide requirements of 150,000 tons per year of cracking catalysts [9]. In general, the rare-earth exchanged form of the zeolites are used, but some catalysts based on NH_4 -Y have been also marketed. At present, all commercial catalysts comprise 5–40% zeolite dispersed in a matrix of synthetic silica-alumina,

semi-synthetic clay-derived gel, or natural clay [10]. It should be noted that such composites can be prepared either by blending a synthetic zeolite with a binder, or by chemical treatments of suitable clays so as to produce the zeolite component *in situ*. There exists no consensus among U. S. refinery operators as to whether one of the types of catalysts is of inherent superiority.

The advantages associated with zeolite-promoted cracking catalysts accrue from high-rates of intermolecular hydrogen transfer coupled with extremely high intrinsic cracking activity [11, 12], (see previous chapter). Data presented by WEISZ *et al.* (Table III) exemplify the effects of hydrogen transfer activity and account for the observations that zeolite catalysts increase yields of light cycle oil, increase the yield and octane of the gasoline product fraction, and decrease the production of coke. The high cracking rates found with zeolite catalysts result in greatly reduced catalyst-oil contact times for given conversion levels, thus leading to further increases in liquid product yields, plus additional advantages such as increased tolerance to poisons, and greater operating flexibility. The relationships between catalyst properties, feedstock composition, and reactor operating conditions are very complex, and have been reviewed recently in several articles that also describe additional benefits of the use of zeolite-promoted cracking catalysts [9, 10].

b) *Hydrocracking for fuels production.* Hydrocracking, catalytic cracking in the presence of hydrogen and a dual function catalyst possessing both cracking and hydrogenation-dehydrogenation activity, is at present the second largest use for zeolite-containing catalysts [13]. In general, such catalysts consist of an acidic, hydrothermally stable, large pore zeolite loaded with a small amount of a noble metal, or admixed with a relatively large amount of an active hydrogenation system such as $\text{NiO} + \text{MoO}_3$ [14, 15].

While several proprietary hydrocracking technologies are in use, the Unicracking-JHC process, in which zeolite catalysts are used exclusively, exemplifies the value of such catalysts in broadening the range of feedstocks that can be handled and in simplifying hydrocracker design and operation [13, 16, 17].

The most elaborate and versatile Unicracking process scheme is the two-stage configuration shown in Figure 1. Feedstock is mixed with hydrogen and admitted to reactor *R-1*, a conventional hydrotreater in which it is substantially freed of nitrogen and sulfur. The product then enters the first stage Unicracker, *R-2*, in which it is hydrocracked, typically at a per-pass conversion of 40–70%. It is especially significant that the zeolite catalysts that have been developed for the Unicracking process can operate stably and efficiently in the presence of hydrogen sulfide and ammonia, thus separation of these substances from the *R-2* feed is unnecessary.

In single-stage Unicracking, the product of *R-2* is treated in liquid-gas separators and fractionated. Additional flexibility in terms of processing refractory feed-

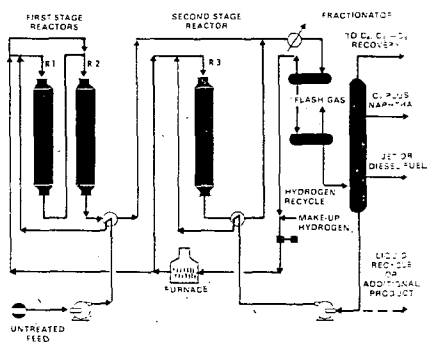


Figure 1
A Two-Stage Unicracking — JHC Plant

stocks is obtained through the use of the two-stage process that is illustrated, in which the fractionator bottoms are recycled through second-stage reactor $R-3$. The recycled gas which is mixed with the $R-3$ feed is essentially ammonia-free, thus the reactor can be operated efficiently at comparatively low temperatures and pressures while maintaining conversion at 50–80% per pass.

In hydrocracking, as with all multi-purpose refinery processes, the relationships between feedstock properties, catalyst type, operating conditions, and product yield and character, are very complex. A number of detailed reviews of these matters have appeared recently [16–19] but it should be noted in general that zeolite catalyzed hydrocracking can efficiently convert a very wide variety of feedstocks, some of which cannot be processed by other techniques, into a range of fuels including LPG, medium octane unleaded motor gasoline, and jet, diesel, and heating oils, or into feedstocks suitable for catalytic cracking, catalytic reforming, or petrochemical manufacture. It should also be noted that zeolite hydrocracking catalysts are now noted for permitting long (2–6 year) periods of highly efficient reactor operation at moderate conditions, and that following such service, many of the catalysts are susceptible to treatments that completely restore their original levels of activity [20].

In considering new applications for hydrocracking, it has been suggested that the process may be used in the future as a means of preparing catalytic cracker feedstocks from special types of crude oils and residua [18].

c) *Special purpose hydrocracking using shape-selective catalysts.* Two special types of hydrocracking processes in which the shape-selectivity of certain zeolite molecular sieves is exploited are in current use.

The Selectoforming process of the Mobil Corporation employs a metal-loaded zeolite of the offretite-erionite variety to selectively hydrocrack the normal-paraffin components of catalytic reformate [13, 21]. The process thus allows either an increase in reformate octane at a particular operating severity, or an increase in reformate yield at a specified octane. The former is the usual mode of operation, with plant experience indicating a typical gain of 2–5 octane numbers.

A second type of shape-selective hydrocracking process is catalytic dewaxing, which has been commercialized by several companies, and which typically employs as a catalyst a metal-loaded tubular pore zeolite such as mordenite [21]. Using such catalyst, long chain normal paraffins, waxes, can be more-or-less selectively hydrocracked to propane, isobutane, and isopentane. Uses for the processes include upgrading of diesel and heating oils, conversion of low-sulfur, waxy crudes directly to fuel oils, and general improvement of lubricating oils.

d) *Paraffin isomerization.* Other than catalytic cracking and hydrocracking, the only well-established commercial process which employs zeolite catalysts at present is the isomerization of normal paraffins into higher octane, branched isomers. The catalyst for the well known "Hysomer" process of the Shell Oil Company is dual functional, and consists of a highly acidic, large pore zeolite loaded with a small amount of a noble metal hydrogenation component [13, 22].

In considering the "Hysomer" process, it is essential to note that the catalyst possesses the hydrogenation-dehydrogenation and acid functions which characterize hydrocracking catalysts. However, since hydrocracking of the "Hysomer" feedstock, which is usually a light, straight run naphtha containing principally pentanes and hexanes, is not desired because it represents a direct reduction of gasoline yield, the process operating conditions are more stringently defined than those for hydro-

cracking. In general, reaction conditions are adjusted to allow the lowest possible reactor temperature consistent with economical production rates, and the lowest hydrogen pressure consistent with economical run lengths. By doing this, yields of the highest octane highly branched isomers are maximized, and hydrocracking is minimized.

In commercial practice, use of the Hysomer process has been found to produce an increase of about 12 octane numbers (RON clear) in suitable naphtha feedstocks. It is interesting to note, however, that the process can be operated in conjunction with the Union Carbide Corporation's "Isosiv" molecular sieve adsorbent procedure for the separation of normal and iso-paraffins in such a manner that complete isomerization of a C_5/C_6 stream can be achieved. The combined process is tradenamed TIP (Total Isomerization Process), and results in octane number increases of about 20 rather than the 12 found with a once-through "Hysomer" treatment [22].

2. Recent developments in zeolite catalysis

In the 1960's, zeolite synthesis systems which included organic cations such as quaternary ammonium species in addition to the traditional alkali metal ions began to receive much attention. Such work continues, and has resulted in the discovery of a number of new families of molecular sieves. One of the groups that was developed at Mobil Corporation laboratories includes the zeolites ZSM-5, -12, and -21, and is characterized by an unusual pore structure, the openings of which are 10-member rings, and highly siliceous frameworks, SiO_2/Al_2O_3 of 20–100 [23–25]. Another group of unusual molecular sieves was recently developed at Union Carbide Corporation laboratories, and includes the large pore silicalite, the first example of a pure silica molecular sieve [26].

The members of the ZSM-5 family of zeolites have been used to prepare some unique catalysts for a variety of processes. In this section, the unusual features of a number of the catalysts will be described.

a) *Xylene Isomerization*. Among the processes for which ZSM-5 based catalysts offer unique advantages, those for the treatment of C_8 aromatics streams for petrochemical use are the closest to becoming firmly established commercially.

The objective of C_8 aromatics processing is the conversion of the usual four component (ethylbenzene and the three xylenes) feedstream into an isomerically pure xylene. Although the bulk of current demand is for the *para* material for polyester fiber manufacture, significant markets for the other isomers also exist [26]. In the execution of such processing, the primary problem is disposing of the 8–40% ethylbenzene that is present in the usually available feedstocks, a task that is complicated by the closeness of the boiling points of ethylbenzene and *p*-xylene. A major secondary facet of the processing is reestablishment of equilibrium concentrations of the xylenes present in the isomer separation train raffinate so as to maximize the yield of the desired isomer [12]. Some schemes which have been devised to achieve these goals include quantitative separation of the ethylbenzene in the feedstock *via* "superfractionation" followed by isomerization and separation of the resulting mixture of xylenes, and use of the Octafining or Isomar processes, vapor-phase hydroisomerization procedures which not only isomerize xylenes, but also convert a portion



of any ethylbenzene present into xylenes, and thus require that only a partial separation of the ethylbenzene in the initial feed be effected.

In what is apparently the most readily adopted C_8 aromatics process based on ZSM-5 and related zeolites, the catalyst is an acid form of the sieve to which is added a group VIII metal hydrogenation-dehydrogenation component [28]. Such catalysts can be used in existing Octafining plants in place of the Pt/silica-alumina ones that were originally developed for the process. Their advantages of higher throughput due to the ability to operate at low H_2 /hydrocarbon ratios, and longer run life between regenerations, can thus be obtained without capital expenditure.

Acidic ZSM-5 type derivatives can be used in other ways to process C_8 aromatics streams, although neither of the techniques can be easily retrofitted to "Octafining" plants. It has been stated, for example, that H-ZSM-5 can, under carefully selected operating conditions, equilibrate the concentrations of xylenes in a four-component C_8 mixture, while causing ethylbenzene to disproportionate about 125 times faster than xylene [29]. Because both benzene and diethylbenzene can be readily separated from the C_8 fraction, with suitable engineering, this liquid-phase selective disproportionation method could be used in processing a mixed C_8 stream, although very little flexibility in operating conditions would be possible.

It has also been stated that under high temperature, vapor-phase conditions using an acid ZSM-5 catalyst in the absence of hydrogen, the xylenes present are merely isomerized to equilibrium whereas the ethylbenzene is partially converted into benzene in such a manner that there is an increase in the number of moles of aromatics present [30]. This unusual reaction could, as in the previous case, form the basis of a C_8 aromatics processing technology.

The mechanism of the conversion of ethylbenzene into benzene as described above is now unknown, but the discoverers speculate that ethylene cracked from the ethylbenzene is "reassembled" into benzene. Another totally unrelated process in which this type of reaction is exploited will be discussed later.

b) *Ethylbenzene Synthesis.* The synthesis of ethylbenzene for styrene production is another process in which ZSM-5 type catalysts are beginning to attract significant amounts of attention. While some ethylbenzene is obtained directly from petroleum, the majority, about 90%, is synthesized. The alkylation of benzene with high purity ethylene is generally accomplished in liquid phase slurry reactors employing promoted $AlCl_3$ catalysts [31]. The chemical can also be prepared by the vapor phase reaction of benzene with a dilute ethylene-containing feedstock obtained by partial purification of catalytic cracker off gases [32]. The catalyst for this process, which is tradenamed Alkar, is BF_3 supported on alumina.

In slurry-type ethylbenzene processes, catalyst handling including disposal of spent aluminum chloride is troublesome, and in both the slurry and solid-catalyzed processes, the catalysts are quite corrosive and necessitate special feed pretreatments and the use of expensive materials of construction. It is these problems that are alleviated through use of the new zeolite catalyst.

It has been reported that a reactor loaded with an acidic ZSM-5 catalyst has been employed successfully to produce ethylbenzene on a semiworks scale, about 4×10^7 lbs./year, using both pure and dilute ethylene sources [33–35]. In both cases, the alkylation was accomplished, somewhat surprisingly, under vapor-phase conditions: about 800°F, 200–300 psig, 300–400 lbs. benzene/lb. cat-hr., and a benzene: ethylene feed ratio of about 30. With both types of ethylene sources, raw material

efficiency in ethylbenzene production exceeded 99%, and heat recovery efficiency was high due to the high temperature at which the reactor was operated. It was noted, however, that the catalyst deactivated moderately rapidly, and required, biweekly oxidative regeneration [34, 35].

c) *The methanol-to-gasoline process.* In a recent paper, [36] workers at Mobil Corporation laboratories described the conversion of methanol and some other oxygenated organic compounds to hydrocarbons using an acidic ZSM-5 catalyst. In the case of methanol, the highly exothermic reaction sequence included the formation of dimethyl ether, and was quite selective in producing an aromatics-rich, gasoline-range mixture of hydrocarbons which was free of oxygenates. It was proposed that the highly charged zeolite framework induced carbene formation, and that these species reacted with each other, methanol or dimethyl ether to form C_2 — C_5 olefins, which were subsequently converted to the final product. The hydrocarbon product contained no compounds with more than 10 carbon atoms, and this, in conjunction with the lower than predicted concentrations of certain multiply alkylated benzenes, was construed as evidence of some shape selectivity due to the moderate pore size of the catalyst.

The interesting transformation described above forms the basis of a pilot-scale methanol-to-gasoline plant that has been developed by Mobil Corporation under a contract with the U. S. Department of Energy [37—39]. Because of the highly exothermic nature of the conversion, the reaction sequence is split into two stages to simplify management of the evolved heat. In the first step, the methanol feed is partially dehydrated to a mixture of methanol, water, and dimethyl ether in a catalyst bed of gamma-alumina. The energy evolved is used to heat the feed to the zeolite catalyst bed in which the gasoline formation occurs; this reactor is operated under vapor-phase conditions at a pressure of about 300 psig and a temperature that increases from about 650 °F to 850 °F along its length. The reactor effluent is cooled, the product recovered and light paraffin gases, which are added as a heat sink, recycled. An auxiliary process is the continuous oxidative regeneration of deactivated zeolite catalyst.

The methanol-to-gasoline process, which is an interesting route from coal to motor fuel, is not yet of commercial interest because, although the processing cost is only about 10 ¢/gallon of gasoline produced, the price of coal-derived methanol leads to a gasoline price 40—50 ¢/gallon more than that of the petroleum product. This situation could, of course, and likely will change [40]. In addition, the gasoline produced using the current catalysts contains enough of the high melting compound, durene (1,2,4,5-tetramethylbenzene) to make it unsuitable for use in some climates. It is stated, however, that this problem can be overcome.

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METALLIC CLUSTERS IN ZEOLITES

By

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Zeolites have been used to prepare metal supported catalyst. The present paper reviews the literature on the preparation of metal clusters in zeolites, on the characterization of the dispersion and of the physicochemical properties of the metal particles.

Introduction

Highly dispersed metals are known as catalysts for several chemical reactions. They are usually supported on a stable inorganic carrier, in many cases alumina. The role of the carrier is not merely that of a dilutant, but it is essential for obtaining a high degree of dispersion and for preventing sintering of the metal phase at high temperatures.

When synthetic zeolites became available in large quantities, their usefulness as a carrier for highly dispersed metals was rapidly recognised [1—4]. By their high cation exchange capacity it is possible to incorporate an important amount of various metals, dispersed as single ions. Although it turned out afterwards to be more complicated, it was postulated that upon reduction the metal remained highly dispersed inside the pore system of the zeolites.

After these early works zeolites loaded with noble metals, especially platinum have been developed into practical catalysts for important industrial processes. Hydrocracking and reforming of hydrocarbons are the most important reactions carried out on an industrial scale making use of zeolite catalysts. Metal loaded zeolites have exquisite properties for these reactions: they act as polyfunctional catalysts, they add to the system a selectivity which is due to the molecular dimensions and the shape of their pores. They make a very efficient use of the costly noble metals by maintaining them in a state of high dispersion. Such catalysts exhibit a remarkable resistance against sulfur and nitrogen bases present as impurities in the hydrocarbon feed [5—13].

It is not the intention to give here an exhaustive review of the use of metal containing zeolites in catalysis. An excellent review on this subject was published by MINACHEV and ISAKOV [14]. It covers the literature till 1973.

The aim of this paper is to review critically the preparation of metal particles in zeolites, to discuss the mechanism of formation of reduced metals in zeolites and

the factors which influence the dispersion. In some systems the zeolite framework participates in redox reactions with transition metal ions. Residual charges on the metal particles influence the stability of the dispersion. In most cases the metal phase is polydisperse, and the methods generally used to measure the degree of dispersion on other substrates are not necessarily applicable to metals on zeolites.

Preparation

Metals can be introduced into zeolites in various ways. The most common technique is that of ion exchange and subsequent reduction using a suitable reducing agent. Adsorption from the gas phase of metal containing compounds (carbonyls) and of metal vapours have also been reported, as well as inclusion of elements during the synthesis of the zeolite. The most interesting elements for catalysis are the transition metals, especially group VIII and group Ib and IIb elements to which this review will restrict itself. Most of the work has been performed on zeolites with the faujasite structure, mainly the synthetic zeolite Y, while other zeolites (A, morde-nite) were less extensively studied.

Ion exchange

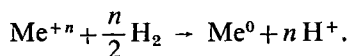
Introduction of transition elements by ion exchange is an easy technique but care must be taken of the chemical properties of the elements. For the more common ions (Ni^{++} , Co^{++} , Cu^{++} , ...) aqueous solutions of the hydrated ions can be used.

The fundamental data on the ion exchange of the transition metals are not very abundant [15—19]. Ion exchange studies are usually carried out in very dilute solutions (0.1 N—0.02 N). Since the solutions of transition metal ions are acidic, partial exchange of protons occurs but this is not so important for the reduction afterwards. More important is the fact that excess transition metals can precipitate due to the basic reaction of the zeolite. This was investigated in detail by SCHOONHEYDT ET AL. [21]. They showed that an important excess of Ni^{++} and especially of Cu^{++} can be fixed on the zeolites Y and even more on X. This excess was present as complex ions when an acetate buffer was used, or as a finely divided hydroxide species probably incorporated in the zeolite pores when the pH of the solution was not controlled. To avoid this complication it is recommended to carry out the ion exchange in dilute solution (<0.05 N), in dilute suspensions (<5%) and at ambient temperature.

One can also exchange transition elements as stable cationic complexes. This is the appropriate procedure for noble metals (Pt, Pd, Ru) which are commonly exchanged as stable amine complexes, but other ions can also be exchanged under complexed form [20]. For the more common ions it is usually attempted to introduce a large amount of metal. Due to the cost, the noble metals are usually exchanged only to a minor fraction of the ion exchange capacity.

Reduction with hydrogen

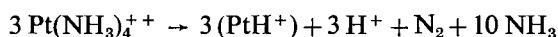
The reduction to the zero valent state is usually done with hydrogen. The overall reaction can be written as follows:



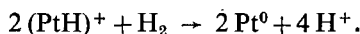
The protons react with the zeolite lattice creating hydroxyl groups. The presence of these hydroxyl groups has been demonstrated with infra-red spectroscopy [30, 31]. They absorb at 3650 cm^{-1} (or in the corresponding OD region), like the acid hydroxyls in HY zeolites. By this acidity the metal loaded zeolites can act as bifunctional catalysts. However, the overall reaction reveals nothing about the fine mechanism of the reduction. Furthermore, slight differences in the reduction procedure may result in quite different degrees of dispersion, an important property of metal catalysts. This reveals that the reduction mechanism is probably complex. Moreover it is not necessarily identical for the different ions or in the different zeolites.

1. *Platinum and palladium*

Because of its importance for practical catalysis, Pt in Y zeolites has been widely studied and a coherent picture has been developed [20–29]. Thermal decomposition of the $\text{Pt}(\text{NH}_3)_4^{++}$ complex results in the formation of an hydride species (PtH^+). The gaseous decomposition products were analysed by WINKLER ET AL. [25] and contain NH_3 and N_2 . MASHCHENKO ET AL. [27] investigated this decomposition reaction by i.r. spectroscopy and observed a band at 2120 cm^{-1} from which they inferred the presence of a surface platinum hydride. A combination of the observations reported in these two works allows us to write the following reaction scheme for this thermal decomposition at 177°C



The (PtH^+) can be reduced with H_2 to metallic Pt.



The reduced Pt seems to migrate and interact with paramagnetic centers in the zeolite, most probably Fe^{3+} ions [25]. When the $\text{Pt}(\text{NH}_3)_4^{++}$ complex is reduced with H_2 immediately, without previous decomposition, a neutral hydride is formed above 90°C [26]. Its decomposition leads to agglomeration of the platinum.

Oxidation of the amine complex prior to reduction with hydrogen influences the dispersion of the metal phase. It has been proved that after a treatment with oxygen at 300°C most of the platinum is present as Pt^{2+} ions located in the supercages. After oxidation at 600°C the Pt^{2+} ions have migrated into the sodalite cages [28, 29]. In this way, when reduction with hydrogen (under moderate condition) is performed after different oxidative pretreatments, the platinum particles are of different sizes and located at different positions. The situation may be summarized as indicated in Fig. 1 [29].

Hydrogen chemisorption, oxygen chemisorption and hydrogen titration have been applied by several authors [22–26, 29, 76] to determine the degree of dispersion, but the results are not in complete agreement. In the first work on platinum zeolites RABO [22] claimed that atomically dispersed platinum could be obtained and suggested that such an atom could sorb two hydrogen atoms. This explanation is not longer followed. GALLEZOT ET AL. [29] assume that atomic Pt in the supercages does not chemisorb hydrogen. Possible reasons for this are that atomic Pt^0 may not have the properties of metallic Pt, or that H_2 , because of its kinetic diameter of 0.289 nm , does not enter into the sodalite cages.

Palladium behaves in a way similar to platinum. After calcination of the amine complex Pd^{2+} ions are present which can be reduced even at room temperature giving almost atomically dispersed Pd^0 . This was demonstrated using X-ray diffraction [32]. The nature of the Pd^0 was studied by sorption of CO and i.r. spectroscopy

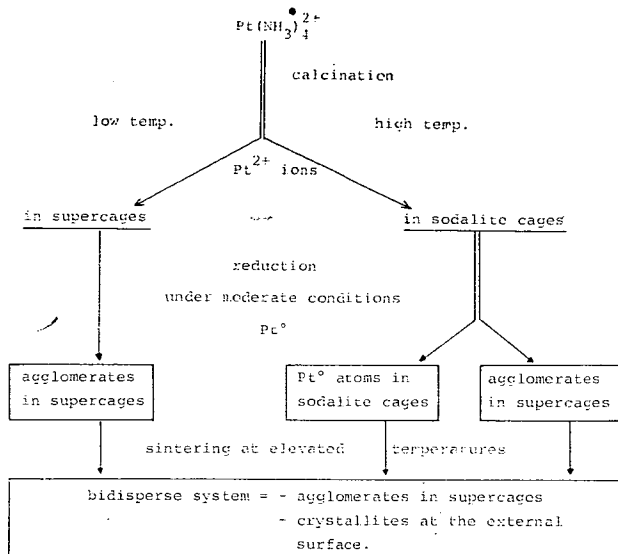


Fig. 1. Reduction scheme of $\text{Pt}(\text{NH}_3)_4^{2+}$ in zeolite Y.

[33]. The Pd atoms are electron deficient: this was derived from the frequency of the CO vibration, and was explained by assuming that the Pd atoms are associated with Lewis acid sites. Pd is very sensitive to sintering. Reduction at 200 °C produces metal crystallites outside the zeolite [33].

2. Other transition metal ions

The reduction of a series of transition metal ions of different nature in zeolite Y was reported by YATES in 1965 [34]. In this early paper it was reported already that during reduction the metal phase can leave the zeolite. Cd, Zn, Ni and Ag crystallites were proved to exist outside the zeolite. It was also shown that metals with a high vapour pressure (Hg, Zn, Cd) could distill out of the zeolite during the reduction.

RIEKERT [35] investigated the interaction between hydrogen and Ni^{++} , Cu^{++} and Ag^+ ions in zeolites T and Y. He treated the stoichiometry of the reaction as an intracrystalline equilibrium between Ni^{2+} and Ni^0 inside the zeolite, following nearly the mass action law. He also observed a slow recrystallization of reduced Ni into larger crystals outside the zeolite.

Of all transition metal ions other than Pt and Pd, Ni has received most attention [36–45]. This is probably because of the usefulness of Ni in practical catalysis, but also because of the applicability of a variety of physicochemical methods to characterize the state of the metal phase. Most authors agree that after reduction the nickel

migrates to the external surface where it agglomerates into relatively large particles. ROMANOVSKII [36, 37] has derived a partition function of nickel particles from magnetization experiments. After reduction at 370 °C there were still particles with dimensions smaller than the diameter of the supercages in zeolite X, but a sintering at 400 °C produced particles too large to be accommodated in the supercages. Reduction of Ni^{++} into Ni^0 accompanied with sintering was reported at temperatures as low as 350 °C for zeolite NiNaA [43, 44], 350–400 °C for zeolite NiNaX [34, 43, 44], 300–440 °C for zeolite NiY [40, 42, 44] and 360 °C in mordenite [44]. All the papers in which quantitative data on the extent of the reduction were reported, agree on the fact that the reduction of nickel is incomplete (except for small Ni contents [40]).

In a recent paper BAGER, VOGT AND BREMER [45] recognize the complex nature of the reduction and of the sintering of nickel in a zeolite Y in which other cations were incorporated (Na, Ca, Ce and NH_4). They investigate the samples by different techniques including chemical analysis, XPS, electron ferromagnetic resonance and electron microscopy. They reported (in NiNaY and NiCaY) a rapid reduction at low temperature (below 350°).

Another part of the nickel contained in these samples was reduced only when the temperature was raised above 420 °C. In NiCeY and NiNH_4Y significant reduction of the nickel occurred only at temperatures above 420 °C. These authors made the important observation that the nickel produced at low reduction temperatures sintered easily and agglomerated outside the zeolite, whereas the nickel reduced at higher temperatures remained in a state of high dispersion. In the NiNH_4Y sample nickel crystallites could never be detected outside the zeolite. The result of the physicochemical determinations were confirmed by catalytic activity measurement for dehydrogenation of cyclohexane to benzene.

Recently [77] the preparation of Ru^0 in several zeolites was reported. The Ru was exchanged into the zeolite as trivalent ions and reduced with hydrogen. Particle sizes are derived from hydrogen sorption. A rather small average crystallite size is found on zeolites X, Y and M. The authors conclude that on these zeolites a large fraction of the metal is inside the zeolite. The sample were good catalysts for benzene hydrogenation.

Experiments were reported to document the influence of the pretreatment [45, 46], the nature of the charge compensating cations [40, 45] and the nature of the zeolite [47] on the reduction and the state of dispersion of the metallic phase after reduction. Despite of the large number of papers, it is difficult for the moment to make general conclusions on the different parameters which influence the reduction of transition metal cations.

Preparation of metal clusters using adsorption of neutral compounds

Zeolites, previously dehydrated, can be loaded with metals by adsorption and subsequent decomposition of neutral compounds containing metals. Preparations with metacarbonyls, acetylacetonates, alkylderivates and others have been reported and patented [66, 67]. The procedure has been "rediscovered" recently. GALLEZOT ET AL. [68] and DEROUANE ET AL. [69] report loading of zeolite Y with Mo, Re, Ru [68] and Ni [99] by adsorption of metal carbonyls and subsequent thermal decomposition. These recent papers use X-ray diffraction, i.r. spectroscopy and ^{13}C -NMR to describe the procedure and the properties of the final product. A definite characterization of the system obtained by this method has not been obtained yet.

Dispersion of the metals in the zeolites

It is obvious from the foregoing that most of the effort was directed to the preparation of a stable nickel phase highly dispersed inside the zeolite system. The major problem to overcome is the existence of bidisperse systems. The particles inside the zeolite have necessarily dimensions smaller than the diameter of the cages. Metal crystallites observed at the outside of the zeolites have dimensions which are greater by almost an order of magnitude.

The adsorption of H_2 , of O_2 and the so-called hydrogen titration are now standard methods to determine the dispersion of metals on classical substrates like alumina and silica. The application of this method to metals on zeolites is questionable. Indeed, if the zeolites are treated under such conditions that a bidisperse system exists, the adsorption experiments estimate an average size which does not correspond to reality. This was demonstrated by KUBO ET AL. [48] for Pt zeolite and by LAWSON ET AL. [42] for Ni zeolites. In their experiments electron microscopy revealed the existence of small and large particles, while H_2 adsorption produced an average value. If the zeolite contains only ultra small particles inside the cavities, the gas adsorption methods might eventually measure the correct order of magnitude. However, not enough attention has been given to the perturbing effect of steric hindrance. It is also questionable whether the adsorptive properties of ultra small particles are the same as those of real metals.

Other physical methods have been used to determine the particle size. Electron microscopy [23, 42, 48, 49] is of course very suitable to determine particle size distributions. However, the ultrafine particles inside the zeolite pores are outside the range of resolution of most of the electron microscopes presently in use.

X-ray diffraction line broadening is another method frequently used [31, 32, 34, 42, 44]. The lower limit of this method reaches only particles of 20–30 Å, and hence it also gives no insight in the state of the metal phase inside the zeolite pores.

Magnetic measurements have been used to characterize the metal phase in the case of Ni zeolites. Susceptibility measurements and ferromagnetic resonance experiments were reported [36, 37, 40, 45]. Again, the appearance of superparamagnetic or ferromagnetic properties was ascribed to larger particles outside the zeolite cages. BAGER ET AL. [45] combine O_2 adsorption with their physicochemical methods (XR, electron microscope, EFR) in order to determine the particle size of intracrystalline Ni^0 particles.

Recently the method of temperature programmed reduction followed by temperature programmed oxidation was proposed by JACOBS ET AL. [50] as a method to distinguish between particles inside and outside a zeolite. The method consists in a reduction with hydrogen, or an oxidation with oxygen in a small volume reactor in which the gas consumption can be followed by measuring the pressure drop. After suitable pretreatments of the samples (outgassing *etc.*) the temperature of the sample was increased at a linear rate of $5^\circ \cdot \text{min}^{-1}$, and condensable gases were trapped out continuously. The rate of gas uptake (first derivative of gas consumption) was determined every 90 seconds and plotted as a function of the temperature. Example of the curves obtained is given in Fig. 2 for CuY zeolite, and in Fig. 3 for NiY zeolite. The temperature at which the peaks occur is indicative of the chemical reaction which goes on, and the intensity of the peaks, since it is proportional to the amount of gas consumed, allows a quantitative estimate. Thus in Fig. 2 the curve r_1 represents

the reduction of CuY. The low temperature peak at about 150 °C is due to the reduction Cu^{++} to Cu^+ , the high temperature peak at 420 °C reflects the transformation Cu^+ to Cu^0 . Temperature programmed reoxidation of this sample results in a peak around 180 °C, which is ascribed to the reoxidation to the Cu^{++} state of all the

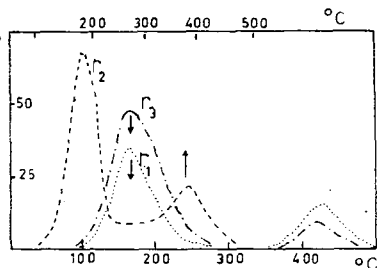


Fig. 2. Rate of gas consumption — $\text{mol g}^{-1} \text{s}^{-1} \times 10^8$ as a function of temperature in TPR/TPO experiment
 r_1 = TPR with hydrogen on CuY
 r_2 = TPO with oxygen on reduced CuY
 r_3 = TPR with hydrogen on reoxidized sample

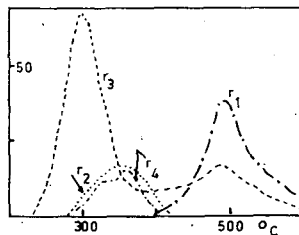


Fig. 3. Gas consumption in $\text{mol g}^{-1} \text{sec}^{-1} \times 10^8$ as a function of temperature in TPR/TPO experiments on NiY zeolite
 r_1 = TPR = rate of reduction on fresh sample
 r_2 = TPO on reduced sample
 r_3 = TPR on reoxidized sample (second cycle)
 r_4 = TPO during second redox cycle

species present inside the zeolite, either as Cu^+ or as ultrasmall Cu^0 particles. A second peak at 400 °C is attributed to the oxidation of large Cu^0 aggregates outside the zeolite which produces a CuO phase. A second TPR of the same sample reveals a peak at 150 °C with a higher intensity than during the first reduction. This is due to the superposition of two phenomena: the transition Cu^{++} to Cu^+ of the copper ions in the zeolite and reduction of a CuO phase outside the zeolite. The high temperature peak at 420 °C has decreased in intensity due to the decrease of the copper content in the zeolite. All these assignments were supported by a detailed characterisation of CuY zeolites during reduction and reoxidation using a variety of physicochemical techniques [51], and by a kinetic study of the reduction and the reoxidation phenomena [52].

Fig. 3 allows a detailed discussion of the behaviour of a NiY. During a first TPR a broad peak at 500 °C appears. An X-ray diffractogram of this sample revealed the presence of a considerable amount of Ni^0 external to the zeolite. TPO on this sample reveals that Ni^0 is completely reoxidised with a maximum in rate at 400 °C. A second TPR on the same sample produces two peaks; the NiO phase formed during the previous TPD is reduced at a lower temperature (300 °C) than the Ni^{++} ions inside the zeolite.

Although the method does not allow a determination of particle sizes, it allows a quantitative distinction between the phases inside and outside the zeolite. Indeed, the total extent of reduction (and oxidation) can be derived from the total gas consumption. The area under the different peaks can be compared to each other and allows conclusions on the relative abundance of the species reduced or oxidized.

Mechanism of the reduction with hydrogen

Reducibility of the cations in zeolites

The formal mechanism of the reduction of the nonnoble transition metals in zeolites has been studied by a few authors [31, 38, 50–56]. For such studies it is important that the zeolite samples are prepared in such a way that the transition metals are only present as exchangeable cations, and that finally divided hydroxide species are avoided [21].

Since we were convinced that the data reported in the literature are often obtained on inhomogeneous samples, we investigated a series of zeolites Y saturated with different cations (Ag^+ , Cu^{++} , Ni^{++} , Co^{++} , Zn^{++}) in very dilute suspensions (zeolite loading of 0.5 g/l) and using a concentration of the transition metal salts (nitrates or chlorides) of 0.005 N. The reducibility of these zeolites was then investigated using the TPR method and by isothermal reduction at different temperatures. AgY can be reduced at very low temperatures ($<100^\circ\text{C}$) [31]. Cu^{++}Y goes to Cu^+Y at low temperature (150°C). Further reduction to Cu^0 goes rapidly at 420°C (TPR) but at 400° several hours were needed to transform 50% of the Cu^+ into Cu^0 [51]. Ni^{++}Y gave a maximum in the rate of reduction (TPR) at 500°C [51]. Under static conditions a temperature of 450°C is needed during several hours to obtain only 36% of reduction. At 350°C reduction proceeded after several hours, to 8% of the total Ni content [57]. Co^{++}Y at 500°C consumed only slight quantities of H_2 corresponding to a degree of reduction of only a few percent, while the CdY , ZnY and MnY could not be reduced at all (unpublished results).

In all these experiments the sample were pretreated by careful outgassing at 500°C . The reducibility could be enhanced by working in the presence of water vapour, or by realising a so-called deep-bed pretreatment.

Table I

Reducibility of metals in zeolites compared to electrochemical potentials and ionisation potentials of the elements

	TPR ^a	Electrochemical potential	Ionisation potential (1st or 2nd) volt
AgY	120 °C	0.7996	6.9
CuY	400 °C	0.158 (Cu^+)	7.72 (1st) 20.29 (2nd)
NiY	500 °C	–0.230	18.15 (2nd)
CoY	b	–0.280	17.05 (2nd)
CdY	b	–0.4026	16.90 (2nd)
FeY	c	–0.409	16.18 (2nd)
ZnY	b	–0.760	17.96 (2nd)
MnY	b	–1.029	15.63 (2nd)

a. Temperature at which maximum occurs in the rate of H_2 consumption in TPR procedures.

b. Reduction not observed.

c. Ref. [78] and [79] —no reduction of $\text{Fe}^{++} \rightarrow \text{Fe}^0$

From these observations we concluded:

(i) The transition metal ions in zeolites have properties which can be compared to the properties of the ions in solution. Indeed, the order of reducibility of the ions follows the electrochemical potentials of the elements as listed in Table I. The reducibility of the metal does not follow the sequence of the ionization potential which is a property of the isolated metal atoms (see also Table I).

(ii) In the previous work reporting a reduction of metal ions which are known to have weak oxidative properties, it is likely that a fraction of the ions was present as a finely divided hydroxyde. The same is probably true for these works where Ni could be reduced at temperatures as low as 300 °C. This remark applies to the experiments on zeolite Y and is not necessarily valid for experiments on other types of zeolite although the precipitation of hydroxydes must still be easier in the zeolites with lower Si/Al ratio (X and A) which give a stronger alkaline reaction than zeolite Y.

These conclusions find support in the observations made by GARTEN [78] and by HUANG AND ANDERSON [79] with Fe^{++}Y zeolites. These authors report that Fe^{++}Y resist reduction with hydrogen. This is in agreement with the position of Fe^{++} on the list of electrochemical potentials. Nevertheless, MORICE AND REES [80] have found that Fe^{3+}CaX could be reduced in hydrogen at 350 °C to give metallic particles.

Mechanism derived from kinetics of H_2 consumption

BEYER ET AL. [31] investigated the kinetics of reduction of AgY at different temperatures. Examples of the H_2 consumption curves are given in Fig. 4. The extent of reduction was dependent on the temperature. Reduction proceeds by another mechanism at low and at high temperature. These results were explained by postulating that the low temperature mechanism applies to the silver ions located in the supercage, while the high temperature reduction affects also the ions in the sites SI. The rate equation for the high temperature mechanism is first order in the concentration of unreduced silver $\left[\frac{dR}{dt} = k[\text{Ag}^+]\right]$ and the activation energy of this mechanism is 97.6 kJ. This is an acceptable value for the activation energy of diffusion of Ag^+ out of the hexagonal prism.

The low temperature mechanism was expressed by the following rate law

$$\frac{1}{P} \cdot \frac{dR}{dt} = k' \frac{1}{R} - k''$$

in which R is the extent of the reduction at time t . That the rate is inversely proportional to the extent of reduction implies that the reaction products slow down the reaction. In all the samples which were studied only two thirds of the Ag^+ ions,

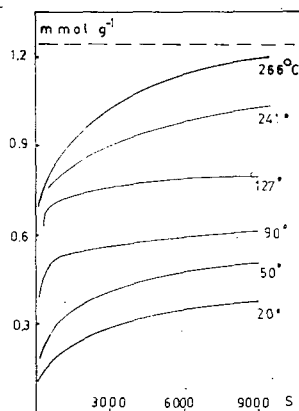
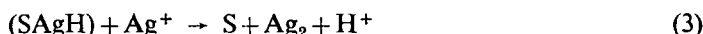


Fig. 4. Hydrogen consumption (in mmol g^{-1}) as a function of time at different temperatures on zeolite AgNaY

normally available in the large cavities for the low temperature mechanism, participate really in the reduction reaction.

BEYER ET AL. [31] further postulate that the reduction is a catalysed process. The hydrogen is activated at some active sites, probably paramagnetic impurities.

The following sequence of reactions accounts for the rate law observed.



in which reaction (3), *i.e.* the regeneration of the active sites, is rate determining. It is assumed that Ag_2 further associated with unreduced silver to form charged clusters Ag_n^+ . From the fact that only two thirds of the silver available in the supercages is effectively reduced in the low temperature mechanism, it was inferred that the silver cluster has an average composition Ag_3^+ , and that such a charged cluster is more difficult to reduce than isolated silver ions.

The assumption that paramagnetic impurities play a role in these processes is supported by a few facts. It has been proved in D_2 — H_2 equilibrium experiments that iron impurities can indeed activate hydrogen in zeolites [58]. Pt reduced in zeolites was shown to agglomerate with iron impurities in the zeolite [25]. Furthermore, BEYER and JACOBS [53] were investigating the reduction of Ag^+ in mordenite, and proved that the rate of the reduction was decreased when the level of iron impurities was decreased previously by an extraction of the iron with dithionate. This extraction does not modify the mechanism of the reaction since the activation energy is the same before and after deferration.

There is only indirect proof that charged clusters are created during reduction of silver at least at moderate temperatures. In BEYER's [31, 58] picture the coulombic interactions between the negatively charged zeolite lattice and the positive clusters prevents the escape of the metal from the zeolite and its agglomeration into a bulk phase. Experimental proof to this hypothesis was recently found by H. BEYER (unpublished). A zeolite AgY was reduced at increasing temperatures (50 to 350 °C), and the existence of metallic particles was checked by the appearance of the (III) line in the X-ray diffraction diagrams. The formation of Ag particles of 210 Å was observed after 4 hours of reduction at 350 °C. At temperatures below 150 °C the formation of extra lattice particles did not occur. When the hydrogen was removed by outgassing at 150 °C, the reduced AgY zeolite could be heated to 350 °C for a long time without formation of silver crystallites detectable by X-ray. One can conclude from this experiment that the Ag particles are in the zeolite cages as a stable entity, probably with a residual positive charge, because sintering occurs only when the temperature is raised in the presence of excess reductant.

Reduction kinetics of NiY were investigated by VERDONCK [57]. At 500 °C only 30% of the Ni present could be reduced to the Ni^0 state. The kinetics of the H_2 consumption could be explained on the basis of the mechanism proposed by BEYER [31]. This implies (i) activation of the H_2 at some surface sites; (ii) diffusion of the nickel ions towards these active sites; (iii) the regeneration of the active site is the rate determining step; (iv) formation of charged Ni_n^{++} clusters. The results allowed to estimate the average size and charge of the clusters to be Ni_3^{++} or Ni_4^{++} . However,

due to the high temperature (500 °C) a considerable sintering of the nickel phase is observed which makes such estimates highly speculative. Another complication arising with the reduction of NiY is the dehydroxylation of the OH groups created in the reduction reactions at the temperatures at which reduction is carried out.

A similar mechanistic study on CuY zeolites was much more difficult. The reason is that reduction proceeds by a two step mechanism: at low temperature Cu^{++} is reduced to the Cu^+ state. Reduction of Cu^+ to Cu^0 request temperatures close to 400 °C and higher [51, 52]. The activation energy of the reduction of Cu^+ to Cu^0 is rather low ($25 \text{ kJ} \cdot \text{mol}^{-1}$) which could mean that the process is diffusion controlled. A full characterisation of a CuY sample partially reduced under specific conditions is a difficult task which request the combination of several techniques. Table II pre-

Table II
Characterisation of a $\text{Cu}_{18}\text{Na}_{19}\text{Y}$ zeolite after reduction and reoxidation

Treatment	Cu^{++} a	Cu^+ a	Cu^0 b	CuO c
(1) Reduction H_2 400 °C (1.25 hr)	0.00	17.38	1.22	—
(2) Reduction H_2 400 °C (10 hr)	0.00	13.07	5.53	—
(3) Reduction H_2 400 °C (20 hr)	0.00	11.09	7.51	—
(4) = 1 + oxidation (1 hr)	18.08	—	—	0.52
(5) = 2 + oxidation (1 hr)	16.01	—	—	2.59
(6) = 1 + oxidation (1 hr)	14.16	—	—	4.44

Figures are in numbers per unit cell.

a. In lattice positions.

b. Inside + outside the zeolite.

c. Measures Cu^0 outside zeolite.

sents an example taken from the work of HERMAN ET AL. [51]. These data were obtained by a combination of methods first applied by HALL ET AL. [59] on Cu^{++} containing hydroxyapatite.

The formation of Ni(I) during the reduction of a NiY zeolite with hydrogen has been reported by GARBOWSKI ET AL. [60]. The evidence presented is based on EPR and electronic spectroscopy but a quantitative estimate of the amount present in that oxidation state is not given. Since the TPR experiments [50] do not reveal a distinct two-step mechanism, it can be assumed that the eventual concentration of Ni(I) must be small and that further reduction to Ni^0 goes fast.

The detailed mechanisms proposed by BEYER, JACOBS ET AL. [31, 50, 57] cannot necessarily be applied to other zeolites than the zeolite Y. Ag mordenite was investigated by BEYER AND JACOBS [53]. The kinetic data showed again a low and high temperature mechanism from which the authors inferred that a similar mechanism as in AgY operated. In the low temperature phenomenon the formation of a Ag_5^+ cluster was postulated.

The reduction of NiX cannot be explained by the mechanism which was found for NiY. GUILLEUX ET AL. [55] advanced a mechanism in which a variable diffusion coefficient ($D = D_0(1 - R)$) is applied. This equation is suitable for low levels of reduction. To interpret data on zeolite NiX over a broad range of reduction levels, VER-

DONCK [57] adopted a mixed type mechanism (SETT AND ROSS) controlled by an interface reaction and by diffusion. When only diffusion is rate determining, the equation

$$\left(\frac{1}{2} - \frac{R}{3} - \frac{(1-R)^{2/3}}{2} \right) = t \quad (\text{time})$$

fits the data. Two straight lines are obtained which intersect at $R=0.4$. VERDONCK concludes from this that two different diffusion mechanism each with a constant diffusion coefficient must exist. Since the NiX contained 27.6 Ni ions per u.c., of which 16 are located in site SI, VERDONCK assumes that the distinction between two diffusion processes can be made on the basis of the location of the cations. The two processes have a different activation energy (100 kJ and 120 kJ). In NiX degrees of reduction approaching 90% could be realised at 550 °C in less than 4 hours. GUILLEUX ET AL. [55] reported the beneficial effect of metallic Pd on the rate of reduction of Ni^{2+} in a zeolite X. The Pd^0 was formed in a (PdNiX) zeolite by reduction with H_2 at 100 °C. To reduce the Ni the temperature was increased to 230°–300 °C. At this temperature the rate of reduction of Ni was increased with increasing concentration of Pd. Heating at 400 °C resulted in a sintering of the Pd and destroyed the activating effect. Similar observations were reported by RABO ET AL. [72].

Reversibility of the reductions and participation of the zeolite lattice in redox phenomena

In most of the papers the possible participation of the lattice in redox phenomena is not considered. TSUTSUMI [49] reported the formation of metallic silver in AgNaY and in Ag mordenite heated in a stream of helium at 600 °C and 750 °C. SEFF [61] recently reported the formation of a Ag_6 cluster in a zeolite AgA. The samples, (single crystals) were dehydrated at 400 °C during two days *in vacuo*, and during two more days in the presence of 100 torr of oxygen, or *in vacuo* at 425 °C during 10 days. The colour of these samples was between brick red and golden yellow. The results of the X-ray diffraction analysis indicated the existence of a Ag_6 octahedral cluster located in the center of the cubooctahedron with their threefold axis oriented towards eight Ag^+ ions in the centre of the 6-rings.

The formation of Ag^0 under these conditions can only be explained by the reduction of Ag^+ by oxide ions of the zeolite lattice. The resulting zeolite lattice must be oxygen deficient.

JACOBS ET AL. [62] observed a similar chemistry with a CuY zeolite. They made a quantitative study of the phenomenon, which they called auto-reduction, by measuring the amount of oxygen evolved. They characterized the oxygen deficient sites in the lattice as Lewis acid centers by adsorption of pyridine and infrared spectroscopy. In the case of CuY the auto-reduction of the Cu^{++} ions proceeded to the Cu^+ state and did not produce metallic copper.

In the case of CuY [62] the auto-reduction was reported to be reversible, the oxygen evolved was readsorbed and the Cu^+ reoxidised when the zeolite was cooled in the presence of oxygen. The existence of an equilibrium pressure of oxygen over a CuY zeolite heated to higher temperatures showed that the reaction was indeed an equilibrium reaction. The reactions can be idealised as in Fig. 5.

Auto-reduction of Pd^{++} in PdX has been reported by MINACHEV ET AL. at temperatures above 140 °C. At that temperature they consider the possible formation of Pd^0 , while at lower temperatures Pd^+ could be stabilized [46].

It was known that the zeolite lattice participated in the reduction of transition metals with hydrogen by accepting the protons to make hydroxyl groups. The experiments described in previous paragraphs show that the oxygen framework of the zeolite can in some cases actively participate in redox reactions also.

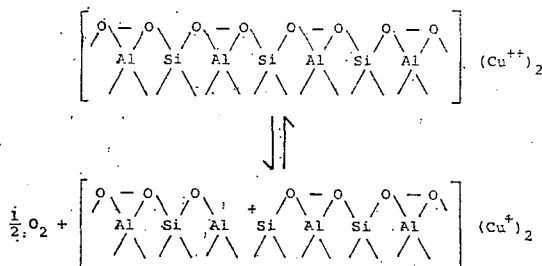
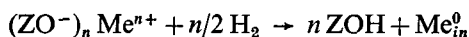


Fig. 5. Participation of zeolite lattice in the reduction of Cu^{++}

We can now consider the question of reversibility of the reduction. Reduced metals can be reoxidized with oxygen. It is generally accepted that reduction-reoxidation of transition metal zeolites using H_2 and O_2 is reversible only when moderate reduction has taken place.

BEYER, JACOBS ET AL. [31, 50—53, 57, 62] have investigated the stoichiometry of hydrogen and oxygen consumption in AgY , CuY , NiY and NiX and in a few other zeolites. They have shown that, in terms of the stoichiometry of the H_2 and O_2 consumption the reduction and reoxidation reaction are virtually reversible, but reversibility is not always realised in terms of the physicochemical properties of the system. Their results can be summarised as follows:

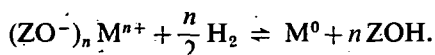
(i) The processes which occur inside the zeolite cavity are reversible in any case. This can be expressed in the following equation in which the subscript (in) indicates that the metal is inside the zeolite cavities.



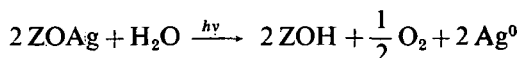
(ii) Irreversibility in the reduction-oxidation cycle is observed when the reduction step was performed at high temperatures so that considerable dehydroxylation had taken place [57] as was the case for NiY .

(iii) If sintering has occurred resulting in a metal phase outside the zeolite, reoxidation of that metal phase produces an oxide species, provided the oxide phase is thermodynamically stable. When the oxide phase is unstable, as is the case with Ag_2O , reoxidation at 350°C will regenerate the initial zeolite. This is important for regeneration of practical catalysts. Reactivation of Pt containing catalysts is done in processes which include an oxidation step to burn off the coke. Since Pt oxides are unstable (decomposition between 400 — 500°C) this reoxidation step might favour a redispersion of the Pt under ionic form, especially when the reoxidation is combined with a controlled rehydration [63].

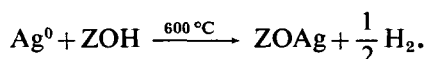
RIEKERT [35], has formally represented the reduction of transition ions in zeolites as an equilibrium reaction



The first experimental proof that this is really so (in some cases) was recently given by JACOBS ET AL. [64]. They reported the release of hydrogen gas from AgY and Ag mordenite previously reduced with hydrogen. The process was not due to the desorption of chemisorbed hydrogen since a concomitant transformation of Ag^0 into Ag^+ was evidenced by CO adsorption and i. r. spectroscopy. The maximum rate of hydrogen desorption in a temperature programmed desorption process was at 600 °C. Only the Ag^0 inside the zeolite pores took part in this process. The reversibility was further proved by applying repeated cycles of reduction with hydrogen and thermal desorption on the same sample of AgY, but dehydroxylation resulted in a progressive decrease of crystallinity of the zeolite. The reversibility of the reduction reaction was used by the same authors for the dissociation of water using a sunlight-activated reduction with water as the reduction step



and a thermal desorption of hydrogen as the oxidation step



Due to the high temperatures and to degradation of the zeolite by dehydroxylation this process has little chance to be of practical application.

Electronic properties of the metal particles in zeolites

As reviewed above, JACOBS, BEYER ET AL. have postulated to existence of charged clusters in zeolites loaded with different types of transition metals. Proof was derived from kinetic experiments.

Even without postulating the existence of such charged clusters, the metallic particles in zeolites were shown to be electron deficient. This conclusion was obtained on the basis of different methods. NACCACHE ET AL. [33] derived this electron deficiency in PdY zeolites from the shift towards higher frequencies of the CO vibration observed in i. r. spectroscopy. CHUCIN ET AL. [70] utilized the same technique on a series of PdY zeolites chemically treated (by Al extraction) in such a way that an increasing number of Lewis sites was created. The electron deficiency of the metal was explained on the basis of electron donation to these Lewis centers. Increased sulphur resistance in catalytic experiments was attributed to this electron deficiency.

Electron deficiency of Pt particles in Y zeolites was also observed by VEDRINE ET AL. [71] in X-ray photoelectron spectroscopy. They also arrive at the conclusion that Pt aggregates associate with Lewis acid sites, and that electron deficiency arises from electron donation from the metal to the zeolite lattice. The particle size ($\leq 20 \text{ \AA}$) did not influence this property.

Alloy formation

Several attempts have been reported to produce alloys by reducing zeolites which contain different types of reducible cations. Ni—Cu, Ni—Cd, Ni—Ag Y zeolites were treated at 500 °C with hydrogen [73]. In the case of Ni—CuY alloy formation was demonstrated using magnetic methods, while no direct evidences for the formation of alloys was given for the other systems.

MINACHEV ET AL. [74] investigated the reduction of Ag—CuY, Cu—NiY and Co—NiY zeolites using XPS. From the changes in the valence band spectra they concluded that the most mobile metal migrates towards the external surface before the other. They also concluded that there is an interaction between Ag and Cu but this is not further characterized. For the Cu—Ni and Co—Ni zeolites it was difficult to obtain unambiguous evidence suggesting the formation of alloys.

JACOBS (unpublished) investigated a few mixed zeolite systems (CuZnY, CuAgY) by the TPR method. He found that the behaviour of these elements in mixture was not different from that in the homo-ionic zeolites. Therefore, alloy formation, as reported by REMAN [73] is probably occurring at the external surface. Indeed, the evidence from magnetic measurements can only be obtained with particles too large to be inside the zeolite.

ROMANOVSKI [75] performed a more detailed magnetic study of the Cu—Ni/Y system. He followed the changes in magnetization during sintering at 450 °C as a function of time for several Cu contents. The systems were previously dried at 350—380 °C. The changes in magnetization were due to two processes going on during sintering: diffusion from the highly dispersed state into crystals at the external surface and homogeneization of the metal phase at the outside of the zeolite crystal. This work also leads to the conclusion that alloy formation occurs as a secondary phenomenon outside the zeolite. A proof of the formation of mixed metal particles inside the zeolite pores has not been produced till now.

Conclusion

The preparation of metallic clusters in zeolites has, in a very short time, stimulated a large amount of research and this is likely to increase. Insufficient data are available for a systematic understanding of the redox behaviour of transition metals and of their complexes in different types of zeolites.

Sintering of the metal phase and agglomeration of large particles outside the zeolite was reported as the general rule, even at low and moderate temperatures. Satisfactory methods to improve the stability of metal particles inside the zeolites must still be found.

Characterization of metal particles inside the zeolites is not an easy task and more work is needed. Gas adsorption experiments fail if bidisperse systems are available, and physical techniques to measure properties of ultra small particles inside the zeolite cavities are still insufficiently understood.

The electronic properties of ultra small metal particles inside the zeolites are probably different from those of larger clusters on the classical amorphous supports. It seems worthwhile to look for special catalytic properties of zeolites loaded with ultra small metal particles.

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A NEW APPROACH OF ZEOLITE ACIDITY. ACTIVITY COEFFICIENTS

By

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Examples are presented of high interactions in zeolites due to the charge density. The comparison with acidic solutions suggests then to define activity coefficients and to consider protons and cations in terms of activity rather than concentration. The consequences of such a concept in the fields of catalysis and adsorption are presented.

The study of the acidity of zeolites has been mainly devoted to the characterization of the nature, number and strength of sites. Since it now appears that zeolites behave also like ionizing solvents [1, 2] or electrolytes [2, 3] it may be interesting to look if other acidic properties of zeolites could not be deduced from the properties of acidic solutions. In this respect the paper will present some experimental facts which may be related to the well known concentration effect in solution.

Introduction

It is known for a long time that interactions between charged species occur in zeolites. For instance, recently the Si K α X-ray emission band energies have been linearly correlated to the aluminium content of various zeolites types [4]. The results imply a regularly increasing destabilization of silicon bonding orbitals as aluminum atoms replace silicium atoms, independently of any zeolite structure effect.

Acidity studies described previously may be a second example. They showed that only a part of the acidity of faujasite-types zeolites is titrable [5]. This part is decreasing as the aluminum content increases. It was deduced that a self-inhibition effect reduced the efficiency of the aluminum atoms in generating titrable acidity. An efficiency coefficient α was defined for the various zeolites. The changes of this coefficient with the aluminum content showed that the introduction of one more aluminum atom in the faujasite structure decreases the efficiency of all the aluminum atoms by 1.45%.

Another series of results concerned with the interactions in zeolite is related to the infra-red wavenumber of acidic hydroxyl groups (high frequency band) which depends on cation and aluminum contents. With alkaline cationic forms progressively exchanged with protons, it has been observed that the hydroxyl IR wavenumber

vary almost linearly with the Si/Al ratio for series of faujasite type zeolites [6] or various zeolites [7, 8]. The Fig. 1 reports results which have been published for 9 different zeolites. Only three of them (n^0 2, 3, 6) belongs to the faujasite family.

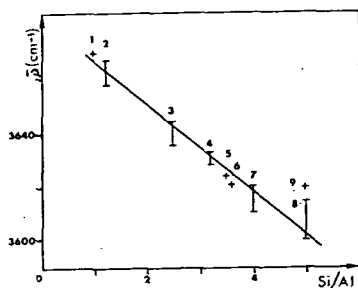


Fig. 1. Wavenumber of the acidic hydroxyls as a function of the Si/Al ratio for the following zeolites: 1: zeolite A [9]; 2: X; 3: Y [6]; 4: L [10]; 5: Ω [11]; 6: Y Al-deficient [6]; 7: offretite [12]; 8: mordenite [13]; 9: clinoptilolite [14]

The zeolites for which a large number of results have been obtained give a range of OH wavenumbers. The low values correspond to high acid strength (low cation content) and upper value to weak acid strength (high cation content). Since for similar weak acid strengths different zeolites give various hydroxyl wavenumbers, it is inferred that the wavenumber alone is not a measure of the acid strength. The decrease in $\bar{\nu}_{OH}$ observed in Fig. 1 as Si/Al increases cannot then be explained only on the basis of the known increase in acid strength. Since the decrease in the aluminum content (rise in Si/Al ratio) decreases the density of charges in the zeolite, the hydroxyl groups are subjected to less intense interactions with the framework and it is suggested that the force constant k of the OH bond is then decreased which shifts the wavenumber to low

values. The average IR wavenumber characterizing each zeolite would then depend mainly on the charges in the zeolite independently of the crystalline structure and of the acid strength.

Activity coefficients

The study of solutions depend whether they are dilute or not. For solutions 0.1 N to 1 N activity coefficients are used and may be calculated. The large number of interactions prevent the calculation of activity coefficients at higher concentrations. It is then interesting to look at the "concentration" of acid sites in zeolites [15]. The Table I reports the unit cell volume of a series of zeolites in $\text{\AA}^3$ and litre [16] and the corresponding proton concentration per litre of zeolites crystal. The proton concentration of the theoretically hydrogen forms lies between 4.76 and 9.5 mol

Table I

Zeolite	Al Al+Si	V unit cell		Theoretical H ⁺ per u. c.	Theoretical H ⁺ per litre	Exchange % for normal solution
		$\text{\AA}^3$	litre (a) (xN)			
X	0.45	15 670	9.03	86	9.5	10.5
Y	0.29	15 350	9.03	56	6.2	16.1
L	0.24	2 794	1.68	8	4.76	21
offretite	0.20	1 160	0.70	3.6	5.16	19.4
mordenite	0.17	2 207	1.33	8.4	6.32	15.8

(a): N=Avogadro Number

of H^+ litre $^{-1}$ which corresponds to highly concentrated solutions. The last column gives the degree of exchange to have an acid concentration of one mole proton per litre. The values obtained are quite lower than those considered for commercial zeolites. Since in solution it is quite usual in all these concentration ranges to consider activity coefficients, it is suggested that activity coefficients might also be defined in zeolites. The activity of a substance is defined by HAMMETT [17] "fundamentally in terms of the statement that the quantity $RT \ln a$ represents the work that can be gained by the reversible transfer of one mole of the substance from the state in which it exists to some standard of reference state at the same temperature. Any force of interactions that tends to bind the substance to other components of the solution must therefore decrease its activity, for the work that must be done against these forces decreases the amount that becomes available when the substance is transferred to the reference state". This definition might be applied to ions and atoms of the zeolite structure.

From what was said just before, the interactions are very important in zeolites. The smaller the charge density, *i. e.* the smaller the $\text{Al}/(\text{Al} + \text{Si})$ ratio, the higher would be the activity coefficient. It then would depend for a large extent on the aluminum content. The Table I shows that it would increase from X to mordenite. In the case of faujasite it would be higher for Y than for X. Then it turns out that the efficiency coefficient defined just before for faujasite zeolites behaves like an activity coefficient. Such a concept of activity coefficient would need of course the definition of reference and standard state on a thermodynamical basis.

Applications to catalysis

The consequences of an activity coefficient concept in acid solids would be at first in the field of catalysis. The rate of a reaction catalyzed by a proton is given by:

$$r = k[\text{S}][\text{H}^+] \frac{f_{\text{S}} \cdot f_{\text{H}^+}}{f_{*}}$$

where $[\text{S}]$ and $[\text{H}^+]$ are the concentrations of the substrate S and of the proton; f_{S} , f_{H^+} and f_{*} are the activity coefficients of the substrate, of the proton and of the transition state.

As far as the activity coefficient of the proton depends on the catalyst, the comparison of the catalytic properties of various zeolites should involve this parameter. Up to now no general classification of zeolites with regards to catalysis has been presented since the results depend on many parameters (nature of the cations, type of reaction, pretreatment and test conditions...). However for a long time it is known that in many reactions X zeolites are less active than Y [18,19] and mordenite more active than Y [19]. In the *isooctane* cracking it has been observed that HKL [20] and HK-offretite [21] zeolites are more active than HKY [22] with similar cation contents. The sequence of activity is parallel to that of activity coefficients deduced from the Table I (inverse of $\text{Al}/(\text{Al} + \text{Si})$ ratio) and to that reported Fig. 1.

It has been postulated that the high acid strength generates a high catalytic activity. Nevertheless it has not been convincingly proved that the stronger acidity offsets the decrease in acid sites number as the $\text{Al}/(\text{Al} + \text{Si})$ ratio decreases [19]. Moreover the stronger acid sites are not necessary in cumene cracking on Y zeolites for example

[23]. The *isooctane* cracking experiments also showed that even at intermediate cation content, *i. e.* similar rather weak acid strength, Y zeolites are less active than L and offretite samples [20—22]. If then the acid strength alone is not able to account for the sequence of zeolites activities, the activity coefficient might be important to consider. It may complete the series of parameters which may be involved [24].

Applications to adsorption

From the extension of the Hammett definition to the case of zeolites it is suggested that activity coefficient may exist for ions other than protons. The cations which are usually considered as the adsorption sites for various adsorbates should then be evaluated in terms of activity rather than concentration. For a given zeolite the number of charges only depends on the aluminum content since the sum (H^+ + cation) is constant. The activity of the cation, like that of the proton, would vary then mainly with the aluminum level. In the faujasite series it would be lower in X than in Y zeolites. The changes in the chemical potential of the sites $\mu = RT \ln a$ would also, in absolute, be lower in X and consequently the free enthalpy of adsorption per site.

This hypothesis could be substantiated by results of adsorption of benzene and cyclohexane on X and Y zeolites with various sodium contents. Integral enthalpies and entropies of adsorption have been calculated for a monolayer [25]. It was concluded that "in X materials each cation adsorbs a smaller amount of hydrocarbon with a smaller heat of adsorption and a smaller change in entropy than in Y zeolites". It follows that, in absolute, the free enthalpy of adsorption per cationic site, ΔG , is also lower in X than in Y zeolites [26] (about 3 times for benzene adsorption). This is in line with the predictions.

The existence of activity coefficients for adsorption sites would then modify the equilibrium of adsorption, the amounts adsorbed and the thermodynamical values of adsorption.

Conclusions

Due to the large interactions in zeolites, it is very likely that cations and protons behave like in concentrated solutions. Activity coefficients should then be defined. It is then necessary to take these activity coefficients into account when comparing the catalytic properties of various zeolites to their number of acid sites. It is also suggested that interactions in other solids may also generate activity coefficients. For instance the characterization of the acidity of amorphous silica-aluminas may very probably make necessary the use of activity coefficients.

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ETHYLBENZENE CRACKING ON AN AGING H-MORDENITE CATALYST

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In accordance with the "Time-on-Stream-Theory" for the cracking of ethylbenzene four different reaction models have been discussed. They differ in the number of active sites involved in the cracking and poisoning reaction step. The apparent activation energies of the partial reactions have been determined.

Introduction

The H-forms of zeolites, particularly H-mordenite, present a high catalytic activity for many reactions which occur by a carbonium-ion-mechanism [1—4]. On the other hand this highly active behavior involves sometimes also catalysis of undesirable side reactions, the products of which can act as inhibitors. In the course of such a reaction an increasing self-poisoning will take place. The poisoning is caused by a blocking of the active sites. This uneconomic aging effect has been studied in detail by WOJCIECHOWSKI and co-workers [5—7] in their "Time-on-Stream-Theory".

In the treatment of catalyst decay WOJCIECHOWSKI considered the poison concentration as constant. If the inhibitor is produced by the reaction itself, however, its concentration is a function of conversion and therefore will be time dependent. Cracking of ethylbenzene on H-mordenite is an example for such a situation.

Experimental procedure

The experiments had to be carried out in such a way that the applied H-mordenite becomes charged only during the actual measurement, because aging of catalyst starts already during the first seconds. A pulse reactor is most suitable for this case.

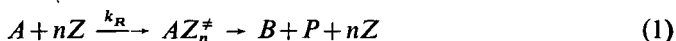
The experimental arrangement consists mainly of a stainless steel differential flow reactor. At the beginning of a run, 5 mg of the pre-purified catalyst were activated in the reactor tube itself under definite conditions at 500 °C. For this purpose the substance was heated to 500 °C [8] at a rate of 9 deg/min in a He-flow (30 ml/min). After a holding time of 30 minutes the catalyst was cooled down to reaction temperature at a rate of 5 deg/min. After 3 hours the He-flow rate was increased up to 490 ml/min and after one more hour the crack experiments started.

A pulse of 10 μ l ethylbenzene was injected by means of a syringe into the He-carrier gas line and after passing the reactor the products were analyzed in a connected gas chromatograph. The reaction temperature was varied in steps of 25 degrees between 300° and 425 °C.

Calculation model

The course of the reaction is determined by the primary cracking reaction at the active sites Z and the poisoning of these sites $Z(t)$. Two assumptions were made:

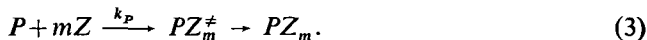
1) Cracking occurs in a first order reaction and n sites are involved in the initial reaction step



A means the initial reactant, B a product and P is also a product molecule, which additionally acts as an inhibitor. Because the reaction takes place in a differential reactor, during the reaction of the pulse the concentration of A can be considered as constant with sufficient approximation, i. e.

$$\frac{dx_A}{dt} = k_R[Z]^n \quad (2)$$

2) In the poisoning process one adsorbed inhibitor molecule P occupies m active sites



Therefore the poisoning reaction is determined by the concentration of P and that of possibly present impurities P' of the initial reactant A . Assuming $c_P \sim x_A$ and $c_{P'} \sim c_A^0$,

$$c_{P, \text{total}} = c_P + c_{P'} = a(c_A^0 - c_A) + bc_A^0$$

Taking $b/a = \eta$; $c_{P, \text{total}} = a \cdot c_A^0 (x_A + \eta)$

$$-\frac{d[Z]}{dt} = k_P a \cdot c_A^0 [Z]^m \cdot (x_A + \eta) \quad (4)$$

Solving the system of equations (2), (4) for different values m and n in order to find the time dependent degree of conversion $x_A(t)$ is cumbersome. If it is necessary to assume parallel reactions at energetically different sites, as in our case, no explicit solution can be found. Because the selected experimental conditions, however, are those of a differential reactor, a different way of solution is possible.

During the passage of the pulse through the catalyst material the concentration of active sites $[Z]$, determining the conversion x_A , decreases according to equ. (4). Dividing the pulse into a large number (>700) of sufficiently small elements allows one to consider $[Z]$ in equ. (2) as well as $[Z]$ and x_A on the right side of equ. (4) as constant within close integration limits. For a better approximation, the conversion in equ. (4), which increases during the passage time t_R of the pulse element i from 0 to x_i , is taken to be the mean value $x_i/2$. The pulse element is chosen as the free volume v_0 of the catalyst material. Therefore, at a pulse v_p this volume can be divided

in $v_p/v_0 = i_M$ elements. The total conversion of the first pulse found by gas chromatography thus results in a mean value of i_M partial conversions

$${}^1x_A = \frac{1}{i_M} \sum {}^1x_i.$$

The superscript is related to the pulse number. To avoid double indices in the following A is omitted.

The evaluation of the experimental data showed that a satisfying curve fitting, especially for the first pulses, can be achieved only by assuming two energetically different sites Z and Z' . The total conversion ${}^\mu X$ of the pulse μ therefore is

$${}^\mu X = {}^\mu x + {}^\mu x'.$$

${}^\mu x$ is determined by k_P , k_R and $[Z_0]$ whereas ${}^\mu x'$ by k'_P , k'_R and $[Z'_0]$. Under the stated assumptions and considering that in equ. (4) x has to be replaced by $x + x' = X$ integration of eqs. (2) and (4) yields for the first element of the first pulse

$${}^1x_1 = k_R [{}^1Z_0]^n t_R$$

and

$${}^1x'_1 = k'_R [{}^1Z'_0]^n t_R \quad (5)$$

respectively.

After the passing of this element the initial concentration of sites has decreased to $[{}^1Z_1]$ and $[{}^1Z'_1]$ respectively:

$$\begin{aligned} [{}^1Z_1] &= [{}^1Z_0] \left\{ 1 - \frac{1}{2} k_P a c_A^0 [{}^1Z_0]^{m-1} ({}^1x_1 + 2\eta) t_R \right\} \\ [{}^1Z'_1] &= [{}^1Z'_0] \left\{ 1 - \frac{1}{2} k'_P a c_A^0 [{}^1Z'_0]^{m-1} ({}^1x'_1 + 2\eta) t_R \right\}. \end{aligned} \quad (6)$$

Simplifying the notation by the substitutions

$$\Omega_m = \frac{1}{2} k_P a c_A^0 t_R [{}^1Z_0]^{m-1}$$

$$\Omega'_m = \frac{1}{2} k'_P a c_A^0 t_R [{}^1Z'_0]^{m-1}$$

$${}^1Y_1 = 1 - \Omega_m ({}^1x_1 + 2\eta)$$

$${}^1W_1 = 1 - \Omega'_m ({}^1x'_1 + 2\eta)$$

$${}^1Y_i = 1 - ({}^1Y_{i-1}^{m-1} - {}^1Y_{i-1}^m) ({}^1x_i + 2\eta) : ({}^1x_{i-1} + 2\eta)$$

$${}^1W_i = 1 - ({}^1W_{i-1}^{m-1} - {}^1W_{i-1}^m) ({}^1x'_i + 2\eta) : ({}^1x'_{i-1} + 2\eta)$$

gives

$${}^1X_1 = {}^1x_1 + {}^1x'_1$$

$${}^1X_2 = {}^1x_1 {}^1Y_1^n + {}^1x'_1 {}^1W_1^n$$

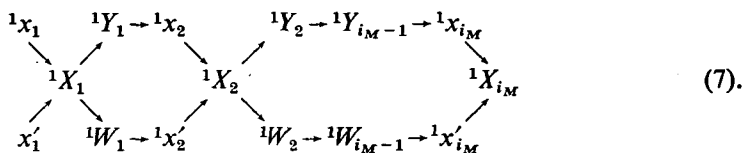
$$\vdots$$

$${}^1X_i = {}^1x_{i-1} {}^1Y_{i-1}^n + {}^1x'_{i-1} {}^1W_{i-1}^n.$$

For the first element of the later pulses μ ,

$${}^{\mu}x_1 = {}^{\mu-1}x_{i_M} {}^{\mu-1}Y_{i_M}^n \quad \text{and} \quad {}^{\mu}x'_1 = {}^{\mu-1}x'_{i_M} {}^{\mu-1}W_{i_M}$$

is valid accordingly. Therefore ${}^1X = \frac{1}{i_M} \sum {}^1X_i$ can be calculated easily with a computer using the following calculation scheme:



The needed input quantities ${}^1x_1$, ${}^1x'_1$, Ω_m , Ω'_m and η in case of primary reactant poisoning are found by fitting the experimental data.

Results and discussion

The cracking conversion as a function of pulse number and reaction temperature has been evaluated from the amount of benzene formed. According to the calculation scheme (7) the optimal curve fittings $\bar{X} = X(\mu, T_R)$ for $m=1$ or 2 and $n=1$ or 2 were determined. The best fitting resulted for $m=2$ and $m=1$ and is shown in Fig. 1. The ethylbenzene used was extremely pure having been fractionated in a gas chromatograph. Therefore $\eta=0$ in (6) was justified.

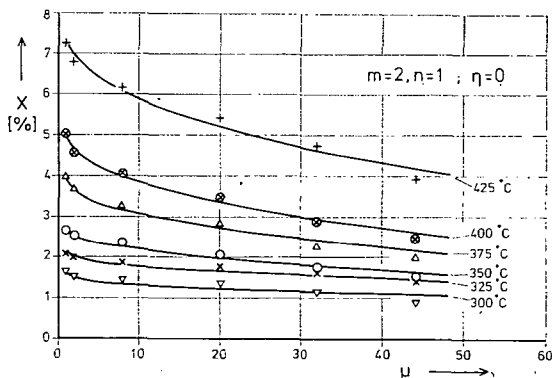


Fig. 1. Conversion of ethylbenzene over H-mordenite at different temperatures as a function of pulse number. The solid lines are calculated for $m=2$ and $n=1$

To test the chosen reaction model ($m=2$; $m=1$) cracking experiments were evaluated in which 0.1, 1, and 2% of pyridine had been added to the ethylbenzene as an inhibitor. The experimental and calculated curves are illustrated in Fig. 2 and show good correspondence.

For the determination of the apparent activation energy E_R for the primary cracking reaction at the sites Z_0 equation (5) is applied, in which the temperature dependent quantities ($^1x_1$, k_R and t_R) yield the Arrhenius equation:

$$\ln (^1x_1 \cdot T_R) = -E_R/R \cdot 1/T_R + \text{const.} \quad (8)$$

Fig. 3 shows the result giving $E_R = 13$ kcal/mol. An analogous plotting of $\ln (^1x_1' \cdot T_R)$ yields $E_R' = 9$ kcal/mol. These apparent activation energies have to be added to the heat of adsorption of ethylbenzene (about 15 kcal/mol) to get the true activation energies.

For the determination of the activation energy of the poisoning reaction E_P , equ. (6) has to be applied, which leads to

$$\ln (\Omega_2 \cdot T_R^2) = -E_P/R \cdot 1/T_R + \text{const.} \quad (9)$$

Fig. 4 shows the Arrhenius diagram, which results in 5.9 kcal/mol for E_P . By analogy, with Ω' , 2.1 kcal/mol for E_P' is found.

In spite of the relative low activation energy found for the cracking, the reaction does not seem to be influenced by diffusion. This follows from the fact that no dependence of conversion on crystal size (about 0.2 to 30 μm) has been found. Besides, no increase of activation energy with increasing pulse number has been found, which should be the case if diffusion hindrance is rate determining.

For the course of the cracking reaction on H-mordenite according to the analysis of the assumed reaction models the following statements seem to be valid: The reaction is of first order (related to ethylbenzene) and there is always one site ($n=1$) in-

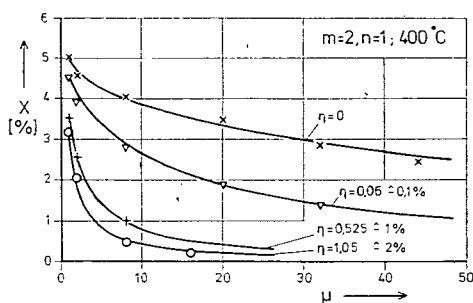


Fig. 2. Conversion of ethylbenzene over H-mordenite at 400 °C for different amounts of catalyst poison added as a function of pulse number. The solid lines are calculated for $m=2$, $n=1$ and η as indicated

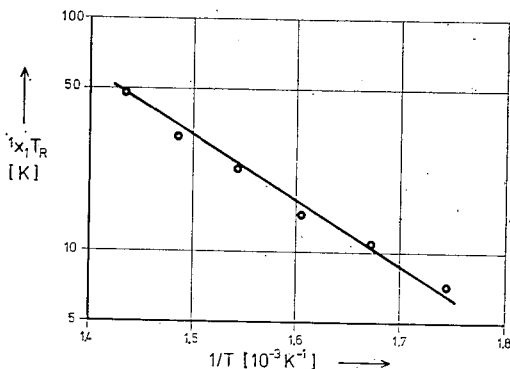


Fig. 3. Arrhenius plot for the cracking reaction

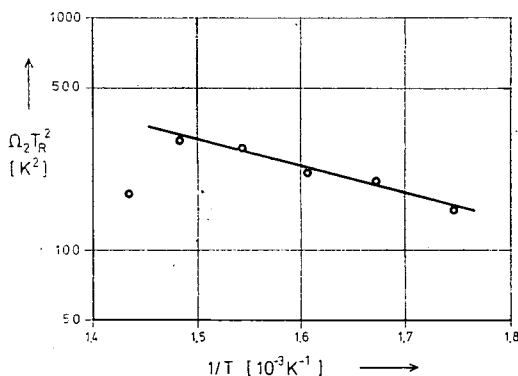


Fig. 4. Arrhenius plot for the poisoning reaction

volved in the initiating rate determining reaction step. Simultaneously a self poisoning of the catalyst takes place: one adsorbed product molecule is able to block two active sites ($m=2$).

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NICKEL ZEOLITE Y CATALYSTS. CATALYTIC ACTIVITY FOR THE METHANATION OF CARBON MONOXIDE USING NICKEL ZEOLITE Y CATALYSTS

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Nickel zeolite Y catalysts have been prepared by ion exchange. The catalysts were characterized for BET surface area and carbon monoxide adsorption. The metal areas were found to increase with degree of nickel exchange. Catalytic activities of these catalysts were measured for the hydrogenation of carbon monoxide in the range of 523–673 K. All the catalysts retain their crystalline structure after reduction with hydrogen at 723 K. Turnover number for methane formation increases with increase in degree of nickel exchange and nickel metal area. The degree of dispersion of the nickel was found to be independent of nickel loading.

Introduction

Hydrogenation of carbon monoxide has been extensively studied using nickel supported catalysts [1–4]. Conventional nickel catalysts are widely used in industry but are highly sensitive to poisoning by sulfur compounds. On the other hand, zeolites have been used in various petroleum refining processes because of their higher activity and better tolerance to sulfur and nitrogen poisoning than the conventional amorphous support [5–8]. Hydrogenation catalysts based on zeolites usually contain platinum or transition metals impregnated, or in a dispersed atomic form. The latter, with active metals being introduced by means of ion exchange, are known to be more catalytically active and resistant to impurities [9, 10]. Virtually nothing has been published on the catalytic activity of nickel-zeolite catalysts for the methanation of carbon monoxide although nickel supported on alumina and nickel supported on silica have been used extensively for this reaction [11].

An attempt has been made to develop and characterize a nickel-zeolite catalyst which would be effective in the methanation of carbon monoxide.

Experimental

Catalyst preparation and materials

The catalyst samples were prepared from Union Carbide molecular sieve SK—40 (1.5 mm extrudates) which is the sodium form of a Y-type zeolite. The catalyst was prepared in two stages. First, the Na-Y zeolite was converted to the Ca-Y form and then to the Ni-Y form by ion exchange [12]. Four different concentrations of Ni-Y catalysts were prepared by repeated ion exchange namely 4.21, 5.69, 6.78 and 6.82 wt.% nickel. All the samples were dried at 373 K for 24 h and subsequently were calcined at 673 K for 16 h before reduction. These catalysts were crushed and screened to $-80+100$ mesh and then stored in a dessicator. All the catalysts were reduced in the reactor in flowing hydrogen ($\approx$ at 100 ml/min) at 723 K for 16 h before the start of a test run. High purity hydrogen and CO (both Matheson 99.95% purity) were further purified before entering the reactor. Argon (99.95% purity) was used as a carrier gas in the chromatographic analyses.

Catalytic activity measurement

Methanation activities were measured in a flow reactor set up described elsewhere [4]. Catalytic activity measurements were carried out with $\approx$ 500 mg of the catalyst in the reactor. Blank runs with Na-Y and Ca-Y zeolites were also carried out in the temperature range 523–673 K under the same flow conditions in order to check their activity. Under these conditions, both zeolites were found to be inactive.

Catalyst characterization

BET surface area, nickel content, degree of nickel exchange, nickel metal area and acidity were determined in order to characterize the catalysts. Average nickel metal crystallite size was calculated from the active metal areas. These values are shown in Table I.

Results and Discussions

It is seen from Table I that there was little difference in nickel concentration ($\approx$ 0.29%) between catalysts SB3-Ni (third nickel exchange) and SB4-Ni (fourth nickel exchange). However, there was a big difference in the degree of nickel exchange between the two catalysts. This behavior can be explained on the basis of different sites such as S_I , S_{II} , S'_I and S'_{II} in the zeolite matrix [14]. During the ion exchange process, nickel (Ni^{2+}) ions are distributed in these sites. Ni^{2+} ions prefer S_I sites and are filled first. Degree of exchange gives an indication of Ni^{2+} ions distributed among these sites. In catalyst SB3-Ni it is likely that Ni^{2+} ions cannot occupy all the available positions and a part of Ni^{2+} ions are sitting outside the matrix, whereas in SB4-Ni most of the sites are occupied although the nickel concentration is nearly same. It has been reported in the literature that the maximum loading limit of the Ni^{2+} ions in zeolite Y is approximately $71 \pm 2\%$ at 318 K [15]. In other words, one might not be able to exceed the nickel concentration by more than 6.82% by ion exchange of zeolite Y, as an exchange of 72.2% was achieved for the catalyst SB4-Ni.

Table I

Analytical Data and Chemisorption Measurements of Ni-Y Zeolite Catalysts

Serial No.	Catalyst	Total Nickel Content (kg Ni/kg Catalyst)	Degree of Nickel Exchange %	BET Surface Area (km ² /kg)10 ³	Nickel ^a Metal Area (km ² /kg)10 ³	Average Crystallite size, nm	% Dispersion ^b	Acidity > H ₂ SO ₄ , 3·10 ⁻⁴ % (moles butylamine / kg)
Supports								
1.	Na-Y	—	—	538 ± 25	—	—	—	0.30
2.	Ca-Y	—	—	530 ± 30	—	—	—	1.13
Catalysts								
3.	SB1-Ni	0.0421	21.2	538 ± 10	20.2	0.90	36.1	1.63
4.	SB2-Ni	0.0569	46.0	560 ± 22	27.9	0.87	36.7	1.70
5.	SB3-Ni	0.0678	61.4	597 ± 10	34.9	0.80	38.5	1.57
6.	SB4-Ni	0.0682	72.2	552 ± 14	35.6	0.78	39.1	1.75
Data from Brooks et. al; [13]								
7.	Ni Zeolon	0.0324	—	—	30	0.50	69.4	—
8.	Ni Dav Z14	0.0592	—	—	22	0.60	33.2	—

a corrected for CO adsorption on the support at same temperature and CO vapor pressure.

b Linear form of CO bonding.

It is important that the zeolite catalysts should not lose their crystallinity during experimentation after ion exchange at 353 K and calcination at 673 K for 16 hr. All the catalysts used in the present study were tested for crystallinity and were found to have retained their crystallinity.

Chemisorption Measurements

The chemisorption data for Ni-Y catalysts are listed in Table I. It is seen that the amount of carbon monoxide chemisorbed increases with increase in nickel concentration. Also, it is interesting to note that the average crystallite size and the nickel dispersion does not vary much with nickel concentration.

It is observed that the zeolite support Ca-Y retains little CO whereas the unreduced nickel zeolite (Ni²⁺-Y) retains a substantial amount of CO implying that the CO chemisorption can occur on nickel cations Ni²⁺. This observation is confirmed by the work of ANGEL and SCHAFER [16] who reported that CO forms adsorptive bonds with Ni²⁺ and Ni⁺, using infrared spectra of zeolite Y. BROOKS AND CHRISTOPHER [13] also observed similar behaviour of CO on nickel zeolon and nickel Dav. Z14 catalysts. As the CO chemisorption occurs both on nickel cations as well as on metallic nickel (Ni⁰), suitable corrections must be applied to calculate the actual nickel metal area. It has also been established that only Ni⁰-Y is responsible for the hydrogenation activity in ethane hydrogenolysis whereas Ni²⁺-Y is inactive [17]. Therefore, a suitable correction was applied in order to measure nickel metal area (*i. e.* Ni⁰-Y area).

Catalytic Behaviour

The catalytic behaviour of all the Ni-Y catalysts is shown in Table II. All the activities are compared at 573 K. The activation energies varied from 71.5 to 79.0 MJ/kmol which are comparable with the reported [11] values between 73 to 130 MJ/kmol. The catalytic activity is expressed as turnover numbers and increases with

Table II
Catalytic behaviour of Ni—Y catalysts in the synthesis reaction

Serial No.	Catalysts	Turnover Number NCH_4 ($s^{-1} \cdot 10^3$) 573 K	Pre-exponential factor A ($s^{-1} \cdot 10^{-3}$)	Activation Energy E_{CH_4} (MJ/kmol)
1.	SB1-Ni	1.35	21.7 ± 6.9	79.0 ± 9.6
2.	SB2-Ni	1.30	10.5 ± 8.6	75.7 ± 18.5
3.	SB3-Ni	5.36	23.1 ± 1.6	71.8 ± 2.4
4.	SB4-Ni	7.68	25.2 ± 3.4	71.5 ± 5.6

increase in nickel concentration and degree of nickel exchange. Calculations show that the metal area expressed per kg of nickel metal increases with increase in the degree of exchange showing that, as the degree of nickel exchange increases, more nickel is uniformly distributed inside the zeolite matrix leading to better dispersion and higher activity.

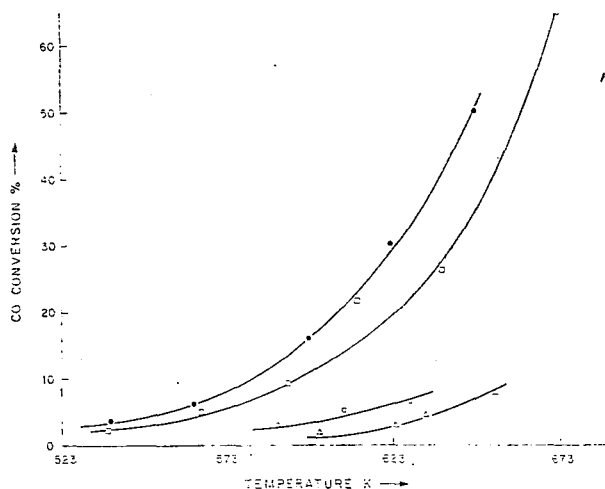


Fig. 1. Effect of degree of nickel exchange on the CO conversion: Δ SB1-Ni; $\circ$ SB2-Ni; $\square$ SB3-Ni; $\bullet$ SV4-Ni. Weight of the catalyst: 500 mg.

Fig. 1 shows the effect of degree of nickel exchange on carbon monoxide conversion in the temperature range 523–673 K. The conversion increases as the degree of nickel exchange increases. It is known that nickel ions (Ni^{2+}) located in S_I positions (interior, sixfold co-ordination with oxygen ions) are harder to reduce than those in the S_{II} positions (surface of the super cage, threefold co-ordination with oxygen ions). Furthermore, since nickel prefers the S_I to the S_{II} position, it is possible that all the locations of S_I are filled with nickel ions in catalysts SB1-Ni and SB2-Ni which results in lower turnover numbers. Fig. 1 shows that the conversion of CO increases sharply after 573 K. This might be due to the internal diffusional resistance which is experienced by the reactant molecules as they are transported through the narrow pores to the catalytic sites within the zeolite matrix crystal. One of the most striking characteristics of zeolite diffusion is its strong dependence on temperature which generally increases exponentially with the temperature [18]. Therefore, it would be expected that the conversion would increase exponentially with temperature under steady state conditions above 573 K as Fig. 1 indicates.

The introduction of a nickel atom in the zeolite matrix is associated with the introduction of a proton and thus, it is expected that the highly loaded catalysts are also catalysts of high acidity. Table I shows that acidity of Ni-Y catalyst is higher than Ca-Y support. Also, the maximum exchanged catalyst (SB4-Ni) shows the maximum acidity. It has been reported in case of Ca-Y zeolite that with cations in S_{II} and S_{III} positions a strong enhancement of the acidity results due to the lower electrostatic shielding in these positions and to the asymmetric charge distribution caused by higher charged cations [19]. During the nickel exchange, as the degree of exchange increased, the nickel ions occupied S_{II} and S_{III} positions beside S_I positions by replacing Ca^{2+} ions and thereby resulted in higher acidity. Furthermore, more Ni^0 atoms are available for the reaction (as Ni^{2+} ions in S_{II} and S_{III} positions are easy to reduce to Ni^0 atoms). It can be concluded therefore that the observed increase in methanation activity is due to increase in the acidity and availability of more Ni^0 atoms for the reaction.

Conclusions

Ni-Y zeolite containing Ni^0 is an active catalyst for the methanation of CO. Chemisorption of CO revealed that a substantial amount of CO is retained by unreduced Ni-Y catalyst indicating that CO chemisorption occurs at Ni^{2+} ions too. The amount of CO chemisorbed increases as the nickel concentration increases. CO conversion and turnover numbers for methane formation increase with increase in the degree of nickel exchanged. The degree of nickel dispersion is independent of nickel loading.

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BUTENE-1 ISOMERIZATION ON ALUMINUM-DEFICIENT NaHY ZEOLITES

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A series of NaHY zeolites with $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio 5.34, 6.70 and 8.45 was prepared. The properties of zeolitic 3550 and 3650 cm^{-1} OH groups and especially their interactions with adsorbed pyridine and butene-1 molecules were investigated using qualitative and quantitative IR spectroscopy. It was also shown that their acid strength increased both with cation exchange degree and with increasing dealumination. 3650 cm^{-1} OH groups are active centres in the catalytic isomerisation of butene-1. Their activity (turnover number) changes parallel to their acid strength.

The aim of the present paper was to investigate the effect of dealumination of NaHY zeolites on their catalytic properties and to correlate it with the acidity of the zeolite which was studied by the infrared spectroscopy.

Experimental

The samples of aluminum deficient NaHY zeolites with $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio 6.70 and 8.45 were obtained from the Institute of Industrial Chemistry, Warsaw. The extraction of aluminum was carried out by treating normal NaY zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio 5.34) with a boiling solution of EDTA. No distinct loss of crystallinity was observed. In the course of the present investigation sodium zeolites were transformed into ammonium form by treating them with NH_4NO_3 solution at 80°C [1]. The conditions were chosen in such a way that 3 series of NaNH_4Y zeolites were obtained showing different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios but very much similar numbers of NH_4^+ ions in a unit cell (Table I).

The hydrogen form of zeolites was obtained by vacuum decomposition of NaNH_4Y zeolites at 400°C for several hours. Such a treatment was always applied "in situ" in the infrared cell or in the catalytic reactor.

The IR spectra of zeolites and molecules adsorbed on them were recorded with a UR-10 Zeiss Spectrophotometer. The detailed procedure of such measurements is given in previous papers [2, 3].

The catalytic measurements of butene-1 isomerisation were carried out in a pulse microreactor (sample of catalyst 0.02 g, hydrogen carrier gas) and the products

Table I
Chemical composition of zeolites

Sample*	Number of NH_4^+ ions per unit cell after cation exchange
NaHY (5.34) 22.4	12.2
NaHY (6.70) 25.6	12.1
NaHY (8.45) 31.0	11.2
NaHY (5.34) 47.5	26.2
NaHY (6.70) 48.8	23.4
NaHY (8.45) 72.7	26.4
NaHY (5.34) 72.5	40.4
NaHY (6.70) 81.5	39.8
NaHY (5.34) 93.6	51.2
NaHY (6.70) 96.0	46.1
NaHY (8.45) 94.5	34.3

* The first figure after NaHY symbol is $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio, the second one the cation exchange degree (in %).

characteristic of silanol $\text{Si}-\text{OH}$ groups increased somewhat with the increasing degree of dealumination. Such OH groups do not react with pyridine nor ammonia molecules and are inactive in the catalytic isomerisation of butene-1.

In the IR spectra of NaOH zeolites two distinct OH bands at about 3550 cm^{-1} (LF OH groups) and 3650 cm^{-1} (HF OH groups) are present. It was stated that positions of both bands are not influenced by the dealumination of zeolites. Similar results for aluminum deficient zeolites were obtained by JACOBS AND UYTTERHOEVEN

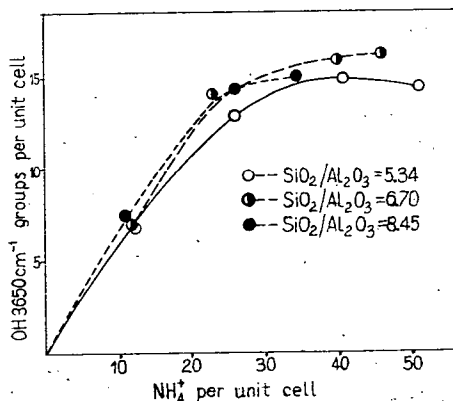


Fig. 1. The concentration of 3650 cm^{-1} OH groups as the function of the number of sodium cations substituted by protons (or NH_4^+ ions) in a unit cell. Particular curves represent the results obtained for the series of zeolites differing by the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio

analysed gas-chromatographically. Further details of the method are given in [4, 5]. Rate constants k were calculated using first order kinetic equation

$$\ln \frac{1-x_0}{x-x_0} = k \cdot \tau$$

where x and x_0 are molar fractions of butene-1 in the products and in the equilibrium state *resp.* τ is contact time.

Results and their discussion

OH groups in NaHY zeolites

Only very weak OH band at 3760 cm^{-1} was present in the IR spectrum of not decationized NaY zeolites with normal $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. The intensity of this band

characteristic of silanol $\text{Si}-\text{OH}$ groups increased somewhat with the increasing degree of dealumination. Such OH groups do not react with pyridine nor ammonia molecules and are inactive in the catalytic isomerisation of butene-1. In the IR spectra of NaOH zeolites two distinct OH bands at about 3550 cm^{-1} (LF OH groups) and 3650 cm^{-1} (HF OH groups) are present. It was stated that positions of both bands are not influenced by the dealumination of zeolites. Similar results for aluminum deficient zeolites were obtained by JACOBS AND UYTTERHOEVEN [6] who investigated the samples prepared — as in our case — by the dealumination of NaY zeolite. On the other hand BEAUMONT ET AL. [7] who dealuminated NH_4NaY zeolite observed the IR bands at 3555 , 3630 cm^{-1} and a shoulder between 3670 and 3695 cm^{-1} . The procedure of dealumination seems therefore to influence the properties of OH groups in zeolites.

The HF OH groups react with adsorbed pyridine molecules forming pyridinium ions. In the case of non-dealuminated NaHY zeolites LF OH groups do not protonate pyridine molecules (some diminishing of the corresponding IR band intensity is explained [8, 9] as the result of hydrogen bond formation). The LF OH groups in aluminum deficient zeolites may protonate pyridine at 150°C . The extent of this reaction increases with the

$\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio [1]. These facts may be interpreted as indicating an increased accessibility of LF OH groups for pyridine molecules or increased mobility of protons bonded in these OH groups.

The intensity of 1545 cm^{-1} band of pyridinium ion increased linearly with the increasing amount of adsorbed pyridine. From the slope of such linear plot the integrated extinction coefficient of this band was calculated ($0.82 \pm 0.08/\mu\text{mole}$). The amount of pyridine molecules necessary to the neutralization of all HF OH groups was also determined and their concentration calculated [1, 3]. The results obtained for zeolites with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio 5.34, 6.70 and 8.45 are given in Fig. 1. It is seen that irrespectively of the dealumination degree the curves are very much similar in their shape. They increase at first almost linearly with the cation exchange degree and then reach a constant value of about 15–16 HF OH groups per unit cell. An analogous result was obtained for NaHY zeolite with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio equal to 5.22 [3]. It is interesting to notice that this highest concentration of HF OH groups observed by us is very close to the number of hexagonal prisms in the zeolite lattice (16 per unit cell). It means that the highest concentration of HF OH groups corresponds to the situation in which there is an average one such group per one hexagonal prism. Similar value was also obtained by JACOBS ET AL. [10] for a zeolite with 70% of cations exchanged.

The acid strength of HF OH groups was estimated by studying thermodesorption of pyridine. This method was based on the assumption that the molecules of pyridine adsorbed on the stronger acid sites are desorbed at higher temperature than those adsorbed on the weaker ones. The B_{500}/B_{350} ratio was assumed as the measure of the acid strength (B_{350} is the intensity of 1545 cm^{-1} pyridinium ion band after adsorption and evacuation at 350°C , B_{500} the same value measured after subsequent desorption at 500°C . In both cases spectra were registered at 150°C). B_{500}/B_{350} ratio expresses the fraction of pyridinium ions remaining after desorption at 500°C . The results given in Fig. 2a show that at the constant concentration of HF OH groups their acid strength increases with the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. On the other hand at the constant $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio the strength of HF OH groups increases with the cation exchange degree [11]. This latter conclusion was also reached by us in a previous study of a series of normal NaHY zeolites. The simultaneous increase in the acid strength of NaOH zeolites with increasing

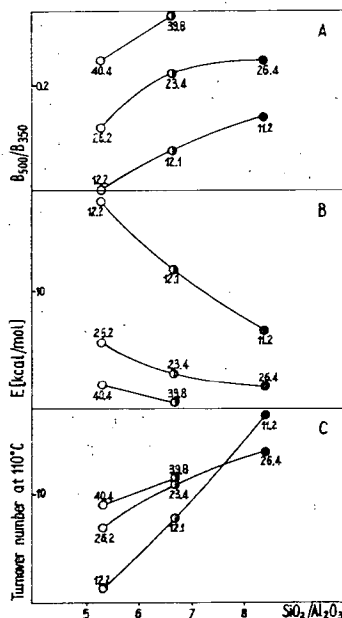


Fig. 2. a. The values of B_{500}/B_{350} ratio characterizing the acid strength of HF OH groups

b. The activation energy of butene-1 catalytic isomerization

c. The turnover number of HF OH groups in the catalytic isomerization of butene-1 at 110°C . All three values are presented as the function of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. The lines are joining the points corresponding to the different values of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio but containing nearly the same number of protons introduced into a unit cell. The exact content of protons in unit cell is given by the numbers at each point.

dealumination and cation exchange degree was observed earlier by BEAUMONT AND BARTHOMEUF [12—14] who determined acidity using titrimetric methods.

Catalytic Properties of Aluminum Deficient NaHY Zeolites

In an earlier research [4] it has been shown by us that in the case of Y zeolites with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio equal to 5.22 only the HF OH groups are catalytically active in the isomerisation of butene-1. Non-decationated NaY zeolites as well as dehydroxylated ones and containing only Lewis acid sites are non active. In addition IR studies have shown [9] that at the temperatures of the catalytic reaction only HF OH groups interacted with butene molecules which manifested by the decrease of the intensity of 3650 cm^{-1} band and simultaneous vanishing of unsaturated character of the olefine. The conclusion concerning the role of HF OH groups reached also by JACOBS ET AL. [10] was verified by us also in the case of dealuminated zeolites which are losing their catalytic activity in the measure as HF OH groups are poisoned by chemisorbed pyridine molecules.

The concentration of HF OH groups determined by quantitative IR spectroscopy was used for calculating the turnover numbers for butene-1 isomerisation. Their values together with the values of activation energies determined within the temperature range $90\text{--}125^\circ\text{C}$ are shown in Figs. 2b and c. It is clearly seen that if the samples contain approximately the same number of protons introduced into a unit cell (and also as Fig. 1 shows the same number of HF OH groups) the turnover number increases with increasing value of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. From the same figure one may conclude that at the constant value of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio the activity is increasing with increasing degree of cation exchange. The increase in the catalytic activity is accompanied in all the cases by a decrease in the activation energy.

The catalytic properties of HF OH groups in NaHY zeolites correlate very well with their acid strength illustrated by the graphs in Fig. 2a. Increased acid strength of HF OH groups seems to be the most plausible explanation of the observed effects of decationization and dealumination.

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THE STATE OF THE PLATINUM IN ZEOLITIC CATALYSTS

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The CaY and Na-mordenite supported Pt with 0.1–5 wt. % Pt showed a linear increase in the specific Pt surface area with increasing amount of metal. The sintering of Pt between 773 and 1073 K is diffusion controlled whereas it is sintering controlled at higher temperatures. The former becomes faster with higher metal content and temperature, being slower with Pt/Na-mordenite than with Pt/CaY. The specific activity for hydroisomerization of *n*-hexane with 2% Pt/CaY varies with the time of calcination at 1073 K and with Pt particle size.

Introduction

Catalytic active metals are commonly employed in the form of supported metal catalysts with the metal dispersed as small crystallites on high surface area supports. This good dispersion renders an optimal economical utilization of the mostly expensive metal. Besides the support separates physically the metal crystallites and thereby hinders the sintering.

Especially at high working temperatures growth of the metal crystallites still occurs. To investigate the influence both of the Pt content and of the structure of the support on the sintering of the noble metal, catalysts with different zeolitic supports — CaY and Na-mordenite — and different Pt contents have been prepared and sintered in air.

Furthermore, sintered catalysts with different Pt crystallite sizes were tested for the specific hydroisomerization activity.

Experimental

Catalyst preparation

As support for the catalysts a commercial Na-mordenite powder (Norton) and CaY zeolite powder were used. CaY zeolite was prepared from NaY (Linde SK-40) by exchanging 86% of the Na-ions by Ca^{2+} . These supports were loaded with $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2 \cdot \text{H}_2\text{O}$. After drying at 393 K and a 2 h calcination at 673 K the catalyst was reduced 2 h at 473 K and 1 h at 673 K with 50 ml H_2 /min.

Measurement of the metal surface area

The structural parameters of the metallic phase of the catalysts, *i.e.* the specific metal surface area, the metal dispersion and the mean metal crystallite size, have been determined by the O_2/H_2 -titration at 573 K by the pulse method in a gas-chromatographic flow apparatus [1]. First the adsorbed water was removed at 673 K with 50 ml N_2 /min. Then the Pt was covered with oxygen 1 h at 573 K with 30 ml dried air/min. At the same temperature the formed Pt oxide was titrated by injection of several H_2 pulses (0.664 cm^3 each) into the carrier gas stream of 20 ml N_2 /min. The non-oxidized H_2 was determined by a heat conductivity cell. A following chemisorption of H_2 on Pt could be neglected at this temperature [1, 2]. This gave good agreement with electron microscopy results.

Catalytic activity measurements (procedure)

The activity for the hydroisomerization of *n*-hexane was tested in a fixed bed tube reactor [3]. For activation the pelletized catalysts were treated in the reactor in flowing H_2 2 h at 473 K and 2 h at 673 K with final cooling down to 473 K. The reaction parameters were the following:

Temperature:	583 K
Pressure:	27.5 bar
Weight of catalyst:	3 g
Feed (<i>n</i> -hexane):	6 g/h
Feed (H_2):	0.4 mol/h

Results and discussion

Influence of the amount of zeolite supported platinum on the metal surface area

The metal surface area per g of catalyst (*S*) and the degree of dispersion (ratio of surface to total metal atoms) was measured for CaY and Na-mordenite supported Pt catalysts all prepared in the same way. Fig. 1 shows that *S* increases linearly with increasing metal content according to

$$\begin{aligned} S &= 0.96 \cdot c_{Pt} && \text{for Pt/CaY and} \\ S &= 1.46 \cdot c_{Pt} && \text{for Pt/Na-mordenite.} \end{aligned}$$

So for the same Pt content the mordenite catalyst has a 50% higher metal surface area than the CaY catalyst.

This can be explained by the different crystal systems and pore structures, respectively, of the supports. Whereas CaY has a relatively open 3 dimensionally accessible pore system with 0.9 nm wide pores, the diffusion of Pt atoms for forming bigger particles is more hindered in the Na-mordenite by the parallel elliptical pores of the size 0.57×0.69 nm which cannot be passed crosswise.

Another reason might be the statistically smaller distance between the freshly reduced Pt atoms in the Pt/CaY as CaY has a higher density of exchangeable cations compared with Na-mordenite. Fig. 1 also shows that the dispersion degree of the Pt in both zeolite catalysts approaches unity for very small metal contents and is decreas-

ing mainly between 0 and 1 wt.% Pt. At higher Pt contents the degree of dispersion and the mean Pt particle size are almost constant with 2.4 nm for Pt/CaY and 1.6 nm for Pt/Na-mordenite, respectively.

Many of the industrially used non-zeolitic Pt catalysts are Pt-on- Al_2O_3 which mostly are prepared by impregnation with H_2PtCl_6 . These catalysts have Pt surface areas increasing only by a lower power function, e.g., by $c_{\text{Pt}}^{2/3}$ [4] or by $c_{\text{Pt}}^{0.3}$ [5].

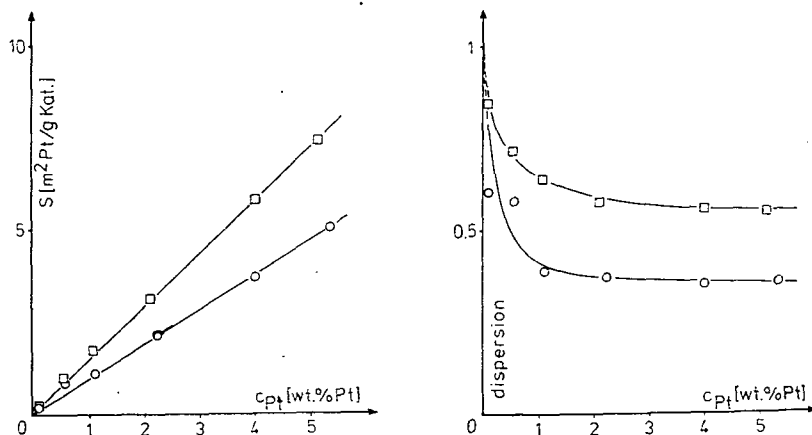


Fig. 1. Specific surface area S and dispersion of Pt as function of content of Pt on CaY (○) and on Na-Mordenit (□)

The sintering of zeolite supported Pt

For testing the influence of the temperature on the sintering of zeolite supported Pt the catalyst 0.5% Pt/CaY was sintered up to 60 h between 773 and 1073 K. Fig. 2 shows little sintering of the Pt at a temperature of 773 K whereas at higher temperatures the rate of sintering is strongly accelerating. For these sintering rates ($dS/dt = -k \cdot S^n$ [6], k : rate constant) the power-law order n showed to be between 6 and 8 for 773–873 K and to be 2 and 3 for 973 and 1073 K, respectively.

Therefore, according to RUCKENSTEIN AND PULVERMACHER [7], the first region means a diffusion controlled sintering whereas at higher temperatures it is sintering controlled. Similar results were found for the 2% Pt/CaY catalyst.

For the investigation of the influence of the support and the metal content on the sintering behaviour Pt/CaY and Pt/Na-mordenite have been sintered in air at 873 K, i.e. under diffusion controlled conditions. With increasing metal content and the same initial Pt dispersion (cf. Fig. 1) an increasing sintering rate was found for

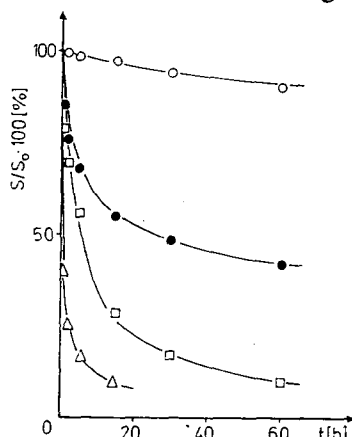


Fig. 2. Relative decrease of Pt surface area by sintering of 0.5% Pt/CaY in air at 773 K (○), 873 K (●), 973 K (□) and 1073 K (△)

both catalysts (see Fig. 3), being explainable by the increasing surface concentration of Pt crystallites. But whereas the sintering rate at Pt/CaY has become very small after 5–10 h this holds for Pt/Na-mordenite only after 30–40 h, presumably also a result of the better diffusion of Pt in CaY.

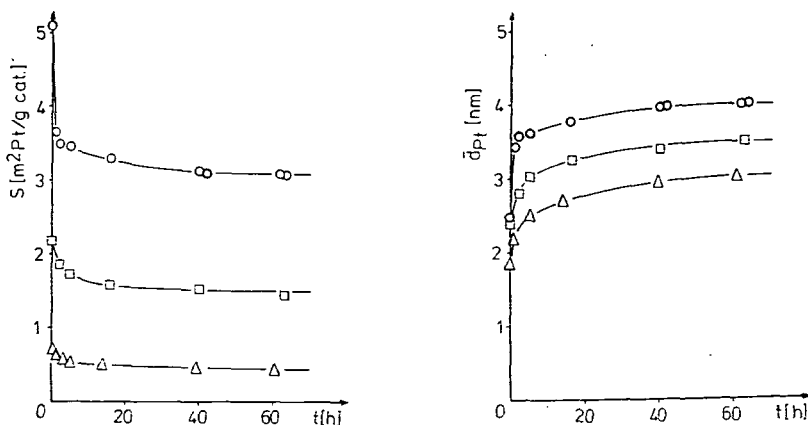


Fig. 3. Decrease of Pt surface area and increase of mean Pt particle size by sintering in air of 0.54% Pt/CaY (Δ), 2.23% Pt/CaY ($\square$) and 5.36% Pt/CaY ($\circ$), respectively

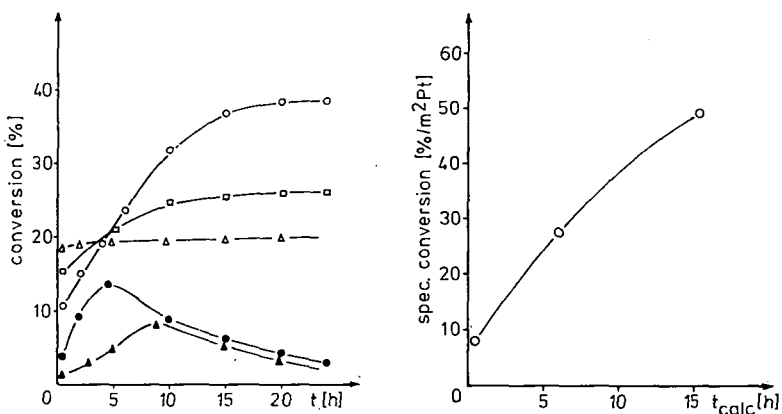


Fig. 4. Conversion and specific conversion of *n*-hexane at 583 K for 2% Pt/CaY (open symbols) and CaY (filled symbols) treated in air at 1073 K for 0.5 h ($\circ$, $\bullet$), 6 h ($\square$) and 15.5 h (Δ , $\blacktriangle$) corresponding to 4.1 nm, 9.1 nm, and 13.9 nm Pt particle size, respectively

Catalytic activity measurements

The catalytic activity of 2% Pt/CaY treated in air at 1073 K between 0.5 and 15.5 h was tested (see Fig. 4). Whereas the supported Pt shows an increasing conversion of *n*-hexane with increasing reaction time becoming constant after about 24 h the activity of the support CaY alone has a maximum. The deactivation is mainly caused by coking. With supported Pt no other products than isomers of *n*-hexane are found. This means that Pt hinders the coking of the catalyst.

As in addition IR-spectroscopy [8] also showed a somewhat different behaviour of CaY and Pt/CaY treated in the same way it was not yet possible to relate the specific conversion exclusively to the metal phase. Instead, the specific conversion was plotted versus the time of heat treatment t_{calc} corresponding to increasing Pt particle sizes for relatively short reaction times (when the support still had only a relatively low activity).

Acknowledgement

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INFLUENCE OF EXCHANGEABLE CATION ON Ni^{2+} REDUCTION AND Ni^0 MIGRATION IN X ZEOLITE

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It was shown that Ni^{2+} reducibility and Ni^0 particle size obtained by hydrogen reduction are depending on Ni^{2+} location, Lewis centers concentration, nature and concentration of other elements present in its environment, pretreatment and reduction conditions.

It was possible to obtain very small particles of Ni^0 (7 Å) stabilized in the zeolitic lattice.

Introduction

In recent years, the reduction of transition metal ions supported on zeolite has been investigated with the aim of obtaining highly dispersed metallic particles of homogeneous size.

In the present work, we have undertaken a comparative study of the hydrogen reduction of Ni^{2+} ions in an X zeolite by varying factors such as

- the Ni^0 concentration by unit cell,
- the initial location of these cations,
- the nature of a second cation present in its environment,
- the acidic degree of the support.

By several methods, we try to determine the Ni^0 formation in order to obtain highly dispersed particles stabilized in the lattice.

Materials

The samples were prepared by exchanging sodium X zeolites (Linde Carbide) with 0.1 N solution of Ni^{2+} and Me^{x+} nitrates ($\text{Me}^{x+} = \text{Ca}^{2+}$, K^+ , Ce^{3+} , La^{3+}) or with ammoniacal solutions of Pt (NH_3)₄²⁺ and Pd(NH_3)₄²⁺ ions.

Table I

Initial sample: $\text{Na}_{86}(\text{SiO}_2)_{106}(\text{AlO}_2)_{88} n \text{H}_2\text{O}$
(unreduced samples)

Composition	Abreviation
$\text{Ni}_{31}\text{Na}_{24}\text{X}$	Ni_{31}X
$\text{Ni}_8\text{Na}_{64}\text{HX}$	Ni_8X
$\text{Ni}_{10}\text{H}_{66}\text{X}$	Ni_{10}HX
$\text{Ni}_{24}\text{Pd}_{0.5}\text{Na}_{12}\text{H}_{25}\text{X}$	Ni_{24}PdX
$\text{Ni}_{12}\text{Pd}_6\text{Na}_{12}\text{H}_{22}\text{X}$	$\text{Ni}_{12}\text{Pd}_6\text{X}$
$\text{Ni}_{17}\text{Pt}_{0.45}\text{Na}_{40}\text{H}_{11}\text{X}$	Ni_{17}PtX
$\text{Ni}_{24}\text{Ce}_6\text{Na}_{16}\text{X}$	Ni_{24}CeX
$\text{Ni}_{10.5}\text{Ca}_{20}\text{H}_{21}\text{Na}_{24}\text{X}$	Ni_{10}CaX
$\text{Ni}_{14}\text{La}_{15}\text{Na}_9\text{H}_4\text{X}$	$\text{Ni}_{14}\text{La}_{15}\text{X}$

The $\text{Na}^+\text{H}^+\text{Ni}^{2+}\text{X}$ samples were prepared by exchanging a partially decationized sample with 0.1 N solutions of Ni^{2+} .

The sample composition was determined by chemical analysis (Table I).

All samples were pretreated for 16 hours under vacuum at 10^{-6} torr and at 773 K.

Experimental methods

The Ni^{2+} location was determined by X-ray analysis using GALLEZOT's method [1].

Kinetic analysis was performed by measuring the rate of the hydrogen uptake in a classic volumetric apparatus at constant hydrogen pressure and at various temperatures. In some experiments successive reduction desorption cycles were carried out. The amount of gas desorbed was measured by a MacLeod gauge and analyzed by mass spectroscopy. Besides some experiments were carried out under dynamic conditions at constant flow of hydrogen and various temperatures.

The magnetization was measured by the Weiss extraction method either in an electromagnet giving 21 K. oe. (measurements at 300 and 77 K) or in a superconductive coil reaching 70 K. oe. (measurements at 4.2 K.)

EPR measurements were made with Varian E_3 spectrometer in X band.

The benzene hydrogenation was studied in a differential steady state flow micro-reactor and the measurements were generally performed at low conversion (normally $\leq 5\%$).

The initial hydrogen and benzene pressure were 702 and 58 torr respectively. A standard temperature of 383 K was chosen in order to make comparison with data already published [2]. Catalysts weights were generally of the order of 300 mg for a total gas mixture flow of 1.4 lh^{-1} . Under these conditions, interdiffusion phenomena were negligible. Reactants and products were analyzed on a 5% Carbowax 20 M on spherical XO B 0.75 column at 353 K.

Results

I — Cationic Location

The cationic location was determined by X-ray analysis based on Debye-Scherrer diffraction diagram. The results corresponding to the different samples studied are given in the following tables:

Examination of Table II suggests the following comments:

- Crystallographic analysis agrees with chemical analysis if we assume that the excess Na^+ located in II (supercages) corresponds to Ni^{2+} ions.
- The Ni^{2+} location is highly depending on the nature of other cations introduced into the lattice and on the Ni^{2+} concentration.
- The results reported in Table III show that Ni^{2+} ions disappear at the same time from sites I (hexagonal prisms) I' (sodalite cavities) and II (supercages). However we know [4] that in Y zeolite Ni^{2+} disappears successively from sites II, I' and I.

The data allowed us to explain kinetic results for the Ni^{2+} reduction in NiNaX and NiNaY .

The study of other samples after reduction is in progress.

Table II
(Reduced samples)

Sample	Atom	Number of atoms per unit cell
$\text{Ni}_8\text{Na}_{64}\text{X}$ $a^* = 24.79 \pm 0.02 \text{ \AA}$ $R^{**} = 0.097$	Na(II) Ni(I) Na(I')	30.1 (9) 5.3 (5) 20.4 (3)
$\text{Ni}_{31}\text{Na}_{24}\text{X}$ $a = 24.47 \pm 0.02 \text{ \AA}$ $R = 0.104$	Na(II) Ni(I) Ni(I')	34 (1) 11.7 (4) 9.6 (5)
$\text{Ni}_{17}\text{Pt}_{0.45}\text{Na}_{40}\text{X}$ $a = 24.54 \pm 0.02 \text{ \AA}$ $R = 0.091$	Na(II) Ni(I) Ni(I')	36 (1) 11.3 (3) 5.8 (3)
$\text{Ni}_{10}\text{Ca}_{20}\text{Na}_{24}\text{X}$ $a = 24.75 \pm 0.02 \text{ \AA}$ $R = 0.103$	Ca(II) Ca(I) Ni(I')	20 (1) 12.1 (4) 7.8 (3)
$\text{Ni}_{24}\text{Ce}_6\text{Na}_{18}\text{X}$ $a = 24.67 \pm 0.02 \text{ \AA}$ $R = 0.120$	Na(II) Ni(I) Ce(I')	24 (1) 11.7 (4) 3.2 (4)
Ni La NaX $a = 24.95 \pm 0.02 \text{ \AA}$ $R = 0.29$	Na(II) Ni(I) La(I')	30 10 10

* a: unit cell parameter

** $R = \sum |F_o - F_c| / \sum |F_o|$ where F_o and F_c are the observed and calculated structure factors (Refinement program ORFLS) [3]

The figures in parentheses correspond to the standard error on the last significant figure.

Table III

Sample	atom	Number of atom per unit cell
$\text{Ni}_{31}\text{X} + \text{H}_2$ (523 K) $a = 24.42 \pm 0.02 \text{ \AA}$ $R = 0.103$	Na(II) Ni(I) Ni(I')	32.8 (9) 11.9 (7) 8.8 (9)
$\text{Ni}_{31}\text{X} + \text{H}_2$ (713 K) $a = 24.42 \pm 0.02$ $R = 0.109$	Na(II) Ni(I) Ni(I')	25 (1) 9.6 (4) 7.6 (6)

II — Kinetic Results

Kinetic studies have shown that the static hydrogen reduction of Ni^{2+} in X zeolite is depending on the Ni^{2+} concentration and on the nature and percentage of the second cation. We have reported in Fig. 1 and 2 the curves $\alpha=f(t)$ where α is the degree of advancement [$\alpha(t) = \text{NiO}/(\text{Ni}^{2+} + \text{Ni}^0)$] of the reaction.

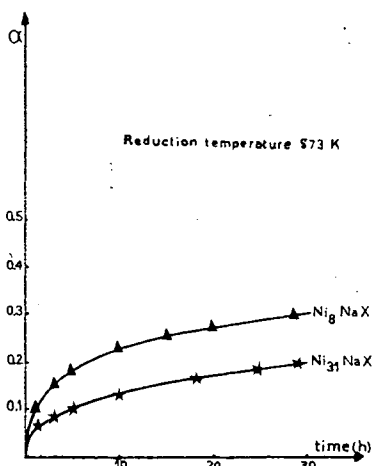


Fig. 1. Curves $\alpha=f(t)$ for Ni^{2+} reduction by hydrogen ($P_{\text{H}_2}=50$ torr) in NiNaX .

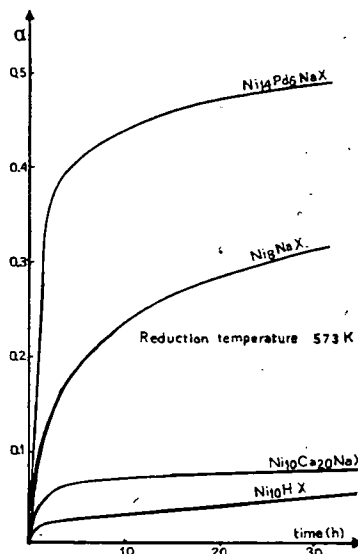


Fig. 2. Influence of other cations on Ni^{2+} reduction by hydrogen ($P_{\text{H}_2}=50$ torr).

It is observed that for $\text{Ni}^{2+}\text{Na}^+\text{X}$ whatever is the Ni^{2+} concentration the curves are superimposable and the activation energy $E=28$ Kcal/mol as long as the degree of transformation for whole ranges of temperature and pressures is the same. The reduction under static conditions is limited by hydrogen diffusion towards Ni^{2+} for which location sites are assumed energetically homogeneous.

For the other samples, it is necessary to consider that several competitive steps are involved in the transformation. For example for $\text{La}^{3+}\text{Na}^+\text{Ni}^{2+}\text{X}$, $\text{Ce}^{3+}\text{Na}^+\text{NiX}$ activation energy is varying when the degree of transformation increases. It is impossible under these conditions to assume the cationic sites to be energetically homogeneous and to define the rate determining step. However, in all cases, diffusion process takes place and reaction products (particularly OH groups) are inhibiting the reduction. Under static conditions it is difficult to obtain a complete reduction at temperatures lower than 673 K.

It was observed in Fig. 2 that the various cations influence the Ni^{2+} reducibility.

So at a given temperature, the lowest value of α is obtained for $\text{H}^+\text{Ni}^{2+}\text{X}$ sample. The vacuum treatment at 773 K. before the reduction reaction leads to the formation

of Lewis acid centres. These centres can behave like oxidizing centres which will therefore favor the redox equilibria towards 2:



Under these conditions the reduction of Ni^{2+} is very difficult and requires fairly high activation energies. In presence of Ca^{2+} , the Ni^{2+} reduction is difficult and we observe by EPR measurements the presence of Ni^+ which is alone in this sample when reduction temperature is lower than 573 K.

Conversely, small quantities of Pt^0 or Pd^0 in the lattice obtained by preliminary reduction of Pt^{2+} /or Pd^{2+} in X zeolite increase the Ni^{2+} reducibility; the higher is the (Pd^0 , Pt^0) concentration, the greater will be the reducibility. Besides, it is possible to obtain the complete Ni^{2+} reduction when $\text{Ce}^{3+}\text{Ni}^{2+}\text{X}$ and $(\text{Pt}^0, \text{Pd}^0)\text{Ni}^{2+}\text{X}$ are treated by a dynamic flow of hydrogen at 623 K. In all cases, the dynamic conditions for a given temperature increase the degree of advancement α .

III — Particle diameters

a) Ni^{2+} is only with Na^+ ($\text{Ni}^{2+}\text{Na}^+\text{X}$). The results obtained by magnetic measurements at 300 and 77 K on NiX show that for reduction temperatures below or equal to 523 K, both very small particles occluded in the zeolitic cavities and larger particles in the 60–100 Å range located on the outside of the surface (Table IV).

Table IV

Samples	Total metal weight per cent	Reduction temperature	Particle diameter in Angström	Rate at 383 K in mol $(\text{C}_6\text{H}_6)\text{S}^{-1}$ $(g\text{Ni}^0)^{-1}/10^{-7}$	E_a Kcal/mol $^{-1}$
Ni_8X	Ni: 3.54	523 K $\alpha = 0.1$ 573 K $\alpha = 0.4$	$\bar{D} \sim 60 \text{ Å}$ $D < 15 \text{ Å}$ $\bar{D} \sim 150 \text{ Å}$	38.2	14 ± 0.5
NiPd^0X		573 K $\alpha = 0.6$	$\bar{D} \sim 30 \text{ Å}$		
NiPt^0X	Ni: 7.34 Pt: 0.65	573 K $\alpha = 0.28$	$\bar{D} \sim 25 \text{ Å}$		
NiCeX	Ni: 10.1	573 K $\alpha = 0.3$	85% $D < 15 \text{ Å}$ 15% $D \sim 30 \text{ Å}$	65.7	13.4 ± 0.5
		Dynamic reduction 623 K $\alpha \approx 1$	85% $D = 7 \text{ Å}$ 15% $D = 30 \text{ Å}$	72	12 ± 0.5
NiPt^0X	Ni: 7.34 Pt: 0.65	Dynamic reduction 623 K $\alpha \approx 1$	$\bar{D} \sim 25 \text{ Å}$	48.9	$12-13 \pm 0.5$

Reduction desorption cycles were carried out on these samples at the reduction temperature. During the desorption runs it was observed a hydrogen desorption and simultaneously a decrease in the magnetization of the sample considered. This can reasonably be attributed to partial reversal of Ni^{2+} ion reduction according to the equilibrium (1).

At higher temperatures >573 K the mean particle diameter increases very rapidly and reaches values greater than $150 \text{ \AA}$. Under these conditions the reduction is no longer reversible.

b) When cations other than Na^+ are present with Ni^{2+} , the results are not the same.

We can see on Table IV. that in presence of Pd^0 , Pt^0 the Ni^0 particle size obtained is very homogeneous ($25\text{--}30 \text{ \AA}$) and does not depend on reduction temperature. Furthermore by carrying out reduction desorption cycles on a given sample $\text{Ni}_{14}^{2+}\text{Pd}_6^0\text{X}$ between $523\text{--}633$ K, it is possible to attain almost complete reduction and to obtain Ni^0 particles of uniform size about $25 \text{ \AA}$.

In the presence of Ce^{3+} magnetic measurements show that the degree of reduction determined by saturation magnetization at 77 K is always very much less than that measured by hydrogen uptake. This suggests that there are very small Ni^0 particles ($\bar{D} < 15 \text{ \AA}$). The mean size of particles saturated at 77 and 300 K is $25 \text{ \AA}$ for samples reduced below 523 K under static conditions.

When the $\text{Ni}^{2+}\text{Ce}^{3+}\text{X}$ is pretreated under oxidizing conditions, static reduction leads to Ni^0 particles which are homogeneously distributed but much larger than before ($\bar{D} \sim 60 \text{ \AA}$). Under dynamic reduction at 593 K it was obtained an almost complete reduction ($\text{Ni}^0/\text{Ni}_{\text{tot}} = 0.85$) and particle diameters determined at 4.2 K were about $7 \text{ \AA}$.

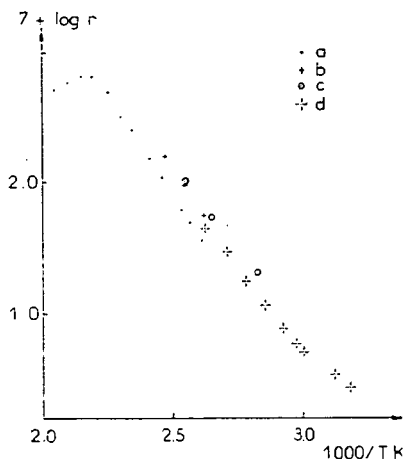


Fig. 3. Arrhenius plot for benzene hydrogenation. Reaction rate in $\text{mol. C}_6\text{H}_6 \text{ S}^{-1} (\text{gNi}^0)^{-1}$
(a: Ni_6X , b: NiCe_6X static reduction, c: NiCe_6X dynamic reduction, d: NiPtX dynamic reduction.)

IV — Catalytic activity

We studied the benzene hydrogenation activity of the metallic nickel particles as a measure of the surface active sites. This reaction is generally considered as a structure insensitive one. The effect of temperature is shown by the Fig. 3. Under our experimental conditions, the plot is linear below 450 K and yields a value for E_{ap} of about 14 Kcal/mol in agreement with the other published results [2, 5]. Nevertheless, we may notice a slight

enhancement of our values. Data reproducibility during temperature cycles indicates that no catalysts deactivation occurs. This result may be interpreted like a good thermostability of reduced and unreduced nickel particles.

The appearance of a maximum of activity with $E \neq 0$, at about 473 K, is also very clear. Theoretical origin for this maximum has been extensively discussed by COENEN et al. [2].

It is interesting to consider now the activity data in relation with the results of the preceeding sections. Primarily we may observe that the order of decreasing is the same as that of reducibility. These observations show that the activity may be considered, in first approximation, as a measure of the superficial metallic nickel. The second point is relative to the effect of static or dynamic reduction treatment. It is also clearly shown that dynamic conditions produce higher rates.

The effect of second element (Ce^{3+} , Pd^0 , Pt^0) on activity is perhaps the more drastic one, when considering the data obtained with NiX and NiCe X for instance (Table IV).

As for the reducibility effect of Pt^0 and Ce^{3+} , the activities of $\text{Ni}^0\text{Ce}^{3+}\text{X}$ and $\text{Ni}^0\text{Pt}^0\text{X}$ are similar.

At last, as it was foreseen, no effect of particle size or of metal location is detected when looking for activity per square meter of metallic nickel. It is noticable that even with various experimental parameters, all catalysts have an activity of the same order of magnitude.

Conclusion

These results show that both reducibility, of Ni^{2+} ions exchanged in X zeolite, and dispersion of the resulting Ni^0 particles, depend greatly on the cation or second metal present in its environment. Besides catalytic activity of the samples for benzene hydrogenation is depending on their reducibility and thermostability. Generally it is observed [6, 7] that the diameter and the stability of metal particles obtained after reduction depend on several factors:

- The acidity or the basicity of the support.
- The eventual existence of redox mechanisms which interact with the energetics of the kinetic process.
- The thermostability of the OH groups formed during the reduction.
- The presence of a modifying element which can interact strongly with the support and with the metal crystallites [8].
- For the samples studied in this work, the above factors influence the reduction process and particle migration.
- For the reduction of $\text{H}^+\text{Ni}^{2+}\text{X}$ which contains a larger number of acidic centres (Lewis sites), it was shown a considerable inhibition to reduction and consequently the formation of large particles. These acidic centres can favor the oxidation process in the redox equilibrium.
- In the presence of Pd^0 or Pt^0 several factors may be involved: these metal particles highly dispersed inside the cavities interact strongly with the lattice and are also active in the Ni^{2+} reduction process by providing atomic hydrogen. Also Pt^0 or Pd^0 clusters decrease the surface acidity and may play the role of donors relative to the strongly acid sites of zeolites.
- In the presence of Ce^{3+} , the reduction of Ni^{2+} ions leads to a highly dispersed metallic state. Now it may be suggested that Ce^{3+} ions could have an important effect on the thermostability of the OH groups formed during the reduction. Ce^{3+} would be a modifying element. Its role is depending on concentration and pretreatment conditions.

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THE CATALYTIC DECOMPOSITION OF FORMIC ACID ON SOME MOLECULAR SIEVES $\text{Na}_{1-x}\text{H}_x\text{Z}$

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On $\text{Na}_{1-x}\text{H}_x\text{Z}$ formic acid is decomposed into $\text{H}_2 + \text{CO}_2$ and $\text{H}_2\text{O} + \text{CO}$. The determination of the reaction mechanisms allows to point out the chemical properties of these solids. Dehydrogenation takes place at high temperature, through the formation of aluminium and sodium formates. Dehydration, which occurs at low temperature, is catalysed by the Brönsted acid sites created during the preparation of the solid or the formation of formates. The strength of this acidity strongly depends on x value.

We have employed the decomposition of formic acid to investigate chemical properties of Z-zeolites in which the parent sodium ions have been partially replaced by H^+ ions. We present our results concerning the overall kinetics of formic acid decomposition and the chemisorption of this molecule as revealed by infrared spectroscopy.

Experimental part

Sample preparation

The cation exchanged zeolites were prepared from Norton sodium Z-type zeolite by treatment with an aqueous solution of nitrate containing various quantities of ammonium ion. $\text{Na}_{1-x}\text{H}_x\text{Z}$ is obtained by decomposition of $\text{Na}_{1-x}\text{NH}_x\text{Z}$. The extent of exchange is given in Table I. Before any experiment the samples were treated at 673 K either in the decomposition vessel or in the IR cell.

Kinetic experiments

Nitrogen, used as the carrier gas, at atmospheric pressure, passes successively through the saturator containing the reactant, the reaction vessel, the traps necessary for the elimination of excess acid and of the water formed, and the IR system for analysis of the carbon monoxide and dioxide formed during the reaction. 10 mg of catalyst are used; the saturator is maintained at 298 K; in this case the amount of formic acid carried over ($11 \cdot 10^{-4}$ moles min^{-1}) is enough to cover completely the catalyst surface, at least at low decomposition rate. The temperature of the reaction vessel is increased from 373 to 573 K in 10 K steps, and the reaction yield is measured when the system is at equilibrium.

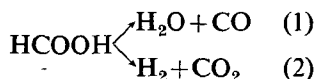
IR Spectroscopy experiments

Formic acid is adsorbed at room temperature on a pellet of the catalyst placed in the IR cell. The acid is desorbed under vacuum at different temperatures increasing from 373 to 573 K. The IR spectrum is recorded on a Perkin Elmer 125 or 225 spectrometer, the sample after each desorption being at the temperature of the IR beam (333 K).

Results and discussion

Determination of the kinetic parameters

We have plotted for each catalyst the variations of $\ln [\text{CO}]$ and $\ln [\text{CO}_2]$ for reactions:



as a function of $\frac{1}{T}$ (Fig. 1). We note first of all that it is often possible to trace these curves by increasing or decreasing the temperature. This shows that these reactions do not poison the active sites of the solids. The kinetic study shows that whatever is

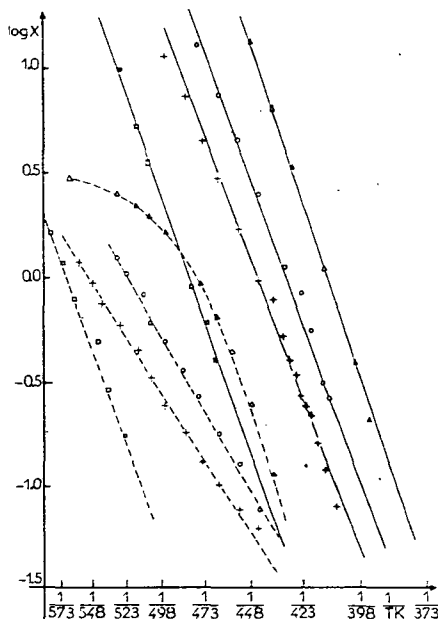


Fig. 1. Arrhenius plots of rate constants for $X=\text{CO}$ (—), $X=\text{CO}_2$ (---) for various values of x : $x=1$ or 0.5 (Δ), 0.2 ($\circ$), 0.025 ($+$), 0 ($\square$).

the exchange, at low temperature, the decomposition is only a dehydration reaction. Its starting temperature depends on the degree of exchange. For $x \geq 0.5$ all the Arrhenius plots coincide (Fig. 1). But for $x < 0.5$, the greater the extent of decatization, the lower the temperature at which the dehydration reaction starts. To obtain the same amount of CO, the Table I shows that the reaction temperature must be increased monotonically with x , from about 393 K for $\text{Na}_{0.5}\text{H}_{0.5}\text{Z}$ to 453 K for NaZ . In all cases, over a temperature range of about 60 K, $\ln [\text{CO}]$ varies linearly with $\frac{1}{T}$. For all the samples studied

the apparent activation energy lies between 20 and 24 kcal mol⁻¹. At higher temperature, the previous straight lines begin to curve owing to a decrease in the coverage of the active sites under the applied experimental conditions or as a consequence of reaction (2).

The case of dehydrogenation is different. Whatever is the value of x ($x=0$) the reaction always starts at the same tempera-

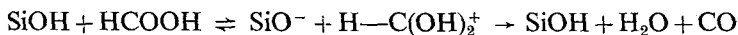
ture 433 K. On NaZ ($x=0$), CO_2 is observed in the gases at 493 K only. As in the case of reaction (1), at higher temperature the Arrhenius plots for all the samples curve toward negative values of $\ln C_{\text{O}_2}$.

IR spectra of chemisorbed formic acid

The IR spectrum of HZ treated at 673 K under vacuum shows the following bands: 3700 cm^{-1} (weak) and 3580 cm^{-1} (strong) characteristic of hydroxyl groups, 1860 and 1620 cm^{-1} due to the lattice. Apart from the 1860 cm^{-1} band, these bands appear during thermal treatment of NH_4Z . The two last ones are found in the other zeolites treated at 673 K under vacuum.

HZ—The IR spectrum of acid adsorbed on HZ at room temperature contains three absorption zones $3500\text{--}3000\text{ cm}^{-1}$, $1700\text{--}1600\text{ cm}^{-1}$ and $1450\text{--}1350\text{ cm}^{-1}$ (Fig. 2). Moreover, the bands at 3700 and 3580 cm^{-1} due to OH groups in the solid are no longer seen because either the O—H bonds are broken or the bands are shifted to low frequencies by strong hydrogen bonding between these OH and the acid molecules. In either case, this result shows that at least part of the adsorbate strongly interacts with the hydroxyl groups of HZ.

Heating at less than 373 K eliminates physically adsorbed acid, which is characterised by an absorption region at about 1700 cm^{-1} . A strong band at 1660 cm^{-1} , typical of strongly interacting $\text{C}=\text{O}$, is then visible. Furthermore, since 393 K is the temperature at which decomposition by reaction (1) begins, it can be deduced that the 1660 and 1400 cm^{-1} bands are attributable to an intermediate stage of the dehydration reaction. The mechanism of this reaction is therefore analogous to that postulated for homogeneous acid media:



The 1660 cm^{-1} band could be associated with either a $\text{C}=\text{O}$ band of an acid molecule in strong interaction with the acid OH groups of the solid, or the antisymmetrical vibration of the $\begin{array}{c} \text{OH} \\ | \\ \text{—C—} \\ | \\ \text{OH} \end{array}$ group. We cannot therefore say whether $\text{H}-\text{C}(\text{OH})_2^+$ is stabilised in the Z-zeolites.

The bands 1610 , 1405 and 1385 cm^{-1} which remain in the spectrum after sample desorption at 393 K characterize the aluminum formate formed on the Lewis acid

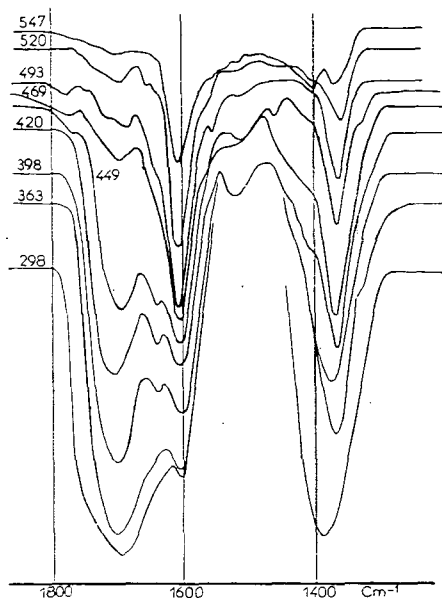
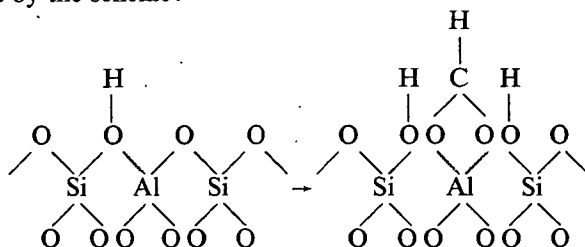


Fig. 2. Infra-red spectra of HCOOH adsorption-desorption on HZ-zeolite

sites of the solid by the scheme:



Compared with the spectrum of aluminum formate [1] we have attributed the bands 1610 and 1385 cm^{-1} to the asymmetric (ν_{as}) and symmetric (ν_{s}) OCO-stretching vibrations and the 1420 cm^{-1} one to the OCO and CH deformation vibration.

The frequencies ν_{as} and ν_{s} are both higher than the corresponding ones in ionic formate HCOO^- (1590 and 1350 cm^{-1} respectively). We deduce that the superficial formate is bidentate and involves a covalent bonding with an aluminum atom.

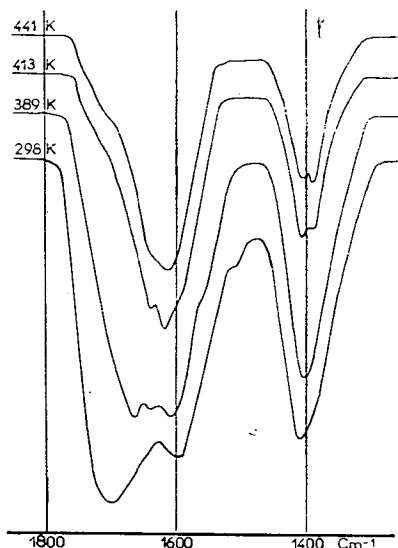


Fig. 3. Infra-red spectra of HCOOH adsorption-desorption on NaZ-zeolite

NaZ — The adsorption of formic acid on NaZ at 300 K leads to the appearance of three bands at 1720, 1605 and 1400 cm^{-1} . The last one contains at least two badly resolved maxima. The second band and the third, partially, can be attributed to sodium formate during the adsorption and which decomposes at about 493 K. This temperature corresponds to the onset of reaction (2) on this solid; we therefore deduce that this formate ion is an intermediate in this dehydrogenation reaction. Formation of this sodium formate implies the release of a proton which must attach itself to an atom adjacent to aluminium and creates an hydroxyl group analogous to those existing on HZ.

The 1720 cm^{-1} band is associated with the $\text{C}=\text{O}$ band of a chemisorbed acid molecule corresponding to an intermediate of reaction (1) since this reaction begins at the temperature at which this band disappears (448 K). But the position of this band shows that the $\text{C}=\text{O}$ bond interacts rather weakly with the OH groups of the solid. This could explain why it is necessary to have a higher temperature than in other cases in order to form HCOOH_2^+ which is required for dehydration of the acid.

$\text{Na}_{0.5}\text{H}_{0.5}\text{Z}$ — We should point out that the spectra for this catalyst contain only the bands for acid adsorbed on HZ, to the exclusion of those detected in the case of NaZ. This proves that the Na^+ cations situated in the small channels of diameter 2.3 Å which link two large channels do not take part in the reaction. This is due to the fact that the HCOOH molecule cannot penetrate into those small channels.

The reactivity of zeolites containing 50% of Na^+ cations therefore owes nothing to the sodium. It is therefore easy to understand why HZ and $\text{Na}_{0.5}\text{H}_{0.5}\text{Z}$ have the same activity if it is assumed that for the same reasons the OH groups situated in the small channels of HZ do not constitute active sites.

Variations of the Brönsted acidity strength with the sodium concentration

We have just seen that the dehydration activity of $\text{Na}_{1-x}\text{H}_x\text{Z}$ zeolites depends greatly on the extent of cation exchange. Now the mechanism of this dehydration involves only the capture of a proton of the superficial OH groups by a molecule of acid. We must therefore conclude that the ease of HCOOH_2^+ formation depends on x value. Two explanations are then possible.

(a) the OH groups of the solid, created during the preparation or the formate formation can interact more or less strongly with the formate, depending on its proximity.

(b) the intrinsic acidity of the superficial OH groups would depend on the nature and the concentration of the cations inside the zeolite. This second hypothesis seems the most plausible for the following reasons.

Table I

Catalysts	1	2	3
HZ	393 K	8	13.98
$\text{Na}_{0.5}\text{H}_{0.5}\text{Z}$	393 K	8	13.98
$\text{Na}_{0.8}\text{H}_{0.2}\text{Z}$	403 K	5.4	6.67
$\text{Na}_{0.9}\text{H}_{0.1}\text{Z}$	410 K	4.8	5.69
$\text{Na}_{0.975}\text{H}_{0.025}\text{Z}$	413 K	4.2	4.20
NaZ	453 K	4	0.40

1 — Experiment temperature $[\text{CO}] = 2.68 \cdot 10^{-3}$ mole $\text{g}^{-1}\text{h}^{-1}$

2 — Total number of Brönsted acid sites per unit cell

3 — $T = 423$ K: Turnover number (mole $(\text{H}^+)^{-1}\text{h}^{-1}$)

We calculated for each value of x the number of Brönsted acid sites per unit cell due to the OH arising from the preparation of the solid and to those coming for the formation of formates on the surface (Table I). We deduced the activity reported to one acid site (Table I). We notice that it is increasing with x . For instance when x increases from 0.2 to 0.5, the turnover number is multiplied by 20.

Conclusion

We have been able to determine the mechanisms of formic acid decomposition on $\text{Na}_{1-x}\text{H}_x$ zeolites. The dehydrogenation reaction occurs at low temperature *via* the aluminium formate ($x \neq 0$) and at high temperature through the sodium formate acting as an intermediate ($x < 0.5$).

Dehydration, which occurs at relatively low temperature, is catalysed by the Brönsted acid sites, OH groups created during preparation of the solid or when the formates are formed.

We have demonstrated that the acid strength of these OH groups depends on the Na—H exchange rate and, consequently, that it is possible to create surfaces with very different Brönsted acidities.

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REGULATION OF THE SELECTIVITY AND STABILITY OF ZEOLITE CATALYSTS CONTAINING TRANSITION METALS

By

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The mixed forms of synthetic zeolites of Y-type containing Ca, Ni and Cr are tested towards the dealkylation and disproportionation of toluene. The introduction of Cr^{3+} or Cr_2O_3 in the nickel-containing samples results in an increase of selectivity and stability, which is attributed to their effect on the dispersity of the metal particles formed after the reduction of Ni^{2+} .

In the search of high-effective catalysts recently much attention is paid to the metal-zeolite catalysts [1]. Their catalytic activity is determined primarily by the type number, amount and state of the transition elements in the zeolite structure [2, 3].

The aim of the present work is to develop catalytic systems based on nickel-zeolite catalysts (obtained by different ways — ion exchange, deposition, mechanical mixing), which should favour the conversion of toluene into benzene, or benzene + xxylenes. Furthermore, the possibilities are examined for regulating their selectivity, stability and regenerability by the introduction of chromium (as Cr^{3+} or Cr_2O_3).

Table I
Composition and method for obtaining the test samples

Sample	Ni content wt %	Cr content wt %	Method of preparation
NiO/CaY	2.5—5.0	—	Deposition by precipitation of $\text{Ni}(\text{OH})_2$
NiO/CaY	3.5—7.5	—	Deposition from Ni-acetylacetonate solution
NiO + CaY	2.5—5.0	—	Mechanical mixing
NiO — CaY	2.5—5.0	—	Precipitation of $\text{Ni}(\text{OH})_2$ in the presence of CaY
NiCaY	3.1	—	Ion exchange with $\text{Ni}(\text{NO}_3)_2$ solution
CrCaY	—	0.5—6.0	Ion exchange with $\text{Cr}(\text{NO}_3)_3$ solution
CrNiCaY	2.7—2.9	0.4—1.2	Ion exchange in NiCaY with $\text{Cr}(\text{NO}_3)_3$ solution
NiCaY + Cr_2O_3	3.1	1.5—2.1	Mechanical mixing

Experimental part

The experiments are carried out on synthetic zeolites of X and Y-type with molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ from 3.2 to 5.0 in calcium form (extent of ion exchange with Ca^{2+} about 80%). The composition and way of obtaining of the Ni-, Cr- and Ni-Cr-containing samples are shown in Table I.

The properties of the catalysts are not noticeably affected by the used amounts of Ni^{2+} and Cr^{3+} . No disturbance of the crystal lattice of the zeolite under these conditions is proved by X-ray analysis.

The catalytic activity of the test samples is determined in a flow system with space velocity of 1.1 h^{-1} at atmospheric pressure in the temperature range 330—470 °C. Ratio hydrogen:toluene = 10. Thermal pretreatment is carried out in hydrogen flow for 2 hours at 450 °C, after the temperature is slowly elevated to this value.

Results and discussion

Recently, catalysts of the type NiO-zeolite are developed [4, 5]. Their activity and selectivity are varied by an appropriate interaction between both components which separately are not active, as in the case of ethylene dimerization [6, 7], or the presence of the second component changes the direction of the conversion, as the alkylation of benzene with ethylene [7, 8].

The catalytic systems NiO/CaY and NiO+CaY used for the conversion of toluene are characterized by the additivity of the activities of the metal and acidic

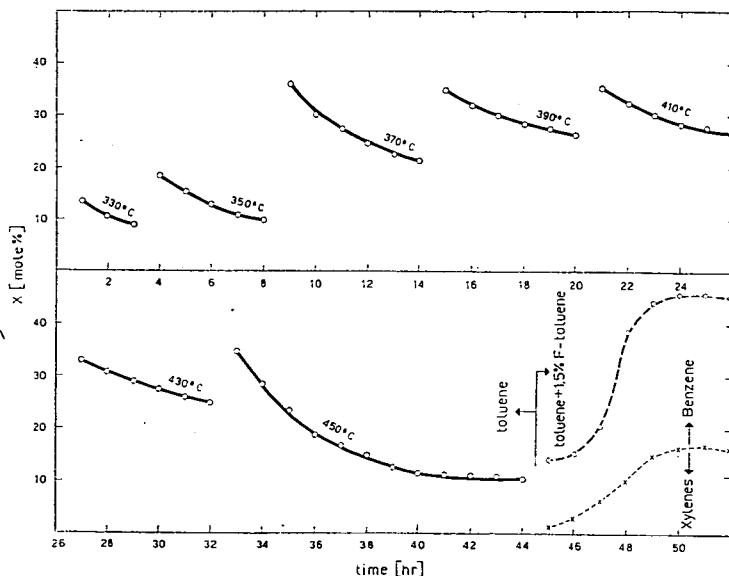


Fig. 1. Consecutive conversion of toluene into benzene and benzene + xylenes on a catalyst NiO/CaY obtained by supporting $\text{Ni}(\text{OH})_2$. Nickel content: 2.5 wt%

component of the two-component catalyst obtained after the reduction of NiO. Initially toluene is converted to benzene on the metal. After the deactivation of the latter, toluene containing about 0.5—1.5% of fluortoluene, bromobenzene, or other halogen-containing substance is passed, *i.e.* under these conditions the "carrier" acts as an independent catalyst. The catalytic activity of the "carrier" is equal to that of the calcium form of the zeolite under the same conditions. The dealkylation of toluene followed by its disproportionation is shown on Fig. 1.

The examined catalytic system provides possibilities for consecutive or simultaneous dealkylation and disproportionation of toluene. It differs from the known similar catalysts by the bifunctional action of the "carrier":

1. The zeolite is used as a carrier. NiO is deposited on it by any of the methods shown on Table I, on which after its reduction, the dealkylation takes place.

2. After the deactivation of the metal, there is a possibility for activating the "carrier" which may act as an independent catalyst for toluene disproportionation.

This catalytic system permits the simultaneous dealkylation and disproportionation of toluene to be performed: Toluene containing 0.5—1.5 wt% of fluortoluene or bromobenzene is passed at temperature of 430—470 °C. Benzene (by both reactions) and xylenes are obtained. When Ni(OH)₂ is precipitated in the presence of CaY, the disproportionation of toluene takes place from the beginning of the process which is probably caused by partial ion exchange. Hence, a new way is shown for obtaining of catalysts for the conversion of toluene to benzene and xylenes, differing essentially from those obtained by ion exchange (see Fig. 2).

The mechanical mixing of Cr₂O₃ to the samples obtained by ion exchange, leads to a significant increase in the selectivity of the catalysts towards disproportionation, their stability and regenerability [9]. This effect is attributed to the influence of Cr₂O₃ on the reduction ability of Ni²⁺ and on the dispersity of the obtained metallic nickel.

In order to elucidate the observed phenomena and to find out new ways for regulating the catalytic properties of the studied catalysts, a series of test samples of CrCaY and CrNiCaY (see Table I) with different Cr³⁺ content are obtained. Under the examined conditions of reduction and reaction, no reduction of Cr³⁺ takes place (at temperatures below 600 °C reduction to metallic state is not observed [3]). The total conversion extent (X) and the sum of the disproportionation products (2/Σ_{xy}l + + 2ΣTMB/) as a function of time for a sample of NiCaY with different Cr and Cr₂O₃ content are shown on Fig. 3. The effect of Cr³⁺ on the activity of the nickel-zeolite samples is illustrated by the comparison of the activities of NiCaY (curve 1) and CrNiCaY (curves 2 and 3), taking into consideration that samples containing only chromium (CrNaY and CrCaY) are not active under the examined conditions. For higher Cr³⁺ contents, as well as for the mechanical mixtures with Cr₂O₃ (curves 4 and 5) the maximal activity is reached slower, which is related to the adsorption-desorption processes preceding the catalytic act.

The changes in the selectivity and stability of NiCaY effected by the introduction of Cr³⁺ are related mainly to the influence of the latter on the dispersity of the nickel particles obtained after reduction. Before reduction Ni²⁺ and Cr³⁺ enter the zeolite structure in the form of hexaquo-complexes. Evidence for the latter is given by the reflection spectra in the visible and UV region and by the ESR-spectra of air-dry samples. The method of FMR yielded some data on the size and form of the nickel particles obtained after reduction. It is known that the line width of the FMR signal is sensitive towards the size and texture of the particle. In Table II the parameters

ΔH and the γ -factors for the three most characteristic samples are presented. It is seen that the chromium-containing samples have a considerably smaller line width after reduction, which is a direct indication for the formation of smaller particles of the mixed Ni-Cr-species.

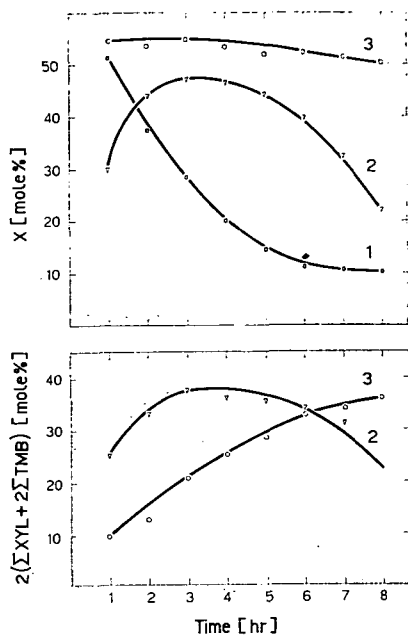


Fig. 2. Total conversion extent and the sum of the disproportionation products ($2/\Sigma_{xyl} + 2\Sigma_{TMB}$) as a function of time at 430 °C for samples obtained by:

1. Supporting of $\text{Ni}(\text{OH})_2$ on CaY
2. Ion exchange
3. Precipitation of $\text{Ni}(\text{OH})_2$ in the presence of CaY.

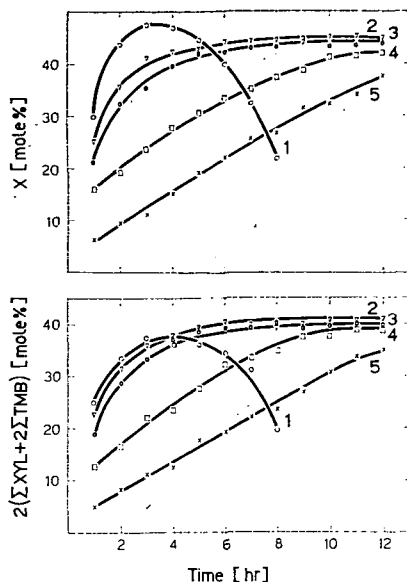


Fig. 3. Total conversion extent and the sum of the disproportionation products ($2/\Sigma_{xyl} + 2\Sigma_{TMB}$) as a function of time at 430 °C for a NiCaY sample containing various amount of Cr^{3+} :

1. NiCaY
2. CrNiCaY (0.4 wt % Cr^{3+})
3. CrNiCaY (0.6 wt % Cr^{3+})
4. CrNiCaY (1.2 wt % Cr^{3+})
5. NiCaY + Cr_2O_3 (1.5 wt % Cr)

Table II
Parameters of the FMR spectra for some samples

Sample	Ion content, wt %		ΔH Gauss	γ
	Ni^{2+}	Cr^{3+}		
NiCaY	3.1	—	820	2.16
CrNiCaY	3.0	0.46	640	2.23
CrNiCaY	2.9	0.67	600	2.23

Furthermore, the nickel particles obtained from Cr^{3+} -containing samples possess an expressed stability towards prolonged treating with toluene at the reaction temperature (the change in ΔH with time is insignificant, which is the most important base for the stable action of these catalysts).

The oxidative treatment during the regeneration leads to an enrichment with Cr^{6+} (proved by the reflection spectra in the visible and UV region), whose strong oxidizing action improves the regenerability of the studied catalysts. Moreover, the obtained Cr_2O_3 is distributed more evenly, thus considerably increasing the selectivity and stability of the regenerated catalysts.

Besides the wide possibilities for regulating the catalytic properties of the studied samples, the obtained results permit to throw light on the important and complicated problem of the mutual interaction between the acidic and metal active sites in the bifunctional zeolite catalysts. In the catalytic systems obtained by mechanical mixing of NiO and CaY (as well as NiNaA and CaY) at different ratios, no experimental support was obtained for a synergism between both functions. The obtaining of more finely dispersed nickel particles in NiCaY by the introduction of Cr^{3+} or Cr_2O_3 contributes to the complete development of the acidic nature of the zeolite, which plays the decisive role for the disproportionation. On the other hand this leads to an enhancement in the hydrogenating capacity of the metal ($\text{Ni}^0 + \text{H}_2$), which results in lower coke-formation.

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INVESTIGATION OF THE SKELETAL ISOMERIZATION OF CYCLOPROPANE ON NaY MODIFIED BY ELEMENTARY Na

By

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It has been shown that by treating NaY zeolite samples with sodium vapour (produced by the decomposition of NaN_3 in the zeolite framework) it is possible to attain the rate of the homogeneous reaction in the case of skeletal isomerization of cyclopropane as a limiting value. Equations are given enabling comparison of apparent first order rate constants obtained from experimental data under different conditions and methods. The rate constant of the true heterogeneous isomerization reaction has been determined ($k = 10^{-2} \text{ s}^{-1}$ at 573 K).

The poisoning effect of sodium atoms is due to charge-transfer between sodium and H^+ ions, though a simple neutralization reaction cannot be excluded either.

No anion vacancies could be produced by treating the zeolite samples with sodium vapour at the temperature (approximately 670 K) and during the short time of contact (only a few seconds) used.

Introduction

The skeletal isomerization of cyclopropane in and over homogeneous and heterogeneous acid catalysts, respectively, received the attention of several investigators in the last two decades. There are at least two recent reviews available about the most interesting details of this reaction [1, 2]. It is generally accepted that cyclopropane reacts with the acidic centres of the catalysts already at relatively low temperatures resulting in carbonium ion type intermediates which decompose further into propylene under regeneration of the acidic centres. The overall reaction is of first order in cyclopropane. As a consequence of the "simplicity" of this reaction, it became a kind of a test-reaction for the investigation of acidic catalysts and supplied valuable information over hydrocarbon reactions in general.

HALL AND CO-WORKERS stated in their papers [3—5] that on silica-alumina catalysts both the Brönsted and Lewis type acidic sites are active. HABGOOD AND GEORGE [6] have found that only Brönsted type acidic centres are active in the case of X and Y faujasites. They were able to set up an order of activity among molecular sieves as catalysts exchanged with mono- and divalent cations. Both group of researchers have found that activity can be influenced by the H_2O content of the catalysts. There is no doubt that the isomerization activity of absolutely pure and dry NaX and NaY catalysts, respectively, is zero. If there is some remaining activity then it is due to di- and three-valent cations as impurities which lead to H^+ ion formation according to a well-known mechanism [6, 7] or to partial hydrolysis of the zeolite [8]. Former investigations by IR [9, 10] and NMR spectroscopy [11] later show that there is a

good correlation between the number of acidic OH groups per u.c. and the content of di- and three-valent cations of the molecular sieves and also the temperature of heat treatment, *i.e.* the degree of dehydroxilation. These results have been substantiated in many ways by LOMBARDO, SILL AND HALL [12] who carried out excellent investigations on the double-bond isomerization of *n*-butene over NaY type catalysts containing variable amount of Ca^{2+} ions. It was straightforward to draw the conclusion that the production of Brönsted centres is the result of a partial hydrolysis of Ca^{2+} ions.

As far as the mechanism of cyclopropane isomerization is concerned, the existing views can be summarized as follows: the first step of the transformation is a relatively fast sorption step (which is partly physisorption and partly a weak chemisorption — heat of adsorption is: $40,19 \text{ kJ mol}^{-1}$ — [6]; the existence of physisorption should be supposed because the sorbed amount of cyclopropane exceeds the number of acidic sites). Using isotopic tracers HABGOOD AND CO-WORKERS [13, 14] came to the conclusion that in the chemisorption step proper or following it a non-classical carbonium cation, a so called edge-protonated cyclopropane is produced. This cation transforms into a classical propyl cation by C—C bond rupture which desorbs as propylene while regenerating the acidic centre.

A similar mechanism has been accepted by HALL AND CO-WORKERS [3], nevertheless, they did not exclude the possibility of a different mechanism on catalysts which have been baked out at high temperatures and therefore might contain Lewis acid sites as well. Here the first reaction step consists of a H^- ion abstraction producing propenyl carbonium cation intermediates. They act as molecular chain carriers by interacting with cyclopropane leading to propylene and reproducing the alkenyl cation. This reasoning has been shown to be valid or at least probable according to a paper by FLOCKHART AND CO-WORKERS [15] who found two maxima in their plot: rate constant *vs.* catalyst activation temperature. This behaviour cannot be regarded as a solid proof of the existence of two types of centres. A smooth transition from Brönsted to Lewis type activity would have been more convincing.

The objectives of the recent paper are the investigation of catalyst activity at very low and at the limit (probable) disappearing H^+ ion concentration and a study of the kinetics in a static "tank" reactor of constant material content.

Experimental

Catalysts used

In the investigations two base catalysts, both of the type SK—40 by the Union Carbide Corp., were used. The lot. No. of *our* catalyst No. 1 is 1280—133, that for catalyst No. 2 3606—224. Catalyst No. 3 has been prepared from No. 1 by repeated ion exchange with a $0,1 \text{ mol dm}^{-3}$ sodium acetate solution. After ion exchange the catalyst was carefully washed using slightly alkaline water ($\text{pH} \approx 10$). Outgoing from catalyst No. 1, the content of Ca^{2+} ions was increased in catalyst No. 4 by exchanging in a 0.25 w% CaCl_2 solution. Catalyst No. 5 is a NaY faujasite synthesized by: L. I. PIGUZOVA (Inst. Neft. Prom., Moscow, USSR).

The Ca^{2+} content of catalysts No. 1—5 has been determined by EDAX (Energy Dispersion Analysis of X-rays) and X-ray fluorescence analysis (XFLA).

Catalysts No. 6—13 are modified samples. The modification consisted in mechanical mixing the zeolite samples with NaN_3 (Merck p. a.) as a solid or imbibing them with its solution in water, respectively.

The details in short are as follows: to get catalyst No. 6. $5 \cdot 10^{-3}$ kg of exsiccator dry catalyst No. 2 has been mixed with $2 \cdot 10^{-2} \text{ dm}^3$ NaN_3 solution in water (concentration of $\text{NaN}_3 = 5 \cdot 10^{-2} \text{ mol dm}^{-3}$) and drying of the mixture under infra-red lamp while mixing it continuously. Catalyst No. 7 has been prepared by mechanical mixing of the catalyst sample No. 2 (previously dried at 473 K) with powdered NaN_3 . The procedure in the case of catalysts No. 8—13 consisted in the digestion of $5 \cdot 10^{-3}$ kg catalyst No. 2 (dried at 473 K) in $4 \cdot 10^{-2} \text{ dm}^3$ solution of NaN_3 in water, in a closed vessel at 353 K for 6 hours. The content of NaN_3 in the solution was varied from sample to sample. The zeolites were filtered off after the digestion on a porous glass filter (G4) and dried. An estimate of the NaN_3 content in the zeolites was possible on the basis of weight increase of the *wet samples* and the content of NaN_3 in the solutions. Analytical and other data are summarized in Table I.

Table I
Unit cell composition of catalysts used

No	Catalysts composition by EDAX						CaO content by	
	Na	Ca	Al	Si	O	Impurities*	EDAX w %	XFLA w %
1	55,0	1,7	59,5	132,5	384	0,43	0,7	0,7
2	58,5	0,8	60,9	131,1	384	0,31	0,32	0,6
3	52,5	1,2	55,2	136,8	384	0,2	0,53	0,68
4	48,2	4,1	57,5	134,5	384	0,4	1,8	1,74
5	58,1	0,3	60,7	131,3	384	0,76	0,12	0,09

Sodium azide content of the modified catalyst samples

No	6	7	8	9	10	11	12	13
NaN_3 content w %	1,28	1,28	0,69	1,83	4,17	6,76	13,1	23,4

* Impurities: Fe, Ti and K

The catalyst powders so prepared were pilled (pelletizing pressure: $5 \cdot 10^8$ Pa), the pellets crushed and sized. The sieve fraction between 0,4—0,6 mm was used after preliminary drying at 473 K. *Separate catalyst samples were used for every kinetic experiment.* Baking out occurred at 723 K under continuous pumping (final pressure: 10^{-2} Pa). The heat treatment at this temperature was continued for two additional hours after which sample and reactor temperature was adjusted for the value of experiment. After temperature stabilization within ± 1 K, the reactant cyclopropane and added nitrogen were introduced into the system.

Kinetic measurement

The skeletal isomerization of cyclopropane was studied in a tank reactor (with constant material content; geometrical volume of reactor and connecting tubing *etc.* 0,1964 dm³; from this the volume of the system at the reactor temperature 0,0707 dm³, at room temperature: 0,1257 dm³), using gas-circulation enabling withdrawal of samples for GC analysis. The investigations were carried out between 473 K and 623 K. The initial reaction mixture consisting of $6.814 \cdot 10^{-4}$ mol cyclopropane and $6.066 \cdot 10^{-3}$ mol nitrogen was used in a typical experiment; the amount of catalyst was $5 \cdot 10^{-4}$ kg. The added nitrogen increased the efficiency of gas circulation.

The isomerization reaction was followed with product analysis by GC (Hewlett Packard type: 5710A*). Gas samples were withdrawn at predetermined reaction times by using a Carlo-Erba type 128—3 sampling valve.

Kinetic curves for reactant and product(s) were plotted on the basis of the analytical data.

For the sake of simplicity the reacting mixture was characterized from kinetic point of view by the rate constants (see later) of the reaction supposing pseudo-first order kinetics as an approximation. The rate constants were determined by linear regression from the measured data.

Results

Figure 1. shows the pseudo-first order rate constants *vs.* CaO content of the catalysts in weight percent. As can be seen there is a good linear correlation between these two parameters. The points lying at very low CaO content show unambiguously that absolutely pure NaY samples have no activity as mentioned earlier. This result has been proved in a more direct way for NaY having no H⁺ ions at all in the case of samples treated with NaN₃. As it is well-known from elementary chemistry NaN₃ decomposes into Na and N₂ at 623 K. The decomposition temperature is probably dependent on particle size, impurities and chemical environment as well. In the cavities of the zeolite (catalyst No. 6) this temperature is higher by approximately 60 K as can be seen in Figure 2. Here the composition of the effluent gas is shown during the temperature programmed heating of the zeolite sample. The analysis for H₂O and N₂ was carried out by a Balzers quadrupole MS. The two maxima at approximately 400 and 430 K are due to physisorbed water and nitrogen; the other two for N₂ at 650 and 690 are supposed to be the decomposition of NaN₃ on the outer surface and in the cavities of the catalyst, respectively.

Similar experiments were carried out by monitoring the pressure change in the reactor system at constant pumping speed (see *e.g.* Figure 3.). The distribution of NaN₃ in- and outside of the NaY crystallites is very dependent on the method of preparation of samples containing NaN₃ and it can be stated that nearly all of the preparation methods used led to relatively poor reproducibility. Even though sodium partial pressure and time of interaction between Na atoms and H⁺ ions are determined by many factors (like content of NaN₃, its distribution, temperature programming,

*) This GC was a donation by the Alexander von Humboldt Foundation.

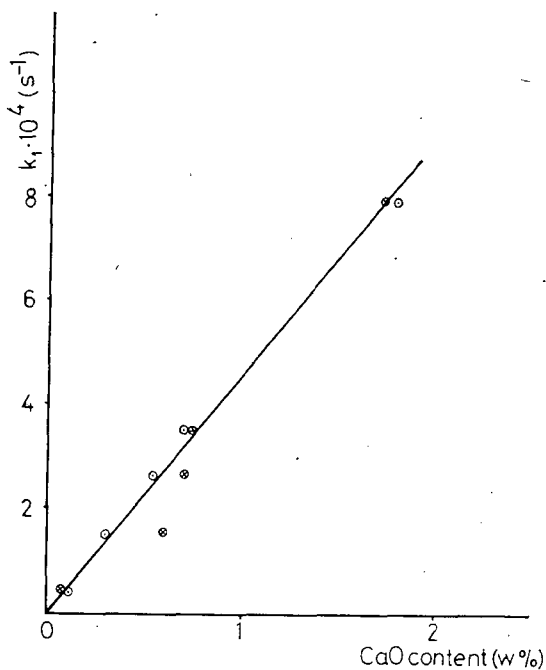


Fig. 1. Measured apparent rate constants as function of the CaO content of NaY zeolites (determined by EDAX: ○ and XFLA ⊗)

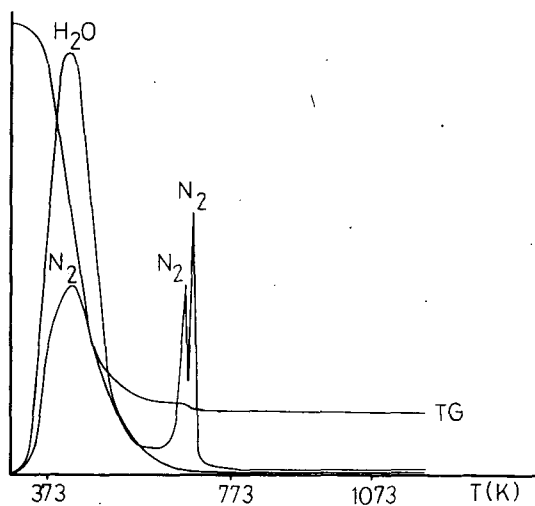


Fig. 2. Thermogravimetry combined with MS product analysis of a NaY zeolite sample containing NaN₃

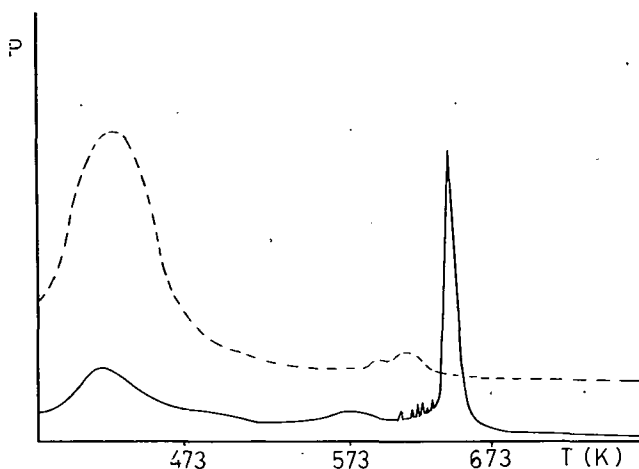


Fig. 3. Monitoring of loss of water and decomposition of NaN_3 by the pressure change in the reactor at constant pumping speed during heat treatment. Continuous line: for catalyst No. 6; dashed line: for No. 7 (shifted upwards)

pumping speed *etc.*) it was possible to achieve a very pronounced decrease and at the limit a complete elimination of H^+ ions in the NaY catalyst samples by increasing the amount of NaN_3 in the catalysts prior to heat treatment.

The decrease of H^+ ion content was a consequence of two reactions, the first corresponding to the reaction:



the other to the neutralization reaction:



where the NaOH is the reaction product of the elementary sodium with the remaining water content of the samples. At present *no clear distinction between these two possibilities exists*. Looking at the Figs. 2 and 3 it is clearly visible that the effluent contains traces or no water at all at the decomposition temperature of NaN_3 . This of course does not mean in any way that water is absent in the α and β pore system while Na is being released, nevertheless, regarding the high decomposition temperature of the azide in the pores, it is probable that the major reaction leading to the disappearance of H^+ ions is the first one.

Figure 4. shows that the decrease in catalytic activity of the initial sample No. 2 is at least two orders of magnitude and for samples with initial NaN_3 content equal to or greater than 1.12 mol kg^{-1} the remaining activity is zero. The very slow residual reaction corresponds to the unimolecular homogeneous decomposition of cyclopropane described in detail in the literature [16, 17].

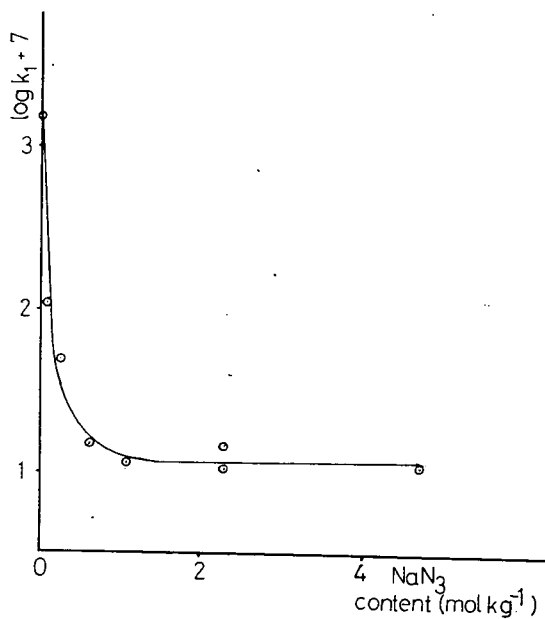


Fig. 4. Catalytic activity as function of the initial NaN_3 content.

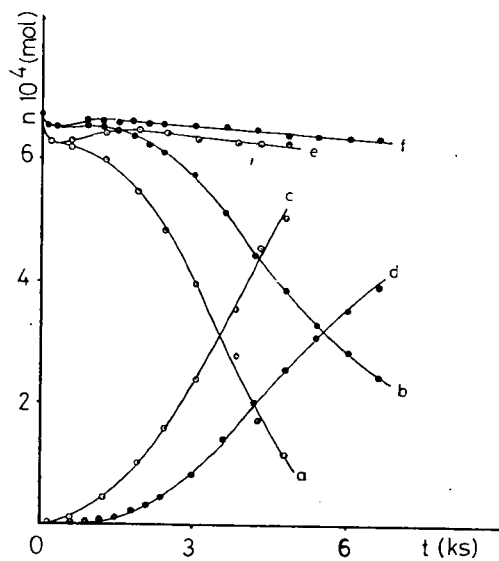


Fig. 5. Kinetic curves for two catalysts containing different amounts of calcium.

Two sets of typical kinetic curves are shown in Figure 5. On the ordinate the total amount of cyclopropane (a, b), propylene (c, d) and the sum of the two (e, f) are shown. The second set of curves in Figure 6. shows the effect of added propylene into the initial mixture.

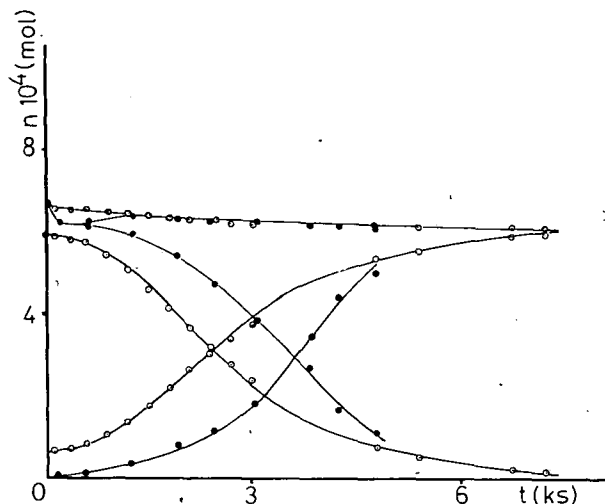


Fig. 6. Kinetic curves showing the effect of added propylene.

Discussion

When looking at Figure 4. the first question, which arises, is whether the levelling off of the curve from the initial NaN_3 content of 1.12 mol kg^{-1} on corresponds to the residual homogeneous reaction? To clarify this very important point it is necessary to find the exact relation between apparent first order rate constants (all of the dimension: s^{-1}) obtained under different experimental conditions.

The apparent first order rate constant corresponding to the rate equation:

$$-\frac{dP}{dt} = k_1 P \quad (3)$$

for a tank reactor which has a heated volume: v_2 (at $T_2 K$) and an additional volume: v_1 at ambient temperature ($T_1 K$) (corresponding to the glass tubing, circulating pump etc.) providing that the rate determining step is the transformation of the non-classical carbonium ion into propyl carbonium ion or propylene, respectively, and the acidic centres are only partially covered with cyclopropane (or with the non-classical cyclopropyl carbonium ion) can be expressed by the equation:

$$k_1 = \left[\left(\frac{k\lambda K\sigma}{N} \right) \cdot \frac{\delta v}{\bar{v}} + k^* \frac{v_2}{\bar{v}} \right] \cdot \frac{T_1}{T_2} \equiv \left(k_2 \frac{\delta v}{\bar{v}} + k^* \frac{v_2}{\bar{v}} \right) \cdot \frac{T_1}{T_2} \quad (4)$$

where:

- k [s^{-1}]: the rate constant of the heterogeneous transformation,
- δv [dm^3]: the apparent volume occupied by the catalyst of mass m ,
- λ (kg^{-1}): the number of acidic centres per unit mass of catalyst,
- σ ($kg\ dm^{-3}$): is the bulk density of the given catalyst sample ($\sigma \equiv m/\delta v$),
- m [kg]: the mass of catalyst used,
- K ($dm^3\ mol^{-1}$): equilibrium constant of sorption,
- N [mol^{-1}]: Avogadro's constant,
- k^* [s^{-1}]: the first order rate constant of the homogeneous transformation of cyclopropane decomposition,
- v_2 [dm^3]: the volume of the heated part of the reactor,
- $\bar{v}$ [dm^3]: is the equivalent volume of the reactor system (referring to ambient temperature) defined by the equation:

$$\bar{v} \equiv v_1 + v_2 \cdot \frac{T_1}{T_2} \quad (5)$$

- v_1 [dm^3]: is the volume of reactor (tubing, circulating pump etc.) at ambient temperature.

If the reaction is carried out in a pulse reactor the exact expression for the apparent first order rate constant for the same reaction:

$$\bar{k}_1 = \frac{k\lambda K\sigma}{N} + k^* \equiv k_2 + k^* \quad (6)$$

where the meaning of the symbols is the same as before.

It is easy to see that the expressions for k_1 and $\bar{k}_1$ are equivalent only if the whole reactor has the same temperature ($v_1=0$, $T_1 \equiv T_2$ and consequently: $\bar{v}=v_2$) and the catalyst is distributed evenly in the reactor volume v_2 . It means in other words that $m/\bar{v} \equiv \sigma$. Otherwise order of magnitude of the apparent rate constant might be very different even for the same catalyst mass and reaction so rendering any comparison impossible.

In the publications it is not easy to find the details characterizing reacting system and equipment to the degree which would be necessary to carry out such a comparison. Nevertheless, on the basis of literature data fairly good estimates are available for the parameters: λ (from the Ca^{2+} content of the catalyst provided that the H^+ ions in connection with $O_{(2)}^{2-}$, $O_{(3)}^{2-}$ and $O_{(4)}^{2-}$ ions at low temperature became mobile and all available for the reaction at temperatures corresponding to the lowest one used), K the equilibrium constant of sorption (from retention data using pulse reactors). From the theory of GC is known that the linear rate of flow w_0 [$m\ s^{-1}$] across a catalyst (or adsorbent) bed (characterized by a catalyst content M [$kg\ m^{-1}$], a void fraction S [$dm^3\ m^{-1}$] and an equilibrium sorption a [$mol\ kg^{-1}$] at a gas concentration c [$mol\ dm^{-3}$]) is reduced by a factor of $1/(1+q)$, i.e. $w = w_0/(1+q)$, where

$$q \equiv \frac{M}{S} \cdot \frac{a}{c} \quad (7)$$

In agreement with this there is a simple relation between the corrected retention time: $t_{R, \text{corr}}$ and the sorption equilibrium constant of the catalyst, K :

$$t_{R, \text{corr}} \equiv t_R - t_0 = \frac{L}{w} - \frac{L}{w_0} = L \cdot \frac{q}{w_0} = \frac{LM\lambda}{w_0 SN} K \quad (8)$$

here L is the length of the catalyst (adsorbent) bed. Values for k^* are available from literature. On the other hand we suppose that the limiting value of k_1 by increasing the initial NaN_3 content is equal to

$$\left(k^* \frac{v_2}{\bar{v}} \right) \cdot \frac{T_1}{T_2}.$$

In other words it is possible to estimate at least order of magnitude of the rate constant of the catalytic reaction (k) from different measurements, *i.e.* from measurements by the pulse technique and the static tank reactor method, respectively.

The rate constant k^* for the homogeneous reaction is at $T_2 = 573 \text{ K}$ [16, 17] $k^* = 2.1 \cdot 10^{-10} \text{ s}^{-1}$. In an empty reactor (*i.e.* in a reactor without catalyst) the measured value of k_1 at 573 K was $1.2 \cdot 10^{-6} \text{ s}^{-1}$ (and because $k_2 = 0$ in this case it means by equ. (4) that $k^* = 3.3 \cdot 10^{-6} \text{ s}^{-1}$) in good agreement with the limiting value of k_1 in Figure 4. This fact proves that Na eliminated all active H^+ ions as expected when more than 1.12 mmol NaN_3 per gram zeolite was present initially. At present no clear explanation exists which would account for the deviation of more than 4 orders of magnitude found for k^* in our experiments and data published in literature. In all probability the impurities on the glass walls and the poor vacuum conditions — not better than 10^{-2} Pa — are both responsible.

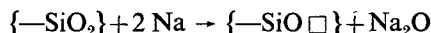
Using equ. (4) the value of k can also be estimated. For catalyst No. 2, as can be seen in Fig. 4, $k_1 = 1.53 \cdot 10^{-4} \text{ s}^{-1}$; from the Ca^{+2} content (providing that $\text{Ca}^{+2}/\text{H}^+ \approx 1$ and all H^+ ions are active [which is probably by far not the case!]) $\lambda/N \approx 5.5 \cdot 10^{-2} \text{ mol kg}^{-1}$; an estimate for the equilibrium constant of sorption is $K = 211 \text{ dm}^3 \text{ mol}^{-1}$ and for the bulk density $\sigma = 0.375 \text{ kg dm}^{-3}$. From all these follows the true rate constant of the heterogeneous cyclopropane transformation: $k = 10^{-2} \text{ s}^{-1}$. With the only exception of a paper [6] the most important data characterizing catalyst and system enabling comparison are missing. HABGOOD AND GEORGE (loc. cit.) measured the k_2 values [see our equ. (6)] in a pulse reactor and got the following results:

$$\begin{aligned} k_2 &= 10^{-2} \text{ s}^{-1} \text{ (in the case of a catalyst baked out at 773 K)} \\ k_2 &= 10^{-1} \text{ s}^{-1} \text{ (for a catalyst containing water).} \end{aligned}$$

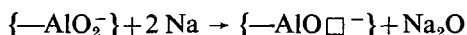
These data are in excellent agreement with the k_2 value computed from our experiments: $k_2 = 4.4 \cdot 10^{-2} \text{ s}^{-1}$, especially if we take into consideration that conditions in the two methods are not strictly the same: under GC conditions cyclopropane and propylene will be more or less separated, therefore, cyclopropane reacts always with fresh catalyst. In a tank reactor mixed adsorption takes place and product propylene chemisorbs more strongly than cyclopropane reducing its coverage.

The constant limiting rate which could be arrived at by initial NaN_3 concentrations higher than 1.12 mol kg^{-1} shows that it is impossible (at least at the highest applied temperature and short time of interaction between elementary Na and zeolite

framework) to create anion vacancies (using for these the notation $\square$) according to the equations:



or (9)

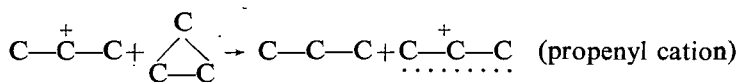
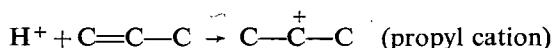


If these reactions occurred a change in activity should have shown up provided FLOCKHART's concept [15] is correct. No increase in activity could be observed actually, therefore, the steps indicated under (9) are improbable.

The analysis of the kinetics of the cyclopropane isomerization (details of which will be given elsewhere) show a few remarkable features:

1. A well pronounced induction period of several minutes could be observed for the reaction suggesting that either the production or the decomposition of the non-classical carbonium ion is a slow process.

Added propylene markedly reduces or eliminates the induction period from the beginning thus it is tempting to believe that the transformation of cyclopropane on Brönsted centres as well follows a mechanism suggested first by FLOCKHART [15]. In the second step propane would then be produced according to the equations:



If propylene or allene in particular is introduced into the system in small amounts before the addition of cyclopropane the duration of the induction period is diminished (in the case of allene nearly to zero) and the rate of reaction becomes *exactly* the same as with cyclopropane only after several minutes. Providing that propenyl cations were chain carriers, as would be no surprise on the basis of their electronic structure [21], their steady state concentration should be exceedingly low.

2. A continuous deactivation of the catalyst could be observed. In previous publications we have shown that this phenomenon is a consequence of the oligomerization of propylene followed by C—C bond rupture and hydrogen transfer reactions leaving inactive carbonaceous deposits on the surface instead of the H^+ ions (for details see [18—20]).

3. The effect of water is extremely interesting: in a few unsuccessful experiments where traces of water remained in the catalyst framework the kinetic curves revealed a higher activity at the beginning ("fast" reaction of H^+ with cyclopropane) than that observed over the same catalyst without water. But later on the activity decreased markedly (interaction of H^+ with NaOH) and fell below of that for the same but dried catalyst. On the basis of similar observations in our praxis and throughout the literature involving acidic catalysts and hydrocarbons (cracking, isomerizations, transformations in the solid zeolite matrix etc.) we believe that the role of water or that of backdonated water should be regarded from an other point of view: under circumstances it helps not only to create Brönsted centres from Lewis acidic sites but,

which we think is more important, greatly improves proton mobility making them available where they are needed at most by the reaction. Water is also a co-catalyst influencing the *topology* of the reactions occurring in zeolitic frameworks.

* * *

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INFRARED STUDY OF ELEMENTARY STEPS OF *n*-BUTENE ISOMERIZATION ON ZEOLITES A COCATALYZED BY SULFUR DIOXIDE

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Adsorption of *n*-butenes on different cation exchanged zeolites type A and their isomerizations at room temperature cocatalyzed by sulfur dioxide are studied by Fourier transform infrared spectroscopy. Attachment to the cations via π bonds effects activation of the butene molecules dependent on the polarizing power of the cation. Back-donation is responsible for stronger perturbation in case of transition metal cations. Except zeolites ZnA and Ca α , where spontaneous isomerization occurs, and zeolite NaA, which is inactive, isomerization is induced by addition of SO₂. Fitting the reaction data by first order laws with respect to *n*-butene and SO₂ points to a direct intervention of the cocatalyst into reaction.

Catalytic transformation of hydrocarbons by zeolites is a rapidly growing area of exploration and there is increasing interest to get insight into the reaction mechanism and the nature of the active sites responsible for catalysis.

In case of isomerization the interconversion of *n*-butenes is one of the common test reactions, as it is the simplest one, where structural, geometrical and skeletal isomerization may occur, respectively. Small amounts of coadsorbed compounds may change the properties of catalysts to increase activity and selectivity. A suitable cocatalyst for isomerization is sulfur dioxide [1, 2].

Despite their low catalytic activity zeolites of type A may be preferred for studies because of their simple, well-defined structure of high symmetry. The electric field inside the supercavity affecting the sorbed molecules may be modified by cation exchange. In order to cover a suitable range of electric field strength A-type zeolites containing lithium, sodium, magnesium, calcium, zinc and silver ions were chosen for our study of elementary steps of isomerization with sulfur dioxide as cocatalyst. The influence of the Si/Al ratio was examined with zeolite Ca α .

Starting material was zeolite NaA synthesized by KACIREK [3]. Ion exchange was performed using chloride or nitrate solutions (reagents of p. a. grade), in some cases under argon atmosphere in order to prevent carbonate formation. In contrast to the stoichiometric ion exchange in all other cases, the zinc uptake by zeolite NaA was much higher amounting to a composition of NaZn₁₁A. Zeolite α (Si/Al=2.47) synthesized by KACIREK [3] was ion exchanged with Ca²⁺ after calcination. The samples were checked on their crystallinity after ion exchange by X-ray diffraction and nitrogen adsorption at 77 K. *Cis*-but-2-ene, *trans*-but-2-ene, and but-1-ene (Linde), stated purity 99%, and sulfur dioxide (Deutsche L'Air Liquide) 99.9%, were used

without further purification. The reaction was studied on self-supporting thin wafers ($5\text{--}7\text{ mg/cm}^2$) outgassed for 36 h at 725 K to a pressure less than $5 \cdot 10^{-7}$ Pa. After degassing no residual hydroxyl groups forming Brönsted acid sites are observed except on zeolite Ca α . The spectra of the adsorbed species were obtained on a Fourier transform infrared spectrophotometer Digilab FTS 14 by ratioing against the background spectrum of the outgassed zeolite. The samples were analyzed by X-ray fluorescence and neutron activation analysis. First of all the sorption behaviour of the *n*-butenes was separately studied. Detailed information about changes of molecular properties upon adsorption can be obtained analyzing the spectra with respect to the number, position, shape and intensity of the bands.

Due to the lowering of their symmetry upon adsorption the butenes show a change of the number and intensities of their infrared bands. A complete analysis is rendered difficult because of band overlap and obscuring the region below 1200 cm^{-1} by lattice vibrations. All *n*-butenes show the preservation of the C=C bond [4]. The frequencies of the CH stretch and bending vibrations are slightly displaced mostly below those of the gaseous molecules. The red shift of the C=C stretch, however, is more pronounced and depends on the cation. On not completely exchanged zeolites two C=C bands are observed, which are assigned to *n*-butene molecules interacting with different cations. Except the transition metal forms a direct correlation between band shift and charge/radius ratio of the cation is observed (Table I),

Table I
Band shift on *n*-butene C=C stretch on zeolites containing different cations

Cation	Charge/radius [V]	But-1-ene [cm ⁻¹]	Cis-but-2-ene [cm ⁻¹]	Trans-but-2-ene [cm ⁻¹]
Na ⁺	15.16	-10	-15	-17
Li ⁺	24.00	-16	-18	-17
Ca ²⁺	29.09	-25	-25	-32
Mg ²⁺	44.36	-28	-33	-47
Ag ⁺	11.44	-50		
Zn ⁿ⁺	38.97	-40	-48	-54

Because of cluster formation the real charge of Znⁿ⁺ is unknown.

indicating that the former is a sensitive indicator for the polarizing power acting on the adsorbed butene molecule. Location near the cations can be proved by identical C=C band shifts on zeolites CaA and Ca α , although the charge distribution in the zeolitic lattice is quite different. In the adsorbed state the rotational fine structure has disappeared, and the fundamentals consist only of one single narrow band (FWHH < 10 cm^{-1} for C=C stretch). In conjunction with the Lorentzian band shape a restricted rotation must be assumed. The separate appearance of two C=C bands in presence of two different cations shows that the residence times of the butenes on the adsorption sites are at least of the same order of magnitude as the half life of an IR event.

Further information about adsorptional interaction can be derived from changes in band intensities. In case of the *n*-butenes the ratio of the C=C stretch intensities to the CH stretch intensities increases upon adsorption, indicating a strong polariza-

tion of the π electrons and a simultaneous lowering of the CH bond dipole moment showing again, that the former is mainly affected by the adsorbent field.

Our experimental results are in accordance with an adsorption in a "side on" mode under formation of a π -complex between the butene and the cation in S1 position. Shielding of the small lithium and magnesium ions by the oxygen of the six-membered ring explains the rather low C=C band shifts on zeolites LiA and MgA. The stronger frequency displacements on zinc and silver ions are caused by the formation of π -sp donor bonds with additional back-donation into π^* orbitals similar to ethylene [5]. In case of some silver complexes the shift of the C=C stretch is inversely related to the ionization potential of the *n*-butenes [6]. With zeolites the different displacements of both but-2-enes in spite of their identical ionisation potentials indicate, that also steric effects and electrostatic interactions due to different arrangements of the adsorption complex [7] are involved. There is no IR spectroscopic evidence for the formation of carbenium ions. Moreover, though in zeolite ZnA excess zinc is assumed to form clusters with oxygen by analogy with nickel and copper [8], no similarity to ZnO with respect to formation of allylic species [9] can be observed.

At room temperature spontaneous isomerization only occurs with ZnA and CaA. On the other zeolites used coadsorption of sulfur dioxide is necessary to induce the reaction except on zeolite NaA, which is inactive in any case. Products are only isomeric *n*-butenes, while isobutene, polysulfones, polymers or fragments could not be detected by IR spectroscopy (in case of zeolite CaA by gaschromatography, either). A quantitative evaluation of the time-resolved IR spectra, provided that Lambert-Beer's law is valid, gives information about the kinetics of isomerization on the catalyst wafer. A rough estimation using RUTHVEN's data [10] shows, that the influence of diffusion may be neglected.

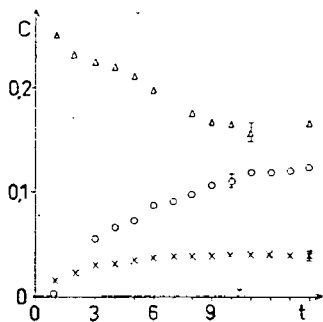


Fig. 1. Isomerization of *trans*-but-2-ene on CaA, composition of reaction mixture, C in arb. un., t in min. Δ *trans*-but-2-ene; $\circ$ *cis*-but-2-ene; $\times$ but-1-ene.

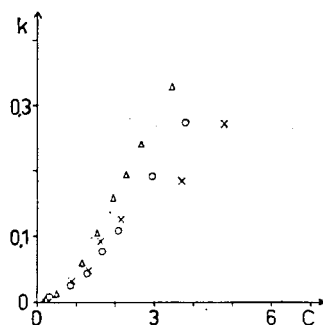


Fig. 2. Isomerization of but-1-ene on CaA, ZnA, MgA rate constant k ($\text{sec}^{-1} \cdot \text{g}^{-1}$) versus SO_2 concentration (10^{-3} Mol/g). $\times$ CaA; $\circ$ ZnA; Δ MgA.

From the variation of composition (Fig. 1), starting with different *n*-butenes on zeolite CaA and with but-1-ene on zeolites MgA, ZnA, and CaA, a closed-loop mechanism between the *n*-butenes must be concluded. No induction period was observed in the triangular isomerization reaction. With fixed amounts of SO_2 the reac-

tion data fit a reversible first order equation (1)

$$\ln(x - x_e) = \ln(x_0 - x_e) - kx_0t/(x_0 - x_e) \quad (1)$$

where k represents the rate constant of the forward reaction, x the concentration at time t , x_0 the initial concentration, and x_e the concentration at equilibrium. On zeolite CaA the reaction rate decreases from *trans*-but-2-ene over but-1-ene to *cis*-but-2-ene approximately following the sequence of C=C band shift as a rough measure of activation. Comparing the results of but-1-ene on zeolites CaA, ZnA, MgA and preliminary ones on CaX leads to a direct correlation between isomerization rate and polarizing power of the cations. In this picture the inactivity of zeolite NaA may be explained with a minimum degree of activation necessary to initiate this reaction. Concerning sulfur dioxide, from a certain minimum amount depending on the butene, direct proportionality between reaction rate and cocatalyst concentration is detectable (Fig. 2), pointing to an immediate intervention into the reaction mechanism. For this reason no change in selectivity can be expected by variation of the SO₂ content, except the small initial range. Upon coadsorption different SO₂ species appear in the spectrum, which are already observed without butene addition [11]. Only on zeolite NaCaA there is some evidence for the formation of a butene-SO₂-complex of sulfone-like structure [12]. According to our results a radical or ionic mechanism on Brönsted sites can be ruled out. Only by IR spectroscopic investigations no distinction at present is possible between a synchron or an ionic mechanism on cations acting as Lewis acid sites.

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A STUDY OF THE REDOX BEHAVIOUR OF COPPER IONS IN ZEOLITES X AND Y BY TEMPERATURE PROGRAMMED REDUCTION

By

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Temperature Programmed Reduction (TPR) has been used to study the redox behaviour of copper ions in X and Y zeolites. Two distinct Cu^{II} to Cu^{I} reduction processes are discernible in both X and Y zeolites. These two processes have been assigned to the reduction of Cu^{II} ions occupying sodalite and supercage sites; a small fraction of the Cu^{II} ions, assumed to occupy hexagonal prism sites, remain unreduced. At 773 K in nitrogen, autoreduction of both sodalite and supercage Cu^{II} occurs in X zeolite, while only supercage Cu^{II} ions are autoreduced in Y zeolite. The reductions are reversible in Y zeolite, but some CuO is formed in X which is subsequently reduced by a third process. Activation energies (kJmol^{-1}) were obtained as follows: Cu^{II} to Cu^{I} (sodalite cages) 84 ± 13 , Cu^{II} to Cu^{I} (supercages) 64 ± 10 and CuO to Cu^0 (X type zeolite) 49 ± 7 .

Introduction

Recent temperature programmed reduction (TPR) studies [1] have shown that the technique can be successfully applied as a "finger print" method for the characterisation of catalysts.

We have studied here the reduction of cupric ions in zeolites X and Y. Previous studies [2, 3] of the type-Y system by isothermal techniques showed that the reduction of Cu^{II} to Cu^{I} occurred by two distinct processes, although a TPR study [4] of the same system did not resolve them. In view of the conditions used in the above study, it seems likely that TPR under milder conditions would yield more detail of the reduction mechanisms involved.

The TPR of (Cu, Na)-X-50 was also studied here to enable a comparison to be made of the redox behaviour of copper in zeolites of different Si/Al ratios. We also report some work on the autoreduction of Cu^{II} in both X and Y zeolites, where TPR is able to shed light on the locations of the ions involved.

Experimental

Apparatus and procedure

The apparatus and procedure used were similar to those described previously [1]. The reducing gas was 4% hydrogen in nitrogen. The samples (200 mg) were held on a sinter (20 mm diameter) in a glass reactor. The reactor was held in a stirred air oven which could be heated linearly at rates up to 20 K min^{-1} . The rate of hydrogen consumption was monitored *via* a katharometer.

Materials

Samples of zeolite Y (LINDE, SK-40) and zeolite X (BDH) were ion exchanged in aqueous copper nitrate solution. Excess nitrate was used to produce (Cu, Na)-Y-68 and the appropriate amounts of nitrate to produce (Cu, Na)-Y-32 and (Cu, Na)-X-50. It has been shown [3, 5] that these methods produce Cu^{II} ion exchanged zeolites. Cylinder gases (BOC and PK MORGAN) were purified by passage over activated charcoal and magnesium perchlorate.

Sample pretreatment

Each sample was pretreated in the reactor under flowing nitrogen or air. The temperature was raised from ambient to 773 K at 30 K min^{-1} , held for 10 minutes then rapidly lowered to 325 K under flowing gas.

Qualitative tests for Cu^{I} , Cu^0 , and CuO

Samples were exposed to carbon monoxide at room temperature, and flushed with nitrogen. The samples were then prepared as nujol mulls and their IR spectra recorded. Absorption at 2145 cm^{-1} was taken as evidence for the presence of Cu^{I} [6]. The presence of the metal or oxide was indicated in some samples by the appearance of characteristic lines in the powder X-ray diffraction patterns.

Results

(Cu, Na)-Y-68, Air pretreated samples

Ten samples were subjected to TPR at heating rates from 2.8 to 17.7 K min^{-1} . A typical spectrum, presented in Fig. 1, consists of two peaks separated by about 100 K. The total amount of hydrogen consumed was $1.00 \cdot 10^{-4} \text{ mol}$, corresponding to 0.47 mol of hydrogen per mol of Cu^{II} in the sample. Before and after the TPR the samples were tested for CuO , Cu^{I} and Cu^0 as described above. The test for Cu^{I} was positive for the reduced samples; all other tests were negative.

When a reduced sample was subjected to the 'air pretreatment' process, and the TPR repeated, identical results were obtained. Thus, the total amount of hydrogen consumed in the TPR of the re-oxidised sample was $9.29 \cdot 10^{-5} \text{ mol}$.

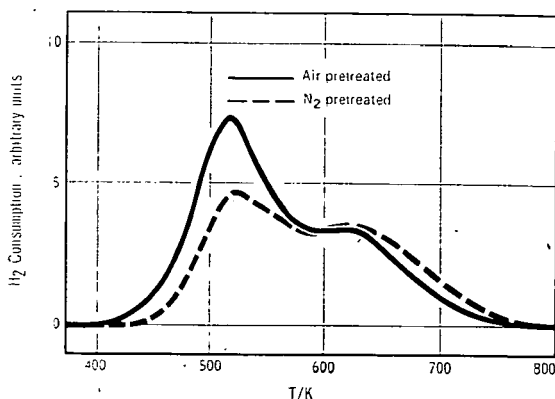


Fig. 1. TPR spectra of (Cu, Na)-Y-68.
 $\beta = 13.5 \text{ K min}^{-1}$, 4% H_2/N_2

(Cu, Na)-Y-68, Nitrogen pretreated samples

Four samples were subjected to TPR at heating rates from 9.3 to 17.9 Kmin⁻¹. A typical spectrum is shown in Fig. 1. As for the air pretreated sample the spectrum consists of two peaks indicating the two separate reduction processes. However, the amount of hydrogen consumed in this reduction ($7.24 \cdot 10^{-5}$ mol) is only 70% of that consumed by the air pretreated sample. It can be seen from Fig. 1 that this difference is due to a diminution of the amount of hydrogen consumed in the low temperature reduction. Tests indicated the presence of Cu^I in samples both before and after reduction. No Cu⁰ or CuO was detected.

When the reduced sample was subjected to the air pretreatment, the TPR results obtained were the same as those obtained for samples that had received only the air pre-treatment. Thus, the re-oxidised sample on subsequent TPR, consumed $9.47 \cdot 10^{-5}$ mol of hydrogen.

(Cu, Na)-Y-32, Air pretreated sample

A single 400 mg sample was subjected to TPR. The spectrum, shown in Fig. 2, consists of two peaks. The total amount of hydrogen consumed was $9.61 \cdot 10^{-5}$ mol.

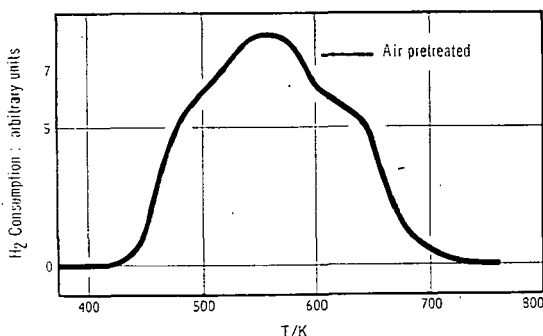


Fig. 2. TPR spectrum of air pretreated (Cu, Na)-Y-32.
 $\beta = 13.5$ Kmin⁻¹, 4% H₂/N₂. 400 mg of zeolite were used

(Cu, Na)-X-50, Air pretreated samples

Six samples were subjected to TPR at heating rates from 3.0 to 18.0 Kmin⁻¹. A typical spectrum is presented in Fig. 3. Again two reduction processes are observed, most of the hydrogen being consumed in the high temperature reduction. The total amount of hydrogen consumed was $9.82 \cdot 10^{-5}$ mol. Tests indicated the presence of Cu^I and Cu⁰ in the reduced samples.

The above processes were not found to be reversible. Thus, after the reduced samples were subjected to the air pretreatment, tests showed the absence of Cu⁰ and Cu^I but gave clear evidence of CuO. A typical TPR spectrum for these samples is shown in Fig. 4. A third low temperature reduction is clearly discernible. The total amount of hydrogen consumed in this reduction was $1.24 \cdot 10^{-4}$ mol.

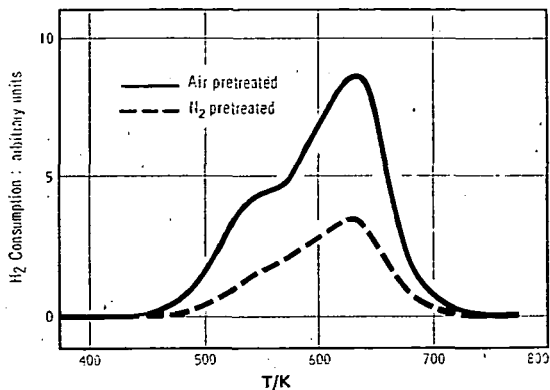


Fig. 3. TPR spectra of (Cu, Na)-X-50.
 $\beta = 13.0 \text{ K min}^{-1}$, 4% H_2/N_2

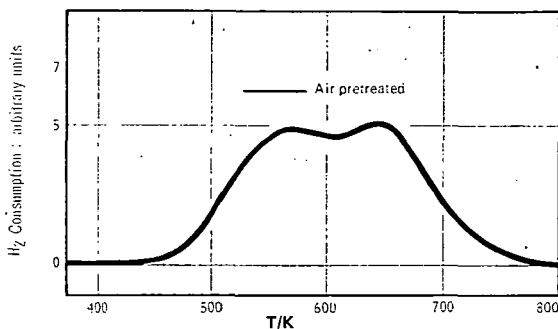


Fig. 4. TPR spectrum of (Cu, Na)-X-50 reduced
 and reoxidised. $\beta = 13.7 \text{ K min}^{-1}$, 4% H_2/N_2

(Cu, Na)-X-50, Nitrogen pretreated samples

Three samples were subjected to TPR at heating rates from 12.9 to 17.9 K min^{-1} . A typical spectrum is shown in Fig. 3. Both reduction processes are apparent. The total amount of hydrogen consumed by the sample $4.18 \cdot 10^{-5} \text{ mol}$. Tests showed the presence of Cu^{I} before reduction and Cu^{I} and Cu^0 after reduction. The sample reduced at 13.5 K min^{-1} was subjected to the air pretreatment and investigated. Tests showed that Cu^{I} and Cu^0 were removed, but that CuO was produced. Subsequent TPR gave the same three peaks as found for the re-oxidised, air pretreated sample (Fig. 4). The amount of hydrogen consumed was $1.58 \cdot 10^{-5} \text{ mol}$, an increase of 25% over the amount consumed by the re-oxidised, air pretreated sample.

Reaction orders and activation energies

Under the conditions used here, the reduction processes were taken as first order in both Cu^{II} concentration [2] and hydrogen concentration [10]. Thus the equation [10]:

$$2 \ln T_m - \ln \beta + \ln [\text{H}_2]_m = E/RT_m + \text{constant}$$

may be used to derive values for the apparent activation energies of the reduction processes (T_m and $[H_2]_m$ are the temperatures and hydrogen concentrations at the rate maxima respectively and β is the linear heating rate).

The reduction processes in (Cu, Na)-Y-68 were found to have activation energies (kJmol^{-1}) of 84 ± 13 (high temperature process) and 64 ± 10 (low temperature process). The same values were found for the analogous processes in (Cu, Na)-X-50. The low temperature process in (Cu, Na)-X-50, Fig. 4, was found to have an activation energy of $49 \pm 7 \text{ kJmol}^{-1}$.

Discussion

The qualitative analyses for Cu^I , Cu^0 and CuO indicate that the reduction of air pretreated (Cu, Na)-Y-68 produces only Cu^I under conditions used here. Moreover, a previous study [3] showed that after reaction using more drastic reducing conditions only 6.5% of the copper in this system was reduced to Cu^0 . Thus, the TPR spectra for the air-pretreated (Cu, Na)-Y-68 show that about 94% of the Cu^{II} is reduced exclusively to Cu^I by two separate reduction processes.

These findings are in accord with the results of a previous study [2] although at the hydrogen pressures used, $P_{H_2} > 13.3 \text{ kNm}^{-2}$, the reduction was found to be zero order in hydrogen. However, a recent TPR study [4] of this system, using hydrogen concentrations of the order of 80 kNm^{-2} , was only able to distinguish a single reduction process of Cu^{II} to Cu^I . Our result that about 6% of the Cu^{II} ions remain unreduced is consistent with the small percentage of ions occupying positions in hexagonal prisms. Furthermore our results showing two distinct reduction processes are in accord with the distribution of the remaining ions between the sodalite units and the supercages [7, 8].

It is thus tempting to assign the low temperature reduction to the reduction of Cu^{II} ions in the supercage and the high temperature reduction to the reduction of Cu^{II} ions in the sodalite units. However, our results indicate that most Cu^{II} ions are reduced by the low temperature process, whereas the distribution of ions in the dehydrated framework shows that most ions are accommodated in the more stable sodalite positions. This anomaly is further highlighted by the results obtained with (Cu, Na)-Y-32. These results, shown in Fig. 2, show the same two reduction processes exhibited by (Cu, Na)-Y-68. X-ray data, for the dehydrated system, indicate however that Cu^{II} ions occupy only hexagonal prisms and sodalite units; on the basis of the above, therefore, only one reduction process would be expected.

The appearance of two distinct reduction processes of Cu^{II} to Cu^I in (Cu, Na)-Y-32 has been attributed to the presence of water in the zeolite framework [2]. We thus suggest that our results are indicative of a partially hydrated zeolite-Y system.

The nitrogen pretreatment of (Cu, Na)-Y-68 was found to reduce about 25% of the Cu^{II} ions to Cu^I . This partial autoreduction has been previously reported for this system [9] and a mechanism has been proposed. A comparison of the TPR spectra for the air and nitrogen pretreated samples (presented in Fig. 1) indicates that the Cu^{II} ions involved in the autoreduction are those involved in the low temperature reduction, and here assigned to supercage sites.

The TPR spectrum of air pretreated (Cu, Na)-X-50, shown in Fig. 3, indicates that the reduction occurs by two separate reduction processes, a result similar to that found for the reduction of (Cu, Na)-Y-68. However, in contrast to the results

found for the Y zeolite, the reduction of (Cu, Na)-X-50 results in the production of Cu^0 in addition to Cu^I . It is somewhat surprising, though, that the hydrogen consumption corresponds to only 0.42 mol per mol of Cu^{II} .

It is assumed [10] that the TPR spectrum is not radically altered by the 'hidden' peak due to the reduction of Cu^I to Cu^0 and that the two peaks refer, as suggested for the Y zeolite, to the reduction of Cu^{II} in the sodalite and supercage positions. Thus the TPR spectrum of air pretreated (Cu, Na)-X-50 shows that, in contrast to air pretreated (Cu, Na)-Y-68, most of the Cu^{II} is reduced in the high temperature reduction process which was assigned above to the reduction of ions in sodalite positions. This result is that expected from the distribution of ions in the dehydrated zeolite. The fact that we would expect the air pretreatment to produce a more dehydrated zeolite than would be the case for the Y zeolite is thus consistent with the above.

The nitrogen pretreatment of (Cu, Na)-X-50 resulted in the reduction of Cu^{II} to Cu^I . The hydrogen uptake during the subsequent TPR was only 43% of that absorbed by the sample subjected to air pretreatment. It is thus apparent that far more drastic autoreduction of (Cu, Na)-X-50 takes place than was the case for (Cu, Na)-Y-68 (see above). The TPR spectrum of the nitrogen pretreated sample (see Fig. 3) suggests, as must be expected, that the reduction involves Cu^{II} from both sodalite and supercage positions.

Using the above assignments, the activation energies obtained for the reduction of Cu^{II} to Cu^I in (Cu, Na)-Y-68 are 84 kJmol^{-1} (for Cu^{II} in the sodalite units) and 64 kJmol^{-1} (for Cu^{II} in supercage positions). These can be compared with values of 111 (sodalite) and 70 kJmol^{-1} (supercage) obtained from an isothermal kinetic study [2]. Activation energies measured for the analogous processes in X-zeolite are not significantly different from those measured for (Cu, Na)-Y-68.

The simplest mechanism for these reductions is the reaction between hydrogen and Cu^{II} ions 'in situ' in the sodalite and supercage positions. An alternative mechanism, invoked previously [2], provides that Cu^{II} ions in sodalite positions must migrate to the supercage before reduction can take place. If this process involves an equilibrium between Cu^{II} ions in the two positions, followed by reduction of Cu^{II} in the supercage, then the difference in activation energies (about 20 kJmol^{-1}) is equal to the difference in energy between Cu^{II} ions in the two lattice positions.

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AMMOXIDATION OF PROPYLENE ON ZnNaY ZEOLITE

By

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Ammonoxidation of propylene on ZnNaY zeolite has been investigated by means of adsorption, pulse, and flow reactors as well as IR spectroscopy. Instead of acrylonitrile acetonitrile has been obtained with high selectivity but low yield. Acetaldehyde and acetic acid react with ammonia to give acetonitrile but oxidation of acetaldehyde is very slow and non-selective. This indicates that acetaldehyde is the most probable intermediate which reacts with ammonia to acetonitrile. On interaction of ammonia with acetaldehyde the absorption band of acetonitrile appears in IR spectrum on both ZnNaY and NaY zeolites, although the latter is completely inactive in ammonoxidation of propylene. Thus Zn-ions perform the role of active centres for initial step of the reactions. Presence of ammonia inhibits the non-selective oxidation of acetaldehyde which otherwise is totally oxidized.

Introduction

Exploratory studies of the activity of ZnNaY zeolite in ammonoxidation of propylene have shown [1] that instead of acrylonitrile usually found on oxide catalysts [2, 3] acetonitrile is formed with high selectivity. It seemed thus of interest to study the mechanism of insertion of oxygen resulting in the elimination of one carbon atom, as well as the role of zinc ions as the active centers.

Experimental part

The samples of zeolite ZnNaY were prepared from sodium faujasite characterized by the formula: $0.98 \text{ Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 5.21 \text{ SiO}_2 \cdot x\text{H}_2\text{O}$. The exchange of sodium ions for zinc ions were carried out three times from 0.02 M ZnCl_2 solution at 100 °C using acetate buffer (pH=5) for stabilization of pH. ZnNaY zeolite has been obtained with chemical analysis: 3.34% Na_2O , 8.56% ZnO , 14.46% Al_2O_3 , 51.34% SiO_2 , and ignition losses 20.92%; percent of exchange about 66.1%.

Adsorption isotherm of CO were determined in semiautomatic constant pressure apparatus at different temperatures [4]. Before measurement the samples of the zeolite were heated and outgassed *in vacuo* 10^{-5} torr for 15 hr at 350 °C. Carbon monoxide was obtained by dehydration of formic acid with concentrated sulphuric acid at 100 °C.

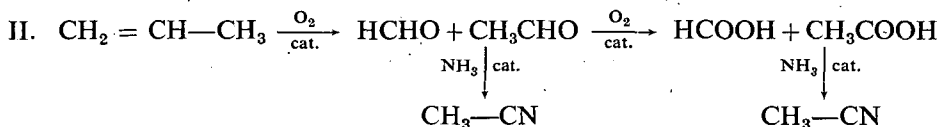
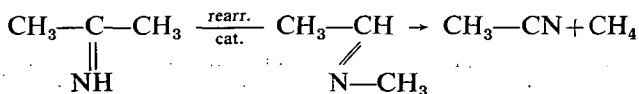
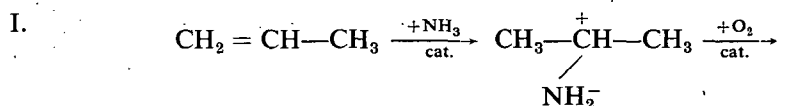
Before every catalytic test in the pulse reactor, the sample of zeolite (0.5 ml) was activated at 400 °C by flow of nitrogen for 4 hr. The chromatographic analysis has been carried out by use of chromatograph Giede 18.03. Conditions of analysis were: column with Carbowax 2 m length, column with succinate 1 m length; detector FID.

Catalytic tests by flow reactor were carried out at 350–480 °C, using feed gases of volume composition: $C_3H_6:NH_3:air=1:1:8$. Propylene used was from Fluka. Ammonia and air were technical grade, dried before using.

IR absorption spectra of adsorbed species on ZnNaY and NaY zeolites were registered by means of spectrophotometer UR-20 (Zeiss). Samples with density about 10 mg/cm² were formed by pressing and placed in vacuum cell equipped with NaCl windows and connected to vacuum system. The sample could be heated *in situ* to 450 °C. Before each run activation has been carried out at 360 °C for 3 hr *in vacuo* 10⁻⁵ torr.

Results and discussion

Two different mechanisms may be proposed *a priori* for the heterogeneous catalytic ammoxidation of propylene resulting in the formation of acetonitrile. They may be represented by following schemes:



Pulse experiments revealed that isopropylamine is not oxidized to acetonitrile on ZnNaY zeolite. The presence of isopropylamine at the surface of that zeolite after contacting it with the mixture of propylene and ammonia also could not be detected, in the IR spectra. Mechanism I could be thus discarded and experiments were carried out to show that Mechanism II is operating and to demonstrate the role of Zn-ions.

Measurements of the adsorption of CO on samples of different degree of exchange showed that the amount of CO adsorbed specifically increases with increasing degree of Zn-exchange. (Fig. 1).

However, the isosteric heat of adsorption ($Q_{isost.}$) as calculated from the Clausius—Clapeyron equation remains practically constant indicating that one type of active centres are involved in specific adsorption of CO independently of the degree of exchange of Zn-ions (Table I).

Table 1
Results of CO adsorption on ZnNaY zeolite (at 0 °C)

Ion exchange %	$Q_{\text{isost.}}$ kcal/mol	N_{Zn}	N_{CO}
44	16.2	11.7	2.0
65	17.7	17.3	3.0
81	18.4	21.6	3.6

N_{Zn} — number Zn^{+2} ions in an elementary cell

N_{CO} — number CO molecules adsorbed in an elementary cell

It should be mentioned that the exchange could not be extended beyond about 80% even by using dehydration, which indicates that the exchange equilibrium was already reached. It may be thus concluded that zinc ions locate themselves firstly in about half of the S_1 positions (every second hexagonal prism) and then occupy statistically all other positions.

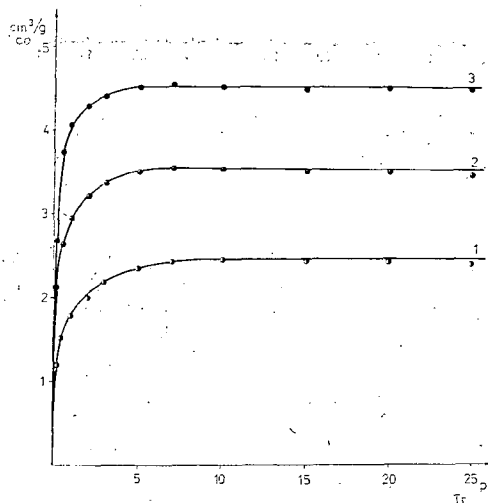


Fig. 1. Specific adsorption of CO on ZnNaY zeolite at 0 °C for ion exchange: 1—44%, 2—65%, 3—81 %

Pulse tests, carried out to prove the primary intermediates of propylene oxidation on ZnNaY zeolite at 400 °C, led to following conclusions:

- reactions of acetaldehyde as well as acetic acid with ammonia to acetonitrile proceed with high yield and high selectivity,
- oxidation of acetaldehyde to acetic acid on ZnNaY zeolite proceeds with difficulty and a variety of different products is obtained.

It may be thus concluded that acetaldehyde is the main intermediate in the ammoxidation of propylene, its reaction with ammonia to form acetonitrile being much faster than its oxidation to acetic acid or other products.

An introductory IR investigation of simultaneous chemisorption of $C_3H_6 + O_2 + NH_3$ mixture on ZnNaY zeolite at 350 °C confirmed the results of catalytic tests showing the appearance of a well developed absorption stretch band of CN group in nitrile (2240—2268 cm^{-1}); however the spectrum is difficult to interpret in the range 1300—1800 cm^{-1} (Fig. 2).

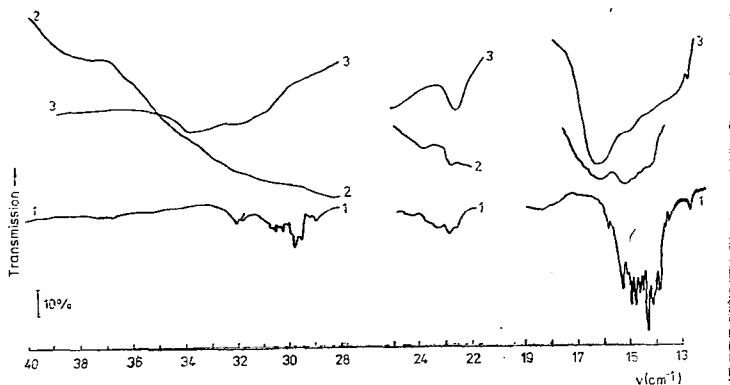


Fig. 2. IR spectra of ammoxidation of propylene: 1 — gaseous CH_3CN
2 — CH_3CN chemisorbed on ZnNaY zeolite at 320 °C,
3 — $C_3H_6 + O_2 + NH_3$ chemisorbed on ZnNaY zeolite at 350 °C

For comparison the spectra of acetonitrile chemisorbed on ZnNaY zeolite at 320 °C, as well as that of gaseous acetonitrile are also shown in this figure.

The mechanism of propylene ammoxidation on ZnNaY and NaY zeolites were then followed in more detail by IR spectroscopy. In the first experiment the mixture of $C_3H_6 + O_2$ (1:1, 26 torr, at 400 °C, contact time 120 s) was chemisorbed on ZnNaY zeolite, then the sample was cooled to 45 °C and outgassed to $3 \cdot 10^{-1}$ torr (Fig. 3). Only H_2O (the stretch band of OH group) and a trace of COO^- were detectable as oxidation products. Then ammonia was introduced into IR cell (3 torr at 45 °C) which was then outgassed to $3 \cdot 10^{-1}$ torr and the sample was heated to 400 °C. From 350 °C the stretch band of nitrile group (about 2280 cm^{-1}) appeared in IR spectrum. The fact that no primary oxidation products could be seen may be connected with very small yield of propylene oxidation which is limiting step in propylene ammoxidation. In spite of a lack of clear appearance of primary propylene oxidation products, their concentration is sufficient for nitrile formation.

In the next experiments the reaction of acetaldehyde with ammonia was investigated. Acetaldehyde was introduced into IR cell and chemisorbed on ZnNaY zeolite and then ammonia to obtain a mixture at room temperature (14 torr, $CH_3CHO : NH_3 = 2:5$) (Fig. 4). Then the zeolite sample was heated to 300 and 400 °C. At 300 °C the nitrile group's stretch band appeared, which persisted after outgassing to 10^{-1} torr the ZnNaY zeolite. The same experiment was carried out using NaY zeolite. The nitrile group's stretch band was also observed but its intensity was much smaller than in the case of ZnNaY zeolite.

An investigation using IR method was also carried out for the sequence: chemisorption of CH_3COOH , addition of NH_3 and heating to 400°C zeolites ZnNaY and NaY . In both cases the absorption bands characteristic for ammonium acetate appeared, and then from 150°C those of acetamide after dehydration of acetate. In both cases the stretch band of nitrile group appeared from about 200°C .

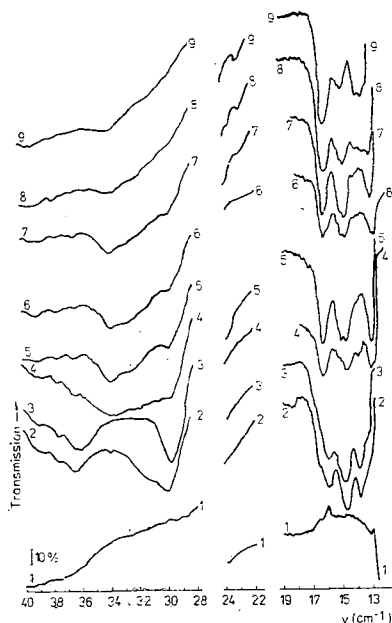


Fig. 3. IR spectra chemisorbed species on ZnNaY zeolite for the sequence: $\text{C}_3\text{H}_6 + \text{O}_2 \rightarrow \text{NH}_3 \rightarrow \text{heating}$. 1 — the background of ZnNaY zeolite, 2 — after chemisorption of $\text{C}_3\text{H}_6 + \text{O}_2$ (1:1, at 400°C , 26 torr, contact time 120 s), 3 — after outgassing to $3 \cdot 10^{-1}$ torr, 4 — after NH_3 dosage and outgassing to $3 \cdot 10^{-1}$ torr at 45°C , 5 — heating at 250°C , 6 — 300°C , 7 — at 350°C , 8 — at 425°C , 9 — at 425°C after outgassing to $1 \cdot 10^{-5}$ torr

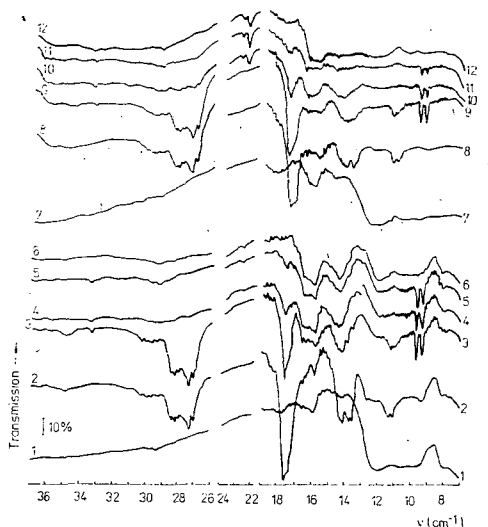


Fig. 4. IR spectra for the sequence: $\text{CH}_3\text{CHO} \rightarrow \text{NH}_3 \rightarrow \text{heating}$ on NaY and ZnNaY zeolites: a) 1 — the background of NaY zeolite, 2 — after chemisorption of CH_3CHO (10 torr, 45°C), 3 — after NH_3 dosage a mixture: $\text{CH}_3\text{CHO}:\text{NH}_3 = 2.5:5$, 15 torr, 45°C), 4 — heating to 300°C , 5 — heating to 400°C , 6 — spectrum after outgassing NaY zeolite sample to $3 \cdot 10^{-1}$ torr; b) 7 — the background of ZnNaY zeolite, 8 — after chemisorption of CH_3CHO (10 torr, 45°C), 9 — after NH_3 dosage (a mixture: $\text{CH}_3\text{CHO}:\text{NH}_3 = 2.5:5$, 14 torr, 45°C), 10 — heating to 300°C , 11 — heating to 400°C , 12 — spectrum after outgassing ZnNaY zeolite sample to $3 \cdot 10^{-1}$ torr

Following conclusions may be formulated on the basis of results obtained:

- the oxidative ammonolysis of propylene on ZnNaY zeolite is very selective, but the conversion is low (2.18% at 450°C); pure NaY is completely inactive which indicates that Zn -ions perform the role of active centers,
- acetaldehyde and acetic acid easily react with ammonia to give acetonitrile, but oxidation of acetaldehyde to acid on ZnNaY is very slow and non-selective; no isopropylamine could be detected in IR spectra; this indicates that acetaldehyde is the most probable intermediate,

- on interaction of ammonia with adsorbed acetaldehyde IR absorption band of acetonitrile appear on both ZnNaY and NaY zeolites, which indicates that Zn-ions play the role in the initial step of the reaction,
- it may be concluded that the ammoxidation of propylene on ZnNaY zeolite, proceeds through a consecutive series of steps, the first being the oxidation of propylene to acetaldehyde with the participation of Zn-ions. Acetaldehyde reacts then with ammonia to form acetonitrile. It is noteworthy that the presence of ammonia inhibits the non-selective oxidation of acetaldehyde which otherwise is totally oxidized.

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TRANSMISSION SPECTRA OF SINGLE CRYSTAL ZEOLITES CONTAINING Ni^{2+} -IONS

By

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Transmission spectra of nickel-exchanged single crystal zeolites are recorded on a single beam microscope-spectrophotometer driven by microcomputer. This digital method yields an improved spectral resolution. Receiving the absorption spectra of transition metal ions present in the zeolite-lattice, both the sodium- and the exchanged forms of zeolites were on-line computed and evaluated. In relation to absorption-maxima of complexed ions in aqueous solutions, the spectra of transition metal complexes surrounded with zeolite network show bathochromic band-shift as well as -broadening and -splitting, respectively. With regard to possible coordination spheres of transition metal ions in the zeolite framework, the spectra are interpreted in terms of ligand field theory. The method presented will also allow an analysis of the sites of hydrocarbons in exchanged zeolites by comparing these spectra with those, which are not loaded with organic compounds, and the spectra of the free organic molecules, respectively.

Introduction

For understanding the role of transition metal ions in zeolite catalysis and for setting up defined starting conditions in reactions of organic compounds in zeolites it is necessary to study, how these ions are incorporated into the zeolite lattice. In addition to EPR-investigations, which are accomplished in cooperation with the Bulgarian Academy of Sciences, the method of electronic excitation spectroscopy in combination with ligand field theory is useful to determine cation positions in zeolites.

Employing large single crystals of defined structure and measuring their absorption spectra in transmitted light, more detailed information can be obtained about particular crystallites eliminating undesired outer-surface effects. Furthermore, compared with the frequently used reflectance technique, in transmission spectroscopic investigations almost no scattering effects are to be found.

Method and apparatus

The transmission spectra of nickel containing single crystal zeolites were carried out with a microscope-spectrophotometer (Leitz) between 220 and 800 nm using mirror objectives (Ealing/Beck) of magnification-factor 74.

The lapse of measurement is driven by microcomputer. Using a stepping motor to push the monochromator, the range of wavelengths can be scanned in 25 000 different steps. At each scanning point an optional number of single values according to the actual intensity of transmitted light is transferred to a calculator (Hewlett Packard 9830A). One to ten data per measuring position are chosen to be recorded and averaged by calculator. Moreover, higher accuracy is received by scanning the whole measuring range repeatedly and by adding and averaging the resulting spectra at each point (cumulative method).

Independently of recording, absorption spectra are evaluated by subtraction of sample- and reference-curves, respectively. Small differences are recognized in comparing sodium zeolites with those containing transition metal ions in small amount.

Preparation of Samples

Synthesis and growth of single crystals were carried out by a method for preparation large crystals of sodium X zeolite (particle sizes 30 to 50 μm in diameter) described by J. F. CHARNELL [1]. The structure of the faujasite type zeolite was confirmed by X-ray diffraction. A Si/Al-ratio of 1.15 was determined by X-ray fluorescence analysis.

Ni^{2+} -ions were introduced into the prepared single crystal zeolites by ion exchange from aqueous solutions of nickel acetate (conc. 0.01—0.5 mol/l, pH 7, $T=80^\circ\text{C}$, degree of exchange 10 to 80 %) [2]. The degree of exchange was calculated on the basis of Ni- and Al-contents in the zeolite, which was determined by atomic absorption spectroscopy.

Adsorption of benzene on sodium and nickel exchanged X zeolites was accomplished by stirring small amounts of zeolites in anhydrous benzene at 50°C for 10 hrs.

Results

Fig. 1 shows the spectrum of a nickel exchanged zeolite (deg. of exchange 75%) compared to the spectra of nickel acetate crystal and an aqueous solution of nickel acetate. The spectra of the nickel acetate crystal and the nickel exchanged zeolite show in addition to the known maxima at 390 to 400 nm and 650 to 730 nm another band in the near UV-region. This maximum has also been observed in the spectrum of aqueous nickel perchlorate solution as a shoulder [3].

To rule out the contribution of the unexchanged sodium X zeolite to the spectrum due to differences in the crystal thickness between sample and reference crystal two sodium X zeolite crystals of different thickness have been measured *vs.* air as reference and *vs.* each other (Fig. 2). Curves a) and b) have a shoulder at about 240 nm. Subtraction of the spectrum of the thinner crystal (approx. 30 μm) from that of the thicker crystal (approx. 50 μm) results in a clear maximum at 240 nm, which corresponds to the absorption of the difference of the two crystals (curve c). This absorption band is due to an electronic transition of Al in the zeolite system and has always to be considered evaluating the spectra of transition metal ion exchanged zeolites.

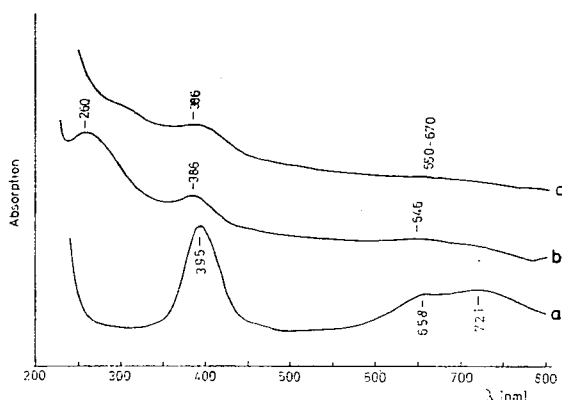


Fig. 1. Absorption spectra of: *a*) aqueous nickel acetate solution; *b*) nickel acetate crystal (ref.: air); *c*) nickel-exchanged (75%) X zeolite crystal (ref.: sodium X zeolite).

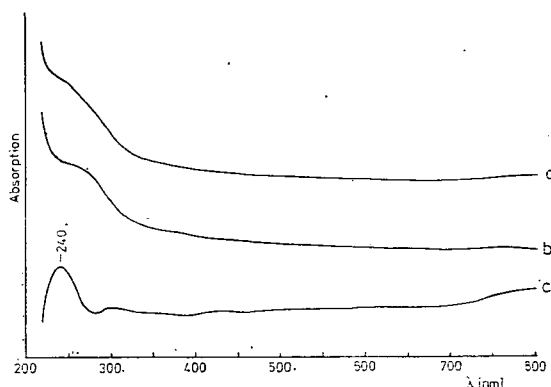


Fig. 2. Absorption spectra of sodium X zeolites: *a*) 50 μm in diameter crystal (ref.: air); *b*) 30 μm in diameter crystal (ref.: air); *c*) 50 μm in diameter crystal (ref.: 30 μm in diameter crystal).

In Fig. 3 the absorption spectra of nickel exchanged zeolites in dependence on the degree of exchange are plotted. In the spectra a bathochromic shift of the two low energy bands is observed depending on the degree of exchange as compared to nickel acetate solution. The shift decreases with increasing degree of exchange. The splitting of the two bands decreases in the same direction. At high degree of exchange only one broad band remains at 650 to 660 nm, which corresponds to the low energy maximum of a nickel acetate crystal (Fig. 1).

Fig. 4 shows the spectra of sodium and nickel exchanged X zeolites after the adsorption of benzene against sodium X zeolite as reference. The vibrational spectrum

of benzene around 250 nm as measured in ethanolic solution can also be clearly observed in both zeolite spectra. No shift of the bands can be seen. Also, the nickel maxima are not significantly shifted as compared to the nickel-exchanged zeolite not loaded with benzene.

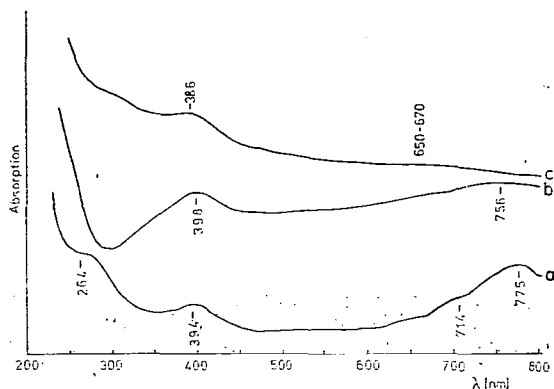


Fig. 3. Absorption spectra of nickel-exchanged zeolite crystals (ref.: sodium X zeolite): a) 12%; b) 47%; c) 75% degree of exchange

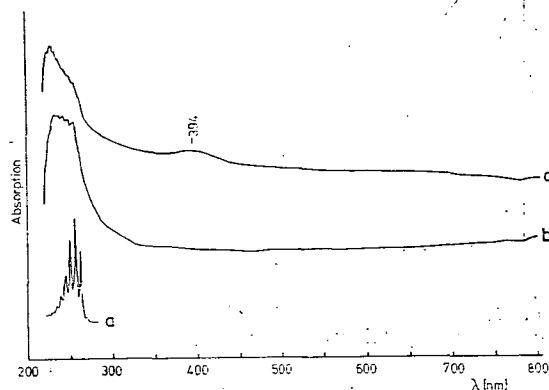


Fig. 4. Absorption spectra of: a) ethanolic solution of benzene; b) benzene loaded sodium X zeolite; c) benzene loaded nickel-exchanged zeolite (ref.: sodium X zeolite)

Discussion

According to [4—6] the Ni^{2+} -ions are incorporated in the zeolite lattice as octahedral $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ -complexes. The maxima at 395 nm, 660 nm and 1180 nm of such nickel ions are interpreted by ligand field theory as the transitions ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ (III), ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ (II) and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ (I) obtained for an octahedral field.

The band found in the near-infrared at 1180 nm could not be measured by our method due to the limited range of the monochromator.

On the basis of the interpretation by REINEN [7] broadening and splitting of the band at 650 to 730 nm in our spectra is due to spin-orbit coupling of the ${}^3T_{1g}(F)$ -term. This leads to an amplification of the higher energy maximum corresponding to the more energetic transition ${}^3A_{2g}(F) \rightarrow {}^1E_g(D)$ to the spin-forbidden ${}^1E_g(D)$ -term of multiplicity 1.

Also, a splitting of band (III) should be seen. Using a Dq-value of 850 cm^{-1} , the Orgel-diagram for octahedral Ni^{2+} -ions [8] results in the overlap of the splitted ${}^3T_{1g}(P)$ -term by the singlet-terms ${}^1T_{2g}(D)$, ${}^1A_{1g}(G)$ and ${}^1T_{1g}(G)$ leading to spin-forbidden transitions.

The base for the explanations as published by REINEN [7] is the assumption of an undistorted octahedral $\text{Ni}(\text{H}_2\text{O})^{2+}$ -complex and a value of Dq corresponding to the band between 1100 and 1200 nm.

Starting from these assumptions, we found it difficult to interpret the maxima in the near UV-region, which we observed especially for nickel acetate crystals and low degree of exchange nickel zeolites, respectively as shoulders in nickel perchlorate solution and high degree of exchange nickel zeolites. These bands as well as the shoulders are of similar intensities as compared to bands (II) and (III) (*cp.* [6]). Within the interpretation scheme of REINEN they have to be explained as intercombination bands ${}^3A_{2g}(F) \rightarrow {}^1E_g(G)$ or ${}^3A_{2g}(F) \rightarrow {}^1T_{2g}(G)$. However, the oscillator strengths of these intercombination bands, which result from the position of the nearest spin-allowed transition (III), should be too small to give observable intensities in the spectrum. On the other hand, the interpretation as a charge-transfer transition would result in much higher intensities of the bands than can be observed.

The D_{3h} -splitting due to the Ni^{2+} -ions discussed by KELLERMAN and KLIER [4] for thermally dehydrated nickel zeolites, where the low energy band at 260 nm is attached to the transition ${}^3A_{2g}(F) \rightarrow {}^3E_{1g}(P)$, can also be excluded in the case of hydrated nickel zeolites and of nickel acetate crystals, respectively.

On the other hand it seems probable to us, that the Ni^{2+} -complex incorporated in the zeolite is slightly distorted. Due to the geometry of the zeolite-lattice especially C_{2v} - or C_{4v} -symmetry should be discussed. This assertion depends essentially on the comparison of the spectra of hydrated nickel zeolite and nickel acetate, respectively, and the circumstance, that Ni^{2+} -ions in acetate crystals have a coordination sphere of D_{4h} -symmetry [9].

Assuming D_{4h} - or C_{2v} -symmetry and taking into consideration the absorption band at 260 nm, an interpretation of this band as the transition ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (III*) should be possible. This would result in correlating the band at 395 nm and the maxima between 650 and 730 nm with the transition ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (II*) and ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (I*), respectively.

In the case of nickel acetate crystal, the maximum at 646 nm would yield a Dq-value of 1548 cm^{-1} . The higher energy band (II*) should therefore appear at 406 nm and the maximum due to the transition (III*) should be at 252 nm according to the equations by SENDODA [5] and to the term-diagram for octahedral d^3 - and d^8 -complexes by TANABE AND SUGANO [10].

Besides spin-orbit-coupling and interaction with the neighboured ${}^1E_{1g}(D)$ -term, the splitting of the band (I*) should be explained, within this interpretation (*e.g.* to D_{4h} - or C_{2v} -symmetry), by lowering of symmetry of the Ni^{2+} -complex upon in-

corporation into the zeolite lattice. On the basis of these assumptions the dependence of this band on the degree of exchange can be cleared up.

The possibility to explain the high energy maxima supports the above interpretation. On the other hand, the necessity of defining a second overtone of the complexed water for the long-wave band at about 1180 nm contradicts this assertion.

The spectra of benzene loaded zeolites indicate that benzene can be absorbed at aqueous zeolites. However, neither a remarkable alteration of the benzene structure nor a noteworthy change of the neighbourhood of Ni^{2+} -ions in the zeolite was seen.

Acknowledgement

For the cooperation concerning the growth and analysis of zeolites we thank PROF. DR. LECHERT and DR. H. KACIREK, University of Hamburg.

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SOME PECULIARITIES OF HYDROCRACKING OF PARAFFINS ON METAL-ZEOLITE CATALYSTS

By

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In the light of recent data on zeolites as catalysts their capacity for polyfunctional catalytic action may be considered as the most important feature. This capacity is related to the presence in zeolites of the catalytically active sites of different nature. The question arises: are general ideas of bifunctional transformations of paraffins on metal-nonzeolite catalysts, considered by WEISZ [1] and THOMAS [2], valid for zeolite systems as well?

One of these regularities — the dependence of the catalyst activity on the activity ratio of acidic and metallic components was confirmed for zeolite catalysts: the rate of hydrocracking was shown to increase significantly with the acidity of a support in the series $\text{Pd/REZ} < \text{Pd/HY}$ [3] or $\text{Al}_2\text{O}_3 < \text{HY} < \text{H-mordenite}$ [4]. As the hydrogenating activity of catalysts falls, the total rate [5] and the yield of isomerized hydrocarbons [6] also decrease.

However, simple schemes of bifunctional transformations listed in [1] may be significantly complicated by a number of factors: 1) olefins, being intermediates of transformations, may promote reactions of cracking and isomerization [7]; 2) metal dispersion in zeolites may result in appreciable changes of their specific catalytic activity toward hydro-dehydrogenation; 3) when metallic component is fixed inside zeolite cavities, diffusional effects may influence the total rate and selectivity of hydrocracking. Taking this into account, the following problems were mainly studied at the Institute of Catalysis: the influence of olefin concentration on the activity of acidic component of hydrocracking catalysts; the influence of the metal component dispersion on its specific activity in hydrogenation of olefins; the influence of the activity ratio of acidic and metallic components and the homogeneity of their mutual distribution on the activity and selectivity of hydrocracking of paraffins. *N*-octane, octene-1, hexene-1 were chosen as model hydrocarbons.

Experimental

A flow-circulation installation supplied with a cracking reactor working at 350 °C and a hydrogenating one working at 150 °C as well as a pulse installation with a catalyst fluidized bed were employed to study the role of olefins during transformation of hydrocarbons on the acidic component of the hydrocracking catalyst (HY

zeolite). This system allowed changing the olefin concentration in the reaction medium over the 10^{-1} — 10^{-8} mmol/l range.

The specific hydrogenating activity of the metallic component in metal-zeolite catalysts was determined by the relation between the rate of hexene-1 hydrogenation measured in the flow-circulation installation at 150 °C and the metal surface area found from the oxygen chemisorption value.

The rate and the selectivity of hydrocracking was measured in the flow-circulation installation (300 and 350 °C, pressure 1.8—20 atm, $H_2:C_8H_{18}=100$). The metal dispersion in zeolites was varied according to the procedures described in [8].

Results and discussion

The decrease in the olefin concentration in the reaction mixture from 10^{-1} down to 10^{-8} mmol/l (Fig. 1) resulted in a sharp (by a factor of 30) fall of the rate of *n*-octane cracking. Moreover, the isomerized to normal reaction products ratio was also decreased by a factor of 2. At low olefin concentrations the catalyst activity is unchanged with time; the process of cracking may be described by the kinetic

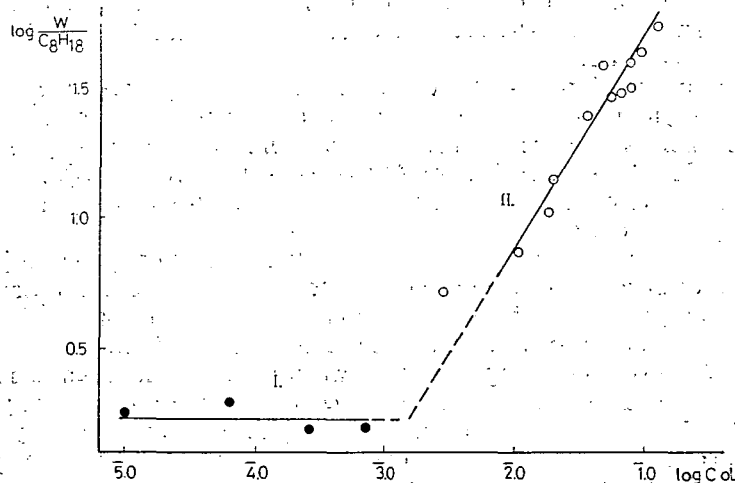


Fig. 1. Influence of the concentration of C_3 — C_5 olefins in the reaction mixture on the rate of *n*-octane cracking, reaction temperature 350 °C

equation of the first order with respect to *n*-octane, $W=K_1C_8$. At high olefin concentrations the rate of cracking depends on the amount of olefins in the reaction mixture, the kinetic dependence is of the $W=K_2C_8C_{olef}$ type. The catalyst activity falls quickly with time.

The rate of octene-1 cracking under standard conditions of cracking is much higher than that of *n*-octane and the rate ratio octene-1:octane is 50:1. As it can be seen from Fig. 2, with the increase of nickel and palladium dispersion in HY zeolite (0.9%-wt Na) the metal specific activity toward hydrogenation of hexene-1 changes

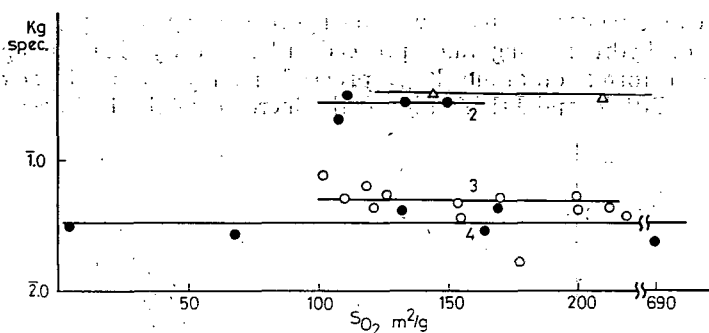


Fig. 2. Rate constant of hexene-1 hydrogenation as a function of the surface area of the metallic component, reaction temperature 150 °C, 1 — zeolite PdHY, 2 — Pd/Al₂O₃, 3 — zeolite NiHY, 4 — Ni/SiO₂

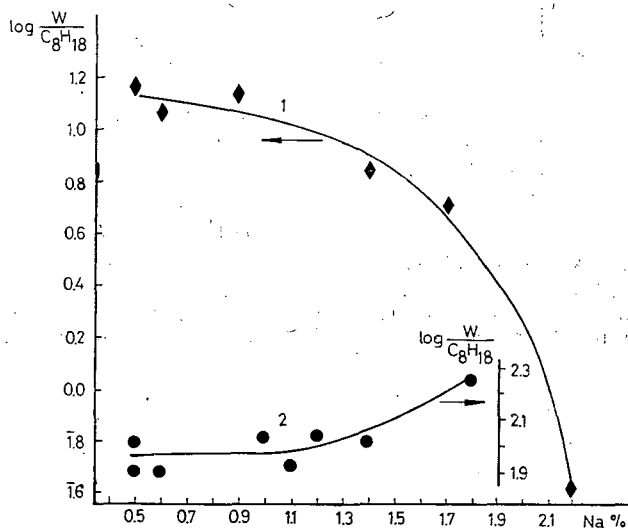


Fig. 3. Influence of sodium concentration in zeolite component on the rate of *n*-octane cracking. Reaction temperature 350 °C, pressure 1.8 atm.; 1 — cracking of *n*-octane on HY, 2 — hydrocracking of *n*-octane on NiHY

slightly and is almost similar to that of these metals in the catalysts considered. The character of variations in the activity of acidic components HY and NiHY depending on sodium concentration has been compared (Fig. 3). The activity of the former one continuously increases with the fall of sodium concentration, for the latter one variations in sodium concentration from 0.5 to 1.2% wt practically do not affect the activity and selectivity. Fig. 4 gives the dependence of the rate of *n*-octane hydrocracking on the activity of the metallic component. The rate of *n*-octane transforma-

tion toward all directions increases with the hydrogenating activity. At $\log K_{\text{hydr.}} < 2.8$ increasing of hydrocracking rates proceeds more slowly than at $\log K_{\text{hydr.}} > 2.8$. *N*-octane transformation at any $K_{\text{hydr.}}$ proceeds mainly toward the acidic cracking. For zeolites PdHY and PtHY (Fig. 5) the increase of the hydrogenating activity

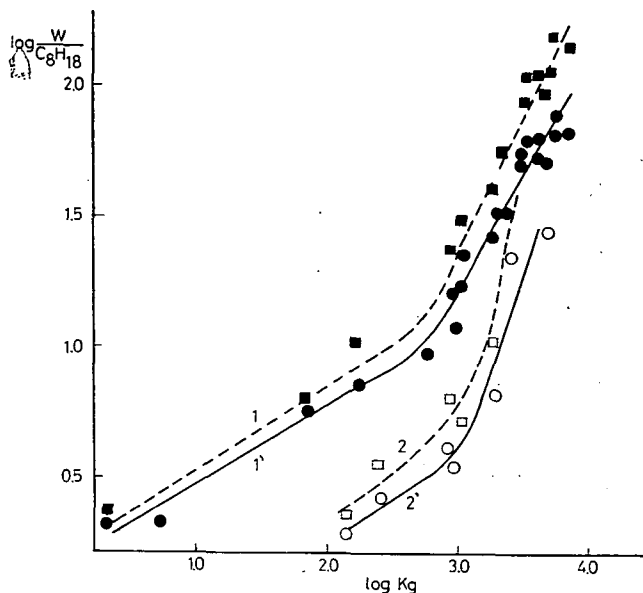


Fig. 4. Influence of the activity of nickel component on the rate of hydrocracking (1,2) and on the rate of product formation of *n*-octane acidic splitting (1', 2'), reaction temperature 350 °C, pressure 1.8 atm; 1,1' — zeolite NiHY, 2,2' — mechanic mixture NiO + HY

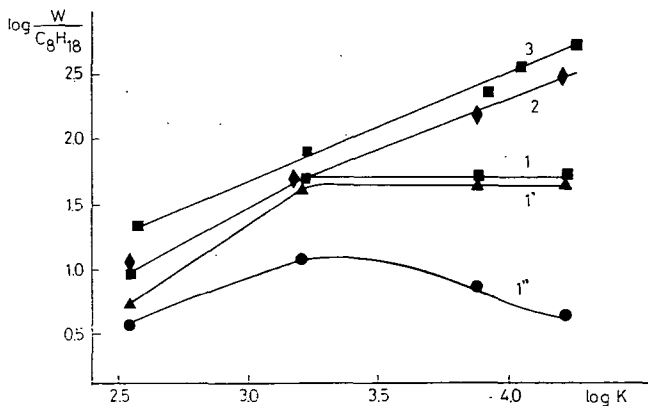
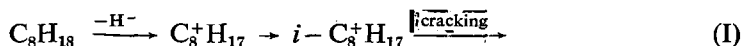


Fig. 5. Influence of the activity of the metallic component in PtHY on the overall rate of hydrocracking of *n*-octane (1) and isooctane (3) in hydrogen and of *n*-octane in helium (2). The yield of products of isomerization (1') and *n*-octane cracking (1'') in hydrogen.

results in the decrease of the selectivity toward the acidic cracking and in the increase of the rate of octane isomers formation. For catalysts with high hydrogenating activities the predominant direction of transformation is hydroisomerization (70—80%). When hydrogen is replaced by helium on zeolites PtHY the formation rate of the acidic cracking products drastically increases, while the rate of hydroisomerization falls. Hydrocracking of *isooctane* on zeolites PtHY is characterised by significantly higher rate than that of hydrocracking of *n*-octane and by the predominant direction toward splitting reactions.

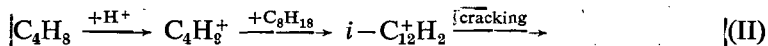
In the case of mechanic mixtures (Fig. 4) at low activities of the metallic component the transformation is primarily directed toward reaction of the acidic cracking (80—90%) while on catalysts with high hydrogenating activities — toward hydrogenolysis reactions (60—70%). In addition, over the whole range of K_{hydr} values the overall rate of hydrocracking, the yield of isomerized products of acidic splitting and isomerization are considerably less than those in the case of homogenized zeolites.

The experimental results (cracking of *n*-octane on zeolite HY, Fig. 1) permit us to determine the region wherein the rate of cracking is independent of olefin concentration. Apparently, at low olefin concentrations the activation of molecules of initial paraffin is due to their direct interaction with the surface active sites, probably, through separation of hydride-ion and formation of carbonium-ion according to the scheme described in [9]:



The rate of acidic splitting, in this case, is rather slow and iso:normal products ratio is close to unity (1.3—1.4).

When the rate of cracking depends on olefin concentrations it may be proposed that olefin must be involved in the intermediate complex, *e.g.* according to the following scheme:

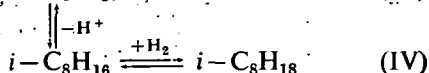
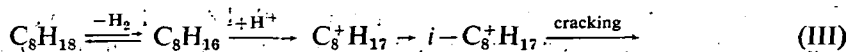


Cracking proceeds at a high rate giving large amounts of isomerized products (*iso/n* = 3—4). However, intensive processes of coke formation are also observed.

Likewise in the case of cracking, under hydrocracking conditions the mechanism and the rate of stages of acidic transformation of hydrocarbons on zeolite component should depend on olefin concentration in the reaction zone. The latter must depend on the activity of the metallic component in the metal-zeolite catalyst. With increasing the activity of the hydrogenating component and, hence, decreasing the concentration of short olefins in the reaction zone, gradual transition from paraffin transformation *via* scheme II to scheme I might be expected. In this case, on the one hand the processes of coke formation will be slowed down, on the other hand, the rate of cracking promoted by olefins should decrease. Actually observed slight increase in the rate of hydrocracking on nickel-zeolite catalysts with their hydrogenating activity in the first region (Fig. 4) may be explained by the decrease in the extent of coke formation on acid sites.

One might expect that further increase of the hydrogenating activity, decreasing the olefin concentration in the reaction zone, should lead to the fall of the rate of hydrocracking. From this point of view, sharp development of cracking (Fig. 4) on catalysts with high hydrogenating activities ($\log K > 2.8$) is unexpected and may

be explained only by transition to another mechanism: from the initial stage of dehydrogenation of *n*-octane to more reactive octenes:



In fact, the increase in the activity of the metallic component is accompanied by a double effect: *i*) the concentration of short olefin products of cracking is decreased due to the growth of the hydrogenation reaction rate, *ii*) the formation rate of octenes — products of dehydrogenation — is increased. Though in the thermodynamic sense the formation of octenes is less probable, the presence of a splitting component results in their quick acidic transformation into the thermodynamically-probable products as well as in the increase of the overall rate of paraffin transformation.

One of the peculiarities of zeolite catalysts is the fact that owing to a high activity of the acidic component, the reaction stage proceeding on a metal is rate-determining. Only by decreasing the reaction temperature down to 300°C and by addition of Pt as a hydro-dehydrogenating component such ratio of activities of acid and hydrogenating components was reached at which the stage of acid-base transformations became rate-determining (Fig. 5). In this case the rate of splitting falls and *n*-octane transformation proceeds primarily toward hydroisomerization. It is likely that, in this case, splitting of the C—C bond in the intermediate (path III) becomes less probable than proton elimination (path IV). The substitution of hydrogen by helium, leading to the termination of hydrogenation (Fig. 5, curve 2), must cause drastic increase in olefin concentration in the reaction zone. In this case, transformation via path III becomes predominant.

The results obtained could be explained assuming that the stages of formation and isomerization of carbonium-ion are reversible (scheme IV). Although the formation of products of cracking is thermodynamically more probable than proton elimination, when increasing the hydrogenating activity the kinetic factor rather than the thermodynamic one may become determining.

If this assumption could be valid, introduction of the hydrogenating reactor in transformation via scheme I should be accompanied by the increased yield of isomerized octanes. However, this fact has not been actually observed. Moreover, during hydrocracking of *isooctane* in the presence of PtHY catalysts the main reaction direction was acidic cracking (Fig. 5). Hence, a more valid proposal may be made which enables the explanation of all above facts, *i.e.* C—C bond breaking must be preceded by the formation of a strongly-isomerized carbonium-ion.

Formation of multi-branched structures may take place after the secondary interaction of short olefins from the gas phase with a carbonium-ion on the catalyst surface. If the activity of a hydrogenating agent is negligible (or it is not used) (paths III and II) the concentration of olefins in the reaction zone is sufficient to carry out reactions of alkylation accompanied by breaking of the C—C bond of the multi-branched structure formed.

Introduction of either a hydrogenation reactor (scheme I) or a strongly-hydrogenating component (PtHY) into the catalyst results in a drastic fall of short olefin concentration. Due to this the possibility for the formation of multi-branched

structures through alkylation of carbonium-ion with olefin is lowered and reactions of C—C splitting are inhibited.

Thus, the change in the ratio of activities of acidic and hydrogenating components in the metal-zeolite catalyst must lead *i*) to the change in the path of paraffin transformation and *ii*) to the change in the rates and the mechanism of the stages of transformation on the catalyst acidic component.

Owing to the fine-pore structure of zeolites and their high activity, the processes of diffusional transfer between various sites may play a significant part in metal-zeolite catalysts.

Thus the increase of the homogeneity of the metal-zeolite system (by addition of a metal inside zeolite cavities) must provide higher (than in the case of mechanic mixtures) rates of paraffin transformation due to weakening of diffusional effects inside zeolite cavities.

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REACTION OF ETHYLENE OVER HYDROGEN MORDENITE, BERYLLIUM MORDENITE, AND LANTHANUM MORDENITE

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The conversion of ethylene over the catalysts hydrogen mordenite, beryllium mordenite, and lanthanum mordenite has been studied using a flow reactor. The reaction yielded light hydrocarbons and polymerisate (coke) as detected by G. C., M. S. and IR. Acid OH groups proved to be the active centers. The IR results suggest rapid formation of carbonium ions in the case of the most acid, highly active hydrogen mordenite, whereas over the less acid beryllium mordenite and lanthanum mordenite initially π -complexes have formed, transforming only slowly to carbonium ions. These results offer an explanation of the differences in activity and life-time of the catalysts.

Introduction

In some previous papers [1—3], we have thoroughly studied the catalysis of benzene alkylation by olefins as well as the inverse reaction (dealkylation). Commercial hydrogen mordenite (HM), the catalyst which was first applied by us for these reactions, exhibited high activity and significant selectivity, due to its special pore geometry (shape selectivity) [1]. Preferentially monoalkylbenzene and, to a smaller extent, only *p*- and *m*-dialkylbenzenes had formed. Unfortunately, the HM was rapidly deactivated. This was attributed to olefin polymerisation (also catalyzed by HM) and subsequent coking. Beryllium mordenite (BeM) and lanthanum mordenite (LaM), prepared by ion exchange from Na-mordenite and being even more selective, exhibited a much prolonged life-time [2—3]. IR evidence suggested that in every case acid OH groups of the zeolite catalysts were the active sites. However, preliminary experiments showed significant differences in the strength of interaction between ethylene and the OH groups of the respective catalysts HM, BeM, and LaM. It was the aim of the present work to study this different behavior of HM, BeM, and LaM in more detail.

Experimental

The IR spectra were run with a spectrometer model 325 (Perkin—Elmer). Our IR cell was a modification of the cell designed by KNÖZINGER ET AL. [4]. The commercial HM was supplied by the Norton Company, Mass. BeM and LaM were exchanged to 59% and 64%, respectively. For technical and experimental details of the IR and catalytic studies see [3] and [5]. Prior to the reaction, the zeolites had

been calcined at the activation temperature T_A (usually 723 K) under dynamic vacuum (usually 1.33×10^{-2} Pa $\approx 10^{-4}$ torr). The reaction temperature T_R was usually 723 K as well. Ethylene/helium mixtures were applied, the partial pressure of ethylene being 3.33×10^3 Pa (≈ 25 torr).

Results

Reaction of Ethylene over HM, BeM, and LaM

Figs. 1a and 1b show the total conversion φ_{tot} of ethylene and the conversion φ_{hc} to light hydrocarbons varying with time t_R . The difference $\varphi_{\text{tot}} - \varphi_{\text{hc}}$ gives the conversion φ_{poly} to polymerisate and/or (at higher temperatures) to coke. The most striking feature in Fig. 1a is the instantaneous onset of the reaction in the case of

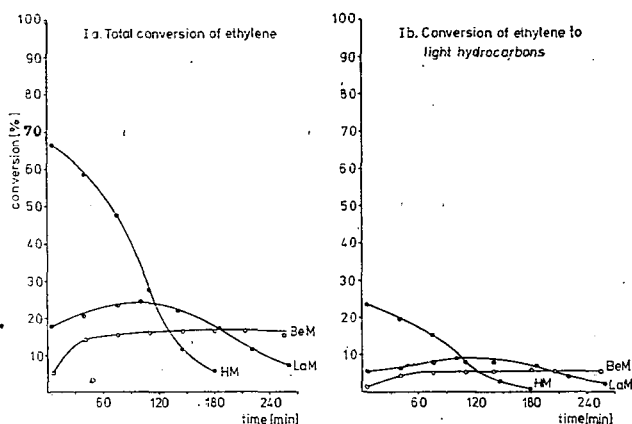


Fig. 1. Conversion of ethylene over HM, LaM, and BeM. $T_A = T_R = 723$ K; pressures: $p_E = 3.33 \cdot 10^3$ Pa and $p_{\text{He}} = 1.00 \cdot 10^5$ Pa; $u = 30$ ml/min. ethylene/helium gas mixture; mass of catalyst: 0.25 g

HM, followed by a rapid decrease of the conversion, whereas BeM exhibits a pronounced incubation period with increasing φ , reaching then a steady state for several hours. With the exception of the incubation period, this φ/t_R dependency corresponds to that observed during the alkylation process [3]. LaM is intermediate between HM and BeM. The situation is quite similar in Fig. 1b (formation of light hydrocarbons). Table I presents the product distributions after $t_R = 40$ min. Over HM, propane had preferentially formed, whereas over BeM propene was mainly produced. The ratio s = saturated hydrocarbons/unsaturated hydrocarbons decreases with the sequence HM, LaM, BeM. The composition of the hydrocarbon mixture varies over BeM only slightly with time ($t_R > 40$ min.). Over HM, s decreases from 3.44 at the beginning of the reaction to 1.44 at $t_R = 2$ h. The same behavior of the conversion φ_{hc} and the product distribution had been observed during the alkylation; i.e., in the presence of benzene, ethylbenzene, etc. With dehydroxylated HM and BeM ($T_A = 973$ K; $T_R = 723$ K), the starting conversions φ_{tot} , φ_{hc} , φ_{poly} amounted to only 10% of those

Table 1
Conversion and Product Distribution in Percent

	Catalyst	φ_{tot}	φ_{pol}	φ_{hc}	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₃ H ₆	C ₄ H ₈	C ₄ H ₁₀	s
$T_A = 723$ K	HM	58.7	39.0	19.7	1.6	2.6	1.9	9.8	2.9	0.9	3.1
	LaM	20.8	14.2	6.6	0.5	0.7	3.8	0.8	0.5	0.3	0.5
$T_R = 723$ K	BeM	14.2	10.0	4.2	0.3	0.5	2.8	0.2	0.2	0.2	0.4
$T_A = 923$ K	HM	5.4	3.7	1.7	0.1	0.1	1.3	—	0.1	0.1	
	LaM	2.4	2.3	0.1	0.05	—	0.07	—	—	—	
$T_R = 723$ K	BeM	1.6	1.4	0.2	0.1	—	0.1	—	—	—	

found over the hydroxylated forms (Table I). In the case of HM the activity decreased further with increasing t_R . In contrast, over BeM the conversion slowly increased with time after three hours had reached the four-fold of the starting value. — Both HM and BeM showed a distinct maximum of φ_{tot} and φ_{hc} at $T_R = 673$ K. (Above 673 K dehydroxylation became noticeable, as could be seen by IR.)

IR spectroscopic investigations

Fig. 2 compares the spectra of (hydroxylated) HM and BeM before and after adsorption of ethylene at 1.33×10^4 Pa ($\cong 100$ torr) and the temperature attained by the sample in the IR beam (B. T. ≈ 373 K). In the case of HM (Figs. 2a, 2b, spectrum 2), the bands of exclusively saturated hydrocarbons appear immediately ($\nu_{\text{as}}^{\text{CH}_3}$: 2950

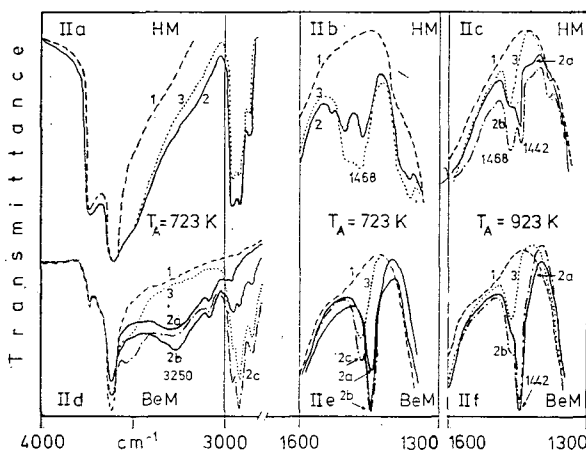


Fig. 2. IR spectra of HM and BeM before (spectra 1) and after (spectra 2) interaction with ethylene at B. T. Ethylene pressure $p_E = 1.33 \cdot 10^4$ Pa, excepted Figs. 2 a, b, d, e — spectra 2 and 2a, where $p_E = 3.33 \cdot 10^3$ Pa. Time of interaction $t_R \approx 15$ min., excepted Figs. 2 d, e — spectra 2c, and 2 c, f — spectra 2b, where $t_R = 15$ h. After pumping: spectra 3. Further details see text.

cm^{-1} ; $\nu_{as}^{\text{CH}_2}$: 2930 cm^{-1} ; $\nu_s^{\text{CH}_2}$: 2860 cm^{-1} and a broad $\delta_{as}^{\text{CH}_2}$ band at 1468 cm^{-1}). The OH band at 3600 cm^{-1} has been weakened remarkably. These changes in the spectrum are practically irreversible at B. T. (Figs. 2a, 2b, spectra 2, 3). In the spectrum of BeM (Figs. 2d, 2e), the sorption of ethylene causes also a significant decrease (about 75%) of the OH band intensity. Simultaneously, a broad band at 3250 cm^{-1} appears, indicating the formation of a π -complex. Further bands (spectrum 2a in Figs. 2d, 2c) are exclusively ascribable to olefinic species (ν^{CH} : 3030 cm^{-1} , δ^{CH_2} : 1442 cm^{-1}). At higher pressures and prolonged time, respectively, also the signals of saturated hydrocarbons appear (spectrum 2c), persisting even during pumping at B. T. Comparing dehydroxylated HM and BeM ($T_A = 973 \text{ K}$), Figs. 2c, 2f demonstrate the appearance of olefinic bands (1442 cm^{-1}) in both cases. Only after a long period of interaction (15 h) could bands of saturated species be detected; these bands remained in the spectrum after pumping. Both dehydroxylated zeolites were only slightly rehydroxylated during the experiment.

At 573 K and $3.33 \cdot 10^3 \text{ Pa}$ (25 torr) the following changes were observed: With (hydroxylated) HM only very weak and vague CH bands were detected, the OH band being less weakened than at 373 K (Fig. 3a, spectrum 2a). Instead, a broad and intensive absorption around 1585 cm^{-1} developed (Fig. 3b, spectrum 2a) due to coke formation [6—8]. The sample became black. In the case of dehydroxylated

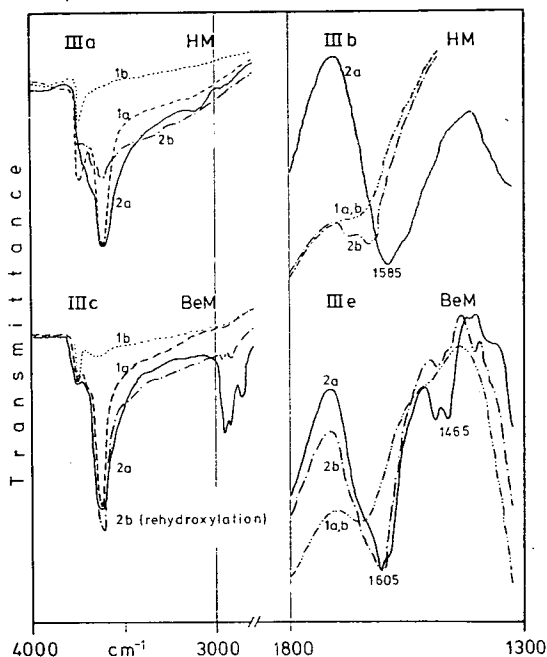


Fig. 3. IR spectra of HM and BeM before (spectra 1) and after (spectra 2) interaction (90 min.) with $3.33 \cdot 10^3 \text{ Pa}$ ethylene at 573 K and subsequent pumping (to $1.33 \cdot 10^{-4} \text{ Pa}$) at B. T. Spectra 2a: interaction with hydroxylated forms (1a); spectra 2b: interaction with dehydroxylated forms (1b). Further details see text.

HM ($T_A=923$ K) no CH bands whatsoever appeared, even at 1585 cm^{-1} (Fig. 3b, spectrum 2b). The sample remained white and was rehydroxylated to a low extent (15 %) (Fig. 3a, spectrum 2b). The differences between hydroxylated and dehydroxylated BeM were less pronounced. In fact, the CH bands appearing on ethylene interaction were more intensive in the first case (Fig. 3c, compare spectra 2a and 2b). However, both forms showed polyolefin formation after a sufficiently long period of interaction (band at 1605 cm^{-1} , being indicative of olefinic groups in a conjugated polyene type structure [6—7]). Similar observations were reported by WEEKS AND BOLTON [9] in their work on olefin-zeolite intermediates, using 1-butene and HY. Surprisingly, the BeM had been completely rehydroxylated during the ethylene interaction (Fig. 3c, spectrum 2b). (The ethylene applied contained traces of H_2O and O_2 .) At still higher temperatures (723 K) one finds in general the same differences between HM and BeM: In the case of HM, there is more significant weakening of the OH band, more polymerizate and subsequent coke formation (band at 1585 cm^{-1}). With BeM, there is a tendency to rehydroxylation, and rather polyene formation (band at 1605 cm^{-1}) after longer exposure. Using BeM, oxidation of the deposit often occurs, indicated by a CO_2 band at 2350 cm^{-1} .

Mass spectrometric investigations

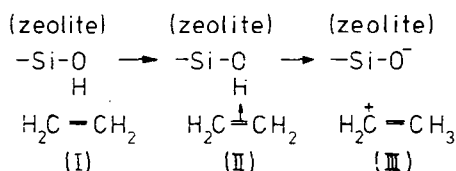
The BeM sample, the spectrum of which is shown in Figs. 3c and 3d, spectrum 2a, has been slowly ($5^\circ/\text{min.}$) heated to 673 K. During the heating mass spectra were run. Above $T_{\text{Des}} \approx 373$ K signals appeared ascribable to desorbed hydrocarbon species: C_2H_4 , C_3H_6 , C_4H_8 , C_4H_{10} and fragments of the approximate composition $\{\text{CH}\}_n$ ($n=1-7$). Table II gives the masses observed, their assignments, and the temperatures of highest signal intensity.

Table II

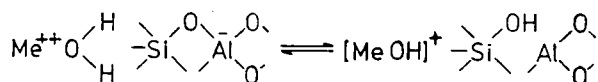
Mass	Species	Mass	Species	T
14, 15, 16	CH_4	12, 13, 14	CH_2	360
26, 27, 28	C_2H_4	37, 38, 39	$\{\text{CH}\}_3$	300
29	C_2H_5^+	50, 51, 52	$\{\text{CH}\}_4$	380
41, 43	C_3H_6	63, 65	$\{\text{CH}\}_5$	380
55, 56	C_4H_8	77, 78	$\{\text{CH}\}_6$	410
57, 58	C_4H_{10}	91, 92	$\{\text{CH}\}_7$	410

Discussion

Obviously, HM contains OH groups of higher acid strength than BeM and LaM, which is in analogy to the results on $\text{HY}/\text{Me}^{++}\text{Y}$. This provides an explanation of the higher starting activity of HM (Fig. 1). Thus, according to



over HM a great number of carbonium ions (structure III) will immediately form upon ethylene exposure, initiating the polymerization. In the case of BeM, the olefin is partially physisorbed, partially bound as a π -complex (structure II, see also Fig. 2d, spectrum 2b). The π -complexes only slowly transform to structure III, as could be evidenced by IR. This causes the incubation period and the lower reaction rate over BeM and LaM compared with HM (Fig. 1). In principle, the formation of polymerizate and consequently the blocking of the active centers (acid OH groups) is the reason for the catalyst deactivation at lower temperatures (≈ 373 K). At higher temperatures the polymerizate is destroyed and the OH groups are partially liberated. However, the increasing amount of coke will obstruct the zeolite pores more or less rapidly. HM shows fast formation of polymerizate and coke, and therefore rapid deactivation (Figs. 1, 2a, b, 3a, b). The longer life-time of BeM is probably due to two effects: (a) the lower conversion φ_{poly} allows for sufficient removal of deposits during the reaction (to some extent by oxidation), and (b) with BeM OH groups may be regenerated via rehydroxylation (Fig. 3c, spectrum 2b). This compensates for the usual loss of activity due to removal of OH groups (dehydroxylation) during prolonged reaction time. The rehydroxylation of BeM can be well understood on the basis of the HIRSCHLER scheme [10]:



Dehydroxylation leads to a reformation of bare Be^{++} cations and not to irreversible changes in the lattice structure as in the case of HM [11–12]. Accordingly, no newly formed Lewis sites could be identified via pyridine adsorption after dehydroxylation of BeM and LaM. Subsequent exposure of the dehydroxylated BeM to H_2O vapor at higher temperatures restores the acid OH centers and $\text{Be}(\text{OH})^+$, according to the above scheme.

The mass spectra run during the desorption shows, in general, the same products as found by GC during the reaction. To a large extent, particularly on HM, the $\{\text{CH}\}_n$ deposits form at the beginning of the reaction. Presumably they are originally richer in hydrogen and can serve as a source for hydrogenation. The role of "carbonaceous deposits" and fragments with C:H ratio close to 1 in intermolecular hydrogen transfer (yielding saturated hydrocarbons) has been studied and discussed by ÖRHALMI AND FEJES [13]. This would offer an explanation for the fact that over (hydroxylated) HM primarily saturated hydrocarbons are formed.

Acknowledgements

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THE PREPARATION OF ULTRA-HIGH SILICON FAUJASITES BY CONTROLLED-RATE ALUMINIUM REMOVAL

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A new technique is described which effects removal of up to 80% of the tetracoordinate aluminium from zeolite Y with retention of 60 to 70% of the crystallinity. Some of the chemical and physical properties of very high SiO₂/Al₂O₃ ratio samples have shed new light on fundamental aspects of faujasite crystal chemistry. These findings should have catalytic significance.

Introduction

It is now well-established that removal of up to about one-half of the tetrahedrally coordinated aluminium significantly increases the thermal and hydrothermal stability of zeolite Y [1—4]. A review of several methods for effecting aluminium removal was recently published [5]. One method which has received wide attention from workers in catalytic studies of zeolites [6] involves the reaction of sodium or ammonium zeolite Y with ethylenediaminetetraacetic acid (H₄EDTA) [2, 3]:

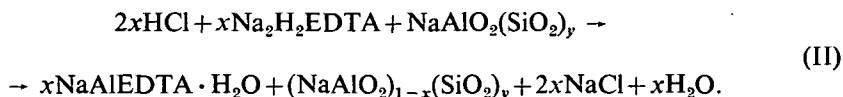


This reaction is conducted in a Soxhlet extractor: the zeolite, slurried in water, is contained in the boiling flask and the H₄EDTA is contained in the Soxhlet thimble. In this way a dilute solution of the acid is added over a 16 to 24 hour period to the zeolite. Attempts to remove more than 50 or 60% of the aluminium *via* this method results in severe losses in crystallinity and thermal stability. The work presented here describes a method for removing 80% of the aluminium with retention of 60 to 70% of the crystallinity. The results of this study shed significant light on some basic aspects of the crystal chemistry of aluminium-deficient faujasites.

Experimental

The new technique consists of carefully controlling the rate of addition of hydrochloric acid to a slurry of the zeolite in a solution of the appropriate di-metal cation dihydrogen ethylenediaminetetraacetate. For example, with the ammonium zeolite, (NH₄)₂H₂EDTA is used; for the sodium zeolite, the acid salt Na₂H₂EDTA

is used. The rate of addition of HCl solution must be such that 10% of the tetrahedral aluminium is removed per day. The overall theoretical stoichiometry of the reaction is:



The reaction products differ from those of reaction I in that sodium chloride is formed in addition to the other products. Thus, the effect of the hydrochloric acid is diminished as the reaction proceeds since the hydronium ion now competes with additional sodium ion, *i. e.*, in addition to sodium ion derived from the sodium zeolite, sodium ion from $\text{Na}_2\text{H}_2\text{EDTA}$ is present in solution.

A typical aluminium removal using this new procedure is described in detail. The ammonium zeolite Y contained 7.47% NH_3 and consisted of 71.4% ash. To exchange one-third of the ammonium ion according to reaction II (and thus at least one-third of the aluminium) from 50.0 g of the ammonium zeolite

$$50 \cdot 0.714 \cdot 0.0747 \cdot \frac{0.333}{17.03} = 0.0518 \text{ moles or } 51.8 \text{ mmoles EDTA}^{4-} \text{ is required.}$$

The 50 g of zeolite was slurried with 51.8 ml of 1 M $(\text{NH}_4)_2\text{H}_2\text{EDTA}$ solution (51.8 mmoles) and 300 ml of water. The mixture was stirred and refluxed while 33.3 ml of 3.14 N hydrochloric acid solution (105 mmoles) was pumped continuously into the zeolite slurry over a period of 3.3 days. The zeolite was then collected on a Büchner funnel and washed with one liter of water. The above treatment was conducted two more times. These three batch treatments were considered necessary to reduce the effect of "excess" ammonium ion in solution which might interfere with the necessary exchange of hydronium ion for ammonium ion in the zeolite. The addition of a total of 100 ml of the hydrochloric acid solution would effect 100% removal of NH_4^+ and Al if reaction II were rigorously obeyed. Small aliquot portions of the reaction mixture were removed at the conclusion of the first treatment and during the last two HCl additions and complete elemental and X-ray diffraction analyses were performed on the zeolite samples.

Results and Discussion

Table I presents a resumé of the experimental results and Figs. 1 and 2 graphically present the most important results. In Fig. 1 the unit cell length, a_0 , and the percent crystallinity are plotted as a function of the number of aluminium ions per unit cell (Al/U. C.). Two straight lines are shown for the a_0 vs. Al/U. C. plot. A mathematical analysis of the data by W. P. BURGESS at the time of his association with this laboratory showed that two straight lines give a better overall fit of the data than does one straight line involving all ten data points. These two lines each have a terminus in the region of 32 Al/U. C. which corresponds to exactly 2 Al and 10 Si per hexagonal prism or 5.00 Si/Al ratio. This observation appears to be highly significant when compared with the results of DEMPSEY, KUHLE and OLSON [7]. They showed that a plot of a_0 vs. Al/U. C. for a variety of synthetic faujasites with Si/Al ranging from 1.00 to about 3.0 best fit three straight lines. One line covers the range correspond-

Table I

ml. HCl added	Wt. % SiO ₂	Wt. % Al ₂ O ₃	$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$	% Al removed	Al/U. C.	$\frac{\text{NH}_4^+}{\text{Al}}$	% cryst.	$a_0, \text{\AA}$
0	74.2	24.6	5.13	0	54	0.91	100	24.795
33.3	78.7	20.0	6.7	24	44	0.80	93	24.654
43.3	76.1	16.9	7.7	33	39.5	0.88	87	24.612
53.3	79.1	15.4	8.7	41	36	0.84	83	24.543
63.3	82.8	13.1	10.8	53	30	0.88	82	24.503
66.6	85.4	12.5	11.7	56	28	0.83	82	24.476
76.6	86.7	11.6	12.7	60	26	0.82	76	24.470
86.6	85.5	9.8	14.9	66	22	0.78	69	24.403
96.6	91.8	7.9	19.7	74	17	0.60	67	24.361
100.0	91.3	6.2	25.2	80	14	0.62 ^a	67	24.335

a — On treatment with NH₄OH, NH₄⁺/Al=0.98.

ing to 6 Si and 6 Al (Si/Al=1.0) and 5 Al and 7 Si per hexagonal prism (1.4 Si/Al). Another line ranges up to 4 Al and 8 Si per prism (Si/Al=3.0). These three lines are displaced in the direction of higher a_0 values as the Al/U. C. range is decreased. Figure 1 shows this same displacement. That the discontinuity in the a_0 vs. Al/U. C. data is real is supported by other aspects of our results. Crystallinity vs. Al/U. C. follows a straight line from 54 Al/U. C. (the zeolite Y starting material) to about 35 Al/U. C. Then the crystallinity remains constant upon further aluminium removal until 26 to 28 Al/U. C. remain in tetrahedral sites. Upon removing still more aluminium to

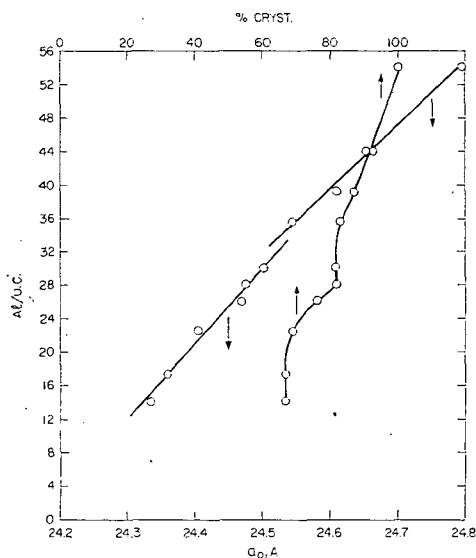


Figure 1. Percent Crystallinity and Unit Cell Parameter vs. Aluminium Atoms Per Unit Cell

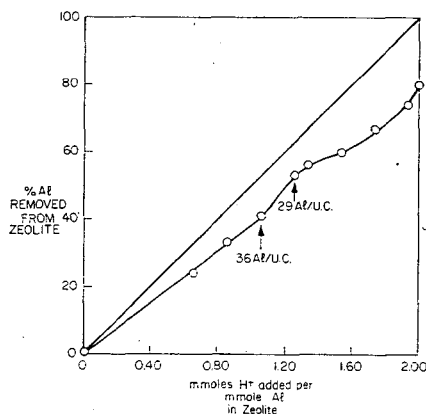


Figure 2. Stoichiometry of Aluminium Removal

the 18 to 20/U. C. level the crystallinity again decreases. The important point is that there is a pronounced inflection in the crystallinity *vs.* Al/U. C. curve in the region of 32 Al/U. C. or one aluminium per six ring.

In Fig. 2, showing the observed stoichiometry compared with that dictated by reaction II (the straight line), an inflection again is apparent in the 32 Al/U. C. region. Indeed, the experimental results indicate that aluminium removal is enhanced in the 36 to 29 Al/U. C. region and then additional aluminium removal becomes more difficult. Note that the final product (80% Al removal) contained only 0.62 NH_4^+/Al but on treatment with NH_4OH this value increased to 0.98 indicating that 40% of the cation sites in the final product are hydrogen or hydronium ion and the four coordinate aluminiums associated with these cations resist hydrolysis and framework removal.

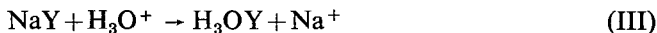
The deviation of the experimental points from the straight line in Fig. 2 over the whole range of aluminium removal is in sharp contrast with the results using the procedure of reaction I where the stoichiometry is very closely followed [2]. The deviation of the experimental points from the stoichiometry of reaction II is attributed in part to the additional ammonium ion in the aqueous phase which depresses hydronium ion exchange into the ammonium zeolite.

The crystallinity data shown in Fig. 1 imply that a portion of the crystalline component becomes amorphous and serves as a source of silica. This raises the questions: (1) what is the composition of the amorphous component? and (2) why isn't all of the available Si used leaving either a very Al rich amorphous phase or no amorphous phase whatsoever?

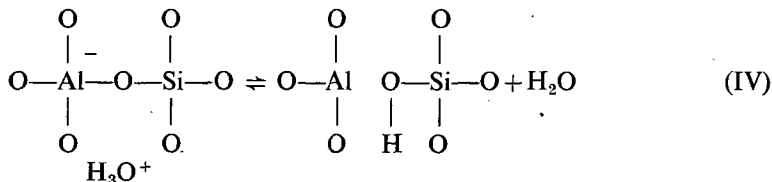
Although the composition of the amorphous phase is not known, it is unlikely to be more Al rich than the crystalline phase. It is also possible that Al in portions of the amorphous phase retaining the short range order of the crystalline phase may possess the same resistance to acid attack as Al in the crystalline phase. In view of the lack of any definitive data concerning this question, we have assumed the two phases to have identical compositions.

The vertical portions of the Al/U. C. *vs.* % crystalline curve of Fig. 1 imply that the Si replacing the removed Al is being supplied solely by the existing amorphous phase in the ranges 28 to 36 and 14–22 Al/U. C. That the Si of the amorphous phase is not completely consumed indicates that some silica fragments are more reactive than others. One would expect that the reactivity of Si would decrease as the number of Si—O—Si linkages increase, *i. e.*, the Si in a 4-ring of Si tetrahedra may be very resistant to Si transport to the crystalline phase.

Further discussion of the significance of 32 Al/U. C. is warranted. In a series of papers, BEAUMONT and BARTHOMIEUF [8–10] showed that about 30 Al/U. C. in a hydrogen zeolite Y contribute strongly acidic sites and that sites associated with more than about 30 Al/U. C. are moderately to weakly acidic. They observed that aluminium removal from zeolite Y, to about the 30 Al/U. C. level using the H_4EDTA method, resulted in a loss in total acidity but no loss in strongly acidic sites. From this observation they drew the logical conclusion that weakly acidic sites and the associated framework aluminiums are preferentially removed by the H_4EDTA method. This is to be expected using the argument that upon treatment of a sodium or ammonium Y with H_4EDTA -water slurries, H_3O^+ is exchanged into the zeolite:



An equilibrium is established between the hydronium form of the zeolite and the hydrogen form:



Obviously the equilibrium would lie to the right of reaction IV for weakly acidic sites and to the left for strongly acidic sites. KERR proposed that aluminium removal involves the hydrolysis of aluminium from the hydrogen zeolite in which disruption of an Al—O bond occurred [2]. Therefore, one would expect the weakly acidic sites to undergo aluminium removal in preference to strongly acidic sites. Also of significance is the observation of BEAUMONT and BARTHOMIEUX that deepbed calcined NH_4Y or ultrastable Y contains about 30 Al/U. C. or that about one-third of the aluminium in the initial NH_4Y of HY undergoes transition from four to six coordinate aluminums. Again, it is the weakly acidic sites which are lost while strongly acidic sites are retained.

As observed previously [2], the thermal stability of zeolite Y increases as the Si/Al ratio increases. The final sample prepared in this series ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 25.2$ or 80% aluminium removal) underwent lattice collapse at 1260° using a DTA test for thermal stability [11]. Hitherto, the two most stable faujasites observed by this test were stable hydrogen zeolite Y (1058°) and rare earth zeolite Y (1040°). A sample of the $25.1 \text{ SiO}_2/\text{Al}_2\text{O}_3$ zeolite was treated with 3 N HCl solution at reflux for 18 hours to yield a 46% crystalline material ($a_0 = 24.259 \text{ \AA}$) which was still crystalline after heating to 1272° , the upper limit of our DTA furnace. This sample contained 99% SiO_2 and 1 to 2% Al_2O_3 or a molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ of at least 50 and perhaps as high as several hundred.

Unquestionably, the most important aspect of the new technique is the rate of addition of hydronium ion and thus, very likely, the rate of removal of aluminum. If it is assumed that silicon atoms or ions migrate into sites vacated by aluminum, as suggested by several workers [12, 13], it is reasonable to assume that this is a slow process at 100° . Thus, if the removal of aluminum proceeds at a faster rate than the migration of silicon into defect sites, then a catastrophic defect situation arises and the crystal structure collapses. Should the exchange of hydronium ion into the zeolite (and thus removal of framework aluminum) proceed at a rate equal to or somewhat less than the rate of silicon migration, then the zeolite can "heal" itself and retain most of the crystallinity even up to quite high levels of aluminum removal. There is nothing unique about the mechanics described in this new technique. It is only a simple and convenient way of carefully controlling the rate of hydronium ion exchange into the zeolite. Indeed, the initial observation that 80% aluminum removal could be effected with retention of most of the crystallinity involved the use of the Soxhlet extractor method with H_4EDTA . In this case, however, a considerably larger scale reaction was conducted than in the past and ten days were required to dissolve and introduce the H_4EDTA into the zeolite slurry rather than the usual 18 to 24 hours. This observation led, ultimately, to the development of the new procedure which involves the removal of 10% of the aluminum per day. When the

new technique was used over a 13.5 day span, the same degree of aluminum removal was achieved but the crystallinity of the final product was about 50%, indicating that the 10% removal per day is critical.

These results suggest that KERR's proposal [3] that aluminum is first replaced by three protons and that upon heating, water is driven from these sites to form new (and somewhat distorted) Si—O—Si bonds is wrong. The first step is reasonable; the second step probably involves the replacement of four protons (total charge +4) by a silicon ion, Si^{+4} .

Acknowledgment

We are indebted to DR. L. D. ROLLMANN for discussions which made this work more significant.

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SZILARD—CHALMERS RECOIL STUDIES IN SYNTHETIC FAUJASITES

By

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Na-X and Na-Y zeolites in which 10, 20, 30, 40, 50 and 60% of the Na^+ ions have been exchanged with Ba^{2+} ions at room temperature have been calcined at various temperatures from 40 to 830 °C. After rapid cooling and rehydration, samples of these zeolites have been eluted with excess quantities of NH_4Cl or BaCl_2 solution at room temperature. These elutions removed all Ba^{2+} and Na^+ ions, when NH_4Cl was the eluent, and all Na^+ ions, when BaCl_2 was the eluent, from the supercages of these zeolites without disturbing the Ba^{2+} or Na^+ ions respectively which were sited in the sodalite cages and hexagonal prisms. The number of these Ba^{2+} or Na^+ ions contained in the "locked" sites was then ascertained by radio-activation analysis.

By means of a novel Szilard—Chalmers recoil technique the distribution of these "locked" Ba^{2+} and Na^+ among the sodalite cages and hexagonal prisms has also been determined. Thermogravimetric analysis, along with chemical analysis for NH_3 of the samples eluted with NH_4Cl solution, has been used to ascertain the zeolitic water content of all samples. From these water contents the thermal stability of the calcined samples has been determined.

Introduction

Synthetic Na-X and Na-Y zeolites containing 85 and 53 Na^+ ions per unit cell (u. c.) respectively have had 10, 20, 30, 40, 50 and 60% of the Na^+ ions exchanged at room temperature ($\sim 20^\circ\text{C}$) with Ba^{2+} ions. These Ba^{2+} ions will only be sited in the supercages of these zeolites [1, 2]. Calcining these samples at various temperatures in the range 40 to 830 °C allows the Ba^{2+} ions to now occupy the sites which were "locked" to them at room temperature *i.e.* sodalite cages (site I') and hexagonal prism (site I) sites. After rapid cooling of the samples to room temperature and slow rehydration, the samples were eluted with solutions containing a large excess of Ba^{2+} while in a second series of experiments elutions with a large excess of NH_4^+ were carried out. The Ba^{2+} elutions removed all Na^+ ions which were sited in the supercages while the NH_4^+ elutions removed all Ba^{2+} and Na^+ which were so sited. By radio-activation analysis of the Ba^{2+} eluted samples it was possible then to ascertain the Na^+ content of the "locked" sites while a similar analysis of the NH_4^+ eluted samples established the Ba^{2+} content of the "locked" sites. Thus the concentration of both Na^+ and Ba^{2+} in the "locked" sites as a function of calcination temperature and degree of Ba^{2+} exchange in both Na-X and Na-Y was obtained.

Secondly, by determining the probability of these "locked" cations recoiling into the supercages on capture of a thermal neutron it has been shown previously

[3–5] that this Szilard—Chalmers process can be used to establish whether the recoiling cation was sited on site I' or site I prior to neutron capture. Thus the distribution of these "locked" Na^+ and Ba^{2+} ions among these two sets of sites could also be established as a function of calcination temperature and degree of initial exchange.

Theory

When a nucleus captures a neutron ~ 8 MeV of binding energy is released in a prompt gamma cascade. It has been shown previously [3, 5] that the mean kinetic energy, $\bar{K}$, of the recoiling species in eV is given by

$$\bar{K} \approx 537 E_\gamma^2 / Mn \quad (1)$$

where E_γ is the sum of the energies in MeV of the n photons released in each cascade and M is the mass of the recoiling nucleus in atomic mass units.

Assuming a hard sphere model it is possible to calculate a mean free path, L_s , for the recoiling species. When this calculation is carried out for a recoiling ^{24}Na atom in zeolite X or Y, L_s is found to be less than the unit cell constant of ~ 2.5 nm. The very short mean free paths allows one to distinguish the different sites from which the recoiling species originated.

Experimental

Tha Na-X was supplied by Union Carbide Corporation, U.S.A. and had a unit cell composition of $\text{Na}_{85}[\text{Al}_{85}\text{Si}_{107}\text{O}_{384}] \cdot 252 \text{H}_2\text{O}$. The Na-Y was supplied by Laporte Industries Ltd., England and had a unit cell composition of $\text{Na}_{53}[\text{Al}_{53}\text{Si}_{139}\text{O}_{384}] \cdot 249 \text{H}_2\text{O}$. The experimental techniques employed in this study are fully described elsewhere [3–7].

In the studies to determine the number of Na^+ ions sited in the "locked" sites as a function of calcination temperature, each of the various Na/Ba-zeolites was divided into 8 small portions and these samples were heated for 24 h at one of eight different temperatures within the range 40 to ca 800 °C. After rapid cooling to room temperature and slow rehydration from the atmosphere the samples were eluted at room temperature with 4 lots of 1 mol dm $^{-3}$ BaCl_2 solution. These elutions had been proved to be sufficient to remove all Na^+ ions from the supercage sites without disturbing the Na^+ ions in the "locked" sites.

In a similar set of experiments to determine the number of Ba^{2+} ions sited in "locked" sites as a function of calcination temperature the same procedure described above was employed but ~ 10 mol dm $^{-3}$ NH_4Cl solution was used as the eluent in place of the BaCl_2 solution. This eluent had been shown to remove all Ba^{2+} ions from the supercages without disturbing the Ba^{2+} ions in the "locked" sites.

These eluted samples, and also the starting materials, were irradiated in the London University 'Consort' reactor ($\sim 1.3 \times 10^{12}$ neutrons cm $^{-2}$ s $^{-1}$) for short times (1–30 minutes) along with suitable standards. The $^{24}\text{Na}^+$ and $^{131}\text{Ba}^{2+}$ activities of these samples were measured with Ge(Li) detector which had 1.9 KeV resolution.

The NH_4^+ contents of samples eluted with NH_4Cl were determined, after dissolution of the zeolite, with Nessler's reagent. From the weight loss found on heating

~10 mg samples to 1000 °C the amount of zeolitic water in the sample could be ascertained. However, allowances had to be made for weight loss due to NH_3 and dehydroxylation in those samples which contained NH_4^+ ions.

After carrying out the radio-chemical analysis of the samples on return from the reactor each sample was divided into two unequal portions and these weighed. The larger portion was eluted at room temperature with 100 cm³ of either saturated NH_4Cl or 1M BaCl_2 solution depending on whether the sample had been eluted with NH_4^+ or Ba^{2+} ions respectively previously. After these elutions the samples were analysed for ^{131}Ba and ^{24}Na activity respectively and these activities were compared with the corresponding activities of the uneluted portions. The percentage elutions, γ , of the ^{131}Ba and ^{24}Na recoils were calculated from equation (2)

$$\gamma = \left(1 - \frac{C_{\text{ext}}}{C_{\text{non}}}\right) 100 \% \quad (2)$$

where C represents the count rate per g of zeolite and subscripts "ext" and "non" represent the eluted and non-eluted portions respectively. Thus γ represent the percentage probability of an ion recoiling from a "locked" site into a supercage site.

From the large number of determinations of γ in this study a value of 20% was taken to represent the most likely value for γ_I , the probability of a ^{24}Na ion recoiling from site I into a supercage and 89% for γ_s , the probability of recoil from site I' into a supercage. The corresponding percentage elution figures for ^{131}Ba were 52% for γ_I and 92% for γ_s . It is then possible from the overall experimental value of γ found for either ^{24}Na or ^{131}Ba to calculate from equation (3) the number, n_I , of Na^+ or Ba^{2+} cations per u. c. residing in site I and $(n_T - n_I)$ the number residing in site I' where n_T is the total number of Na^+ or Ba^{2+} ions locked per u. c.

$$n_I \gamma_I + (n_T - n_I) \gamma_s = n_T \gamma \quad (3)$$

Results and Discussion

Figs. 1, 2 and 3 show the respective numbers of Na^+ , Ba^{2+} and positive charge locked in zeolite X as a function of calcination temperature and degree of Ba^{2+} exchange. When Na-X is exchanged to completion with Ba^{2+} at 20 °C 16 Na^+ ions still remain in each unit cell [1]. These 16 Na^+ ions are assumed to be sited in the sodalite cages and hexagonal prisms of Na-X and, therefore, inaccessible to Ba^{2+} exchange at 20 °C. Thus Figs. 1 and 2 show that on raising the temperature to 40 °C Ba^{2+} ions now enter these cages and replace Na^+ ions. As the calcination temperature increases more Ba^{2+} ions migrate from supercage to "locked" sites but this process levels out above 300 °C. At 400 °C, therefore, roughly one third of the Ba^{2+} ions are located in "locked" sites with the remainder remaining in the supercages.

In Fig. 1 an immediate reduction in the Na^+ content of the "locked" sites from 16 to between 6 and 11 Na^+ ions per u. c. in the samples containing 60 to 10% respectively is demonstrated on calcination at 40 °C. Although the Ba^{2+} content of these sites increases as the temperature is raised the Na^+ content does not correspondingly decrease. Approximately one seventh of the available Na^+ ions are located in the "locked" sites.

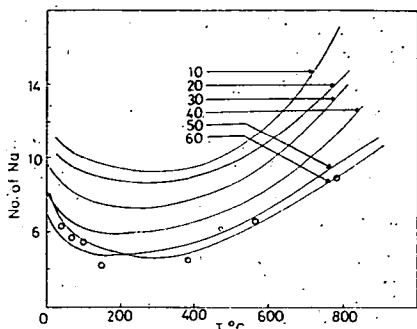


Fig. 1. Number of sodium ions per u. c. in the locked sites of Ba/Na-X zeolite as a function of calcination temperature and degree of barium exchange

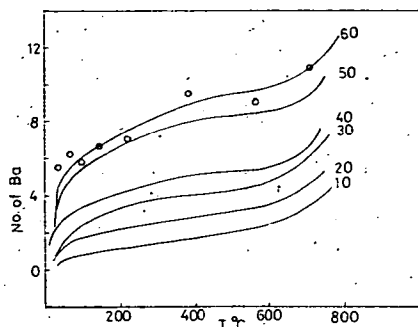


Fig. 2. Number of barium ions per u. c. in the locked sites of Ba/Na-X zeolite as a function of calcination temperature and degree of barium exchange

If there are 16 "locked" sites per u. c. in zeolite X then a random distribution of cations would give somewhat less than one in five ions sited in "locked" sites (*i.e.* 16/85th). Thus Ba^{2+} ions prefer the "locked" sites while Na^+ ions prefer, or are forced, to be sited in the supercages of zeolite X.

The total positive charge due to cations in "locked" sites increases with calcination temperature after the decrease which usually occurs on heating from 20 to 40 °C

(see Fig. 3). This total positive charge is well below 16 per u. c. for the 10–40 % Ba exchanged samples but, approximately, equal to 16 for the 50–60% exchanged samples when the calcination temperature is less than 100 °C. However, it is possible that in the preparation of these samples a small degree of hydrolysis may have occurred. This would give low values for the total positive charge. On increasing the temperature above 100 °C the total positive charge in "locked" sites increases. The 10 and 20% exchanged samples still exhibit values well below 16 until the calcination temperature is ~ 550 °C. The 30 and 40% exchanged samples have values slightly above 16 at calcination temperatures in excess of 400 °C while the 50 and 60% exchanged samples are found to have interesting large values of 22–25 in the

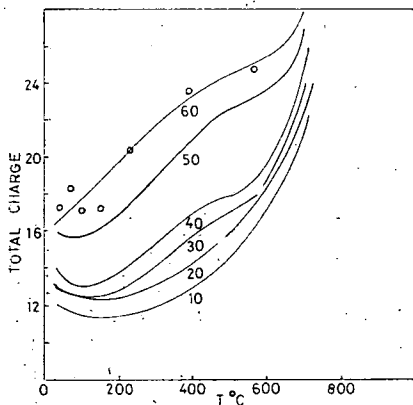


Fig. 3. Total positive charge per u. c. in locked sites of Ba/Na-X zeolite as a function of calcination temperature and degree of barium exchange

temperature range 400–600 °C. It is interesting to note that in these latter, most highly Ba exchanged samples, the total number of cations in "locked" sites is about 16 per u. c. when the calcination temperature is 600 °C *e.g.* the 60% Ba sample has $9.9 \text{ Ba}^{2+} + 7.0 \text{ Na}^+ = 16.9$ ions while the 50% Ba sample has 16.7 ions.

When the calcination temperature is increased to 700 °C and above the zeolitic water content of these samples (after cooling and rehydration) begins to decrease demonstrating the start of lattice breakdown. The decrease amounts to ~10% at 710 °C increasing to ~15% at 780 °C. Because of the partial collapse of the lattice the rapid increase in the cation content of the "locked" sites which occurs at temperatures greater than 700 °C must be ignored as some of these cations may not be trapped in sodalite cages and hexagonal prisms.

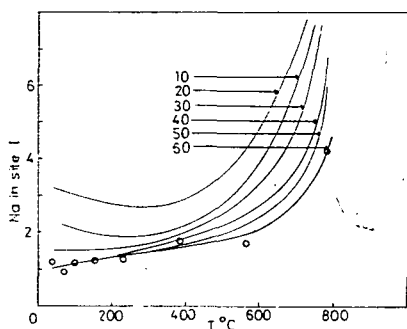


Fig. 4. Number of sodium ions per u. c. in site I of Ba/Na-X zeolite as a function of calcination temperature and degree of barium exchange

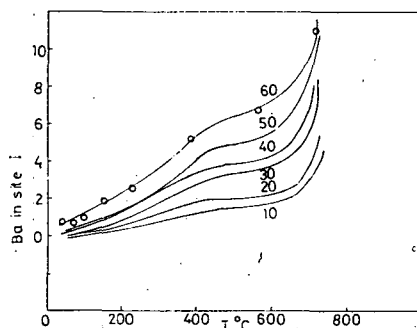


Fig. 5. Number of barium ions per u. c. in Site I of Ba/Na-X zeolite as a function of calcination temperature and degree of barium exchange

If we now consider the overall elution percentages, γ , determined for all of the above samples it is possible to distinguish between those "locked" cations which are sited in the sodalite cages and those which are sited in the hexagonal prisms. In Figs. 4, 5 and 6 the respective amounts of Na^+ , Ba^{2+} and total positive charge "locked" in site I per u. c. are presented as a function of the calcination temperature. Site I is seen to be almost devoid of cation in these Na/Ba-X zeolites as prepared and, also, after calcination at low temperatures. Increasing the temperature to 600 °C has little effect on the population of site I by Na^+ ions. Even in the 10% Ba exchanged sample, which has 73 Na^+ ions per u. c., there are still only 2 Na^+ ions per u. c. occupying hexagonal prism sites at 500 °C.

The Ba^{2+} content of site I in the 60% Ba exchanged sample increases, approximately, linearly with temperature up to 600 °C. This sample has 6.7 Ba^{2+} ions per u. c. located in site I at 570 °C. As this sample has a total of 9.1 Ba^{2+} ions per u. c. in "locked" sites there are 2.4 Ba^{2+} ions per u. c. in the sodalite cages at 570 °C. In the other samples the

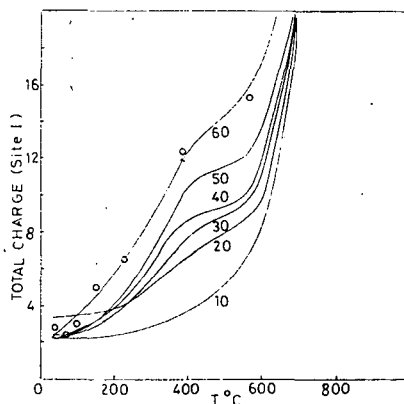


Fig. 6. Total positive charge per u. c. in site I of Ba/Na-X zeolites as a function of calcination temperature and degree of barium exchange

Ba^{2+} content of site I increases from nearly zero at $\sim 200^\circ\text{C}$ to about 5 for the 50% exchanged zeolite down to 2 for the 10% exchanged sample at $\sim 600^\circ\text{C}$. After calcination at 600°C the total positive charge in site I is seen in Fig. 6 to decrease from ~ 15 to 8 as the Ba^{2+} content of the zeolite decreases. Although this represents a total number of 10 cations per u. c. in site I in the 60% Ba/Na-X, all the other samples have 8 or less cations in site I at 600°C .

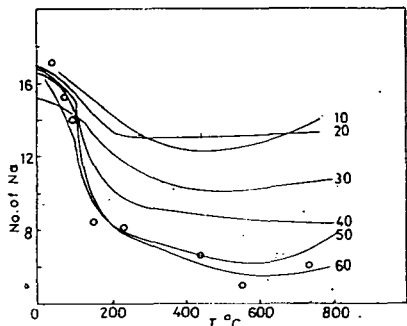


Fig. 7. Number of sodium ions per u. c. in the locked sites of Ba/Na-Y zeolite as a function of calcination temperature and degree of barium exchange

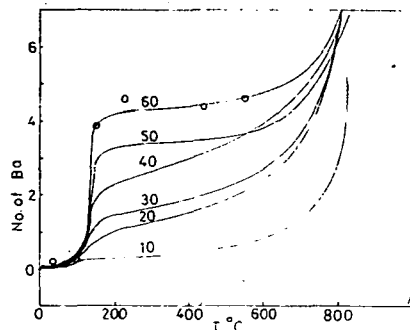


Fig. 8. Number of barium ions per u. c. in the locked sites of Ba/Na-Y zeolite as a function of calcination temperature and degree of barium exchange

In Figs. 7, 8 and 9 the curves for Ba/Na-Y zeolite corresponding to those in Figures 1, 2 and 3 respectively for Ba/Na-X are presented. By comparing these two sets of figures significant differences in the behaviour of zeolites X and Y can be readily seen. For example, Fig. 7 shows that all samples contain $\sim 16 \text{ Na}^+$ ions per u. c. in "locked" sites while Figure 8 shows that few Ba^{2+} ions are accommodated in these sites when the calcination temperature is $\leq 70^\circ\text{C}$.

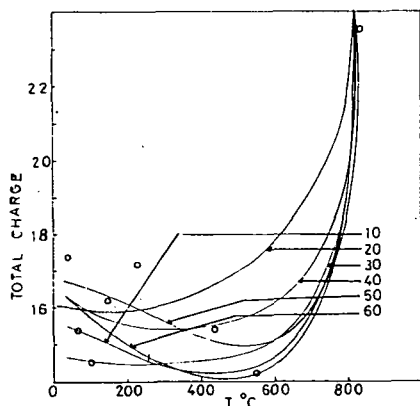


Fig. 9. Total positive charge for u. c. in locked sites of Ba/Na-Y zeolite as a function of calcination temperature and degree of barium exchange

When the temperature is raised above 120°C Ba^{2+} ions now readily occupy the "locked" sites while a corresponding decrease in the Na^+ ion population of these sites occurs. The number of Ba^{2+} ions in the "locked" sites of the 50 and 60% Ba exchanged samples, remains constant at calcination temperature between 250 and 600°C . The other four Y zeolites show some increase in the Ba^{2+} content of these sites in this temperature range. At 400°C the 10–60% Ba exchanged Y zeolites have 0.5, 1.5, 2.0, 3.0, 3.5 and 4.5 Ba^{2+} ions per u. c. in "locked" sites with corresponding Na^+ contents of 12.0, 13.0, 10.2, 8.8, 6.6 and 6.0 respectively. These two sets of figures indicate, as shown in Fig. 9, that the total positive charge due to

cations in "locked" sites remains at ~ 16 per u. c. although there is some indication that in some samples this figure may be as low as 14 per u. c.

The water contents of these Y zeolites indicate little or no lattice collapse in samples which had been calcined up to 730°C . When this temperature is raised to 830°C about 10% loss in water content is found in the 60, 50 and 40% Ba exchanged Y zeolites; some 25% loss in capacity in the 30% exchanged sample while the 10 and 20% exchanged samples show almost total framework collapse. The water content of these latter two samples was only 30–35% of the uncalcined samples. Interesting differences in the thermal stability of the Ba exchanged X and Y zeolites are thus demonstrated. The Y zeolites are more stable at 730°C and the 40–60% Ba exchanged Y zeolites are more stable at 830°C . However, the 10 and 20% Ba exchanged Y zeolites are very unstable at 830°C and, although the corresponding X zeolites were not heated above 780°C these figures suggest that Y zeolites containing 10 and 20% Ba^{2+} are less stable than their X zeolite counterparts. It is difficult to explain why the introduction of only 2.9 or 6.5 Ba^{2+} ions per u.c. in these 10 and 20% exchanged samples respectively should render the zeolite unstable to temperature.

The rapid increase seen in Fig. 8, in the Ba^{2+} contents of the "locked" sites of the 50 and 60% Ba exchanged Y at 830°C is not due to lattice collapse. This rapid increase in selectivity of the "locked" sites for Ba^{2+} ions occurs without any corresponding decrease in the Na^+ population of those sites. Thus the total positive charge resident in "locked" sites also increases rapidly to around 22–23 per u. c. at 830°C .

At 400°C approximately three tenths of the available Na^+ ions are resident in "locked" sites. The corresponding Ba^{2+} distribution decreases from three tenths to one fifth as the degree of Ba exchange decreases from 60 to 10% in these Y zeolites. Thus the more highly exchanged samples show similar selectivities for these two ions in "locked" sites and a reduced preference for Ba^{2+} at low Ba^{2+} loadings. A random distribution over all sites would give $16/53=0.30$ of the ions to "locked" sites. Thus, apart from a preference of Ba^{2+} for supercage sites at low Ba^{2+} loadings, the distribution of cations in zeolite Y at 400°C is a random one.

From the recoil probabilities of the "locked" Na^+ and Ba^{2+} ions it is possible, by the use of equation (3), to calculate the number of these "locked" cations sited

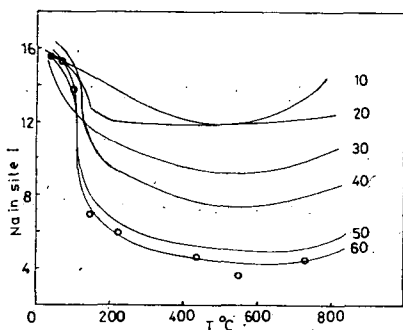


Fig. 10. Number of sodium ions per u. c. in site I of Ba/Na-Y zeolite as a function of calcination temperature and degree of barium exchange

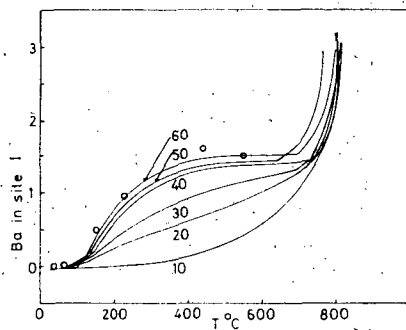


Fig. 11. Number of barium ions per u. c. in site I of Ba/Na-Y zeolite as a function of calcination temperature and degree of barium exchange

in site I and I' of zeolite Y. In Figs. 10, 11 and 12 the number of Na^+ , Ba^{2+} and total positive charge per u. c. residing in site I is plotted as a function of calcination temperature and degree of Ba exchange. These curves may be compared with the equivalent curves for zeolite X in Figs. 4, 5 and 6 respectively. Zeolite Y shows a completely different behaviour from that found in zeolite X. At low temperatures ($\leq 100^\circ\text{C}$) nearly all "locked" Na^+ ions are sited in the hexagonal prism sites. As there are few, if any, Ba^{2+} ions in either sites I or I' these various Ba/Na-Y zeolites have few, if any, cations in their sodalite cages if they have never been heated above 100°C . When these zeolites are heated from 100 to 150°C , however, there is a rapid depopulation of site I by Na^+ and a much smaller occupation of these sites by Ba^{2+} ions. At 600°C the Na^+ content of site I is reduced from 16 per u. c. to about 12, 12, 9.2, 7.3, 4.8 and 4 in the Y zeolites containing 10, 20, 30, 40, 50 and 60% Ba respectively. The corresponding Ba^{2+} contents of site I are approximately 0.6, 1.0, 1.3, 1.3, 1.5 and 1.5 respectively. The total positive charge residing in site I at 600°C is shown in Fig. 12 to be 12.5, 14.5, 11.0, 10.2, 7.6 and 7.0 respectively in these

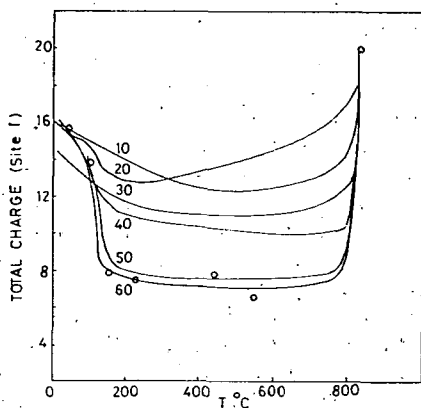


Fig. 12. Total positive charge per u. c. in site I of Ba/Na-Y zeolite as a function of calcination temperature and degree of barium exchange

six zeolites. These figures indicate that on heating samples of zeolite Y which have large Ba^{2+} contents a rapid depopulation of site I occurs. Even samples which have a small Ba^{2+} content still exhibit a small depopulation of site I on heating to 600°C .

Although on calcination above 220°C there is some occupation of the sodalite cages by Na^+ these ions always show a very distinct preference for the hexagonal prism sites. Ba^{2+} , on the other hand, shows little desire to occupy site I even at 600°C . Approximately one third of the "locked" Ba^{2+} ions are sited in these hexagonal prism sites at 600°C .

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CALORIMETRIC STUDY OF ZEOLITE ACIDITY

By

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The microcalorimetric technique has been applied to investigate the adsorption of ammonia, pyridine and *n*-butylamine on A, X, Y and mordenite zeolites modified by the ion exchange and aluminium extraction. The results show that the sodium ions weakly bound with the framework are the strongest adsorption sites. The heats of adsorption measured on hydrogen zeolites are higher than in the case of cationic forms. Aluminium extraction of H-zeolites reduces the number of protonic acid sites.

The results imply that the heats of the adsorption of bases are quite sensitive to the variations of zeolite acidity induced by chemical treatment. A new approach to represent the acidity spectra from calorimetric values is described.

The search for a way to determine the number and the strength of acidic sites remains one of the most important problems of zeolite catalysis. Nearly all investigations along this line were concerned with the measurements of the adsorption of certain bases on zeolites. In our laboratory an extensive calorimetric research has been undertaken to study the behaviour of bases sorbed by the zeolites with different structure and chemistry. Ammonia, pyridine and *n*-butylamine, which are currently among the most widely used bases for the acidity measurements, were selected as sorbates.

The isotherms and the heats of adsorption were measured by a Calvet type microcalorimeter connected with a volumetric system. Before the measurements all samples were evacuated for 100 hours at 480 °C.

Adsorption of ammonia on NaA, NaX and NaY zeolites

By comparing the isotherms it is seen that sodium A, X and Y sieves adsorb different amounts of ammonia. At high coverage the forms of isotherms are exactly similar and they fit the same curve when properly displaced along the ordinate. The variations in the adsorption can be thus ascribed to the different amounts of NH_3 consumed by zeolites at low pressures. Under these conditions a greater influence of the specific zeolite type is to be expected since the ammonia molecules interact with the strongest sites, the strength and the number of which depend on the frame-

work structure and chemical environment. The differences in the adsorption heats are also the most pronounced at low coverage, whereas at the increased loadings the variations in the heats for single zeolites are rather small (Fig. 1).

The data for the adsorption of NH_3 on Na-zeolites indicate that the sodium cations function as adsorption sites. They further suggest that the cations less tightly

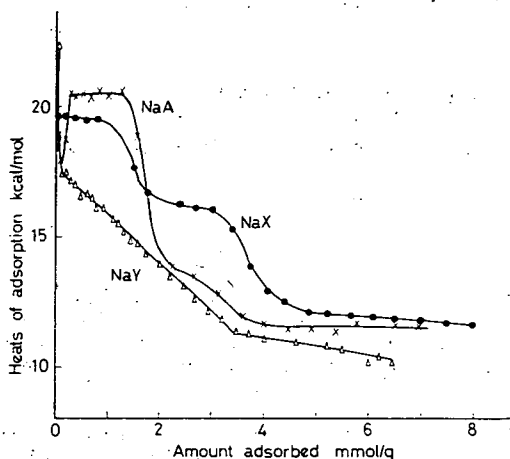


Fig. 1. Adsorption heats of ammonia on NaA, NaX and NaY zeolites

bound in the lattice interact with ammonia molecules more strongly than the cations which are more completely screened by the framework oxygen. Ammonia molecules seem to prefer unlocated cations as adsorption sites at low coverage.

One unit cell of NaA zeolite contains 4 slightly bound cations. A sharp decrease in the adsorption heats from 20 to 14 kcal/mole corresponds to the NH_3 uptake equal to 4 molecules per unit cell. The same cations apparently occupy the large cavities in NaX zeolite and that leads to the similar initial heats obtained for both zeolites. On the contrary a very limited number of unlocated cations in NaY zeolite accounts for the drastic decrease of the adsorption heats at

low coverage. As the adsorption of NH_3 molecules by the cations loosely bound with the lattice is completed, the cations located in 6-rings become involved in the interaction with ammonia.

With the decrease in aluminium content in zeolites the heterogeneity of the rings increases in the series: $\text{NaA} \rightarrow \text{NaX} \rightarrow \text{NaY}$ and the heats of adsorption for NaY show a monotonic decline, while the curves for NaX and especially for NaA zeolites reveal a step-shape decrease.

Kinetic measurements supported the suggestion about the preferential adsorption of NH_3 on loosely bound cations. In addition a slow penetration of ammonia molecules into sodalite cages was observed.

Adsorption of ammonia on mordenite

The heats of NH_3 adsorption have been measured on Na-mordenite and on acid-treated samples with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of 12.6, 20 and 47 (Fig. 2). Compared to other Na-forms, sodium mordenite adsorbs ammonia with the highest heats at low coverage, apparently due to the poor Al content in the lattice and relatively weak interaction of cations with the zeolite framework. Step-shape curve for Na-mordenite indicates the location of cations in several different crystallographic positions.

Ion exchange of Na^+ by protons doesn't alter the total number of the adsorption centers but modifies the nature of the sites as evidenced by the enhancement of ad-

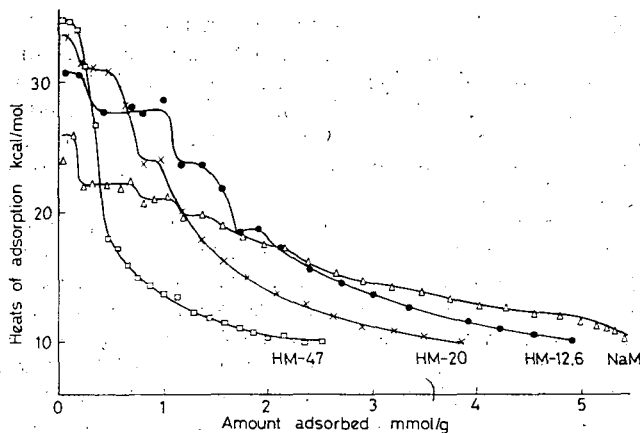


Fig. 2. Adsorption heats of ammonia on mordenites

sorption heats. By progressively increasing the Si/Al ratio the initial heats increased, however, they decreased more rapidly with the filling. Such behaviour may be explained by two opposing effects resulting from Al extraction: the increase of acid-strength of protonic sites and the decrease of the number of the sites.

*Adsorption of *n*-butylamine on decationized and dealuminized zeolites*

NaY zeolite adsorbs *n*-butylamine with heats of ~ 25 kcal/mol over a wide range of coverage [1]. After removing the cations the heats increase to reach the ~ 37 kcal/mol level. The sample exchanged to 20% shows behaviour similar to NaY zeolite [2]. The highest increase in the adsorption heats (from 26 to 35 kcal/mol) was observed when the extent of decationization was raised from 20 to 45%. This suggests that removal of exchangeable cations from 6-rings creates strong protonic sites capable of converting butylamine molecules into butylammonium ions. The further NH_4^+ ions contribute little to the adsorption heats, probably because of poor accessibility or/and weak acidity of protons associated with high exchange levels.

The enhancement of the initial adsorption heat from 30 to 47.5 kcal/mol caused by decationization of mordenite is greater than in the case of Y zeolite [1]. Another feature of hydrogen mordenite is a significant decrease of the adsorption heat with coverage, that indicates a heterogeneity of the acidic sites.

To evaluate the effect of Si/Al ratio on the acidity of Al deficient samples, the

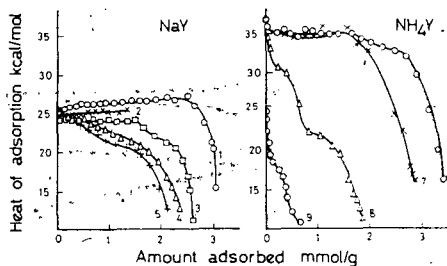


Fig. 3. Adsorption heats of *n*-butylamine on aluminium deficient NaY and NH_4Y zeolites with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of 4.7 (curves 1 and 6), 7.1 (curves 2 and 7), 10.1 (curve 3), 22.6 (curves 4 and 8), 104 (curve 5), curve 9—silica gel

adsorption of *n*-butylamine has been investigated on two series of NaY and NH₄Y zeolites (Fig. 3). Al removal was accomplished by treating Na- and NH₄-zeolites with different amounts of EDTA. The initial heats were not changed by the extraction of aluminium but the fraction of butylamine sorbed with elevated heats decreased progressively as Si/Al was increased. Since no enhancement of the adsorption heats was observed for either series, the generation of more strong sites by extraction was not detectable with *n*-butylamine.

The curves, obtained for the samples from which more than 30% of Al has been removed, showed a distinct step near 20–22 kcal/mol at the high loadings. This suggests the formation of new adsorption centers resulted from dealumination which interact with the sorbed molecules more weakly than either the cations or the protonic sites do. A parallel IR study has established the appearance of additional OH-bands at 3745 cm⁻¹ in aluminium deficient samples. Intensities of this band increased as Si/Al ratio was increased. This band may be thus ascribed to silanol Si—OH groups which, in contrast to cations or protonic sites, interact only weakly with *n*-butylamine through H-bonding.

Acid treated mordenite with SiO₂/Al₂O₃=20 adsorb *n*-butylamine with ~5–7 kcal/mole lower heat than parent hydrogen sample. Again it seems that Si—OH groups are responsible for the adsorption at high coverage. The strongest acidic centers appear to associate with readily removable Al atoms.

Comparison of the adsorption heats of the bases

The data concerning the adsorption of different bases indicate that the sorbed bases interact with zeolites more strongly than hydrocarbons of similar structure and molecular weight. Increased adsorption heats on NaY may be related to coordinative bonding between sodium ions and nitrogen atoms. In this case the highest value was found for pyridine (Fig. 4) apparently because the coordinate bonding is superimposed by the interaction with π -ring. Replacement of Na⁺ by protons results in the ~8–9 kcal/mol higher adsorption heats of ammonia and butylamine. Pyridine is a somewhat weaker base and Py-ion formation is accompanied by lower heat effect. The

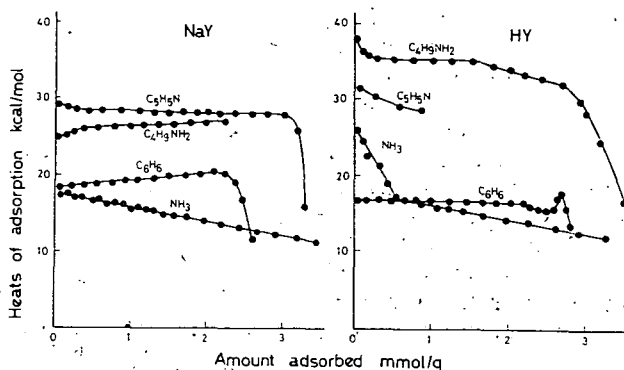


Fig. 4. Comparison of adsorption heats of bases on NaY and HY zeolites.

heats of pyridine adsorption are virtually the same both on sodium and hydrogen zeolites. Thus pyridine seems to be insensitive probe molecule for counting the number of protonic sites by calorimetric technique [3].

Thermochemical study of adsorption on zeolites is fraught with considerable difficulties. The main problem comes from a very slow attainment of the heat equilibrium. Moreover in many cases this technique fails to distinguish between cations and protonic sites due to the insufficient selectivity of the adsorption. Finally, the sorbed amounts of large molecules such as pyridine and butylamine are very limited by the definite void volumes of zeolites. In the case of ammonia complications arise because of penetration of NH_3 molecules into the small cages.

In spite of the difficulties outlined above, adsorption heats provide a valuable information about zeolite acidity. A quantitative approach may be undertaken with the help of acidity spectra calculated from the adsorption heats.

Acidity spectra of zeolites

In some cases the variation of the adsorption heats with progressive filling is represented by step-shape curves. Adsorption heats of NH_3 on NaA and NaY zeolites are typical (Fig. 1). Such behaviour may be associated with the discrete surface heterogeneity due to the existence of several energetic levels. In analyzing the adsorption equilibrium on these surfaces an equation has been derived to describe the change in the adsorption heats with filling.

If the homogeneity of the sites within the single energy level is assumed, the applicability of Langmuir equation can be postulated. Under condition of equilibrium the sorbed amount a is distributed through all levels and the pressure over all parts of the surface would be equal. By using this assumption and taking the adsorption on the first level as independent variable, the adsorption on other levels a_i and the total uptake a can be then determined:

$$a = \sum_{i=1}^n a_i = \sum_{i=1}^n \frac{a_i a_{mi}}{\gamma_i a_{m1} - (\gamma_i - 1) a_1} \quad (1)$$

where a_{mi} — limiting value for the adsorption on the level i , γ — selectivity coefficient.

Once the adsorption and the heat of adsorption for the sites of either type is known, the differential heat of adsorption may be given by:

$$q_a = \frac{\sum_{i=1}^n \frac{q_i a_{mi} \gamma_i}{[\gamma_i a_{m1} - (\gamma_i - 1) \cdot a_1]^2}}{\sum_{i=1}^n \frac{a_{mi} \gamma_i}{[\gamma_i a_{m1} - (\gamma_i - 1) \cdot a_1]^2}} \quad (2)$$

In order to describe the experimental plot of adsorption heats against filling, by the equations (1) and (2), the values of a_{mi} , q_i and γ_i should be found by trial-and-error method. The constants thus evaluated can be represented as energetic spectrum which for the adsorption of bases is spectrum of zeolite acidity. Such spectra are depicted in Fig. 5.

There is still another approach to find acidity spectra. Assuming that the variations in the adsorption heats coincide with energy distributions, a graphical differentiation of the experimental curve and the construction of the plot of $\frac{da}{dq}$ vs. q should produce the spectrum. For step-shape curves the agreement between the spectra

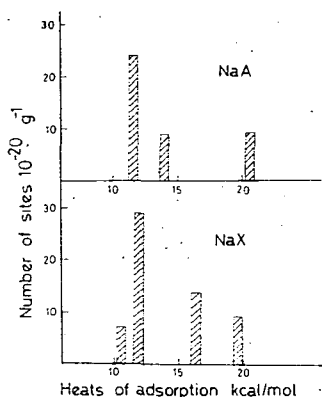


Fig. 5. Acidity spectra for NaA and NaX zeolites

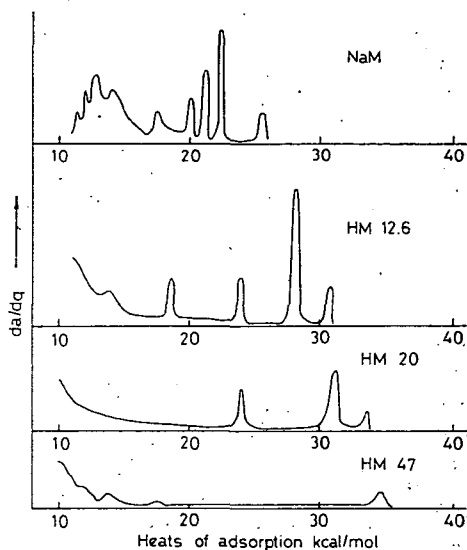


Fig. 6. Acidity spectra for mordenites. Spectra have been obtained by graphical differentiation of the curves in Fig. 2.

obtained by this method and the results of the calculations according to (1) and (2) is very satisfactory.

Fig. 6 represents the acidity spectra calculated for mordenites by using the graphical treatment of the curves in Fig. 2. The variations in the strength and in the number of adsorption sites following aluminium removal are evident.

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TO THE NATURE OF THE CATALYTIC ACTIVITY OF DECATIONIZED AND STABILIZED FORMS OF Y-ZEOLITES

By

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The influence of decationization, stabilization and dehydroxylation of Y type zeolites on their catalytic activity was investigated. It was shown, that the active centres formed by these processes played a different role in the interaction with propylene, ethylene and deuterium.

The catalytic activity of HY zeolites is of common knowledge, while the nature of this activity has not been quite clear. We were interested therefore in the nature of active sites responsible for the catalytic interaction with propylene, ethylene and deuterium. The number and the type of the active centres was changed by the degree of decationization, by the stabilization of zeolites and by their dehydroxylation.

The decationization of the zeolites increased from NaY, $H_{20}Na_{30}Y$, $H_{40}Na_{60}Y$ to $H_{70}Na_{30}Y$ (shortly *e.g.* HY-70). The ratio Si/Al was in all cases 2.5, the sorption capacity of Ar was 10.4–11.2 mmol/g (all weights relate to a dried sample). The samples were prepared from the ammonium form *in vacuo*: the hydroxylated samples at 300, 350 or 400 °C (further denoted as Z_{300} , Z_{350} ...), a partially dehydroxylated sample at 500 °C (Z_{500}). The HY-70 zeolite was stabilized under selfsteaming conditions at 570 and 770 °C [1], *resp.* The latter sample was denoted as St-E, the former St-C₁ and St-C₂. The preparation of these two last samples differed in the kinetic parameters of stabilization. The sorption capacity decreased with stabilization up to 9.4 mmol/g. The extra-lattice aluminium atoms per unit cell (removed by the extraction with 0.1N NaOH) increased from 2.9 to 6.6 from St-C to St-E. The stabilized zeolites were also treated in *vacuo* at 400 °C (Z_{400}) or 500 °C (Z_{500}). The zeolite-propene interaction was investigated at the pressure of 1.7 kNm⁻² by setting the IR instrument (Perkin-Elmer 621) to scan repeatedly over the 3800–1200 cm⁻¹ region [2]. The pyridine was adsorbed at 300 °C and after evacuation of the cell at the same temperature, the IR spectra at the temperature of the IR beam were recorded [1]. The interaction of propene and ethylene with individual zeolites was also studied at 80 °C by the gravimetric method at the pressure of 5.3 kNm⁻² [3]. The exchange of deuterium at 400 °C with 0.075 g of zeolite was investigated at the pressure of 0.19 kNm⁻² (Soviet mass spectrometer MCH 1302) [4].

Results

HY zeolites-interaction with propene and ethylene

The structural hydroxyls were present on all our samples of HY sieves, as resulted from IR spectra-bands at 3640 cm^{-1} (HF) and 3550 cm^{-1} (LF). In the interaction with unsaturated hydrocarbons only OH groups located in the large cavities were involved. Their number in the unit cell was calculated from the height of the HF band on the basis of the data from [5] (see Table I). Assuming that the removal of two hydroxyls gives rise to one Lewis acid-base pair, the number of the latter ones in a u. c. formed in dehydroxylated samples was determined.

The formation of hydrogen-bonded $\text{OH} \cdots \begin{array}{c} \text{C} \\ || \\ \text{C} \end{array}$ complexes with HF hydroxyls was observed after the adsorption of C_3H_6 on HY sieves. An attenuation of the 3640 cm^{-1} band occurred and this was accompanied by a development of a broad band at positions given in Table I and by a band of propene. The intensity of these

Table I
HY-zeolites, interaction with propene and ethylene

Propene				Ethylene		
HF/u. c.	k_{CH_3} [cm ² g ⁻¹ min ⁻¹]	$k_{\text{CH}_3/\text{HF}}$ [cm ² g ⁻¹ min ⁻¹]	ν_{OH} [cm ⁻¹] $\begin{array}{c} \text{C} \\ \\ \text{OH} \cdots \\ \text{C} \end{array}$	$k_{\text{et.}}$ [mg g ⁻¹ min ⁻¹]	$k_{\text{et.}}/\text{Lw}$ [mg g ⁻¹ min ⁻¹]	
HY-70	$\begin{cases} Z_{320} & 22.1 \\ Z_{400} & 20.5 \\ Z_{500} & 4.8 \end{cases}$	$\begin{cases} 5.8 \\ 6.1 \\ 5.9 \end{cases}$	$\begin{cases} 0.26 \\ 0.30 \\ 1.22 \end{cases}$	$\begin{cases} 3180-3190 \\ 3180-3190 \\ b \end{cases}$	$\begin{cases} <0.05 \\ <0.05 \\ 5.5 \end{cases}$	$\begin{cases} - \\ - \\ 0.64 \end{cases}$
	$\begin{cases} Z_{400} & 15.3 \\ Z_{500} & 6.3 \end{cases}$	$\begin{cases} 2.9 \\ 1.8 \end{cases}$	$\begin{cases} 0.19 \\ 0.28 \end{cases}$	$\begin{cases} 3200 \\ 3200 \end{cases}$	$\begin{cases} <0.05 \\ 1.6 \end{cases}$	$\begin{cases} - \\ 0.36 \end{cases}$
	$\begin{cases} Z_{400} & 8.4 \\ Z_{500} & 3.6 \end{cases}$	$\begin{cases} 0.35 \\ 0.30 \end{cases}$	$\begin{cases} 0.04 \\ 0.09 \end{cases}$	$\begin{cases} 3230 \\ 3230 \end{cases}$	$\begin{cases} <0.05 \\ 0.38 \end{cases}$	$\begin{cases} - \\ 0.16 \end{cases}$
NaY	$\begin{cases} Z_{500} & 3.6 \\ Z_{400} & 0 \end{cases}$	$\begin{cases} 0.30 \\ 0 \end{cases}$	$\begin{cases} 0.09 \\ 0 \end{cases}$	$\begin{cases} 3230 \\ 0 \end{cases}$	$\begin{cases} 0.38 \\ <0.05 \end{cases}$	$\begin{cases} 0.16 \\ - \end{cases}$

b the HF groups were so rapidly covered by saturated compounds that the position of this band could not be located.

bands decreased during oligomerization, when branched saturated hydrocarbons were formed. For the comparison of the catalytic activity the intensity A_{CH_3} (normalized on sample thickness) on the 2950 cm^{-1} band of CH_3 groups in a saturated chain was used. The activities order was confirmed by the intensity-time plots of the $\text{C}=\text{C}$

band, the CH_2 band and the OH band in $\text{OH} \cdots \begin{array}{c} \text{C} \\ || \\ \text{C} \end{array}$ complex. The extent of spectral

changes together with the measurement of the weight increase showed that gas molecules also participate in the building of chains. With regard to possible transport limitations, the rate of the CH_3 intensity changes k_{CH_3} given in Table I was determined

from the early stage of reaction. In the next column this value related to 1 HF group is shown.

From these data the following conclusions could be made: *i*) the activity of both hydroxylated and dehydroxylated samples in propene oligomerization drops with the decationization; *ii*) the position of the OH band in the $\text{OH} \cdots \begin{array}{c} \text{C} \\ \parallel \\ \text{C} \end{array}$ propene complex moves to a higher wavenumber with decreasing decationization; *iii*) the dehydroxylation usually decreases the total activity. However, the activity per HF group increases, particularly with the HY-70 sample.

Hydroxylated forms of HY zeolites were found to be inactive with respect to the ethylene oligomerization; this reaction proceeded on the dehydroxylated samples only. In the Table I, the rate of the weight increase k_{et} was used for the characterization of total activity. The rate related to one L. acid-base pair, formed by dehydroxylation, is shown in this table, too. From these data follows, that the effect of dehydroxylation on the catalytic activity in ethylene oligomerization is most remarkable with HY-70 sieve and lowers with decreasing decationization.

Stabilized zeolites-interaction with propene and ethylene

Bands of OH groups typical for stabilized forms were present in the infrared spectra of St-C and St-E samples — see Fig. 1. The zeolite St-C₁ contained in addition OH groups with a 3630 cm^{-1} band which was at similar positions as structural hydroxyls bands in HY samples.

Both ethylene and propene interacted with 3690 cm^{-1} hydroxyls of St-E zeolite giving rise to hydrogen bonded complexes ($\nu_{\text{OH}} = 3440, 3490 \text{ cm}^{-1}$ for adsorbed propene and ethylene, *resp.*). This zeolite was found to be inactive.

The activity of St-C samples in the oligomerization of ethylene was found to be still low and to be increased by dehydroxylation. The substantial differences were observed in the rate of propene oligomerization on the St-C₁ and St-C₂ samples together with the negative influence of dehydroxylation (Table II). The activity of St-C₁ zeolite pretreated *in vacuo* at 400°C was similar to that one of parent HY-70 sieve. The catalytic reaction in the St-C samples was accompanied by the decrease of 3690 and 3670 cm^{-1} bands, in the case of the St-C₁ sample also by the disappearance of the 3630 cm^{-1} band.

From the interaction with pyridine it follows in respect to the propene and ethylene interaction: *i*) the amount of Brönsted centres which forms pyH^+ ions is by one order lower on St-E than on the parent HY-70 zeolite in its

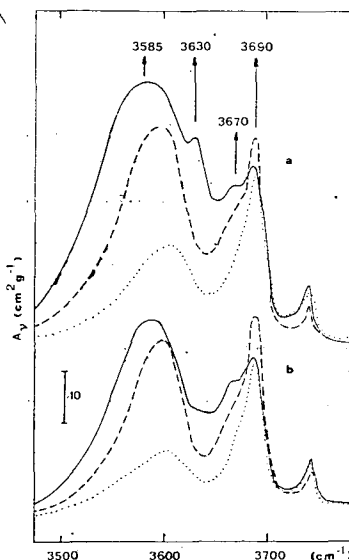


Fig. 1. IR spectra of stabilized zeolites. Full line: St-C₁; dashed line St-C₂; dotted line St-E; after 18 hrs evacuation at *a* 400° and *b* 500°C .

Table II

Stabil. Zeolites — interaction with propene and ethylene

		propene k_{CH_3} [cm ² g ⁻¹ min ⁻¹]	ethylene $k_{et.}$ (mg g ⁻¹ min ⁻¹)
St-C ₁	Z ₄₀₀	6.0	0.3
	Z ₅₀₀	3.5	1.3
St-C ₂	Z ₄₀₀	1.7	0.2
	Z ₅₀₀	0.6	0.8
St-E	Z ₄₀₀	0.09	<0.05

hydroxylated form; *ii*) the number of these sites is 3—4 times higher on St-C than on St-E sieves and decreases with dehydroxylation, *iii*) the band of 3630 cm⁻¹ hydroxyls of St-C sieve disappears.

Exchange with deuterium

Both types of D₂ exchange with zeolites were evaluated from one measurement using the initial non-equilibrated mixture of D₂ and H₂ [6]: the exchange of D₂ with zeolitic hydrogen groups (hetero-exchange) and the exchange of D₂ + H₂ catalyzed by zeolite but not including the hydrogen of OH groups (homo-exchange).

Table III

Total number of the OH groups and the rates of hetero- and homo-exchange

		NaY	HY-20	HY-40	HY-70	St-C ₁	St-C ₂	St-E
OH/g × 10 ⁻²⁰	Z ₄₀₀	0.7	8.4	14.7	19.1	28.4	24.9	10.1
	Z ₅₀₀	0.7	5.8	6.8	8.7	12.6	12.6	7.1
R _{hetero} × 10 ³ [atom min ⁻¹ g ⁻¹]	Z ₄₀₀	—	3.5	2.7	1	4	2	3.5
	Z ₅₀₀	—	12	7	5	9.5	8.8	5
R _{homo} × 10 ⁻¹⁸ [atom min ⁻¹] per OH	Z ₄₀₀	6.5	3.1	4.2	1.1	1	1	3.5
	Z ₅₀₀	6.5	9.3	9.3	69	6.4	4.5	3.5

In Table III, the rates for hetero-exchange and homo-exchange together with the total numbers of OH groups taking part in the hetero-exchange are shown.

The rates of hetero-exchange per OH group increased with decreased decationization and are also higher for stabilized zeolites than for the parent zeolite HY-70. The dehydroxylation always increased the hetero-exchange rate; an extraordinary high rate of homo-exchange was found for dehydroxylated HX-70 zeolite, but this effect was lowered with decreased decationization and increased stabilization.

Discussion

For the oligomerization of propene and ethylene on hydroxylated HY zeolites the carbonium ion mechanism is suggested. Proton transfer is supposed to involve tunneling *via* a strong hydrogen complex [7]. Our results support this opinion by the parallelism found between the activity of samples and the position of the OH band in the hydrogen bonded complex. The wavenumber shift related to unperturbed hydroxyls provides information about the OH bond weakening and in this way about their acidity strength. The diminishing of this shift with decreased decationization shows that both the acidity strength and the number of OH groups are responsible for the catalytic activity. The lack of ethylene oligomerization under our experimental conditions is probably caused by the lower basicity of ethylene in comparison with propylene and by the necessity of primary carbonium ion formation from ethylene as was already supposed by CANT [7]. The appearance of ethylene conversion with dehydroxylation evidently depends on the presence of Lewis acid-base pair centres. The maximum efficiency calculated per one pair of these centres was found with HY-70 and it decreased towards NaY. Propene conversion is catalyzed both with Brönsted and Lewis acid centres as can be seen from the comparison of propylene and ethylene interactions.

Homo- and hetero-exchange was found to be in antibatic dependence on the presence of Brönsted acid centres: it is of lowest value with HY-70 in hydroxylated form and increases with the increasing number of Na^+ ions. Na^+ ions could play an active role in deuterium exchange. The Lewis acid-base pair centres catalyze strongly the homo-exchange, especially on HY-70.

The properties of stabilized zeolites strongly depend on the stabilization conditions: the effect of dehydroxylation is of lesser importance. The zeolites stabilized at 770 °C were found to be practically inactive in hydrocarbon conversion probably due to the annihilation of the Lewis acid-base pair centres during the high temperature

stabilization of the lattice. The shift of the OH band due to the formation of OH... $\begin{smallmatrix} \text{C} \\ \parallel \\ \text{C} \end{smallmatrix}$ complexes indicated a low acidity of the 3690 cm^{-1} hydroxyls located in the large cavities. This finding was in accordance with pyridine adsorption. This adsorption was higher with zeolites stabilized at 570 °C in a similar way as their activity in propene conversion. Hetero-exchange was found to proceed with a higher rate on stabilized zeolites than on HY-70, likely owing to some lattice defects. The homo-exchange on slightly stabilized zeolites is similar to that on the parent HY-70 zeolite.

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CATALYTIC PROPERTIES OF Pd-ZEOLITES IN ETHYLENE OLIGOMERIZATION

By

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Pd-zeolite catalysts display activity in C_2H_4 conversions under atmospheric pressure, the principal reaction products being dimers, trimers and other oligomers of C_2H_4 . On the [3% Pd] 0.75 CaNaY zeolite, the conversion of C_2H_4 at 50–100 °C equals 29–34%, while on [0.1% Pd] 0.4 CaNaY at 200° the yield of C_4 hydrocarbons is as high as 70% based on converted C_2H_4 . The conversion of C_2H_4 on the PdCaNaY ion-exchanged zeolite grows as the content of Pd increases and the extent of Na^+ exchange with Ca^{2+} becomes greater. Zeolite pretreatment with various gases, in combination with the XPS technique, made it possible to establish that in C_2H_4 conversions the catalytic activity is displayed by Pd in the cationic form, while Pd metal is inactive. Pd on amorphous silica-alumina behaves similarly. It is concluded that the presence of Pd in the cationic form, in conjunction with proton acidic sites, is essential for obtaining an active C_2H_4 oligomerization catalyst.

Introduction

Pd-containing zeolites are active in ethylene oligomerization [1–3]. However, the nature of catalytic effect of these catalysts and also the structure of the oligomerization active site have not been studied in sufficient detail. We investigated the properties of Pd-zeolites in this reaction and also the nature of their catalytic activity.

Experimental part

Runs were carried out in a flow system under atmospheric pressure [3]. The ion-exchanged catalysts were prepared by introducing 0.01–3.0 wt.% Pd in zeolites: Na-mordenite ($SiO_2/Al_2O_3 = x = 10$), NaY, CaNaY ($x = 4.3$), CaNaX ($x = 2.5$) using an aqueous solution of $[Pd(NH_3)_4]Cl_2$. The extent of Na^+ exchange with Ca^{2+} in CaNaY and CaNaX zeolites was 20–75 and 48 eq. % respectively. A number of catalysts were prepared by impregnating carriers with aqueous solutions of H_2PdCl_4 and $[Pd(NH_3)_4]Cl_2$. The catalysts prepared by ion exchange are designated as [Pd] zeolites, and those by impregnation as Pd-zeolites.

The X-ray photoelectron spectra (XPS) of catalysts discharged from the reactor in Ar were recorded by an ES-100 spectrometer [4].

Prior to each run, the catalysts were heated in an air stream (450°, 8 hrs, space velocity 800 h^{-1}). Run duration was generally 30 min, the time of C_2H_4 contact being 2 s (space velocity 900 h^{-1}).

Discussion

The effect exerted by the technique of Pd incorporation and the temperature on C_2H_4 conversions was studied in the 50—200°C temperature range (Table I). Ethylene conversion (A) of ~30% was obtained on the type Y ion-exchanged zeolite at 100°, and at 150° in the case of impregnated specimen containing the same amount of Pd. The yield of C_4H_8 based on C_2H_4 converted was higher (20—30%) for the impregnated catalyst than for the ion-exchanged one, the overall yield of C_4 hydrocarbons (Y_b) on both catalysts at 100—200° being ~30%, and that of $i-C_4H_8$, 0.1—0.5%.

Table I
Effect of method of preparation and zeolite type on ethylene oligomerization

Catalyst	T °C	C_2H_4 conversion (A), %	Yield based on converted ethylene, %						$K = \frac{2\text{-butenes}}{1\text{-butene}}$
			C_2H_6	$C_3H_8 + C_3H_6$	C_4H_{10}	C_4H_8	C_5-C_8	adsorbed hydrocarbons	
[1% Pd] 0.75 CaNaY	50	15.0	3.1	0.4	9.3	10.3	38.2	38.7	11.7
	100	31.9	5.3	1.1	15.3	16.8	31.2	30.3	7.6
	150	38.3	6.5	1.2	14.4	11.7	29.5	36.7	6.5
	200	31.4	8.4	2.2	22.4	8.0	25.3	33.7	5.6
1% Pd -0.75 CaNaY	50	10.5	2.8	0.5	12.4	30.3	54.0		13.7
	100	22.3	3.8	0.3	8.6	20.0	36.5	30.8	8.9
	150	31.8	4.6	0.5	7.9	19.8	39.0	28.2	6.6
	200	31.6	4.3	0.7	8.7	22.4	40.1	23.8	5.5
[1% Pd] 0.48 CaNaX	200	21.9	—	0.9	3.4	35.0	33.3	27.4	5.3
1% Pd -0.48 CaNaX	200	14.6	—	2.3	7.9	60.4	1.8	27.6	5.4

As the temperature increases from 50 to 200°, A grows, while on the ion-exchanged zeolite the yields of C_4H_8 decrease, but C_4H_{10} yields increase, Y_b remaining practically unchanged. As the temperature increases, $K = \beta - C_4H_8/\alpha - C_4H_8$ diminishes.

Pd-containing X zeolites are less active than type Y zeolites, but display higher selectivity as regards C_2H_4 dimerization.

The 0.01% Pd-containing catalyst at 100° is inactive in C_2H_4 oligomerization, but on the 3% Pd-containing zeolite A equals 28.9% even at 50° (Table II). With respect to T_{min} required for obtaining A equal to 28—31%, the [Pd] 0.75 CaNaY catalysts are arranged in the order: 0.01% Pd > 0.1% Pd > 1% Pd > 3% Pd.

The degree of Na^+ exchange with Ca^{2+} (α) in zeolites affects C_2H_4 oligomerization (Table II). On the 0.1% Pd-containing catalysts, the growth of α from 0 to 75 eq. % results at 200° in a 41-fold increase of A and a 2.5-fold decrease of Y_b , the yield of higher hydrocarbons being simultaneously increased. Process selectivity as regards C_2H_4 dimerization experiences diminution.

With respect to the growth of A at 200°, the catalysts containing 0.1% Pd are arranged in the order [Pd]NaY $\cong$ [Pd] 0.2 CaNaY < [Pd] 0.4 CaNaY < [Pd] 0.75 CaNaY

Table II

Effect of palladium content and the degree of Na⁺ exchange with Ca²⁺ on ethylene oligomerization

Catalyst	T, °C	C ₂ H ₄ conversion (A), %	Yield based on converted C ₂ H ₄ , %						K = $\frac{2\text{-butenes}}{1\text{-butene}}$
			C ₂ H ₆	C ₃ H ₈ + C ₃ H ₆	C ₄ H ₁₀	C ₄ H ₈	C ₅ - C ₈	Ad-sorbed hydrocarbons	
[0.01 % Pd] 0.75 CaNaY	100	0.8	not analyzed						
	200	18.5	1.5	1.4	16.3	10.0	41.5	29.3	6.4
	250	28.1	3.1	2.4	16.9	14.5	38.8	24.3	4.8
[0.1 % Pd] 0.75 CaNaY	100	9.4	2.0	1.4	13.7	31.9	51.0		10.3
	200	28.8	6.9	1.7	11.7	16.0	31.4	32.3	5.2
[3 % Pd] 0.75 CaNaY	50	28.9	8.5	0.5	8.6	8.8	39.8	33.8	13.7
	100	34.4	10.4	0.5	6.0	8.3	41.2	33.6	7.3
[0.1 % Pd] NaY	200	0.7	0.7	Not analyzed					
[0.1 % Pd] 0.2 CaNaY	200	1.0	1.0	Not analyzed					
[0.1 % Pd] 0.4 CaNaY	200	9.6	1.8	0.8	10.6	59.5	7.0	20.3	6.0

the order of selectivity of these catalysts for C₄ hydrocarbon formation being reversed. The maximum values of Y_b (70%) and C₄H₈ yield (59.5%) were observed at 200° for the [0.1 % Pd] 0.4 CaNaY zeolite.

Hence, in type Y zeolites the growth of acidity as the value of α increases [5, 6] results in A rise, Y_b diminution and hydrogen redistribution enhancement which manifests itself in greater yields of some paraffins.

The role played by the acidity of Pd-zeolites is also seen from the fact that practically nonacidic Na-forms of mordenite containing 0.1 and 1 % Pd are devoid of activity for C₂H₄ oligomerization, while Y zeolites are more active than X zeolites (Table I).

On all Pd-zeolites, A maximum is observed, in accordance with [3], after pretreatment with air (450 or 380°). The ion-exchanged and impregnated zeolites dried in the air at 100—120° after 1 % Pd incorporation and next treated with H₂ are inactive for C₂H₄ conversions. The ion-exchanged zeolite is also inactive on being treated with Ar due to complex ion [Pd(NH₃)₄]²⁺ decomposition to form Pd metal [7].

The results of heat treating the catalysts with diverse gases, in combination with XPS data, showed A to depend on the Pd cationic form share in the catalysts [8].

The spectrum of Pd3d_{5/2} electrons of the starting zeolite is close to the spectrum of [Pd(NH₃)₄]Cl₂, the bond energy of Pd3d_{5/2} electrons (E_b) being 338.2 eV. After treatment with the air (at 380 or 450°), E_b declines by ~1 eV. An analogous shift in the spectrum due to [Pd(NH₃)₄]²⁺ decomposition and partial Pd²⁺ reduction to Pd⁺, as well as due to Pd²⁺ clustering to form PdO was observed for the PdX zeolite [4, 9].

The maximum value of A is observed for zeolites that contain all Pd in the cationic form. Treating the starting sample with H₂ or Ar at 380° results in reducing the palladium in [Pd(NH₃)₄]²⁺ to Pd⁰, as shown in [4, 9], the value of A being 0.2%. After treating the [3% Pd] CaY zeolite with Ar or H₂, followed by treatment in the

air, there appears in XPS a signal analogous to that observed for the zeolite treated with the air alone and containing all the palladium in the cationic form. Here, the value of A is maximal (33—37%).

In C₂H₄ oligomerization on zeolites treated with the air (4 hrs, 380°) and then with H₂ (2 hrs at different temperatures), zeolite activity and C₄ hydrocarbon yield based on the C₂H₄ feed (Y_b') experience symbatic variation with the cationic Pd share (Fig. 1). The data on the degree of Pd reduction are in agreement with [10].

ESR data show the catalytically active [3% Pd] CaY zeolite treated with the air and then with H₂ at room temperature to contain Pd⁺, this being in agreement with [11].

The ratio of intensities of Pd3d_{5/2} and Si2s, which equals 0.24 in the stock zeolite

containing [Pd(NH₃)₄]²⁺ exclusively, increases after treatment with either air or argon to 0.4 and 0.58, respectively, presumably because of Pd⁰ migration into the surface layer and oxidation.

Ethylene, like CO and H₂ [12], reduces Pd²⁺ to Pd⁰ in zeolite. In the course of experiments, A and the share of cationic palladium decreases.

Palladium supported on active carbon, SiO₂ or Al₂O₃, in contrast to Pd-zeolites,

is inactive for C₂H₄ oligomerization under the investigated conditions after treatment with both air and H₂. The Pd-impregnated amorphous synthetic silica-alumina (Pd-ASA) displays maximum activity after treatment with air and is devoid of activity after H₂ treatment. The catalyst obtained by impregnating ASA with an aqueous solution of [Pd(NH₃)₄]Cl₂ displays greater selectivity for C₂H₄ dimerization and higher stability than does the catalyst prepared using H₂PdCl₄. In the 20—250° temperature range the C₂H₄ conversion and C₄H₈ yield pass through a maximum (Fig. 2), the yield of C₄H₈ being up to 97.6% based on converted C₂H₄.

Hence, in C₂H₄ oligomerization, palladium is active in the cationic form. Rela-

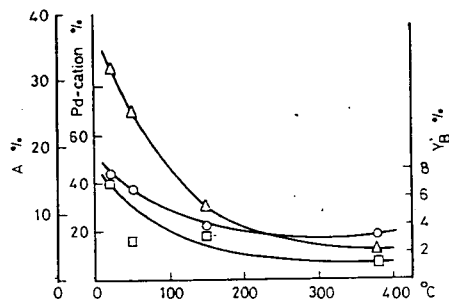


Fig. 1. Effect of temperature of hydrogen treatment of [3% Pd] 0.75 CaNaY zeolite preheated in air stream on the state of Pd in zeolite and ethylene conversions. Δ — C₂H₄ conversion (A), %; ○ — share of palladium in cationic form, %; □ — yield of C₄ hydrocarbons based on C₂H₄ feed (Y_b), %.

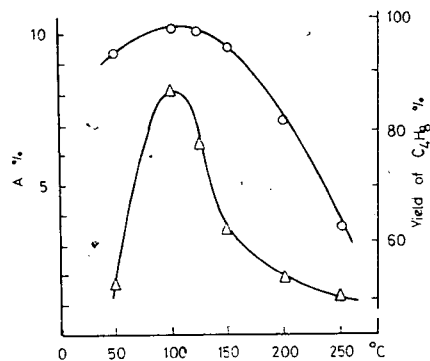


Fig. 2. Effect of temperature on C₂H₄ dimerization in the presence of 4%-ASA catalyst. Δ — C₂H₄ conversion (A), %; ○ — yield of C₄H₈, %.

tionships between the activity of Pd-zeolites, the degree of Na^+ exchange with Ca^{2+} and also the zeolite type, and absence of activity of palladium supported on carbon, SiO_2 or Al_2O_3 make it possible to conclude that, in the same way as in Ni-silica-aluminas [13, 14], in Pd-silica-aluminas in the formation of an oligomerization active site there participate acidic sites, apart from palladium in the cationic form. Proton sites are, presumably, essential for the formation of Pd^{2+} cation from PdO according to the scheme: $\text{PdO} + 2 \text{H}^+ \rightarrow \text{Pd}^{2+} + \text{H}_2\text{O}$ analogous to the scheme suggested for Ni-zeolite catalysts [15].

* *

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NMR-STUDIES OF THE MOBILITY OF AROMATICS IN FAUJASITES

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The inter- and intramolecular part of the second moment of the proton resonance of C_6H_6 in NaX at about 100 K show four molecules above the S_2 -sites rotating around their hexagonal axis. Other possible sites seem to be the windows between the large cavities. With increasing temperature tipping motions can be shown between these sites by relaxation measurements. Above 300 K translation is the predominating mobility mechanism, the characteristic parameters of which are drawn from T_1 -measurements on C_6H_6 , C_6H_5F and C_4H_4S in NaX and NaY. For cavities with almost no ions in the zeolites LaY, HY and "Ultrastable"-Y for benzene two regions with different mobility can be observed, the relative amount of which and the exchange rate of the molecules between them depend on temperature and the zeolite type.

Informations on the mechanism of molecular mobility in zeolite pores are important for an explanation of the catalytic properties of these substances. We have studied the mobility of benzene and related aromatics with NMR-methods in a variety of faujasites with low paramagnetic impurity between 77 and 450 K.

In NMR theory, the mobility is described usually in terms of correlation time τ_c , which can be regarded as the inverse of the jump frequency. τ_c is directly related to the nuclear relaxation times T_1 and T_2 , where the exact relation depends on the special motional mechanism. The temperature function of T_1 shows a minimum for each kind of motion, T_2 usually decreases with decreasing temperature and becomes constant for molecules in fixed positions possibly, with a definite state of reorientation [1]. At the minima of T_1 holds $\tau_c \omega_L \approx 0.6$, from which τ_c can be obtained. ω_L is the frequency of the NMR-experiment. Further is there $T_1/T_2 = 1.6$ if motion of the molecules is isotropic with only one τ_c [2, 3]. Any deviation from this situation leads to an increase of this ratio. Usually τ_c is assumed to obey an Arrhenius law. The respective activation energy can be obtained by a measurement of the T_1 -minimum for different ω_L . For molecules in fixed positions, the second moment M_2 of a wide-line spectrum will give valuable information of the adsorbed phase. For nuclear dipole-dipole interaction and molecules undergoing rotational reorientations, M_2 obeys a relation [4].

$$M_2 = \sum_i K_i (3 \cos^2 \theta - 1)^2 (3 \cos^2 \gamma_i - 1)^2 r_i^{-6} \quad (1)$$

where the K_i contains the magnetic moments of the interacting nuclei, r_i is their distance and γ_i the angle of the internuclear vector and the axis of the rotation. θ is the angle of this axis with the applied magnetic field. For powders, the term containing

θ must be averaged over all possible θ . The K_i of the ^1H — ^1D interaction is much less than that of the ^1H — ^1H interaction. Therefore, from a comparison of the M_2 , measured on C_6H_6 and $1,3,5\text{-C}_6\text{H}_3\text{D}_3$, the contributions of the protons in the same and in different molecules can be separated [5]. Measurements on samples with 4 and 5.2 molecules in a large cavity show below 150 K and intramolecular M_2 of 0.84 Gauss² which is exactly the value obtained from Eq. 1. for a benzene molecule rotating around its sixfold axis. For lower coverages the M_2 indicate additional freedoms of motion. The intermolecular M_2 for 4 molecules in a large cavity is 0.28 Gauss². It can be assumed, that the molecules lie flat on the walls above the S_2 -sites [6]. To simulate the rotation, four circles with the diameter of a benzene molecule have been arranged in the described position. In steps of one degree, the distances, r_i , of the points of one circle to all points of the other circles have been calculated as well as the angles γ_i of the vectors r_i with the axis of the first circles. These values have been inserted into Eq. 1 and averaged for different distances of the benzene molecules. The measured value of 0.28 Gauss² is explained best by a distance of 3.1 Å of the benzene from the S_2 -ion, which is in good agreement with the value obtained by GESCHKE [6] from CNDO-calculations.

The intermolecular M_2 for 5.2 molecules in a cavity is 0.4 Gauss². Because of the strong dependence of M_2 on the r_i of the interacting nuclei, from the explanation of this value a sensitive check of the possible positions of this molecule can be expected. We have carried out calculations with the fifth molecule in the center of the large cavity and in the window between the two cavities perpendicular and parallel to the window plane. Only the position parallel to the window can explain the measured intermolecular M_2 . The values for the other situations are two to five times too large. This result allows conclusions on the sorption mechanism.

The maximum sorption capacity, observed for benzene in NaX, lies at 5.2—5.4 molecules in a large cavity [7]. The limit of our model is at 6 molecules. Further, the rather good mobility observed above 250 K, can be easily explained to take place via a tipping from the sites above the S_2 -ions into the sites in the window or vice versa, or from an occupied S_2 -site to an unoccupied one. The mobility at higher temperatures has been studied by relaxation measurements. The analysis of the temperature functions of T_1 for C_6H_6 , $1,3,5\text{-C}_6\text{H}_3\text{D}_3$ and mixtures of C_6H_6 — C_6D_6 shows for about 4 molecules in a large cavity a distinct maximum of the intermolecular relaxation rate at about 200 K, which is in good agreement with the discussed tipping motions (Fig. 1). The behaviour for full loading is somewhat difficult to survey, but not in

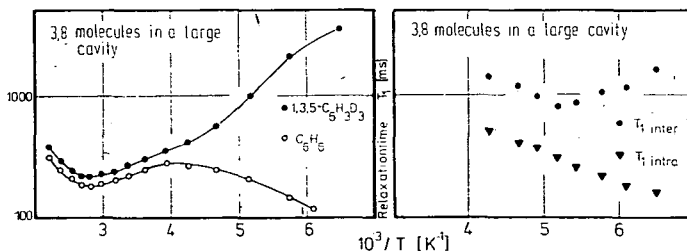


Fig. 1. Temperature behaviour of T_1 for samples with about four molecules benzene in a large cavity of NaX in different deuteration states, and separation of the inter- and the intramolecular contribution to T_1 .

contradiction with the suggested model. A striking effect of these measurements is, that the T_1 of the protons does not depend on deuteration near and above the T_1 -minimum. According to PREIFER's [2] "relaxation analysis" scheme this means that the relaxation occurs via an interaction with the residual paramagnetic impurities of the zeolite, being about 5 ppm Fe^{3+} . Because of the large distances of these Fe^{3+} ions, translational diffusion must be the predominating mobility mechanism in this temperature region. From the average distance of the Fe^{3+} and the value of T_1 at 300 K an approximate self diffusion coefficient $10^{-8} \text{ cm}^2 \text{ sec}^{-1}$ can be estimated. For a more exact analysis of the temperature function of T_1 , the theory of TORREY [8] and KRÜGER [9] has been used, describing the dipolar relaxation caused by translational diffusion. In this theory, the relaxation times are given by rather complicated functions of τ_c , the concentration of the paramagnetic centers, the mean jump distance and the shortest possible distance of the molecule to the paramagnetic centers. Using the τ_c from the temperature function of T_1 and the activation energy of the motion, obtained from the T_1 -minima at different ω_L , the measured temperature behaviour of T_1 has been fitted, varying the mentioned parameters of the theory. The results for NaX are summarized in the Table I. The self diffusion coefficient D , included in this

Table I
Parameters of the Translation-Relaxation-Model for Benzene in NaX-Zeolite

Coverage Molecules /Cavity	Temp. in K	D in cm^2/s		$\sqrt{\langle r^2 \rangle}$ in Å	E_{act}		Temp. of $T_{1\text{min}}$ for 60 Mc
		direct	Model		kJ/mol direct	Model	
5.3	374	$1.4 \cdot 10^{-7}$	$8.8 \cdot 10^{-8}$	4.9	—	35	391
3.7	374	$1.8 \cdot 10^{-7}$	$1.1 \cdot 10^{-7}$	4.4	16	14	382
	364	$1.6 \cdot 10^{-7}$	$1.1 \cdot 10^{-7}$				
	354	$1.3 \cdot 10^{-7}$	$1.0 \cdot 10^{-7}$				

D Self-Diffusion-Coefficient.

$\sqrt{\langle r^2 \rangle}$ Mean Jump Distance.

E_{act} Activation Energy.

table, has been obtained from the jump distance and the correlation time by the Einstein relation. Additionally it has been measured directly on especially synthesized large crystals using the method of TANNER and STEJSKAL [10], as shown in the Table I. The agreement between these values of D and those obtained from the fit of the temperature function of T_1 is fairly good.

For benzene in NaY, the minima of T_1 lie at temperatures, where the benzene desorbs already from the sample. A fit of the described kind is, therefore, not possible. An estimation shows, that the mobility is distinctly restricted compared with NaX, which has been observed already in earlier studies [11, 12].

The respective values for thiophene and fluorobenzene are summarized in Table II. Both adsorbates show an increased mobility, which is best demonstrated by the lower temperatures of the T_1 -minima. The self diffusion coefficient usually increases with decreasing coverage. For C_6H_6 and $\text{C}_6\text{H}_5\text{F}$ the activation energy from full to

Table II
Parameters of the Translation-Relaxation Model for
 C_6H_5F and C_4H_4S on NaX and NaY

Sample	Coverage Molecules /Cavity	D for 320 K cm^2/s	$\sqrt{\langle r^2 \rangle}$ in Å	E_{act} kJ/mol	Temp. of T_{1min} for 60 Mc
C_6H_5F in NaX	4.2	$2.2 \cdot 10^{-8}$	2.7	34	336
	3.0	$9.5 \cdot 10^{-8}$	3.5	20	309
	1.2	$3.5 \cdot 10^{-7}$	3.6	27	279
C_6H_5F in NaY	4.6	$1.8 \cdot 10^{-8}$	2.9	24	369
	3.2	$5.8 \cdot 10^{-8}$	3.7	13	345
	1.3	$1.7 \cdot 10^{-7}$	3.8	30	303
C_4H_4S in NaX	5.1	$5.2 \cdot 10^{-8}$	2.9	12	323
	3.5	$9.8 \cdot 10^{-8}$	3.3	13	296
	2.0	$1.7 \cdot 10^{-7}$	3.5	17	286
	1.0	$1.6 \cdot 10^{-7}$	3.8	16	294
C_4H_4S in NaY	5.3	no T_1 -minimum			
	3.7	no T_1 -minimum			
	2.0	$1.1 \cdot 10^{-7}$	4.2	14	323
	1.2	$1.3 \cdot 10^{-7}$	4.2	17	313

D Self diffusion-Coefficient.

$\sqrt{\langle r^2 \rangle}$ Mean Jump Distance.

E_{act} Activation Energy.

half coverage decreases, whereas the activation energy for C_4H_4S remains rather constant over the observed range of coverages. It can be concluded that the small dipole moment of C_6H_5F and C_4H_4S leads to a partial orientation of the molecules in the strong fields of the S_2 -ions which disturbs the strong interaction of the π -electrons with these ions as it is observed for the benzene molecules.

To study the influence of the S_2 -ions samples of LaY, HY and "Ultrastable"-Y have been prepared. The temperature functions of T_1 and T_2 of these samples have been summarized in the Figure 2. The distributions of correlation times are considerably broadened compared with the NaX and NaY. In LaY, two regions of different T_2 are observed, the relative amounts of which vary almost over the whole range of temperatures. T_1 shows only one component. Here from an average life time of the molecules in the state with the lower mobility of 10 ms can be estimated for 300 K. HY shows two regions in T_1 and T_2 indicating rather low exchange rate between the two states of a strong bonding of the fixed molecules. The "Ultrastable"-Y shows the rare case of a T_2 minimum, indicating the presence of a small region with a short correlation-time and a variety of states with long τ_c which are in a rapid molecular exchange. Summarizing, the removal of the cations result in an increased mobility of the regions with good mobility which can be seen from the decreased temperatures of the T_1 -minima compared with NaY. In all three types sorption sites with varying strength and ability to exchange molecules with the more mobile phase can be observed, which seem to be characteristic for the type of the modified zeolite. The nature of these sites may be best characterized by definite lattice defects created by the sample preparation.

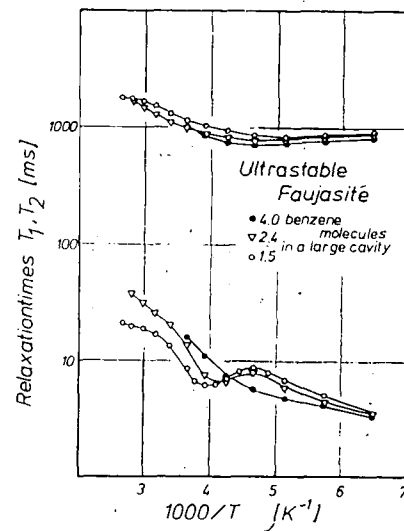
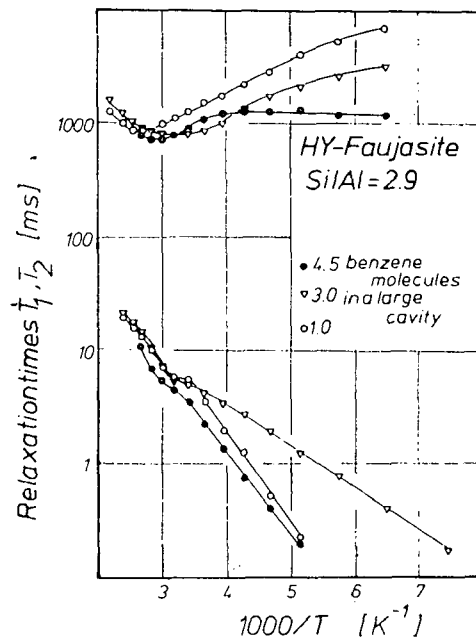
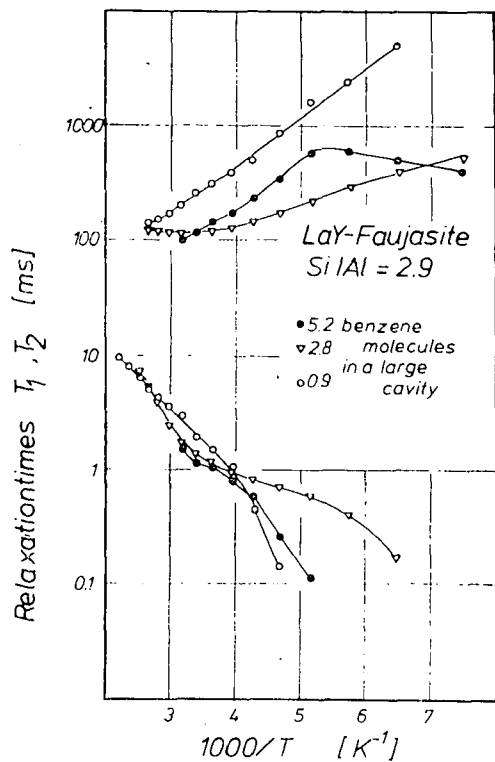


Fig. 2. Temperature behaviour of the relaxation times T_1 and T_2 for benzene in LaY, HY and "Ultrastable"-Y.

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ISOMERIZATION AND CRACKING OF SATURATED HYDROCARBONS ON HYDROGEN-MORDENITE AND PLATINUM-HYDROGEN-MORDENITE CATALYSTS

By

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Cracking and isomerization of *n*-hexane, 2-methylpentane, 2,4-dimethylpentane and *isooctane* have been studied at 250 °C and 400 °C on hydrogen-mordenite and 0.6% platinum-hydrogen-mordenite.

On hydrogen-mordenite, at 400 °C, no isomerization is observed and the selectivities are roughly those expected from a classical carbonium ion mechanism in which the adsorption-desorption of the alkanes constitutes the rate-determining step. At 250 °C, products from cracking are mainly saturated hydrocarbons with very small quantities of C₁, C₂ but comparatively large amounts of C₄, C₅ resulting from bimolecular reactions among the products.

Isomerization occurs on platinum-hydrogen-mordenite at both temperatures, but only at 250 °C on hydrogen-mordenite. Hence it is suggested that the rate-limiting step is no longer the formation and desorption of carbonium ions but rather their isomerization and β -scission.

Introduction

Cracking and isomerization of hydrocarbons constitute the major industrial application of zeolite catalysis in petroleum chemistry [1]. Synthetic mordenites in particular are known to be very active in this field [2-4] and their use will probably become more and more widespread in the near future.

Carbonium ions are the most commonly proposed intermediates for the acid catalyzed isomerization and cracking of alkanes [4, 5] according to the mechanism presented in Fig. 1. The most frequent ways of forming carbonium ions from alkanes, (reactions (1) and (4)), are: direct cracking of alkanes by protons, hydride abstraction by Lewis acid sites or protons of Brønsted acid sites, or intermolecular hydride transfer from the alkane to a preadsorbed carbonium ion. These carbonium ions can then undergo what POUTSMA calls "three basic reactions" [4]: intermolecular rearrangements (2), β -scission (3,3') and hydride transfer.

Our objective was to study the main factors that can affect the formation and transformation of carbonium ions and, therefore, change the selectivities of the reaction. The effect of the structure of the reactant itself was studied by using 4 alkanes: *n*-hexane, 2-methylpentane, 2,4-dimethylpentane and *isooctane*. The influence of the reaction temperature was investigated by comparing the results obtained at

400 °C and 250 °C. Finally, the effect of the addition to the mordenite, of a metal component which can dehydrogenate the alkane into alkenes (reactions (1') and (4')), and hence facilitate the formation of carbonium ions, was studied by using a platinum-hydrogen-mordenite catalyst.

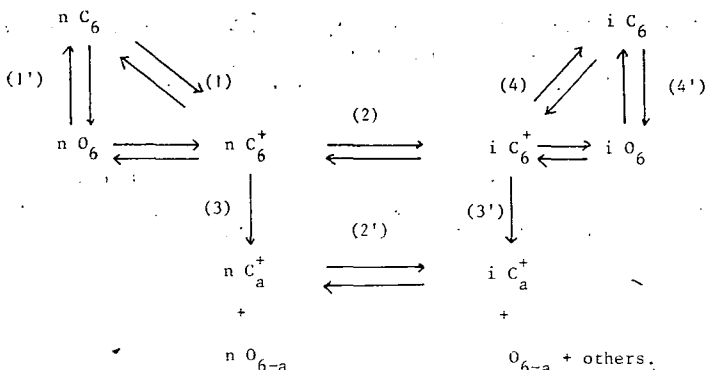


Fig. 1. Carbonium ion mechanism for *n*-hexane cracking and isomerization: *n* normal; *i* isomeric; C_6 hexane; O_6 hexene; C^+ carbonium ion $1 \leq a \leq 4$

Experimental part

All the reactants were Fluka pure grade reagents percolated through alumina before use.

The 900-H zeolon hydrogen-mordenite (H-M) was purchased from Norton. Each sample was preheated overnight at 500 °C under hydrogen. The platinum-hydrogen-mordenite (Pt-H-M) was obtained by impregnation of the hydrogen-mordenite with an aqueous solution of H_2PtCl_6 and reduced overnight in hydrogen at 500 °C. The H_2 — O_2 gravimetric titration of the 0.2, 0.6 and 1 w% Pt-H-M gives respectively a metal surface area of 0.37, 0.6 and 1.0 m² per gram of catalyst (Pt dispersion 80%, 42% and 36% respectively).

All the results were established in a dynamic flow reactor with 0.1 atmosphere hydrocarbon pressure and 0.9 atmosphere hydrogen pressure.

Table I

Activities (Mole hr⁻¹g⁻¹) of Hydrogen-Mordenite (H-M) and 0.6% Platinum-Hydrogen-Mordenite (0.6% Pt-H-M) after 20 min reaction time (a_{20}) and after deactivation extrapolated at zero conversion (a_0)

Catalysts		Isooctane		n-Hexane		
		$10^4 a_{20}$	$10^4 a_0$	$10^4 (a_1)_0$	$10^4 (a_c)_0$	$(a_1)_0 / (a_c)_0$
		(cracking)		(Isomerization)	(cracking)	
H-M	400 °C	45	5.5	0.05	2.2	0.02
	250 °C	10-15	1.5	0.6	0.75	0.8
0.6 % Pt-H-M	400 °C	1200	400	160	200	0.8
	250 °C	55	15	10	1.5	6.6

The analysis of the reaction mixture was performed on a Perkin-Elmer F—20 gas-chromatograph equipped with a S. C. O. T. capillary column of squalane.

The activity of all the catalysts decreased very rapidly during the first 2 hours of use, then became stable. For *isooctane* cracking, the activity after 20 minutes reaction time (a_{20}) of the hydrogen-mordenite is approximately 10 times the extrapolated activity after deactivation (a_0), while on platinum-hydrogen-mordenite $a_{20} \approx 3a_0$ (Table I). The product distribution was determined after deactivation of the catalyst and at a very low conversion (less than 5%).

Results and discussion

Hydrogen-mordenite

At 400 °C, the main products are those expected from carbonium ion β -scission (Tables II and III). The distribution is almost the same as on silica-alumina [6]: *n*-hexane and 2-methylpentane give mainly C_3 products, 2,4-dimethylpentane mainly C_3 and C_4 products and *isooctane* C_4 products. However, if one looks at the product distribution in detail, it appears not to correspond exactly to a primary cracking of carbonium ions resulting from the reactant.

The amounts of C_1 and C_2 are always larger than the amounts of the complementary heavy products: one finds 4.4% C_1 and 16.6% C_2 from *n*-hexane while the corresponding amounts of C_5 and C_4 are only 0.5% and 10.5% respectively (Table II).

Table II

Cracking of *n*-hexane and 2-methylpentane. Product composition (mole %)

Starting material	Catalysts Products	H—M		0.6 % Pt—H—M	
		400 °C	250 °C	400 °C	250 °C
<i>n</i> -Hexane	Methane	4.4	0	0.2	0
	Ethylene	12	0	0	0
	Ethane	4.6	0.5	4.7	1.3
	Propene	28.5	0.2	6.3	0
	Propane	39.5	43.9	72.2	31.2
	Isobutene	1.7	0	0.9	0
	Isobutane	3.6	22.1	4.7	39.2
	<i>n</i> -butane	4.2	17.1	6.3	8.3
	2-butene	1	0	0.5	0
	Isopentane	0.5	7	1.8	15.7
	<i>n</i> -pentane	0	9.2	2.4	4.3
2-methyl-pentane	Methane	6.3	0	0.75	0
	Ethylene	12.5	0	0	0
	Ethane	4.6	1.2	4.9	4.6
	Propene	33.2	0.85	1.3	0
	Propane	30.7	33.9	81.5	21.4
	Isobutene	0.4	0	0.05	0
	Isobutane	6.7	34.15	4.1	42.5
	<i>n</i> -butane	1	14.45	4.3	7.7
	2-butene	0.8	0.2	0.1	0
	Isopentane	3.8	12.8	2.25	21.6
	<i>n</i> -pentane	0	2.45	0.75	2.2

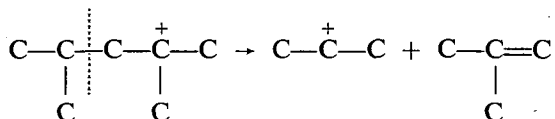
Table III
Cracking of 2,4-dimethylpentane and isooctane. Product composition (mole %)

Starting material	Catalysts Products	H—M		0.6% Pt—H—M	
		400 °C	250 °C	400 °C	250 °C
2,4-dimethyl-pentane	Methane	0.4	0.05	0.4	0
	Ethylene	2.1	0	0	0
	Ethane	0.2	0.15	2.2	0
	Propene	38.6	2.45	1.1	0
	Propane	7.0	27.4	47.0	42.0
	Isobutene	4.2	0.6	4.6	0
	Isobutane	45.0	47.6	34.7	46.5
	n-butane	0.2	9.5	7.3	3.0
	2-butene	2.1	0.15	0.4	0
	Isopentane	0.2	6.7	0.2	4.8
	n-pentane	0	1.2	0.1	0.5
	Hexanes	0	4.2	2.0	3.2
Isooctane	Methane	11.4	0	2.5	0
	Ethylene	3.7	0	0	0
	Ethane	2.8	0	2.2	0
	Propene	14.6	0.8	0	0
	Propane	9.7	13.7	7.2	7.8
	Isobutene	15.8	7.6	16.0	0
	Isobutane	28.35	54.8	54.5	74.0
	n-butane	1.8	11.6	15.0	11.5
	2-butene	7.1	0.4	0	0
	Isopentane	2.6	7.9	1.4	5.1
	n-pentane	0.8	1.9	1.2	1.1
	Pentenenes	1.3	0.7	0	0
	Hexanes	0.05	0.6	0	0.5

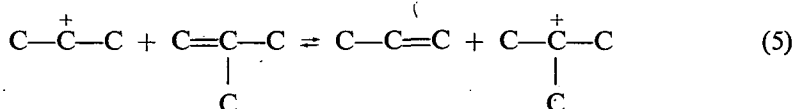
This implies that the alkenes or carbonium ions formed in reactions (3) and (3') undergo a secondary cracking before desorption.

The quantity of alkenes is in every case smaller than the amount of alkanes. This result is generally supposed to be due to hydrogen transfer with formation of aromatics or coke [7]. No aromatics are detected here, but the catalyst is deactivated by coke formation (Table I).

Another observation is that 2,4-dimethylpentane yields *isobutane* and *propane* (Table III) instead of *propane* and *isobutene* according to:



This indicates that a reaction of proton transfer (reaction (5)) takes place very readily on the surface:



No isomers of the starting material are detected but one observes an unexpected formation of *i*-C₄ from *n*-hexane (Table II) and *n*-C₄ from *isooctane* and 2,4-dimethylpentane (Table III). The fact that no isomers of the starting material are observed means that (1) and (4) or (2) are slow compared to (3) and (3'). Since isomeric fragments are found among the products, reactions (2) and (2') must take place at an appreciable rate. Moreover it is known that butanes are much more difficult to isomerize than larger alkanes [8—9]. Thus, the principal way in which the isomeric fragments are formed is probably (2) followed by (3'). One must then conclude that the carbonium ion formation and desorption are rate-determining.

At 250 °C, the selectivities differ markedly from what is observed at 400 °C and one notices especially that isomerization now accompanies cracking except for *isooctane*.

The light products are formed in very small quantities but the C₄, C₅ and C₆ products are found in rather large amounts (Tables II and III). For example, no C₁ and C₂ are formed from *n*-hexane whereas one finds respectively 16% and 39% of C₅ and C₄. However, no products heavier than the reactant are found. All the products are mainly saturated and very few alkenes are found. The large amount of heavy products (C₄, C₅ and C₆) can only be accounted for by supposing that a bimolecular intermediate is formed, either between two molecules of reactant, or one molecule of reactant and one molecule of product, or between two molecules resulting from a primary cracking of the reactant. The primary products of cracking (alkenes and carbonium ions) are highly reactive and may interact together very readily through alkylation which is the reverse reaction of β -cracking of carbonium ions. This reaction will occur very rapidly especially if small, unstable, primary carbonium ions are involved [10], with a consequent decrease in the amount of light hydrocarbons and alkenes and an increase in the amount of heavier products. The formation of a dimer of the rather unreactive starting alkane [11] is unlikely without its previous transformation into alkenes. Moreover this should lead to products heavier than the reactant, but this is not observed.

At this temperature, cracking is only 3 to 4 times slower than at 400 °C (apparent activation energy: 5 kcal mole⁻¹) whereas isomerization is up to 10 times faster at 250 °C than at 400 °C (Table I). The existence of isomerization shows that at 250 °C the cracking of carbonium ions (3 and 3') is no longer infinitely faster than their desorption (4) as it is the case at 400 °C. Adsorption-desorption of alkanes is no longer rate-limiting. Moreover, the peculiar enhancement of the overall isomerization rate (Table I) leads one to suppose that the formation and desorption of the carbonium ions (1 and 4) themselves occur at a higher rate than at 400 °C. This phenomenon can easily be accounted for by assuming that these reactions involve intermolecular hydride transfer between alkanes and carbonium ions at the surface. This exchange would be more important at a lower temperature because of a larger concentration of adsorbed species on the catalyst.

Platinum-hydrogen-mordenite

At 400 °C the fact that platinum has been deposited on the mordenite has an effect similar to a lowering of the reaction temperature: disappearance of alkenes among the products and also a decrease in the amount of C₁, C₂ products and an increase in that of C₄, C₅ and C₆ (Tables II and III). But the main point is that the cracking

activity is considerably increased and that an important isomerization activity appears (Table I). The isomerization to cracking ratio in the case of *n*-hexane increases in the same way as when the reaction temperature is lowered on hydrogen-mordenite.

The effect of platinum content (Figure 2) or metal area on the activity is typical

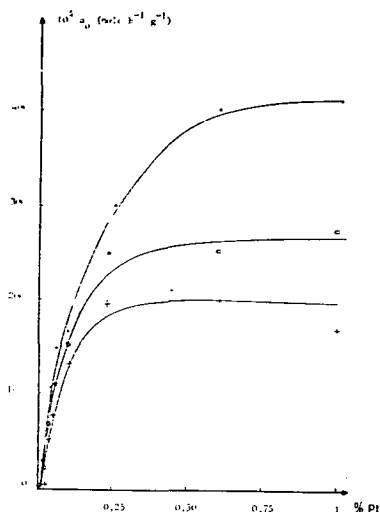


Fig. 2. Influence of platinum content on the activity of platinum-hydrogen-mordenite at 400 °C: • cracking of isooctane; ○ cracking of *n*-hexane; + isomerization of *n*-hexane.

plied by 15 (Table I). Thus, the ratio of isomerization to cracking is highly increased. One can again assume that the rate of adsorption-desorption of the alkane is increased by adding (1') and (4') to (1) and (4). The weakness of the effect of platinum deposit is probably due to the fact that at this temperature the metal area is not sufficient to attain the equilibrium between the alkanes and corresponding alkenes.

Conclusion

The classical mechanism involving carbonium ions as intermediates can explain the results of cracking and isomerization of alkanes on hydrogen-mordenite and platinum-hydrogen-mordenite. At 400 °C, the formation and desorption of carbonium ions is rate-determining for cracking. Isomerization does not take place because the desorption of isomeric carbonium ions is slow compared to their β -scission. A decrease in reaction temperature or an addition of platinum to the hydrogen-mordenite improves the rate of adsorption and desorption of carbonium ions and consequently favors isomerization compared to cracking. The alkenes and carbonium ions resulting from cracking react together. This reaction is faster at 250 °C because of the larger concentration of adsorbed species.

of a bifunctional behaviour: the activity first increases proportionally to platinum content, then remains constant. For *n*-hexane a metal area of approximately 0.4 m²g⁻¹ (0.2 w% Pt) is sufficient to obtain the maximum level of activity. On the catalysts with high platinum content (metal area >0.4 m²g⁻¹) the carbonium ion formation occurs readily through dehydrogenation of the reactant into alkenes (1'). The limiting step for the cracking reaction becomes the β -cracking of the carbonium ions (3 and 3') while (2) is the limiting step for isomerization. This effect of platinum demonstrates that an increase in the rate of carbonium ion formation improves the selectivity in isomerization as opposed to cracking, and this provides good evidence for our interpretation of the effect of lowering the reaction temperature.

At 250 °C the effect of platinum is much less pronounced than at 400 °C. The activity for *n*-hexane cracking only doubles while the isomerization activity is multi-

Acknowledgments

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STABILITY AND REGENERABILITY OF COPPER-EXCHANGED ZEOLITE CATALYSTS FOR THE CYCLODIMERIZATION OF BUTADIENE

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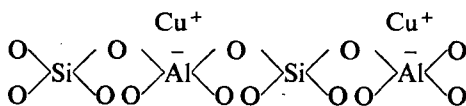
A study has been made of the stability and regenerability of monovalent copper-containing zeolite Y catalysts for the selective cyclodimerization of butadiene to 4-vinylcyclohexene. It is shown that the stability of catalysts prepared by reduction of divalent copper-exchanged zeolites can be considerably enhanced when ammonia is used as the reducing agent and the activation conditions are chosen such that ammonia remains selectively chemisorbed on acidic sites. In addition such catalysts, in contrast to those prepared by direct exchange with monovalent copper, are fully regenerable.

Introduction

Copper-exchanged zeolites, particularly those having the faujasite structure (*i.e.* zeolites X and Y), have been shown to be highly active and selective catalysts for the cyclodimerization of butadiene to vinylcyclohexene [1—3]. In the active form of the catalyst the copper is in the monovalent state. The active form can be prepared in the following two ways:

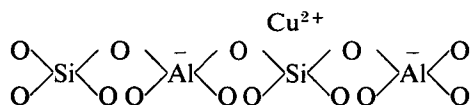
- (1) by direct ion exchange of the parent sodium form of the zeolite with a solution containing monovalent copper in the absence of air (denoted Cu⁺-zeolite catalysts);
- (2) by ion exchange of the parent zeolite with a solution containing divalent copper, followed by mild *in situ* reduction to the monovalent form (denoted Cu²⁺-zeolite catalysts).

In the first case the stoichiometric structure is quite simple, with each Cu⁺ ion balancing the negative charge associated with one tetrahedrally coordinated aluminium in the zeolite framework:



However, in the second case, the stoichiometric structure prior to reduction is such that each Cu²⁺ ion balances the negative charges on two framework aluminium ions:

i.e.



Hence, on reduction of divalent copper to the monovalent form a charge imbalance arises between the zeolite framework and the exchangeable cations.

Previous kinetic studies [4] on the reduction of divalent-copper-exchanged zeolites X and Y with mild reducing agents, such as butadiene and ammonia, showed that the rate of reduction was second order in the copper concentration. This suggested the involvement of (divalent) oxide ions in the reduction. A mechanism was therefore proposed according to which, in the presence of zeolitic water (lower dehydration temperatures), BRÖNSTED acid sites are formed.

In the present paper it is shown that this difference in stoichiometric structure is particularly important with regard to stability and regenerability of the catalysts used for the butadiene cyclodimerization reaction.

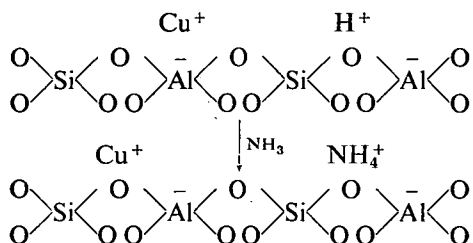
Results and discussion

Catalyst stability

Although monovalent copper-containing zeolites are highly selective catalysts for the dimerization of butadiene to 4-vinylcyclohexene, catalyst stability is often quite low. The deactivation is almost certainly caused by the deposition of polymers of butadiene on the surface of the catalyst.

In agreement with previous observations [3] we have also found that catalysts prepared by direct exchange with monovalent copper ions are more stable than those prepared by reduction (in this case using butadiene feed as reducing agent) of divalent-copper-exchanged zeolites (see Fig. 1). This is readily understood in terms of the differences in stoichiometry which, as previously discussed, lead to the formation of BRÖNSTED acid sites in the latter case. Thus the surface acidity introduced into reduced Cu^{2+} -zeolite Y leads to a higher rate of deposition of butadiene polymer on the surface of the catalyst and hence a faster rate of deactivation.

However, as previously demonstrated [3, 4], ammonia is also a very effective reducing agent for the preparation of monovalent copper from Cu^{2+} -zeolites. In this case excess ammonia could conceivably react with the acid sites generated during reduction to form ammonium ions which should be stable under the rather mild reaction conditions (90–100 °C), *i.e.*



This points to a possible method of neutralizing the surface acidity and thereby increasing the catalyst stability. However, this requires activation (nitrogen stripping) conditions such that excess ammonia is removed from the dimerization sites (*i.e.* monovalent copper) but remains chemisorbed on the acid sites. In general, the decomposition of ammonium ions on zeolites takes place at temperatures above 300 °C [5], indicating that, with the correct choice of catalyst activation temperature, ammonia neutralization of acid sites should be feasible.

The results obtained by reducing a Cu^{2+} -Y zeolite catalyst with ammonia at 200 °C (6 h at 3 NI/h) and then stripping it with N_2 (16 h at 3 NI/h) at temperatures of 200 and 300 °C are shown in Fig. 2a. Clearly, the results fully confirm predictions in that the lower activation temperatures results in a catalyst with a lower initial activity but a considerably higher stability (*i.e.* 0.06 and 0.45 conversion percentage points loss per hour for 200 and 300 °C, respectively). In fact, the stability following activation at 200 °C is now comparable with that attained using Cu^+ -Y catalysts (see Fig. 1).

Further evidence in support of the above conclusions is obtained from thermogravimetric and mass spectrometric data (see Fig. 3a) of a spent Cu^{2+} -Y catalyst. Mass spectrometric analysis of effluent gas during programmed heating in a nitrogen atmosphere clearly indicates that residual ammonia is present on the spent catalyst and is only removed at 450 °C. Such a temperature is consistent with the decomposition of ammonia bound to strong acid sites [5].

Catalyst regenerability

In the previous section it has been shown that by the appropriate choice of reducing agent and activation conditions Cu^{2+} -Y catalysts can be prepared which are comparable in stability to those prepared by direct exchange with monovalent copper *i.e.* Cu^+ -Y catalysts. However, even at this level of stability (*i.e.* approximately 0.05 conversion percentage points loss per hour) long-term continuous operation will necessitate periodic restoration of the original catalytic activity. Since rejuvenation

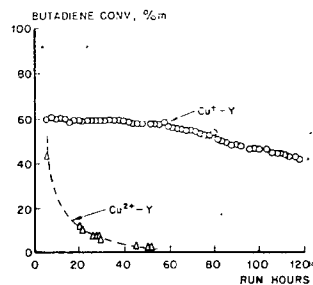


Fig. 1. Comparison of catalytic stabilities of Cu^+ -Y (butadiene-reduced) and Cu^{2+} -Y catalysts, N_2 activation 300 °C, $T = 100$ °C, $P = 25$ bar, $\text{LHSV} = 1.1 \text{ l.l}^{-1} \cdot \text{h}^{-1}$.

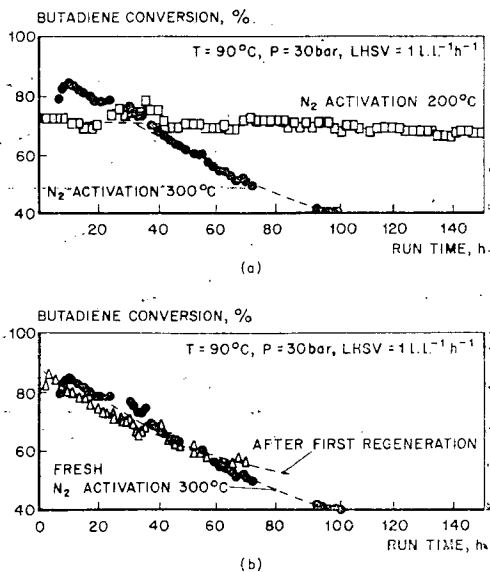
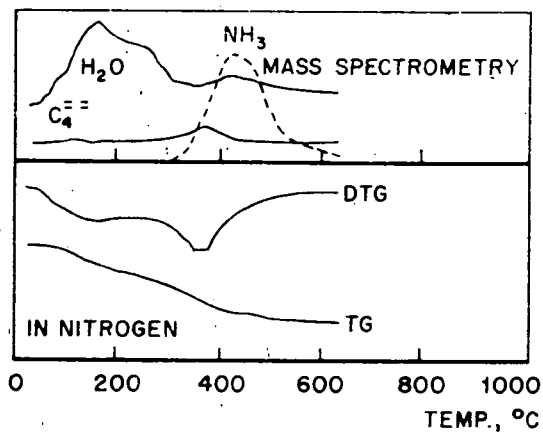
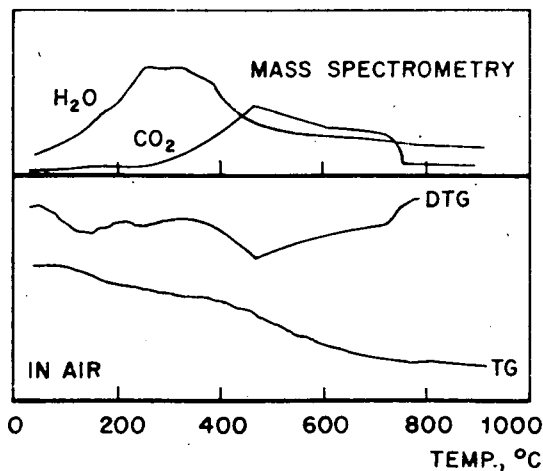


Fig. 2. Butadiene dimerization over Cu^{2+} -Y catalyst

of the catalyst would be preferable to replacement, we have investigated the relative merits of $\text{Cu}^+ \text{-Y}$ and $\text{Cu}^{2+} \text{-Y}$ catalysts with regard to regenerability. Powder X-ray diffraction studies showed that on heating $\text{Cu}^+ \text{-Y}$ in air, above 330°C , CuO is formed irreversibly as a separate crystalline phase. This is not the case for $\text{Cu}^{2+} \text{-Y}$ which displays good thermal stability up to 800°C and is therefore a promising candidate



(a)



(b)

Fig. 3. Thermogravimetry (TG) and differential thermogravimetry (DTG) (with effluent gas mass spectrometry) of spent $\text{Cu}^{2+} \text{-Y}$ catalyst

for regeneration. Thermal analysis data, obtained in air, for a spent Cu^{2+} -Y catalyst (see Fig. 3b) show that even under continuous temperature programming all carbonaceous residues are removed at 760 °C and that the zeolite structure remains intact up to 850 °C (consistent with the X-ray data).

A polymer burn-off was accordingly carried out on a spent Cu^{2+} -Y catalyst which, over a 100 h operating period, had declined in activity from 85 to 40% butadiene conversion (see Fig. 2b). As shown in Fig. 2b, the initial activity and the rate of decline in activity of the regenerated catalyst are, within experimental error, the same as those of the fresh catalyst.

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CARBON-13 NMR STUDY OF *n*-BUTENE ISOMERIZATION IN CaNaY TYPE ZEOLITES

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Measuring highly resolved carbon-13 nmr spectra, the isomerization of *n*-butenes adsorbed on CaNaY type zeolites has been investigated at temperatures from 300 to 350 K. Relative equilibrium concentrations as determined from nmr line intensities fairly well agree with known data for the thermal equilibrium of *n*-butene isomers in the gas phase. The application of partially ¹³C enriched but-1-enes enabled a detailed study of the transformation of the different groups during the double bond isomerization. If but-1-ene $^*\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3$ (* denotes the labeling) was used an enrichment of carbon-13 nuclei was only found in the methyl groups of *cis*- and *trans*-but-2-ene molecules. In agreement with this finding the group $=^*\text{CH}-$ of but-1-ene $\text{CH}_2=^*\text{CH}-\text{CH}_2-\text{CH}_3$ is transformed to the analogous group of *cis*- and *trans*-but-2-enes. Intermediates were not detected under the present conditions of measurements.

At higher temperature additional resonance lines indicate the occurrence of polymerization reactions.

1. Introduction

Some years ago it could be shown that the application of carbon-13 Fourier transform nmr techniques enables the investigation of highly resolved nmr spectra of adsorbed molecules with natural abundance of carbon-13 nuclei [1—3]. In this work a simple conversion (double bond isomerization of *n*-butenes adsorbed in CaNaY zeolites) will be studied to check which statements on a heterogeneous catalytic reaction are possible. The main problem is to correlate the resonance lines occurring during the catalytic process to carbon atoms of molecules or intermediates of the sorbate. For that purpose the use of carbon-13 enriched molecules is of great importance. Thus, after a description of experimental conditions (Chapter 2) spectra are discussed which resulted after conversions of but-1-ene with a carbon-13 enrichment in positions $=\text{CH}_2$ and $=\text{CH}-$, respectively (Chapter 3). Conclusions are summarized in Chapter 4.

2. Experimental conditions

Using an HX 90 Fourier transform nmr spectrometer, the ¹³C nmr spectra have been measured at 22.63 MHz. The cylindrical sample glass tubes have an external diameter of 10 mm. The capillary containing the lock substance (DMSO-d₆) is fixed in the axis of the tube so that it is uniformly surrounded by the sorbate. This special kind of sample preparation excludes the investigation of fast reactions.

CaNaY type zeolites (0...88% of Na^+ replaced by Ca^{++} ions) were prepared by means of ion exchange starting from a NaY type zeolite ($\text{Si}/\text{Al}=2.6$, VEB Chemiekombinat Bitterfeld-Wolfen, G.D.R.).

First of all the zeolites were slowly heated up to 670 K and evacuated during 20 h resulting in a final pressure of about 10^{-3} Pa. Then the butenes were adsorbed in vacuo at 77 K. This treatment yields total numbers of zeolitic OH groups as shown in Table I which have been measured by means of proton nmr wide line techniques [4].

Table I

Number N_{OH} of hydroxyl groups per large cavity (± 0.4 OH per large cavity) for different n CaNaY type zeolites (n denotes the percentage of Na^+ ions replaced by Ca^{++})

n	0	20	40	63	74	88
N_{OH}	0.2	0.4	0.5	0.6	0.9	1.0

The sorbates were normal but-1-ene purum (Fluka AG., Buchs-Switzerland), $^*\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3$ and $\text{CH}_2=^{**}\text{CH}-\text{CH}_2-\text{CH}_3$ with a carbon-13 enrichment of 15% (*) and 50% (**), respectively. For the preparation of the labelled species at first butanols were synthesized starting from $\text{Ba}^{13}\text{CO}_3$ (Isotop, Moscow-U.S.S.R.) The dehydration of the respective butanols was carried out in a flow reactor with a γ -alumina catalyst.

3. Results and Discussion

^{13}C -spectra of normal but-1-ene adsorbed on various CaNaY type zeolites

On pure NaY type zeolites a catalytic reaction can be observed in the spectra only when the samples are heated up to 430 K for some hours. If the Ca^{++} exchange is increased to about 65%, the carbon-13 nmr spectra of the adsorbed but-1-ene molecules remain only unchanged if the temperature is less than 330 K. The chemical shifts of the various resonance lines with respect to the neat liquids are slightly less than those of butenes adsorbed in NaY type zeolites [1, 2]. For but-1-ene molecules adsorbed on 88 CaNaY (88% of its Na^+ replaced by Ca^{++}) the conversion rate at room temperature is so fast that the process cannot be studied by observing the line intensities unless the temperature is lowered. Thus, the present investigations were carried out with (65...70) CaNaY zeolites allowing a convenient measurement at room temperature or higher temperatures. In the interval from 330 to 350 K the intensities of $=\text{CH}_2$ and $=\text{CH}-$ resonances of the normal but-1-ene (*cf.* [2]) decreased while an olefinic resonance line occurs with a resonance shift of $\sigma \approx 1.3$ ppm (upfield with reference to benzene $\sigma_{\text{C}_6\text{H}_6}=0$). The dublett splitting of this line in the spectra without proton decoupling indicates the presence of a $=\text{CH}-$ group. An assignment of this line to the $=\text{CH}-$ groups of *cis*- and *trans*-but-2-ene (which overlap mutually in the beginning of the reaction is not unambiguous since their CH_3 - resonances are difficult to detect. Presumably, the methyl resonance of *cis*-but-2-ene overlaps with the CH_3 group of but-1-ene.

¹³C-spectra of $^*\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3$ adsorbed on 67 CaNaY type zeolites

In Fig. 1 spectra for a pore filling factor of $\theta=0.6$ are given which show the intense line of the labelled $=\text{CH}_2$ group besides signals due to the other carbon nuclei of but-1-ene with natural abundance of ¹³C nuclei. The weak line at $\sigma \approx 1.3$ ppm (upfield with reference to benzene) is obviously due to but-2-ene impurities (about 10% *cis*- and 4% *trans*-but-2-ene in this sample). After heating to 330 K a resonance line appears at 118 ppm (initially overlapping with the weak signal of the unenriched methyl group of but-1-ene). Simultaneously, the fairly weak resonance at 1.3 ppm becomes more intense. These peaks unambiguously indicate the presence of *cis*-but-2-ene. The signal at $\sigma \approx 112$ ppm is characteristic for the formation of *trans*-but-2-ene. This change in the spectra with time (first order reaction, time constant $t_{1/2} \approx 200$ min at 333 K) demonstrates that the carbon in the terminal group $=\text{CH}_2$ of but-1-ene is converted into methyl groups of *cis*- and *trans*-but-2-ene, respectively. In the equilibrium the *cis/trans* ratio is equal to 1.6 if one takes the carbon-13 nmr peak areas approximately as a measure for the concentration of species. The neglect of possible differences between the Overhauser factors seems to be no source of error because the equilibrium concentrations of but-2-enes (94%) and but-1-ene (6%) at 300 K roughly agree with values obtained by KALLÓ and SCHAY [8] for the thermal equilibrium of butene isomers in the gas phase.

Similar results have been obtained for pore filling factors of $\theta \approx 0.2$ (Fig. 2). Especially, there were also no additional lines which point to an intermediate state or to further conversions.

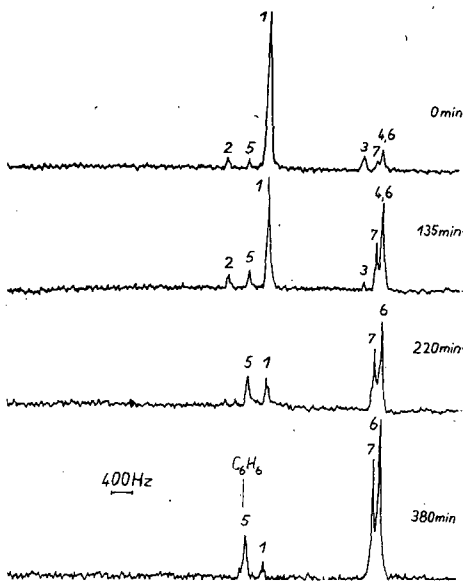


Fig. 1. Carbon-13 nmr spectra of but-1-ene: $^*\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3$ (* denotes a 15% enrichment with carbon-13 nuclei), adsorbed on a 67 CaNaY type zeolite with a pore filling factor of $\theta \approx 0.6$, during the double bond isomerization: Temperature of measurement 333 K, 4 K scans, pulse interval 0.2 s. Assignment of carbons: but-1-ene: 1 ($=\text{CH}_2$, enriched), 2,3,4($=\text{CH}-$, $-\text{CH}_2-$, $-\text{CH}_3$, respectively, with natural abundance of nuclei) *cis*-but-2-ene: 5 ($=\text{CH}-$), 6 ($-\text{CH}_3$, enriched with ¹³C after reaction) *trans*-but-2-ene: 5 ($=\text{CH}-$), 7 ($-\text{CH}_3$, enriched with ¹³C after reaction)

¹³C spectra of $\text{CH}_2=^*\text{CH}-\text{CH}_2-\text{CH}_3$ adsorbed on 67 CaNaY type zeolites

All nmr spectra measured here had a width of 12.5 kHz and were centered near the ¹³C nmr resonance of benzene. Since in the low frequency domain no lines appeared, only the right half of these absorption spectra is plotted in Fig. 3.

In this Figure typical spectra are shown for systems with a pore filling factor of $\theta \approx 0.6$ and a carbon-13 enrichment of 17%. Besides signals of the labelled group

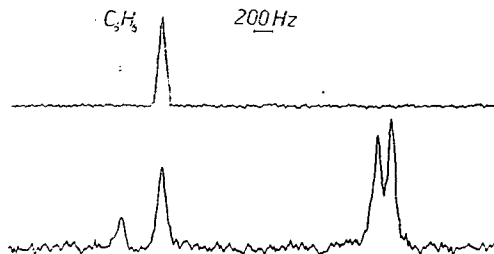


Fig. 2. Carbon-13 nmr spectra of but-1-ene $^*\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3$ (* denotes a 15% enrichment with carbon-13 nuclei) adsorbed on a 67 CaNaY type zeolite with a pore filling factor of $\theta \approx 0.2$: Top spectrum (8 K scans): measurement at room temperature. Bottom spectrum (4 K scans): measurement during the reaction at 333 K.

$=\text{CH}-$ of but-1-ene no other peaks could be detected below 310 K which should be attributed to other carbon-13 enriched groups. At 323 K and higher temperatures the group $=\text{CH}-$ of but-1-ene transforms into the group $=\text{CH}-$ of the but-2-enes. The assignment of the new line is based upon its resonance frequency ($\sigma \approx 1.3$ ppm upfield to benzene) and its doublet structure in spectra without proton decoupling.

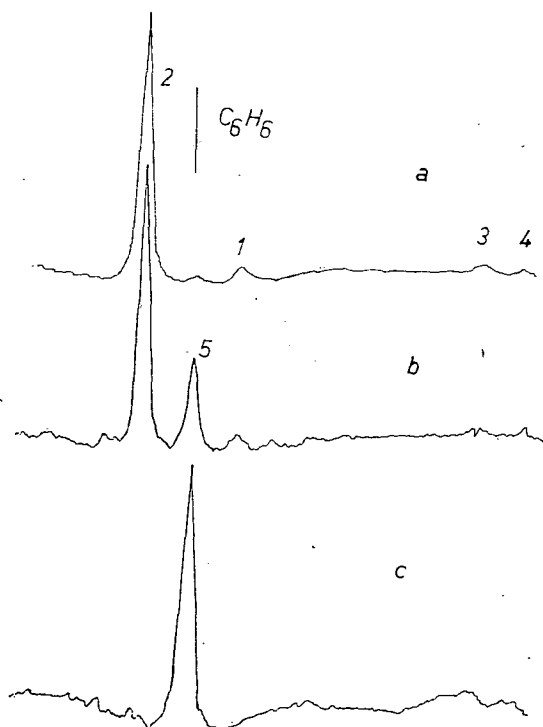


Fig. 3. Carbon-13 nmr spectra of but-1-ene $\text{CH}_2=^*\text{CH}-\text{CH}_2-\text{CH}_3$ (* denotes a 17% enrichment with carbon-13 nuclei), adsorbed on 67 CaNaY type zeolites with a pore filling factor of $\theta \approx 0.6$, during the double bond isomerization. Measurements a) at 300 K before reaction (16 K scans), b) at 350 K during the reaction (8 K scans), c) at 300 K after reaction (8 K scans). Pulse interval 0.16 s.

Assignment of carbons:
but-1-ene: 2 ($=\text{CH}-$, enriched), 1,3,4 ($=\text{CH}_2$, $-\text{CH}_2-$, $-\text{CH}_3$, with natural abundance, respectively)
but-2-enes: 5 ($=\text{CH}-$, enriched after reaction).

In agreement with the former spectra (where the methyl resonances of but-2-enes were observed when starting with the $^*\text{CH}_2=$ labelled but-1-ene) this signal can be attributed unambiguously to but-2-enes. It was possible to obtain results also for very low pore filling factors ($\theta=0.07$) in the case of but-1-ene enriched with 50% ^{13}C nuclei in the position $=\text{CH}-$ (Fig. 4). Similarly, a transformation of this group of but-1-ene into the respective group of but-2-ene molecules was found as a consequence of double bond isomerization. The absence of further signals again is typical for the experiments so far. However, as will be discussed in more detail elsewhere [5], much more involved spectra are obtained after heating the samples to temperatures above 360 K. This is due to polymerization reactions where the presence of numerous overlapping lines leads to fairly broad resonances even in the case of high carbon-13 enrichments. This line broadening is probably the reason for the (apparent) single line spectrum mentioned in [2].

4. Conclusions

i) The application of carbon-13 Fourier transform nmr technique enables the observation and investigation of highly resolved nmr spectra of adsorbed molecules. As could be shown in this work the nmr method is a powerful tool for studying heterogeneous catalytic reactions *in situ*.

ii) The use of molecules enriched with carbon-13 nuclei in defined positions, not only facilitates the assignment of the lines and the measurement of signal for very low pore filling factors, but also enables the investigation of the change of the bond of the respective carbons during the catalytic reaction. Hence, new insights into elementary steps of catalytic processes become possible.

iii) As an example, the *n*-butene isomerization has been investigated at room temperature and higher temperatures using CaNaY type zeolites where 67% of Na^+ ions were replaced by Ca^{++} . This catalytic process has been chosen not only because of the great number of kinetic and spectroscopic work already done [6–10], but also because of the lack of further reactions in the case if the measurements are restricted to a certain temperature interval (300 to 350 K). At temperatures above 350 K polymerization reactions occur which can be inferred from the overlap of numerous lines in that region of ^{13}C resonances where in general signals of aliphatic CH_n ($n=0, \dots, 3$) groups appear.

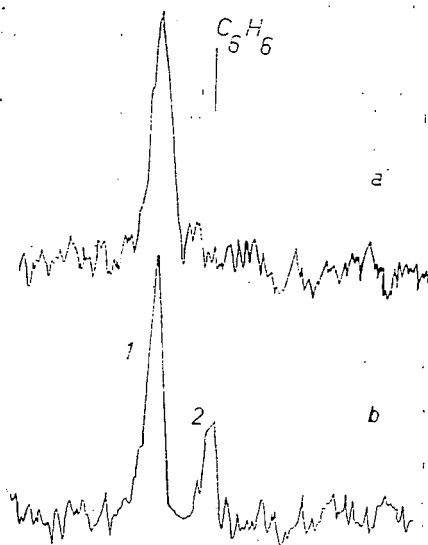


Fig. 4. Carbon-13 nmr spectra of but-1-ene $\text{CH}_2=^*\text{CH}-\text{CH}_2-\text{CH}_3$ (* denotes a 50% enrichment with carbon-13 nuclei), adsorbed on 67 CaNaY type zeolites with a pore filling factor of $\theta \approx 0.07$. Measurements (16 K scans) a) at 300 K before reaction, b) at 340 K during reaction. Pulse interval 0.16 s. Assignment of carbons: 1 and 2 ($=\text{CH}-$ groups of but-1-ene and but-2-enes, respectively). Carbons with natural abundance of ^{13}C nuclei were not detected.

The interpretation of data is based on conversions of but-1-enes which were partially enriched with carbon-13, viz.



and



where * denotes the carbon-13 labelling which amounts to 15 and 50%, respectively.

iv) Within the limits of experimental error the labelled nuclei were found only in the $-\text{CH}_3$ groups and $-\text{CH}=\text{}$ groups of *cis*- and *trans*-but-2-ene if the reaction started with but-1-ene molecules of type (1) and (2), respectively. Hence, a cyclic intermediate structure with four identical carbons can be excluded which, when participating in the conversion, should lead to a random distribution of carbons in the but-2-ene molecules formed.

v) In agreement with conclusions of WEEKS and BOLTON [9], the double bond isomerization of *n*-butenes is a pure intramolecular reaction.

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A THEORETICAL STUDY OF THE SITE SELECTIVITY OF THE CATIONS IN ZEOLITE A. FOR ANTICIPATION OF CATION SITES AND CATALYTIC ACTIVITY

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A theoretical approach was attempted for the interpretation of the site selectivities of the exchangeable alkali and alkaline earth metal cations in zeolite A. The cation-lattice interaction energies comprising the electrostatic, polarization, dispersion, repulsion and charge transfer energies were calculated for the cation at the six- and eight-membered oxygen ring sites in a simplified model of zeolite A structure. As a result, the site selectivities of the cations were determined as follows: Li^+ , Na^+ , Ca^{2+} and Sr^{2+} ions prefer the six-membered oxygen ring site, whereas K^+ , Cs^+ and Ba^{2+} ions prefer the eight-membered oxygen ring site. These results are in good agreement with those obtained experimentally.

Synthetic zeolite A is a crystalline aluminosilicate well known for its industrial applications as an adsorbent and molecular sieve [1]. The characteristic properties of zeolite A are due to the crystal structure which contains interconnected channels and cavities of uniform sizes. In $\text{Na}_{12}\text{-A}$ [2], of which the ideal chemical composition is $\text{Na}_{12}(\text{AlSiO}_4)_{12}$, 12 Na^+ ions are distributed among three kinds of site, i.e., four-, six- and eight-membered oxygen ring sites, and for brevity they are named site III, site I and site II, respectively. The eight sites I in a unit cell are occupied by 8 Na^+ ions and the three sites II are occupied by 3 Na^+ ions. The twelfth Na^+ ion occupies one of the eight sites III. These cations are exchanged easily with various others. The exchangeable cations have their own intrinsic site preferences [3, 4], that is to say, the three kinds of sites in Na-A zeolite are occupied in an order, not at random, by the incoming cations. This site selectivity of the cation is of great importance in understanding of physicochemical properties of zeolite A, such as adsorption and catalysis, because the adsorption of reactant molecules is prevented partly or completely when the large cations are presented at sites II. The site selectivity of cations was first suggested on the basis of adsorption experiments BRECK [1] and REES and BERRY [4] and has been partly confirmed by X-ray diffraction studies. However, there is no theoretical information available in the literature on the site selectivities of various exchangeable cations. We present here a theoretical interpretation of the site selectivity of cations in zeolite A, which are alkali and alkaline-earth metal ions. This is done by evaluating the cation-zeolite lattice interaction energy at each cation site.

Simplified Structure Model of Zeolite A

The bond lengths and angles chosen are those from a single-crystal X-ray diffraction analysis of dehydrated $\text{Na}_{12}\text{-A}$ zeolite [2]. The structure adopted is a simplified model with high symmetry, which allows easy calculation of the potential energy: bond length (Si, Al)-O = 1.66 Å, bond angles O-(Si, Al)-O = 109.4°, Si-O-Al = 154.4°.

According to PAULING, the amount of ionic character of the (Si, Al)-O bond can be calculated to be 50% from the electronegativity difference between (Si, Al) and O atoms. This indicates that both ionic and covalent bonding components of the framework of zeolite A must be considered in the calculation of the cation-lattice interaction energy. In the case of a purely ionic crystal, the framework is made up of Si^{4+} , Al^{3+} and O^{2-} ions strongly joined together throughout the crystal by ionic forces. In the case of a purely covalent crystal, the framework is composed of Si^0 , Al^- and O^0 atoms strongly joined together by covalent forces.

In both cases, it is assumed that the cation is located at a position where the potential energy is minimum at each site.

Energy Calculation

Coulombic electrostatic energy Φ_E

The electrostatic energy between the cation at a given site and zeolite lattice ions can be calculated for various points in the site from the formula

$$\Phi_E = \sum_i \frac{q_M q_i}{r_{Mi}} \quad (1)$$

where q_M and q_i represent the charge of cation (M) and those of zeolite lattice ions (i): +3.5 for Si and Al, -2.0 for O in ionic structure and -1.0 for Al in the covalent structure, respectively, and r_{Mi} is the distance between the cation and lattice ion.

The potential energy of the cation was calculated in order to find the optimum position on the axis throughout the center of each site [2, 5], and the position which gives the minimum electrostatic potential available for the following energy calculations. The axes I and II and the positions of the cation are shown in Fig. 1.

Polarization energy Φ_P

Polarization energy can be represented by the following expression

$$\Phi_P = \frac{1}{2} \alpha_M \left(\frac{d\Phi_E}{dr} \right)^2 \quad (2)$$

where α_M is the polarizability of cation, $(d\Phi_E/dr)$ is the electrostatic field at the cation position along the axis and is obtained from a large scale plot of Φ_E as a function of axial distance, r .

Dispersion energy Φ_D

Several formulae have been proposed to express the dispersion energy. We shall adopt the formula of Kirkwood and Muller for the inverse sixth term and of Kiselev for the inverse eighth and tenth terms.

$$\Phi_D = \sum_i \frac{A_i}{r_{Mi}^6} + \sum_i \frac{B_i}{r_{Mi}^8} + \sum_i \frac{C_i}{r_{Mi}^{10}} \quad (3)$$

where A_i , B_i and C_i are the functions of m (the mass of an electron), c (the velocity of light), α (polarizability) and χ (magnetic susceptibility).

Repulsion energy Φ_R

For calculation, we shall adopt the Lennard-Jones form D/r^{12} as follows:

$$\Phi_R = \sum_i \frac{D_{Mi}}{r_{Mi}^{12}} \quad (4)$$

where D_{Mi} is a constant characteristic of the interacting pair, involving contributions of the electrostatic, polarization and dispersion terms, and this can be calculated on the basis of balancing of attractive and repulsive forces at the cation position.

Stabilization energy due to charge transfer Φ_{CT}

The charge transfer in the ionic structure of zeolite A can be left out of the consideration because of instability of the charge transfer structure. This energy is considered only in the case of the covalent structure. If a cation is present near the center of the six- and eight-membered oxygen rings, the unoccupied orbitals on the cation effectively overlap with delocalized unshared-pair orbitals on the ring oxygen atoms, and some degree of transfer of the unshared-pair electron to the unoccupied orbitals may occur. The stabilization energy is produced by this transfer of an electron. The calculation of the energy is carried out based in Mulliken's charge transfer theory [6]. In a system comprising a cation and several oxygen atoms surrounding it at a given site, the energy of the no-bond structure, E_{NB} , consists of the electrostatic energies between charged ions (cation (M^{n+}) and the framework ions), and one-electron energy of a delocalized unshared-pair orbital on the ring oxygen atoms obtained separately. The energy of the system in the charge transfer structure, E_{CT} , consists of the electrostatic energies among the ring oxygen ions donated an electron, $O^{\delta+}$, and Al^- ions in the framework, the cation accepted an electron $M^{(n-1)+}$ and other cations, M^{n+} , and one-electron energy of the unoccupied orbital on the cation. The latter is ap-

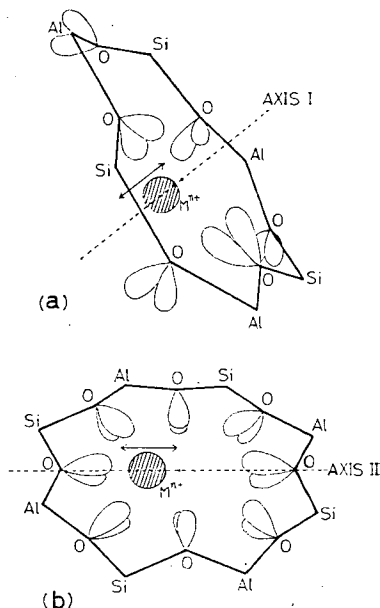


Fig. 1. (a) Site I and symmetry axis I. Unshared-pair orbitals are shown by two lobes on each oxygen. (b) Site II and symmetry axis II. Unshared-pair orbitals are shown by two lobes on each oxygen.

proximated by the electron affinity of the cation. The energy of the resonance structure between the no-bond and charge transfer structures, E_{RES} , is obtained by the roots of the following secular determinant:

$$\begin{vmatrix} E_{\text{NB}} - E_{\text{RES}} & H_{\text{III}} - G_{\text{III}} \cdot E_{\text{RES}} \\ H_{\text{III}} - G_{\text{III}} \cdot E_{\text{RES}} & E_{\text{CT}} - E_{\text{RES}} \end{vmatrix} = 0$$

where G_{III} is the group overlap integral between the two structures and can result in the overlap integral between the delocalized unshared-pair orbital on the ring oxygen atoms and the unoccupied orbital on the cation, and H_{III} is the resonance integral which is estimated by Helmholtz—Wolfsberg approximation. The stabilization energy due to charge transfer, Φ_{CT} , is obtained by the following equation:

$$\Phi_{\text{CT}} = E_{\text{RES}} - E_{\text{NB}} \quad (5)$$

Potential energy of cation in the resonance structure

In ionic and covalent structures, the potential energy of a cation at sites I or II due to the cation-lattice interaction may be expressed as sum of the following terms, respectively:

$$E_{\text{ion}} = \Phi_E + \Phi_P + \Phi_D + \Phi_R \quad (6)$$

$$E_{\text{cov}} = \Phi_E + \Phi_P + \Phi_D + \Phi_R + \Phi_{\text{CT}} \quad (7)$$

The “real” cation-lattice interaction energy in the “real” structure, *i.e.*, the resonance structure between 50% ionic and 50% covalent structures, is obtained as follows:

$$E_{\text{real}} = \frac{1}{2} E_{\text{ion}} + \frac{1}{2} E_{\text{cov}} \quad (8)$$

Analysis of the Energy Calculation Results

Site selectivity of cations

The E_{real} calculated here by eq. (8) is the result for the first incoming cation into dehydrated zeolite $\text{Na}_{12}\text{-A}$ by ion exchange. The energy at site III was not calculated since the Na^+ ion at site III seems to be energetically the most unstable of the twelve Na^+ ions. In fact, the potential energy of the Na^+ ion at site III (-5.77 eV) was much smaller compared with those of other sites. Other cations also may not occupy this site from the beginning of ion exchange. The values of E_{real} at sites I and II are summarized in Table I. Most of the E_{real} value is due to Φ_E and other terms such as Φ_P , Φ_D , Φ_R and Φ_{CT} make less contributions to the value. In Table I there is an appreciate difference in the values of E_{real} for sites I and II. It is reasonable to assume that the cation introduced by ion exchange occupies preferentially the site possessing higher potential energy and that it is more stabilized. Thus, from the comparison between sites I and II in E_{real} , the site selectivity of the exchange cation can be determined (the fourth column in Table I).

Table I
Cation-Lattice Interaction Energies in Zeolites A and Site Selectivities

Cation	Site	E_{real} eV	Site Selectivity	
			this method	experimental
Li ⁺	I	-9.46	I	I [7]
	II	-9.13		
Na ⁺	I	-9.52	I	I [3, 5]
	II	-8.81		
K ⁺	I	-8.51	II	II [4, 8]
	II	-8.63		
Cs ⁺	I	-7.85	II	II [9]
	II	-8.83		
Ca ²⁺	I	-24.21	I	I [5, 8]
	II	-22.90		
Sr ²⁺	I	-23.86	I	I [10, 11]
	II	-22.81		
Ba ²⁺	I	-22.30	II	No data available
	II	-22.52		

Comparison with experimental results

As can be seen in Table I, there is good agreement for all cations between the present and experimental results, except for Ba²⁺ ion. It is interesting that Ba²⁺ ion prefers site II, unlike other alkaline-earth metal cations. Unfortunately, there is no information delineating the cation sites and site selectivity of Ba²⁺ ion in dehydrated Ba-A, because the thermal stability of zeolite A is reduced considerably when Ba²⁺ ions introduced into the crystal, and structure collapse occurs on calcination of hydrated (Ba^{ex}, Na)-A. We expect that the site selectivity of Ba²⁺ ion supposed here will be confirmed by a refined X-ray diffraction analysis when a stable dehydrated sample is obtained.

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RING TRANSFORMATION OF TETRAHYDROFURAN INTO TETRAHYDROTHIOPHENE OVER ALKALI METAL CATION EXCHANGED ZEOLITES

By

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The reaction of tetrahydrofuran and hydrogen sulfide to give tetrahydrothiophene over alkali metal cation exchanged zeolites has been studied. The tetrahydrothiophene yield of 94% is reached with NaX at 340 °C. The catalytic activity is considerably suppressed by adding either hydrogen chloride or pyridine to reactants feed. The reaction mechanism is proposed: Hydrogen sulfide molecules dissociate on basic sites, forming protonic acids and SH⁻ groups and protons thus formed interact with and activate tetrahydrofuran molecules, which, in turn, react with SH⁻ groups to form tetrahydrothiophene. The dissociation of hydrogen sulfide over NaX is confirmed by infrared spectroscopy.

Introduction

Synthetic zeolites usually act as acidic catalysts and have very high activity for the major hydrocarbon transformations *via* carbonium ions such as cracking, alkylation and isomerization. For these reactions, HY zeolites or alkaline earth exchanged zeolites are the most active catalysts, and alkali metal cation exchanged zeolites are the least active [1]. In a previous work, however, it was found that, for the reaction of γ -butyrolactone and hydrogen sulfide, alkali metal cation exchanged zeolites have high activity, while HY has very low, and concluded that the basic sites play important roles in the dissociation of hydrogen sulfide [2]. In another work it was reported that, for the ring transformation of tetrahydrofuran (THF) into pyrrolidine, the presence of protonic sites is essential for the ring-opening step of THF [3]. In this work, the reaction of THF and hydrogen sulfide to give tetrahydrothiophene in order to obtain further information on the role of basic sites in catalysis by alkali metal cation exchanged zeolites and on the mechanism of ring transformation reaction.

Experimental part

THF was distilled prior to each run. Hydrogen sulfide was used as received from commercial source. NaX and NaY were obtained from the Linde Division of Union Carbide Corp. Various cation forms of Y-zeolites were prepared by conventional cation exchange procedure using salt solution. The cation exchanged zeolites were pelleted without a binder and crushed and sized into 9–16 mesh. A continuous flow reactor was used under atmospheric pressure. The reactor was a silica tubing (13 mm

i. d.) placed in a vertical furnace. Tetrahydrofuran was pumped into preheating zone of the reactor containing 10 ml quartz powder. Nitrogen was used as diluent for regulating the initial pressure of reactants. The gaseous materials were fed through flowmeters. Reaction products collected in the receiver were withdrawn at certain intervals during the run and were analyzed by gas chromatography.

Results and discussion

Effect of reaction temperature

The effect of the reaction temperature on the tetrahydrothiophene yield was examined with NaX as a catalyst. The activity decreases gradually with stream hours, and the extent of deactivation increases with reaction temperature. In Fig. 1, the conversion of THF and the yield of tetrahydrothiophene were plotted as a function of reaction temperature. The values of the conversion and the yield are obtained at the stream hours of 2–3 hr. The yield increases with reaction temperature up to 350°C, and through the maximum, decreases at higher temperatures. The selectivity to tetrahydrothiophene is almost 100% below 350°C and decreased at higher temperatures.

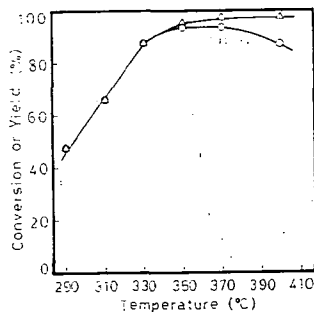


Fig. 1. Effect of reaction temperature on the conversion of THF (Δ) and the yield of tetrahydrothiophene ($\circ$) NaX, $W/F=15.9 \text{ g} \cdot \text{h} \cdot \text{mol}^{-1}$.

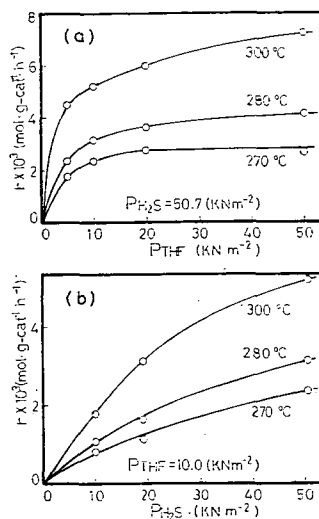


Fig. 2. Dependence of the reaction rate (a) on the partial pressure of tetrahydrofuran (P_{THF}) and (b) on the partial pressure of hydrogen sulfide.

Effect of contact time

Effect of contact time [W/F , W : weight of the catalyst (g), F : molar flow rate ($\text{mol} \cdot \text{h}^{-1}$)] on the yield of tetrahydrothiophene was examined at 340°C with NaX catalyst. The yield increases with contact time and reached 92% at $W/F=15.7 \text{ (g} \cdot \text{h} \cdot \text{mol}^{-1})$. The selectivity to tetrahydrothiophene is always 100% at this temperature.

Kinetics of the reaction

The reaction kinetics was examined with NaX catalyst in the temperature range 270–300 °C under small contact time conditions. The effects of the partial pressures of THF (P_{THF}) and of hydrogen sulfide ($P_{\text{H}_2\text{S}}$) on the reaction rate (r) are shown in Fig. 2. The kinetics could be expressed as

$$r = kP_{\text{THF}}^{0.3}P_{\text{H}_2\text{S}}^{0.7}$$

The apparent activation energy is calculated to be 34 kJ · mol⁻¹.

Catalytic activity of various forms of zeolites

The catalytic activities of various zeolites were examined at 340 °C and the results are given in Table I, from which one can see the following features of the reaction.

- (1) Catalytic activities of alkali cation exchanged zeolites are high, while those of acidic zeolites (HY, MgY) are low.
- (2) Alkali cation exchanged X-zeolites are more active than the corresponding cation forms of Y-zeolites.

These features are same as those found in the reaction of γ -butyrolactone and hydrogen sulfide [3], and are in sharp contrast with those found in ordinary carboniogenic reactions, for which HY is most active and alkali cation zeolites are inactive and Y-zeolites are more active than X-zeolites.

Effect of hydrogen chloride and of pyridine

The above results indicate that basic sites play an important role in the catalysis. In order to get further information on the active centers, the effects of addition of hydrogen chloride and of pyridine on the catalytic activity was examined. MATSUMOTO ET AL. [4] reported that the cracking of cumene over NaY was greatly enhanced by addition of hydrogen chloride to the system. The enhancement of the catalytic activity was ascribed to the formation of Brönsted acid sites by the interaction of hydrogen chloride with NaY. Addition of hydrogen chloride was carried out by passing the hydrogen sulfide stream over the concentrated hydrogen chloride aqueous solution. The result is given in Fig. 3(a), which shows that hydrogen chloride completely inhibits the catalytic activity as found in the reaction of γ -butyrolactone and hydrogen sulfide. It was confirmed that the treatment with hydrogen chloride does not destroy the crystallinity of the zeolite. Thus, it may well be assumed that the deactivation is associated with the poisoning of the active centers, presumably the basic sites by hydrogen chloride.

Pyridine is often used to poison acidic centers. The effect of addition of pyridine on the ring conversion was examined. As seen in Fig. 3(b), the addition

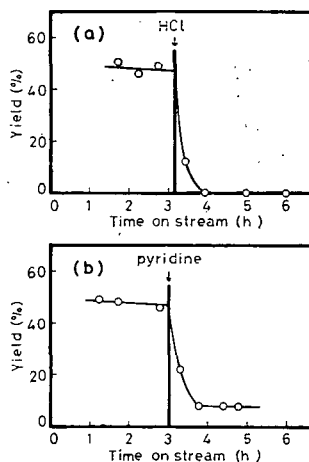


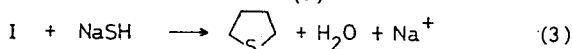
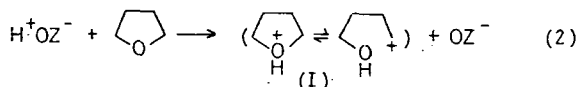
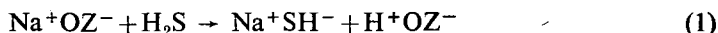
Fig. 3. Effect of hydrogen chloride and of pyridine on the reaction rate. NaX 300 °C, Pyridine added 1.8 mol %

of pyridine to the reactant feed greatly suppressed catalytic activity. The extent of the activity depression depended on the partial pressure of pyridine added. This result is in sharp contrast with that found in the reaction between γ -butyrolactone and hydrogen sulfide, for which the pyridine does not poison but enhances the catalysis.

This result suggests the participation of acidic centers in the reaction. Since NaX has no acidic centers, they must be produced during the reaction, presumably by the dissociation of hydrogen sulfide.

Reaction mechanism

For the reaction of γ -butyrolactone with hydrogen sulfide, the authors proposed a mechanism in which hydrogen sulfide dissociates on the basic sites (AlO_4^-) to form protonic centers and NaSH. The protonic centers may interact with and activate THF molecules. This explains why the presence of pyridine depressed the catalytic activity. The mechanism may be written as



The steps (1)—(2), and (2)—(3) could be concerted. The mechanism is not incompatible with kinetic results.

Dissociation of hydrogen sulfide has been confirmed by IR spectroscopy. Introduction of hydrogen sulfide to NaX produced an OH band at 3650 cm^{-1} and a SH band at 2560 cm^{-1} . Furthermore, the introduction of hydrogen sulfide to NaX preadsorbed pyridine gives a band by pyridinium ions at 1540 cm^{-1} , confirming that the dissociation of hydrogen sulfide gives protonic centers. The same phenomena have been observed by KARGE AND RASKÓ [5], who showed also that the dissociation is easier over NaX than NaY. This is in conformity with the fact that the activity is higher with NaX than NaY.

The main difference of the reaction of THF and hydrogen sulfide and that of γ -butyrolactone and hydrogen sulfide [2] is that the former is retarded by pyridine,

Table I
Comparison of the catalytic activities of various zeolites

Catalyst	Yield (%)	Catalyst	Yield (%)
LiX	60	NaY	21
NaX	70	CsY	27
KX	62		
RbX	51	HY	2
CsX	49	MgY	3

340°C , $W/F = 7.95 \cdot \text{g} \cdot \text{h} \cdot \text{mol}^{-1}$, molar ratio
($\text{H}_2\text{S}/\text{THF}$) = 5

but the latter does not. This means the protonic acid is essential for the activation (probably for ring opening) of THF. Similar phenomena were observed also in the reactions of THF/ γ -butyrolactone and amines. For the ring conversion of THF to pyrrolidine, only the acidic catalysts are active [3], while for the ring conversion of γ -butyrolactone to pyrrolidinones, the alkali cation exchanged zeolites have comparable activity with HY [6, 7]. This has been attributed to the ease of the ring opening of the lactone due to the presence of polarizable carbonyl group.

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SO₂-INDUCED ISOMERIZATION OF *n*-BUTENES OVER X- AND Y-TYPE ZEOLITES

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The promoting action of SO₂ for the isomerization of *cis*-2-butene over X- and Y- type zeolites has been characterized. Different kinetic behaviour observed for the SO₂-induced *cis*-*trans* isomerization and double-bond migration of 2-butenes on cation-exchanged zeolites shows that the two reactions take place with different mechanisms over different active sites. The *cis*-*trans* isomerization is accompanied by the copolymerization of SO₂ and 2-butenes. The double-bond migration is caused by acidic OH groups newly generated through the reaction of SO₂ with basic OH groups. On HY zeolite, the creation of basic sites by dehydroxylation is essential for the promoting action of SO₂. SO₂ adsorbed on the basic sites may enhance the acid strength of BRONSTED sites by its attracting negative charge from the catalyst.

Introduction

The favourable action of guest molecules to reactant transformation has been recognized, specifically on zeolites [1, 2] with a few exceptions [3]. The promoting action of SO₂ for hydrocarbon conversion such as cracking, alkylation or isomerization over X- and Y-type zeolites has been reported in patents over ten years ago [4, 5]. However, not detailed study on this subject has since been reported. Hence, in order to elucidate the promoting action of SO₂ in zeolite catalysis, we have investigated kinetics of the SO₂-induced isomerization of olefins over cation-exchanged-X, NaX and HY zeolites. The reaction mechanism and the nature of the active sites are discussed.

Experimental

All the zeolites used were prepared by an usual ion exchange method of NaX and NaY zeolites with aqueous solution of the appropriate chlorides. The percentages of exchange were as follows: LiX (60), KX (79), RbX (61), CsX (64), MgX (76), CaX (83), SrX (94), BaX (81), LaX (83), CeX (84), NdX (87), NH₄Y (100).

The apparatus employed was a conventional gas circulating system with 225 ml dead volume. Prior to every run, the catalyst was calcinated in dried oxygen and degassed *in vacuo* for 2 hr at 500 °C. HY zeolite prepared by decomposition of NH₄Y zeolite under vacuum at various temperatures was subjected to the run without calcination in oxygen. At 25 °C, SO₂ was adsorbed on the catalyst and the reaction was started by feeding *cis*-2-butene (1.3×10^{-3} mol). The initial rates of the two types of isomerizations, $R_{c \rightarrow t}^0$ and $R_{c \rightarrow i}^0$, were calculated from the amount of *trans*-2- and 1-butene produced within 7 min, respectively.

Results and discussions

Cation-exchanged zeolites

Addition of SO_2 onto LiX, NaX and KX zeolites induces geometrical isomerization of *cis*-2-butene but no double-bond migration. No isomerization of 1-butene has been further confirmed. The reactions did not occur on RbX and CsX zeolites. SO_2 on alkaline earth- and rare earth-X zeolites induces the two isomerizations of *cis*-2-

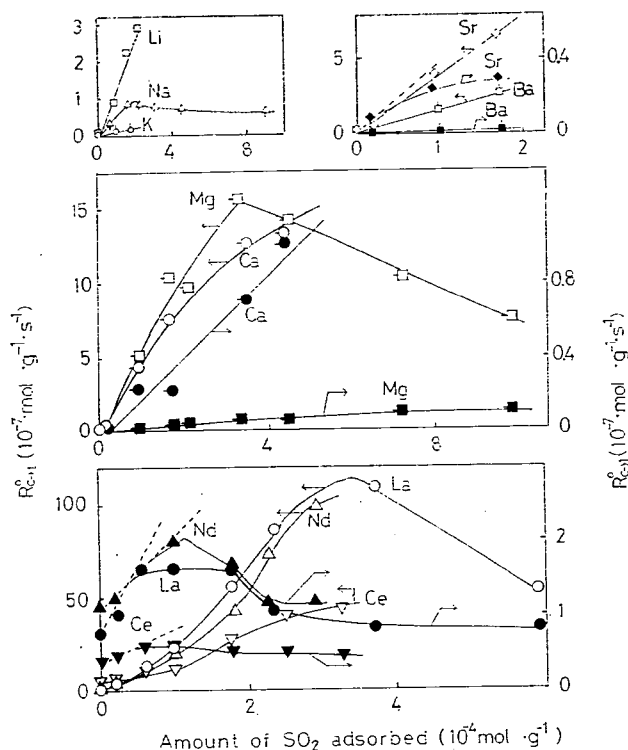
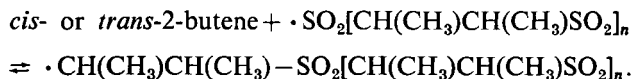


Fig. 1. Rate of SO_2 -induced isomerizations of *cis*-2-butene as a function of the amount of SO_2 adsorbed on cation-exchanged-X zeolites. Open signs $R_{c \rightarrow t}^0$; filled signs $R_{c \rightarrow 1}^0$.

-butene. The effect of SO_2 concentrations on the initial rates, $R_{c \rightarrow t}^0$ and $R_{c \rightarrow 1}^0$, is shown in Fig. 1. The promoting action of SO_2 is unusually greater on geometrical isomerization than on double-bond migration. Nitric oxide in an amount of 1% of preadsorbed SO_2 poisons geometrical isomerization strongly, but does not affect the rate of double-bond migration.

Reaction mechanism for *cis-trans* isomerization

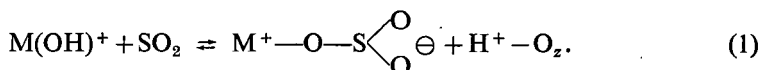
The selective *cis-trans* isomerization can be explained by the addition and elimination of 2-butene molecules at the terminal of the polysulfone formed in the adsorption layer [6—8]:



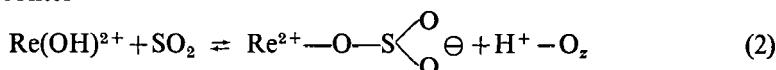
The *cis-trans* isomerization on alkali and alkaline earth zeolites shows an acceleration of its rate with reaction time, being attributed to the accumulation of a radical intermediate. The selective poisoning of nitric oxide to the reaction must be due to its effective quenching of the terminal radical of the polysulfone. The decrease in the rate of *cis-trans* isomerization with increase in the amount of SO_2 under high SO_2 concentrations can be ascribed to an interference of the diffusion of butene molecules by the formed polysulfone in the narrow pores of zeolites. The activities for the zeolites in Fig. 1 for the *cis-trans* isomerization increase with a rise in the electrostatic potential of the exchangeable cations of the zeolites, suggesting the initiation of the reaction under the influence of metal cations.

Active site for double-bond migration

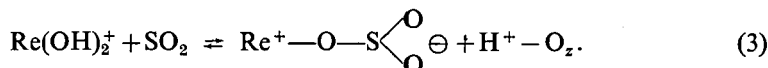
The SO_2 -induced double-bond migration over alkaline earth- and rare earth-X zeolites can be interpreted by assuming generation of acidic hydroxyl groups on SO_2 adsorption at the expense of basic hydroxyl groups [2, 9, 10]. In the case of alkaline earth zeolites, new acidic OH groups may be generated as follows:



For rare earth zeolites



or



The rate of SO_2 -induced double-bond migration is expressed as follows:

$$R_{c \rightarrow 1}^0 \propto [\text{H}_{\text{new}}^+] \quad (4)$$

$$[\text{H}_{\text{new}}^+] = K[\text{M}(\text{OH})^+][\text{SO}_2] \quad (5)$$

where K is the equilibrium constant of equation (1). Table I shows the slopes of the linear portion of the curves for the double-bond migration in Fig. 1 at the low concentration of SO_2 . The concentration of $\text{M}(\text{OH})^+$, produced by the dissociation of water molecules in the electrostatic field around the divalent cations in zeolite, must increase in the order of $\text{Ba} < \text{Sr} < \text{Ca} < \text{Mg}$ as the electrostatic potential of the cations increases [11—14], while K must decrease in the same order because of an expected decrease in basicity of $\text{M}(\text{OH})^+$. Thus, it is reasonable that the number of

Table I

Activities of the zeolites for SO₂-induced double-bond migration of *cis*-2-butene

Zeolites	BaX	SrX	CaX	MgX	NdX	CeX	LaX
Activities (10 ⁻⁴ ·s ⁻¹)	0.075	3.70 ^a	2.18	0.133	15.3 ^a	17.5 ^a	15.1 ^a

^a: obtained from the dotted lines in Fig. 1.

new acidic OH groups, or the promoting action of SO₂, over alkaline earth zeolites is highest in SrX (Table I). The high promoting action of SO₂ for rare earth zeolites might be attributed to the presence of Re(OH)₂⁺ which has greater basicity than M(OH)⁺.

HY and NaY zeolites

For HY zeolites prepared by the decomposition of NH₄Y zeolite at 200–350 °C, SO₂ acts as a weak poison for the two isomerizations. Its promoting action appears on HY zeolites degassed in a vacuum at temperatures higher than 400 °C. SO₂-enhanced rates on HY and NaY, R(SO₂), or the differences between rates measured in the presence and absence of SO₂, are plotted against the degassing temperatures and the reaction temperatures (zeolites degassed at 600 °C) in Fig. 2 (a) and 2 (b),

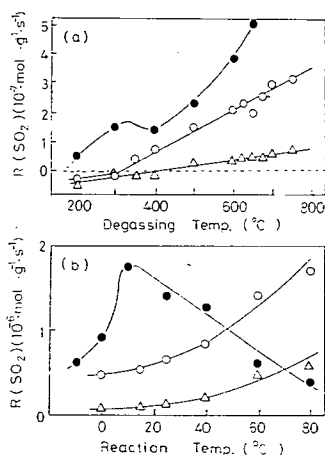


Fig. 2. Effect of (a) degassing temperatures of zeolites ([SO₂] 2.2×10⁻⁵ mol/g) and (b) reaction temperatures ([SO₂] 9.4×10⁻⁵ mol/g for HY, 3.8×10⁻⁵ mol/g for NaY; the degassing temperature 600 °C) on the rate of SO₂-induced isomerizations of *cis*-2-butene. ○ HY(c→t); △ HY(c→l); ● NaY(c→t)

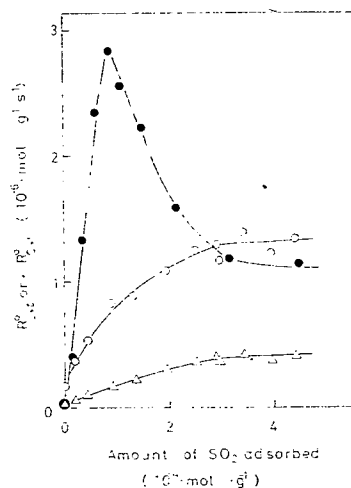
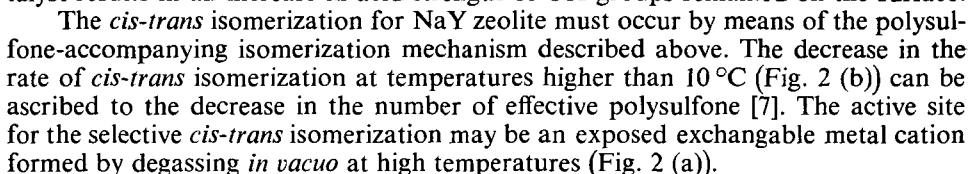


Fig. 3. The plots of net rates of isomerizations against the amount of SO₂ adsorbed. The catalysts were degassed at 600 °C. ○ HY(c→t); △ HY(c→l); ● NaY(c→t).

In the case of HY zeolite, the similar kinetic behaviour for the two isomerizations (Figs. 2, 3) suggests that they proceed *via* a common reaction intermediate on a common active site. The fact that the promoting action of SO₂ emerges on the catalysts treated at temperatures higher than 400°C implies that the dehydroxylation of the catalyst, shown below [15], is necessary.



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THE CATALYTIC ACTIVITY OF COPPER(II)-IONS IN ZEOLITES AS COMPARED TO COPPER(II)-OXIDE AND COPPER-ALUMINIUM-SPINEL

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1. Introduction and Scope

The object of the present investigation was to compare the catalytic activity of various copper compounds in oxidation reactions, including Cu^{2+} -exchanged zeolites. Zeolites are generally supposed to be particularly active as catalysts, due to the high degree of dispersion of the catalytically active species within the porous structure of the crystals.

It appears doubtful, however, whether this expectation must be true in general. If the reactivity of lattice oxygen is responsible for the catalytic properties of a bulk oxide (*e.g.* CuO) then a zeolite containing the same cation (*e.g.* Cu^{2+}) may not exhibit a corresponding catalytic activity, the reactivity of its oxygen in the silica-alumina framework being not affected by the cation-composition. On the other hand, if the cations in the surface of an oxide are the catalytically active species, then a zeolite containing the same cation should exhibit catalytic activity, corresponding to the high degree of accessibility of the cations in the zeolite-lattice for the reactants. A well defined quantitative measure of catalytic activity is necessary in order to resolve this question by experiment. Such a measure is the rate constant of the reaction at a fixed temperature, provided it is not affected by mass- or heat transfer in the reactor and the reaction-order (rate low) is the same for the various catalysts to be compared. The rate constant has to be defined per unit amount of catalyst, which could be unit of mass, volume, surface area or amount of catalytically active species; the choice of this basis being essential to a meaningful comparison of different solids.

The kinetics of oxidation of CO and of propane



were studied on copper oxide (CuO), copper-aluminum spinel (CuAl_2O_4) and on Cu^{2+} -exchanged zeolites Y and mordenite in order to compare the catalytic activity of these solids in oxidation reactions.

2. Experimental

a) Catalysts

CuO was obtained in the form of porous cylinders (4 mm diameter) by pressing $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ (Merck, No 2722) into tablets and heating to 550°C for two hours.

CuAl_2O_4 (copper-aluminum spinel):

8 g $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ was dissolved together with 51 g $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ in 100 ml H_2O and the water evaporated. The remaining solid was heated to 900°C for 10 days.

The resulting red-brown powder analyzed 35 wt% Cu and 30 wt% Al; its X-ray diffraction pattern corresponding to that of the spinel-structure, no other phase being detectable.

Zeolite Y was synthesized following the procedure described by BRECK [1] from sodium aluminate, NaOH and silica sol (27 wt% SiO_2). Crystallization at 75°C for six days yielded crystals from 2 to 10 μm in diameter analyzing $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot (\text{SiO}_2)_{4.16}$.

Zeolite mordenite was obtained from the Norton company (type 100, analyzing $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3(\text{SiO}_2)_{10}$ as a crystalline powder with particle sizes between 2 and 12 μm .

Cu^{2+} -ions were incorporated into these zeolites by partial ion-exchange with a solution of 0.1 mol/l $\text{Cu}(\text{NO}_3)_2$ in a citrate buffer at pH 6.0 (in order to avoid hydrolysis of Cu^{2+} -eq.). No phases other than the zeolite structures were detectable by X-ray diffraction in the ion-exchanged materials:

Structure	Faujasite (Y)		Mordenite		
Designation	Y0	Y22	M0	M5	M12
% of Na^+ exchanged by Cu^{2+}	0	22	0	5	12

The spinel as well as the zeolites were pressed into tablets of 4 mm diameter before being used as catalysts.

b) Characterization of solids

The surface area of CuO and CuAl_2O_4 was determined by adsorption of N_2 at 77 K using the two-parameter BET-equation and assuming a monolayer capacity of $1 \cdot 10^{-5}$ mol N_2 per m^2 .

According to SCHOLTEN and KONVALINKA [2] the amount of CO-chemisorption is a measure of the number of accessible copper-ions in a surface. CO-adsorption isotherms were determined volumetrically at 357 K and $p \leq 0.6$ bar after degassing the solids at 625 K and $p < 0.3$ Pa.

The chemisorbed amount was obtained by extrapolating these isotherms to $p_{\text{CO}}=0$; in the case of the zeolites this amount was equal to the increment of CO adsorption observed at a given pressure on the Cu^{2+} -exchanged zeolite as compared to the parent material.

c) Reaction rate measurements

The rates of total oxidation of propane or of carbon monoxide, *resp.*, were obtained from the conversion in an integral reactor at atmospheric pressure, containing 1.5 cm^3 of catalyst. Catalyst materials were compacted into tablets of 0.4 cm diameter.

The absence of appreciable concentration gradients of reactants in the porous pellet was established in two ways

- (1) by estimating the Thiele modulus and effectiveness factor of the pellet on the basis of an effective diffusivity of $2 \cdot 10^{-3} \text{ cm}^2 \text{ sec}^{-1}$ as its lower limit;
- (2) by locating the temperature-range where the effectiveness factor η is essentially unity ($0.9 \leq \eta \leq 1$) from an observation of the rate over a wide range of temperatures as described previously [3].

Reaction mixtures were less than 0.013 mol% of C_3H_8 in air or 0.05 mol% CO in oxygen, corresponding to adiabatic temperature rises of 10 K or 5 K, *resp.*, at total conversion so that the temperature rise in the reactor was limited to 1 K under the conditions of the experiments. A gas chromatograph with flame-ionization-detector was used to analyze the gas mixtures before and after the reactor; analysis for the very low content of CO was possible by hydrogenating CO on a nickel catalyst prior to detection in the FID.

Since the concentration of excess oxygen is constant, the rate coefficients k_i per unit of mass of catalyst can be defined by the equation

$$-\frac{1}{m} \cdot \frac{dn_i}{dt} = k_i \cdot c_i^\alpha \quad (1)$$

($i = \text{CO}, \text{C}_3\text{H}_8$) where m is the mass of catalyst, c_i the concentration of reactant i and α the order of reaction with respect to i . In the case of first order ($\alpha = 1$) integral conversion X_i and volumetric flow rate $\dot{v}_0$ are related to the mass m of catalyst in the reactor and to the rate constant k by equation (2):

$$\dot{v}_0 \ln \frac{1}{1 - X_i} = k_i \cdot m \quad (2)$$

k_i is obtained in $\text{cm}^3 \text{ g}^{-1} \text{ sec}^{-1}$.

3. Results

a) Surface area and CO-chemisorption

BET surface areas and corresponding numbers of N_2 -adsorption sites in a monolayer, CO-chemisorption at 357 K and Cu-content are shown in the following Table I:

Table I

Catalyst	CuO	CuAl_2O_4	Y22	M5	M12
BET surface in m^2/g N_2 -sites in mol/g	2.0 $2.0 \cdot 10^{-5}$	5.4 $5.5 \cdot 10^{-5}$	—	—	—
CO-chemisorption n_{CO}/m in mol/g	$1.8 \cdot 10^{-5}$	$1.45 \cdot 10^{-5}$	$1.3 \cdot 10^{-4}$	$2.3 \cdot 10^{-4}$	$4.2 \cdot 10^{-4}$
Cu-content n_{Cu}/m in mol/g	$1.26 \cdot 10^{-2}$	$5.51 \cdot 10^{-3}$	$5.3 \cdot 10^{-4}$	$1.1 \cdot 10^{-4}$	$2.5 \cdot 10^{-4}$
Density of pellets in g/cm^3	1.6	2.5	1.3	1.1	1.1

The CO-chemisorption capacity of the bulk oxides corresponds to the amount of Cu^{2+} expected at the surface, as far as the order of magnitude is concerned. In the Cu-containing mordenites roughly 2 molecules are chemisorbed per Cu^{2+} -ion, whereas only 0.25 molecules of CO are chemisorbed per Cu^{2+} -ion in zeolite Y, indicating that Cu^{2+} in zeolite Y is only partially accessible for CO-chemisorption as has already been reported in the literature [4, 5].

b) Kinetics of oxidation reactions

The kinetics of reactions (I) and (II) were found to be first order in the concentration of CO or C_3H_8 , *resp.*, the coefficients k in eq. (2) being independent of space velocity and initial concentrations at least up to 0.05 or 0.013 mol %, *resp.* Rate coefficients k per unit of mass of catalyst as a function of reciprocal temperature are shown in Figs. 1 and 2 on a logarithmic scale; all results were reproducible when the temperature was increased or decreased. The region where the observed rates of reaction are affected by mass transfer limitations can be detected in the $\log k$ *vs.*

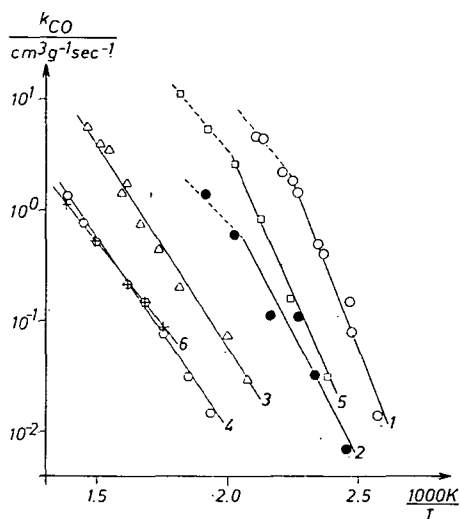


Fig. 1. Arrhenius plot of rate constants (CO-oxidation) 1=CuO, 2=CuAl₂O₄, 3=Y22, 4=Y0, 5=M5, 6=M

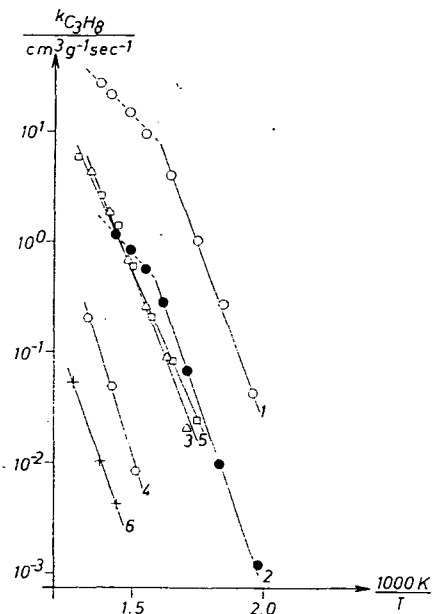


Fig. 2. Arrhenius plot of rate constants (C_3H_8 -oxidation) 1=CuO, 2=CuAl₂O₄, 3=Y22, 4=Y0, 5=M5, 6=M

$1/T$ -plot, since the slope will change by a factor 0.5 as soon as concentration gradients in the porous pellets are significant. Mass transfer limitations exert an influence on the observed rates only if k is greater than $1 \text{ cm}^3 \text{ g}^{-1} \text{ sec}^{-1}$, as can be seen from Figs. 1 and 2 (dotted lines). Time constants of diffusion of small molecules in zeolite crystals are very small compared to the time constants R^2/D_{eff} of diffusion in the macropores of pellets made from these crystals [6]. It can be concluded, therefore,

that the observed rates of reaction are also not affected by mass-transfer limitations in the zeolite crystals if k is smaller than $1 \text{ cm}^3 \text{ g}^{-1} \text{ sec}^{-1}$.

The rate per unit of mass of catalyst on the pure Na-forms of the zeolites is less than 10% of the value observed on the same zeolites after partial ion-exchange with Cu^{2+} .

4. Discussion

In the following Table II rate data which are not influenced by mass effects are compared for different catalysts at two arbitrarily chosen temperatures (440 K for CO-oxidation, 570 K for C_3H_8 -oxidation). In a few cases the values given have been obtained by extrapolating the Arrhenius plot at low-temperatures ($\eta=1$) to the reference temperature, any influence of mass transfer resistance being eliminated in

Table II

	CuO	CuAl_2O_4	Y22	M5	M12
Reaction: normalized rate data CO-oxidation (440 K):					
(1) k in $\text{cm}^3/\text{g}\cdot\text{sec}$	1.4	$6.3 \cdot 10^{-2}$	$5.2 \cdot 10^{-3}$	0.115	
(2) $k \cdot m/n_{\text{CO}}$ in $\text{cm}^3/\text{mol}\cdot\text{sec}$	$8.2 \cdot 10^4$	$4.3 \cdot 10^3$	$4.0 \cdot 10^4$	$5.0 \cdot 10^3$	
(3) $k \cdot m/n_{\text{CO}}$ relative to CuO	(1.00)	$5.3 \cdot 10^{-2}$	$4.9 \cdot 10^{-4}$	$6.1 \cdot 10^{-3}$	
C_3H_8 -oxidation (570 K):					
(4) k in $\text{cm}^3/\text{g}\cdot\text{sec}$	0.94	$3.8 \cdot 10^{-2}$	$1.4 \cdot 10^{-2}$	$2.4 \cdot 10^{-2}$	$5.3 \cdot 10^{-2}$
(5) $k \cdot m/n_{\text{CO}}$ in $\text{cm}^3/\text{mol}\cdot\text{sec}$	$5.5 \cdot 10^4$	$2.6 \cdot 10^3$	$1.1 \cdot 10^3$	$1.0 \cdot 10^3$	$1.3 \cdot 10^3$
(6) $k \cdot m/n_{\text{CO}}$ relative to CuO	(1.00)	$4.7 \cdot 10^{-2}$	$1.95 \cdot 10^{-3}$	$1.9 \cdot 10^{-3}$	$2.3 \cdot 10^{-3}$

this way. The highest rate per unit of mass of catalyst (lines (1) and (4)) is observed with CuO for both reactions, however, mordenite M5 reaches 8% of the value observed with CuO. A comparison on the basis of unit of mass of catalyst does not appear very meaningful, however, if one wants to characterize the catalytic activity of a given species in different environments, since in the bulk oxides only the surface can be involved in the catalytic reaction. The rate constants k per unit of mass have therefore been normalized by the amount of CO-chemisorption per unit of mass (lines (2) and (5)). The resulting quantities $k \cdot \frac{m}{n_{\text{CO}}}$ can be considered as rate coefficients per unit amount of active species or sites and will thus be proportional to turnover-numbers, provided CO-chemisorption measures the amount of active species or active sites. Again these numbers are highest for CuO; ratios of $k \cdot \frac{m}{n_{\text{CO}}}$

relative to the values observed on CuO are given in line (3) and (6). Whereas the rate per CO-adsorption-site on CuAl_2O_4 is roughly 5% of the value observed on CuO, it does not reach 1% of this value in the zeolites. Since CO-chemisorption measures the amount of Cu^{2+} which is accessible to the reactants, one can conclude that Cu^{2+} is not the active species in these oxidation-reactions. There is strong evidence that lattice oxygen is an intermediate in catalytic oxidation on oxides as has been shown by several authors [7—9] particularly by BORESKOV and his school [10—12]. This view is in agreement with the above conclusion, since the properties of oxygen in the lattice of CuO or CuAl_2O_4 can be expected to be very different from those of oxygen in a zeolite-framework.

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ISOMERIZATION OF XYLENES ON H-MORDENITE AND H-CLINOPTILOLITE OF NATURAL ORIGIN

By

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There are large deposits of two important zeolites, clinoptilolite and mordenite, in Hungary in the rhyolite tuffs of the Tokaj mountains as microcrystalline rock-forming minerals. The H-derivatives of these zeolites prepared by Ag^+ -exchange and subsequent reduction are very active and stable catalysts in xylene isomerization, as opposed to the H-derivatives obtained by acid treatment or ion-exchange with NH_4^+ ions. By means of TG—MS measurements we have established the concentration of OH groups in the various catalysts prepared, the conditions of their formation and their thermal stability. The experimental results help explain the differences between the catalytic properties of the $\text{Ag} \rightarrow \text{H}$ -mordenite and those of the other H-mordenites.

Introduction

On the H-forms of zeolite catalysts the following reactions of C_8 alkylaromatic compounds occur depending on the conditions: isomerization of xylenes into each other, metathesis, partial or complete dealkylation of xylenes and of ethyl-benzene. The acidic insulator catalysts are active without regeneration only for a very short time (between a few seconds and 1-2 days). Their activity can be stabilized by the incorporation of metals or metal oxides into their structure. This, however, requires consideration of active centers other than those of the acidic type, which may promote additional reactions. In this paper the catalytic properties of acidic derivatives of natural clinoptilolite and mordenite prepared in different ways are described. Our aim was to obtain zeolites in the H-form with a stable activity and selectivity in order to study the isomerization of xylenes, regarding the other possible processes as undesirable side-reactions.

Experimental

Preparation and characterization of the catalysts

There are large amounts of microcrystalline mordenite and clinoptilolite in Hungary as rock-forming minerals. The mordenite and clinoptilolite content of these sedimentary rocks varies but in samples from certain locations may be as high as 70—80%. On the basis of X-ray diffraction and electron microscopic data, we have established that in both zeolite-containing rocks, used as starting materials for

the catalysts, the main crystalline non-zeolitic mineral is quartz (occasionally some feldspar); the rock contains also amorphous rock glass.

Table I shows the chemical composition of the *rock* rich in mordenite and clinoptilolite. It is seen from Table I that the rocks contain a small amount of iron oxide, too. When using natural zeolites as catalysts, it is often feared that the non-zeolitic



Fig. 1. Transmission electron micrograph of a mordenite-containing rock (the bar denotes 1 μm)

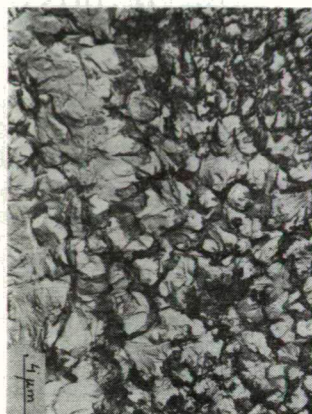


Fig. 2. Transmission electron micrograph of a clinoptilolite-containing rock

components may have a disturbing effect. We have proved experimentally that in our case these components — including iron oxide — do not influence the catalytic behaviour of the rock and do not lead to aging of the catalysts, either.

By means of electron microscopy we have established the shape and size of the zeolite crystals (Figs. 1—3). In Fig. 1 well developed mordenite crystals, 5—10 μm in length and a few tenth of a μm in width and thickness, are to be seen. On transmission electron micrographs the clinoptilolite crystals are not clearly seen (see Fig.

Table I
Composition (wt. %) of the rocks
containing mordenite
(MR) and clinoptilolite (CR)

Component	MR	CR
Na ₂ O	1.37	0.24
K ₂ O	4.11	3.24
MgO	0.28	0.89
CaO	1.87	1.82
Al ₂ O ₃	10.78	10.12
SiO ₂	70.93	70.96
Fe ₂ O ₃	1.41	1.30
TiO ₂	—	0.07
Weight loss on heating at 1000 °C	9.23	11.28

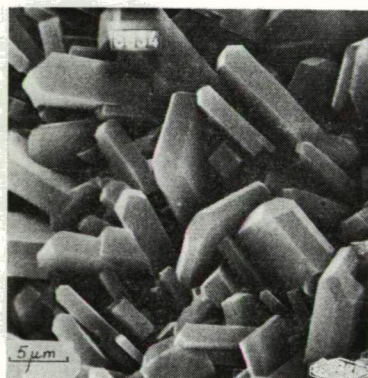


Fig. 3. Scanning electron micrograph of a clinoptilolite-containing rock

2), but scanning electron microscopy permits to obtain pictures of a crystalline region (Fig. 3).

Starting from a 1.0—1.6 mm particle size fraction grist of the mordenite- and clinoptilolite-containing rock the partially or fully protonated H-forms were prepared in 3 different ways: by acid treatment with HCl, and ion-exchange with NH_4NO_3 and AgNO_3 solutions. (Acid treatment with 0.1 N, 1 N and 3 N hydrochloric acid, ion-exchange with 2 N NH_4NO_3 and AgNO_3 , 3×4 hrs with fresh solutions, were carried out by refluxing. For 100 g zeolite grist 400 ml solution was applied. From the NH_4 - and Ag-form we have prepared the H-forms by a deammoniation or reduction at a suitable temperature.) Comparative catalytic investigations were made on the three mordenite and clinoptilolite samples; the corresponding 2 samples were always prepared under the same circumstances. In all cases the mordenite catalysts proved to be more active and the aging experiments showed that the activity of the H-mordenite prepared by Ag ion-exchange practically did not change. The differences in the activity of clinoptilolite and mordenite catalysts are supposed to be due to differences in the structure, because the reaction occurs in both cases on the surface of the crystallites, and there are no significant differences between the surface of the various catalysts. (Earlier adsorption investigations have shown that natural mordenite is a narrow-pore solid [1]). Comparison of the activities shows that the most active are the H-forms prepared by Ag ion-exchange, a somewhat lower activity is observed for the derivatives prepared by NH_4NO_3 ion-exchange, and the acid treated forms have the smallest activity. Changes in the chemical compositions owing to various treatments were followed by X-ray microanalysis of the mordenite [2, 3] crystals, which can be readily indentified on the electron micrographs. The electron beam can be focused on a single crystal, thus permitting to analyze the zeolite phase proper. The measurements prove that by Ag^+ -exchange all K-, Na- and Ca-ions are removed, while treatment with NH_4NO_3 leads to a full exchange of Na, ca. 90% exchange of Ca and ca. 50% exchange of K. Upon acid treatment the extent of ion-exchange further decreases, thus the sequence of activity can be explained on this basis. The stable activity of the Ag^+ -exchanged derivatives in time is remarkable. The origin of this phenomenon was studied by TG—MS measurements with special reference to the formation and stability of the acidic centers. For elucidation of the mechanism of catalysis, the kinetics of xylene isomerization have been studied.

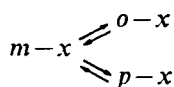
Xylene isomerization on H-mordenite catalysts

This reaction has been investigated by many authors because of its relevance to numerous petrochemical processes [4]. Also, it is very suitable test reaction for characterizing the activity of such catalysts (see *e.g.* [5]).

In our experiments isomerization was followed starting from the individual xylene isomers, in a flow reactor, at 200—400 °C and at total pressures of 5—60 atm and at various hydrogen/xylene partial pressures. By changing the space velocity, so called conversion isotherms were recorded. The following conclusions can be drawn partly from the direct conversion data, partly from the kinetic parameters calculated from the conversion isotherms:

a) Starting from each xylene isomer under the above circumstances on all three H-mordenite catalysts the main reaction is the intramolecular isomerization of xylenes, which is accompanied to a small extent by the metathesis of xylenes. (This does not exceed 5% for the equilibrium xylene composition.)

b) Starting from individual xylene isomers it has been established that the inter-conversion of the 3 xylene isomers follows the scheme:



there being no direct route from ortho to para xylene. The consecutive processes indicate that no equilibrium exists between the adsorbed species. In accordance with this, we have found that the initial rate of *m*-xylene isomerization can be described by a Langmuir isotherm which holds in the case of a rate-determining surface reaction.

c) The selectivity of *m*-xylene isomerization into *o*- and *p*-xylene (selectivity means here the ratio of *p*- to *o*-xylenes formed) is the same for all three H-mordenite catalysts and is independent of the temperature. The activation energy of *m*-xylene isomerization is also the same on the various H-mordenite catalysts: 38 kcal/mol, the chemisorption heat of *m*-xylene is 16 kcal/mol. From these facts one can conclude that on all three mordenite catalysts prepared in different ways, the adsorption of the xylene molecule occurs on the same Brönsted acid centers, *i.e.* the first step is a fast (equilibrium) adsorption of the species followed by the rate-determining surface reaction (1 → 2 methyl transfer along the ring), the catalytic cycle being closed by the fast desorption of the product.

The same selectivity and activation energy values on different H-mordenites permit the conclusion that metallic silver formed by the reduction of the Ag ion-exchanged form has no catalytic effect on the above reaction. This conclusion is supported by the fact that re-conversion of the H-form into the Na-form with a NaCl solution produces a fully inactive catalyst.

From the chemical analysis of ion-exchanged mordenite and its catalytic activity, it can be concluded that the acidic centers optimal in xylene isomerization with respect to their position and acid strength are only formed by total ion-exchange and they are responsible both for the high activity and stability.

Concerning the nature (characterized by thermostability) and quantity of acid centers on the three H-mordenite catalysts prepared in various ways, results were obtained by so-called TG—MS measurements.

Combined thermogravimetric-mass-spectrometric (TG—MS) measurements on the starting mordenite and the catalysts prepared from it

The literature discusses almost exclusively the thermostability of synthetic H-mordenites prepared by NH_4^+ -exchange [6—9]. BEYER *et al.* [10], however, discussed in detail the properties of a synthetic Ag(H)-mordenite obtained from Ag-mordenite, too.

The thermogravimetric experiments were carried out on a Mettler thermobalance combined with a Balzers mass spectrometer QMG—101, under N_2 atmosphere, with a heating rate of 4 °C/min.

Experiments were made with the original mordenite-containing rock and the above derivatives. (The Ag^+ -exchanged sample was reduced *in situ* and the measurement carried out under reductive conditions in order to prevent silver from reoxida-

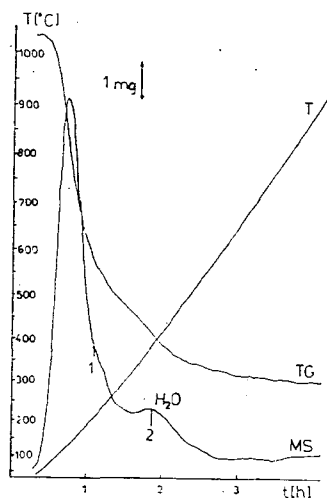


Fig. 4. TG—MS diagram of the original mordenite sample

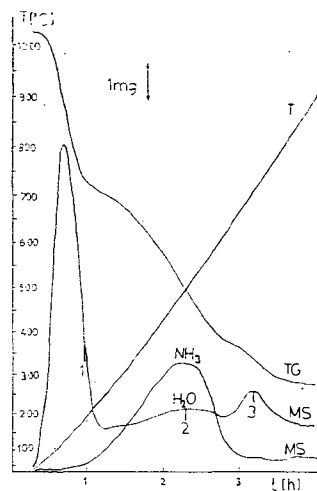


Fig. 5. TG—MS diagram of the NH_4^+ -exchanged mordenite

tion.) Figs. 4, 5 and 6 show TG—MS diagrams for the original, NH_4^+ -exchanged and Ag^+ -exchanged samples, respectively.

In the TG—MS diagram of the original mordenite (Fig. 4) three types of water are to be distinguished desorbing at various temperatures. The so-called zeolitic water, adsorbed physically, desorbs in two overlapping steps up to 250 °C (marked in Fig. 4 by 1); thereafter, in a third, better separated region the desorption of water bound to cations of the mordenite begins (marked by 2). For the lack of space the diagrams concerning the three acid-treated derivatives are omitted. The diagram shows the formation of various OH groups as a consequence of the acid treatment (quantitative data are summarized in Table II).

Table II

Concentration of acidic centers
in catalysts prepared in different ways

Preparation of catalysts from mordenite	Concentration of acidic centers (mmol/g)
Treated with 0.1 N HCl	0.2
Treated with 1 N HCl	1.0
Treated with 3 N HCl	0.8
NH_4^+ -exchanged	1.7
Ag^+ -exchanged	1.8

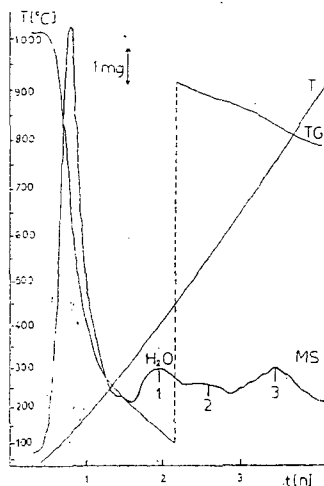


Fig. 6. TG—MS diagram of the Ag^+ -exchanged mordenite

Upon thermal decomposition of the NH_4^+ -mordenite (Fig. 5) the other product observed in addition to water was NH_3 . It is to be seen in Fig. 5 that the deammoniation begins after the removal of physically adsorbed water at ca. 200 °C and lasts till ca. 630 °C. In parallel to the deammoniation, part of the OH groups is immediately removed (region 2 in Fig. 5). The removal of water between 620 and 800 °C proves the presence of strongly bound structural OH groups.

In the TG—MS diagram of the H-mordenite produced by reduction of the Ag^+ -exchanged sample (Fig. 6), in addition to the desorption of zeolitic water, 3 different types of water are removed between 300 and 850 °C. The two overlapping peaks with the NH_4^+ -mordenite in region 2 correspond here to two clearly distinguishable steps.

The calculated concentrations of the OH groups for the three H-mordenite types prepared in different ways are presented in Table II.

Conclusions

a) By acid treatment — in our experimental conditions — the alkali and alkaline-earth cations can be only partially exchanged for protons.

b) Owing partly to unsatisfactory ion-exchange, partly to the high temperature needed for deammoniation (where dehydroxylation also occurs, consequently, the number of the acidic centers decreases), it is not possible to obtain the fully exchanged H-form from the NH_4^+ -form either. During its use as a catalyst only part of the OH groups originally amounting to 1.7 mmol/g, remains in the zeolite.

c) Presumably the H-mordenite formed by reduction of the Ag^+ -exchanged form, contains all the possible types of OH groups distributed in various positions, which is due partly to complete ion-exchange, partly to the low temperature (~ 320 °C) needed for reduction.

The above facts permit interpretation of the observed catalytic properties of the H-mordenites prepared in different ways.

Acknowledgement

The authors are indebted to DR. FERENC TYLL and MRS. ANDREA ZSOLDOS-BÁRCZAY (Research Laboratory for Inorganic Chemistry, Hungarian Academy of Sciences) for the TG—MS measurements.

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STABILIZED Y-TYPE ZEOLITES WITH HIGH CONTENT OF Na CATIONS

By

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A series of stabilized forms of NaHY zeolites has been prepared containing 87, 67, 53 and 31 % of the total amount of Na cations in the NaY zeolite, respectively. The composition, structural character and sorption properties are described and discussed.

The stability of these zeolites does not depend on the degree of stabilization, the intensities of phenomena connected with the process of stabilization depend on the Na⁺ content and the temperature of stabilization.

Ultrastable Y zeolites, their synthesis and properties have been first described by MCDANIEL and MAHER [1]. Since that time, several methods have been reported for preparing, from Y-type zeolites, materials with ultrastable properties [2—4]. A number of articles has been published concerning their crystal structure [5, 6], infrared spectra [7—10], formation mechanism [2—4] and acidic properties [11, 12]. These materials are of considerable interest for their catalytic properties.

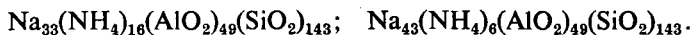
As follows from the patent literature [13], the ion exchange capacity of the ultrastable (US) zeolite is substantially lower than that of the parent zeolite.

A concentration of residual Na cations higher than 1 % by weight of Na₂O is undesirable as it lowers the catalytic activity neutralizing the acidic centres on the catalyst [14].

On the other hand, a stabilized form containing an appreciable amount of sodium cations exhibits a higher ion exchange capacity. Such a form has the faculty of combining the properties of a metal exchanged Y zeolite with those of a stabilized Y zeolite. We have therefore investigated the products resulting from the stabilizing process on zeolites with a high concentration of metal cations.

In the present paper we describe and discuss the composition, structural character and sorption properties of a series of stabilized Y zeolites containing 87, 67, 53, and 31 % of sodium cations, respectively, present in the original NaY form.

As starting material for preparing stabilized NaHY zeolites four types of NaNH₄Y were used, their unit cell compositions being:



Thermal decomposition of the ammonium forms was performed in an electric furnace at 550 and 770° C, respectively. The sample geometry and the stabilization procedures used in this study were described previously [15].

The following denotation of the US samples is used: USC for samples stabilized at 550° C, USE for those at 770° C. These letters are followed by a number, giving the percentage of the residual Na cations in the US forms with respect to the original NaY form, e.g.: USC-87, USE-53.

The extraction of extralattice aluminium was effected by slurring 10 g samples of the stabilized zeolite in 1000 ml of 0.1 N NaOH solution for 24 hrs, filtering, washing with 500 ml of water, and drying. The same procedure was applied in the case of aluminium extraction with 1 N NH_4OH aqueous solution. In special experiments aliquots of the US samples were extracted with potassium-sodium tartarate ($\text{KNaC}_2\text{H}_4\text{O}_6$) aqueous solution. The extracts were analyzed for aluminium and the composition of the sample calculated from the amount of aluminium extracted. The removal of only extralattice aluminium by all the above mentioned procedures was tested using NaNH_4Y zeolites as a blank. No traces of aluminium were found in the extracts of the blank.

Sorption capacity measurements and X-ray diffraction data were used to establish the degree of structural collapse of various materials and the contraction of the lattice of stabilized samples. The sorption capacities of Ar and H_2O were measured with a quartz balance. The details of the infrared measurements have been described previously [16]. The heats of adsorption of model adsorbates were calculated from the data obtained by gas chromatography. The treatment in hydrothermal conditions was realized by the repeating the following cycles: full hydration of the zeolite at room temperature followed by desorption of H_2O at 370° C *in vacuo* (10^{-4} torr).

Sorption capacities of Ar and water were established for all samples in order to test the possible changes of the volume of the zeolite cavities, which may be caused either by partial loss of crystallinity or by presence of voluminous cationic aluminium

Table I

Sorption capacities a_0 of Ar at -198° C and H_2O at 25° C,
the influence of repeated treatment in hydrothermal conditions (THTC)
and Al extraction a_0 mmole g^{-1}

Zeolite	a_0 after THTC		a_0 after Al extr.		Relative increase of a_0 in %	
	Ar	H_2O	Ar	H_2O	Ar	H_2O
NaHY-31	5.08	—	—	—	—	—
USE-31	9.71	15.40	10.63	17.92	9	16
USC-31	10.70	16.68	11.32	18.53	5	11
NaHY-53	6.31	—	—	—	—	—
USE-53	9.75	15.29	10.50	17.57	8	15
USC-53	10.62	16.74	11.17	18.31	5	9
NaHY-67	6.11	—	—	—	—	—
USE-67	3.11	amorphous	—	—	—	—
USC-67	10.26	16.30	10.78	17.00	5	4
NaHY-87	5.34	—	—	—	—	—
USE-87	2.50	amorphous	—	—	—	—
USC-87	10.34	18.02	10.48	17.94	1	0

in the cavities. The respective data for all zeolites studied in this work are shown in Table I. Y zeolites containing 50% or less of the original Na cations can be stabilized also at 770° C. A higher content of Na⁺ excludes the positive effect of stabilization at the temperature 770° C. The increment for water adsorption capacity after complete Al cation exchange in comparison to the increment for argon may be in connection with the fact, that sodalite cages are accessible for water but not for Ar molecules.

Table II

Zeolite	SiO ₂ /Al ₂ O ₃ mole ratio	% Al removed	Unit cell nm
NaNH ₄ Y-31	5.24	—	2.468
USE-31	5.97	12.18	2.453
USC-31	5.72	8.35	2.457
NaNH ₄ Y-53	5.11	—	2.467
USE-53	5.70	10.41	2.452
USC-53	5.49	6.85	2.456
NaNH ₄ Y-67	5.84	—	2.463
USC-67	6.11	4.46	2.454
NaNH ₄ Y-87	5.84	—	2.463
USC-10	5.85	0.27	2.459

Table II summarizes the analytical data of cationic aluminium content and unit cell sizes for our US zeolites. Besides a general decline in cationic aluminium content with the increasing Na⁺ content in a sample, the data also show the positive influence of temperature on the formation of Al cations for zeolites with Na⁺ ≤ 50%. The data also show a unit cell shrinkage proportional to the extralattice aluminium content.

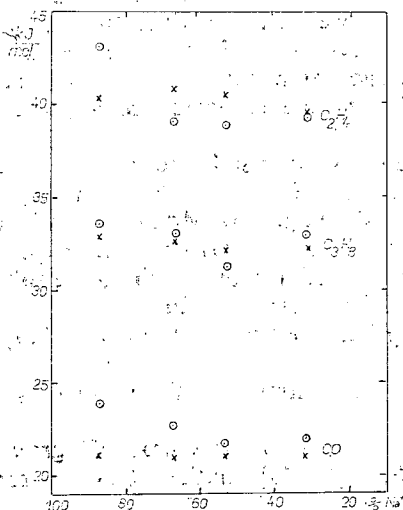


Fig. 1. Dependence of the adsorption heats for US and HY zeolites [17] on the Na⁺ cation content. Adsorbates: ethene, propane, and carbon monoxide

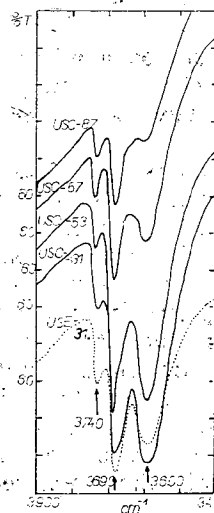


Fig. 2. Infrared spectra of the US samples

Dependences of differential heats of adsorption on the Na^+ content in stabilized Y zeolites are plotted in Fig. 1. When comparing these results with the former ones [17] obtained with nonstabilized NaHY zeolites, the influence of Na cations on the energy of adsorption for adsorbates possessing the ability of specific interaction is lowered by the process of stabilization.

The stabilization of Y zeolites is connected with the formation of structural OH groups whose wavenumbers are shifted to higher values in comparison to OH groups of the nonstabilized forms [18, 19]. The IR spectra of our US zeolites investigated

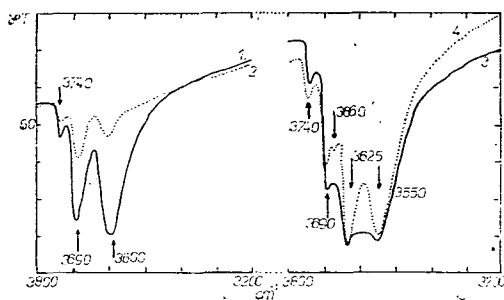


Fig. 3. Infrared spectra of the US samples after treatment with NH_4OH and potassium-sodium-tartrate solutions

curve 1 USE-31

curve 2 USC-31, both after the treatment with tartarate salt solution

curve 3 USE-31

curve 4 USC-31, both after the treatment with NH_4OH aqueous solution

in the OH stretching region are presented in Fig. 2, the wavenumbers correspond to the data of the quoted literature. The intensities of high frequency (HF) and low frequency (LF) bands are proportional to the degree of decationation and inversely to the temperature of stabilization. Fig. 3 represents the OH stretching spectrum of USC-31 and USE-31. Both samples were treated with 1 N NH_4OH (aqueous solution). Two new types of OH groups are observed, nearing to the HF and LF bands in HY zeolites. Even these materials are stable after repeated hydrothermal treatment. In the same figure the IR spectra of USC-31 and USE-31 are shown, the samples were treated with sodium-potassium

tartarate solution in order to remove the extralattice aluminium. In the OH stretching region no changes, corresponding to the absence of possible OH groups connected with Al cations, were observed. The stability of these extracted samples was preserved.

The results of the presented study have shown that stable forms of a Y zeolite, containing up to 90% of the original Na cations present in NaY, can be prepared. This fact is in contradiction to the hypothesis developed by MCDANIEL and MAHER [1, 20] but in agreement with the results of KERR summarized in the review [21], and JACOBS and UYTTERHOEVEN [18]. All our treated Y zeolites exhibit the following common properties, which are characteristic for a stabilized form.

1. Structural stability, *i.e.* constant sorption capacity and full crystallinity after repeated hydration-dehydration treatment.

2. Shrinkage in the unit cell, resulting in a contraction of the lattice by about 0.3–0.6%.

3. The wavenumbers of the valence vibrations of structural OH groups are identical with those reported by other authors [18, 19] for the ultrastable form of Y zeolites.

4. A part of the aluminium atoms is extracted from its framework lattice positions and removable from the zeolite matrix with NaOH, NH_4OH or complex forming agent solution.

5. Lowered energetical inhomogeneity of the surface layers of our US zeolites has been found, resulting in different sorption and catalytical properties in comparison with those of nonstabilized NaHY zeolites.

From the quantitative point of view all these properties are influenced by the $\text{Na}^+ \rightarrow \text{NH}_4^+$ cation exchange and by the temperature of the stabilization.

We have prepared stable structures differing significantly as to the intensities of the phenomena (Na^+ , $\text{Al}(\text{OH})_x^{(3-x)+}$ content u. c. dimensions *etc*), accompanying the stabilization of the lattice. According to the X-ray spectroscopic study of KÜHL [22] such a structure may be formally taken for a hybrid form of the true HY and the USY, the ratio of both types depending on the concentration of cationic Al. Such a formal conception agrees with some results of our IR measurements, showing in Fig. 3 the presence of absorption bands in the hydroxyl stretching region characteristic for a HY zeolite [18]. Presuming, nevertheless, the validity of the conception of two independent parts of structure; a partial destruction must follow after treatment under hydrothermal conditions. But we have found that even these structures are stable as no decrease in adsorption capacities after the THTC was observed. According to this fact and to the observed independence of stability on the degree of stabilization we conclude that the changes during the stabilization process influence the properties of the whole structure. This conception agrees with the observed shrinkage of the whole zeolitic lattice.

The aluminium extraction from its lattice positions during the stabilization process is a necessary condition. But, as we have shown, its presence in the stabilized structure is unnecessary.

The formal comparison of the presented data of adsorption heats leads us to the conclusion that the stabilization process suppresses the sorption activity of the cationic adsorption centres. Nevertheless, we have to take into account the possible redistribution and the possibility of the removal of some Na^+ due to the influence of water vapour during the stabilization process. This influence will be especially remarkable on the surface layer and will probably decrease towards the centre of the monocrystal. Under the dynamic conditions of the gas chromatographic method the information obtained refers mainly to the properties of the surface layers of zeolitic monocrystals where the adsorption equilibrium is attained. The hypothesis mentioned above accounting for the differences in the distribution of Na cations is supported by our results published earlier [15, 23] concerning the differences in sorption and catalytic behaviour of the surface layer and the bulk of the zeolite monocrystal.

Presented results of the X-ray photoelectron spectroscopy show that the content in silicon and aluminium at the surface can be widely different from the bulk composition of the NaY zeolite [24], and that the surface NH_4^+ content in NaNH_4Y zeolites is about 1/2 of that of the bulk [25]. These observed differences in compositions confirming the heterogeneity of the structure may grow during the stabilization process.

To conclude: the study presented has shown the possibility of preparing a stable Y zeolite with high cation-exchange capacity. The stabilization process is considered to influence the whole structure of the zeolitic monocrystal.

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EFFECT OF ALUMINUM CONTENT ON THE ACIDITY AND CATALYTIC PROPERTIES OF DEALUMINATED ZEOLITES

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The properties of dealuminated with EDTA faujasite type zeolites and synthetic samples with identical Si/Al ratios have been compared. It is concluded that the properties of faujasite structure zeolites depend not only on the Si/Al molar ratio but also on the absolute number of aluminum atoms in the unit cell.

Studying dealuminated by EDTA zeolite samples obtained from one initial sample BEAUMONT and BARTHOMEUF [1—3] have suggested that the nature of the acidity change depends solely on the number of aluminum atoms in the unit cell. By devising a mathematical model of dealumination MIKOVSKI and MARSHAL [4] reaffirmed the suggestion that the rising degree of dealumination brings about a parallel rise of strong acid sites. Moreover, the extraction of each aluminum atom causes a qualitative change in the acidity of the residual ones.

The present investigation is a further attempt to develop the ideas considering the role of the absolute number of aluminum atoms in the unite cell on the acidic

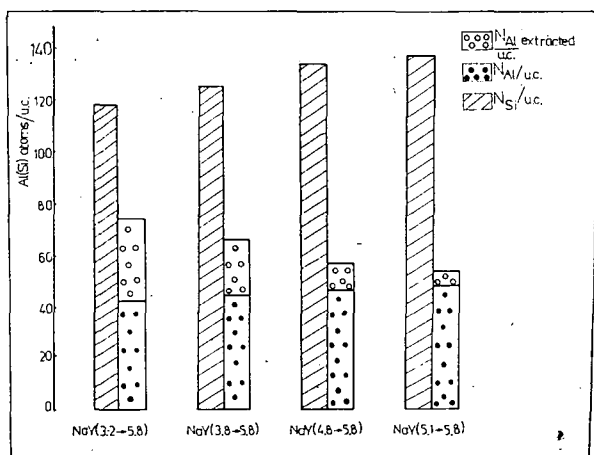


Fig. 1. Histograms for the preparation of dealuminated samples with equal Si/Al ratio from different initial samples

and catalytic properties of zeolites. The faujasite samples of various Si/Al molar ratios modified by dealumination represent a convenient basis for such a study, because it makes possible a directed and controlled variation of the contents of the two constituent unit cell's elements *i.e.* Al and Si and their ratio.

For one series of initial samples with a molar $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 3.2, 3.8, 4.8 and 5.1 and an increasing Si content, to obtain samples with the same new Si/Al ratio (*e.g.* 5.8) through dealumination different quantity of Al must be extracted. Considering the fact that the Si content in the unit cell remains unchanged under the employed conditions of treatment with EDTA [5, 6], to preserve an equal ratio between the two elements in the new dealuminated series, the absolute number of Al atoms/u. c. must be different — least in the sample obtained from the initial one with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 3.2 and greatest in the $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.1$ one. Similarly, the number of Al atoms will be different in every two samples of the same Si/Al ratio, the one obtained through direct synthesis, the other — through dealumination of a sample with lower Si content.

These theoretical considerations have been confirmed by data from chemical analyses of the series of dealuminated samples obtained in the present study. It is clear that in all cases the number of Al atoms/u. c. in the dealuminated samples is lower than that of the synthetic ones having the same Si/Al ratio.

Table I

Indexes of the samples	Molar Si/Al ratio		Unit cell composition
	before dealum.	after dealum.	
HNaX(2.6)	2.6	—	$\text{H}_{35.6}\text{Na}_{47.6}(\text{AlO}_2)_{83.5}(\text{SiO}_2)_{108.5}$
HNaX(2.6 → 3.2)	2.6	3.2	$\text{H}_{22.2}\text{Na}_{46.3}(\text{AlO}_2)_{68.5}(\text{SiO}_2)_{108.5}$
HNaY(3.2)	3.2	—	$\text{H}_{33.4}\text{Na}_{40.4}(\text{AlO}_2)_{73.8}(\text{SiO}_2)_{118.8}$
HNaY(3.2 → 3.9)	3.2	3.9	$\text{H}_{39.0}\text{Na}_{21.3}(\text{AlO}_2)_{60.3}(\text{SiO}_2)_{118.8}$
HNaY(3.8)	3.8	—	$\text{H}_{42.8}\text{Na}_{23.4}(\text{AlO}_2)_{66.2}(\text{SiO}_2)_{125.8}$
HNaY(3.8 → 4.8)	3.8	4.8	$\text{H}_{26.0}\text{Na}_{26.6}(\text{AlO}_2)_{52.6}(\text{SiO}_2)_{125.8}$
HNaY(4.8)	4.8	—	$\text{H}_{34.6}\text{Na}_{21.4}(\text{AlO}_2)_{56.0}(\text{SiO}_2)_{136.0}$
HNaY(4.8 → 6.2)	4.8	6.2	$\text{H}_{32.6}\text{Na}_{10.9}(\text{AlO}_2)_{43.5}(\text{SiO}_2)_{136.0}$
HNaY(4.8 → 7.8)	4.8	7.8	$\text{H}_{33.0}\text{Na}_{11.9}(\text{AlO}_2)_{34.9}(\text{SiO}_2)_{136.0}$
HNaY(3.2 → 5.8)	3.2	5.8	$\text{H}_{31.0}\text{Na}_{9.7}(\text{AlO}_2)_{40.7}(\text{SiO}_2)_{118.2}$
HNaY(5.1 → 5.9)	5.1	5.9	$\text{H}_{38.0}\text{Na}_{8.4}(\text{AlO}_2)_{46.4}(\text{SiO}_2)_{138.0}$
HNaY'(5.8 → 8.8)*	5.8	8.8	$\text{H}_{17.4}\text{Na}_{9.6}(\text{AlO}_2)_{27.0}(\text{SiO}_2)_{118.2}$
HNaY'(5.9 → 8.9)	5.9	8.9	$\text{H}_{18.9}\text{Na}_{11.7}(\text{AlO}_2)_{30.6}(\text{SiO}_2)_{138.0}$

* Samples designated with „'” have been obtained by second dealumination.

The samples obtained by this method have proved particularly appropriate for studying the individual role of Al, by way of comparing the properties of samples with identical Si/Al ratio but with different Al content.

The variation of the acidic function and catalytic activity, depending on the Al content in samples with identical Si/Al ratio, has been followed. The method of high temperature adsorption and thermodesorption of NH_3 [11] and toluene disproportionation [12] as a model reaction has been employed.

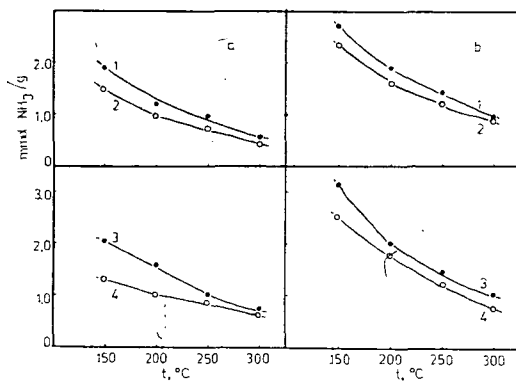


Fig. 2. Relationships between the quantity of ammonia chemisorbed and the temperature of adsorption for dealuminated and synthetic samples with the same Si/Al ratio (a): 1-HNaY (3.2→3.9), 2-HNaY (3.8), 3-HNaY (3.8→4.8), 4-HNaY (4.8), and dealuminated ones, prepared from synthetic samples with various initial Si/Al ratios (b): 1-HNaY (3.2→5.8), 2-HNaY (5.1→5.9), 3-HNaY' (5.8→8.8) and 4-HNaY' (5.9→8.9)

The data obtained from the chemisorption of NH_3 indicate that dealuminated samples adsorb larger quantities of ammonia than the initial samples despite their identical Si/Al ratios. The same regularity has been observed in dealuminated samples with practically identical Si/Al ratio obtained from different initial samples. Consequently in both cases higher acidity is observed in samples with a lower number of Al atoms/u. c. regardless that the ratio of the two elements, *viz.* Al and Si may be the same.

These result should be associated not only with the difference in the absolute number of Al atoms in the comparable samples but also with their positions in the lattice. In all probability, during dealumination a selective extraction of a part of the Al atoms takes place at definite places and order in the structure. This will affect the modification of their acidic properties.

The thus observed acidity relationships of the samples affects their catalytic properties in the same manner (Fig. 3). As it can be seen from this figure, a good correlation exists between the number of Al atoms after dealumination, the quantity of NH_3 adsorbed at 200° C and the catalytic activity. Similarly to the cracking reaction of *isooctan*

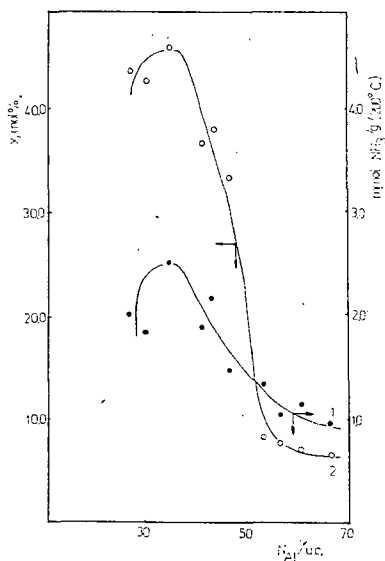


Fig. 3. Acidity (adsorption of ammonia at 200° C) and catalytic activity as a function of the Al content

[1] and cumene [10], and toluene disproportionation on bi-functional catalysts, containing Ca cations [7], maximum activity is observed in the samples containing about 35 Al atoms/u. c.

It should be emphasized, however, that the acidity differences of samples with identical Si/Al ratios, but different absolute number of Al atoms in the unit cell are much more distinct than those arising in their catalytic activity. Because of this, probably, previous studies [8, 9] based only on catalytic data do not provide information on differences from samples with the same Si/Al ratio. Besides, both acidic and catalytic differences are more pronounced when the difference of the aluminum content is higher in the comparable pairs with identical ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ (e.g. in the samples HNaY (3.2→5.8) and HNaY (5.1→5.9). This can be clearly seen from Fig. 3.

On the basis of these results the conclusion can be made that the properties of the zeolites with faujasite structure depend not only on the Si/Al ratio but also on the individual number of Al atoms in the unit cell. In all probability dealumination results in a selective extraction of Al at definite positions which causes new redistribution of the remaining atoms in the lattice. It influences their electrostatic interactions and is one of the major factors of zeolite acidity function and catalytic properties.

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ACTIVE SITES IN ZEOLITES. DEALKYLATION AND DEHYDRATION ON ALKALINE EARTH-Y ZEOLITES

By

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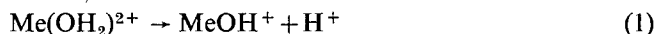
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Dealkylation of 2-butylbenzene and dehydration of 2-butanol were studied on MgY, CaY and BaY zeolites of different water content, using temperature programmed desorption (TPD) and microcatalytic technique. The dealkylation on MgY and CaY was considerably increased when water was added, whereas that on BaY was independent of water content. On MgY and CaY the TPD maxima (of benzene) were shifted to lower temperatures, when water was added, indicating a higher cracking activity. Two maxima appeared on CaY. The dehydration of 2-butanol was studied only on MgY and found to be independent of water content.

Introduction

It is well known that very active cracking catalysts show high acidity. Three kinds of acidic centers have been discussed:

a) Protons of OH groups, originated through the interaction of cations with water molecules (Brönsted acidity)



b) Tri-coordinated Al atoms (Lewis acidity) with high electron pair acceptor (EPA) strength

c) Cations accessible to the reactant (Lewis acidity).

With IR spectroscopic methods, WARD [1] has found Brönsted acidity to have a maximum between 450 and 600° C and decreases steeply at higher temperatures. The Lewis acidity mentioned in b) has been found to increase and to be much more pronounced, within the temperature range of 700—800° C, than Brönsted acidity.

NOLLER [2] has suggested cations to be indispensable active centers for reactions on polar catalysts. The interaction between an EPA site (cation) of the catalyst and an EPD (electron pair donator) site of the reactant (leaving group OH or C₆H₅ in this study) is assumed to be essential for the catalytic activity.

The purpose of this study is to contribute to the question concerning the nature of the active centers. The temperature programmed desorption (TPD) and the microcatalytic technique were used. The dependence of activity upon the content of water and the percentage of exchange was studied. Catalytic results were compared with the TPD characteristics of samples subjected to treatments as similar as possible.

Experimental

The starting material was a NaY zeolite (SK 40) from Union Carbide. The cation exchanged zeolites were prepared by treating this sample with 0.1 n solutions of the cation to be introduced for 3 h at 90° C. The anions were chlorides.

For TPD, the catalysts were activated at 540° C for 15 minutes in a reactor of quartz glass evacuated to 13 Pa, and cooled to room temperature. The zeolites treated in this way are denominated 'anhydrous'. Secondary butyl benzene (SBB) was injected through a septum (and adsorbed). The pressure was always adjusted to 10 000–13 300 Pa. After 3–5 minutes the reactor was again evacuated for some minutes in order to remove weakly adsorbed species. Then the catalyst was heated with a rate of 50° C/min. The desorbing substances were detected in a quadrupole mass spectrometer connected to the reactor. The reactor was also connected, through a valve, to a vacuum pump. To prevent water from diffusing back through the vacuum pump to the zeolite, a liquid air trap was placed between the valve and the pump. The valve was heated to 70–80° C to prevent condensation of water.

The masses 78 (representative for benzene) and 77 (representative for SBB) were continuously recorded. A somewhat larger mass range was cyclically covered by the mass spectrometer. Water was injected before introduction of SBB to study its influence. The figures given in the spectra and tables indicate the amount of water injected per weight of catalyst.

For the microcatalytic technique (dealkylation of SBB, dehydration of 2-butanol) the zeolites were similarly activated at 540° C for 15 min in a He carrier gas flow, previous to reaction. The elution of the reaction products and the non-converted reactant was observed with a thermal conductivity detector and recorded. At the maximum of the elution process, 0.3 ml gas was taken out with a gas syringe and injected into a gas chromatograph with a 1.3 m Carbowax 1540 on Teflon 20–60 mesh column and an FID. For studying the effect of water a measured quantity was injected to the catalyst, previous to the reactant.

Results and Discussion

Temperature programmed desorption

Catalysts studied: Ca₄₀-Y, Ca₅₈-Y, Ca₁₀₀-Y, Mg₃₂-Y and Mg₆₂-Y (subscript: degree of exchange in percent of Na⁺ ions exchanged).

Ca₄₀-Y did not show cracking activity for SBB, not even after treatment with water (Fig. 1). The only substance desorbed (at 300° C) was SBB. All Ca²⁺ ions are located on SI sites, where they are not accessible to the reactant and hence inactive. (The appearance of mass 78 in the mass spectrum does not indicate formation of benzene, but corresponds to the mass spectrum of SBB.)

Anhydrous Ca₅₈-Y gave a desorption maximum of benzene at 480° C. It was shifted to 475° C, when a small amount of water was injected, and a second maximum of benzene appeared at 375° C (Fig. 2).

In our opinion, the cracking activity should not be ascribed to Brönsted sites, for several reasons: The anhydrous zeolite exhibited activity. If this was due to some remaining Brönsted sites, the maximum at 480° C should be increased on adding

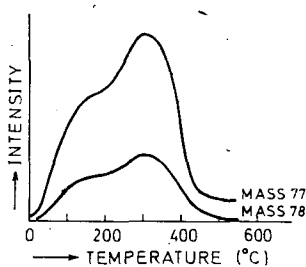


Fig. 1a. TPD spectra on anhydrous $\text{Ca}_{40}\text{-Y}$

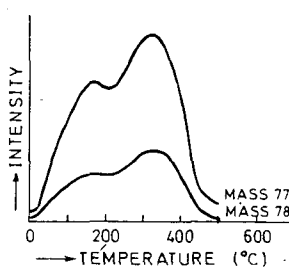


Fig. 1b. TPD spectra on $\text{Ca}_{40}\text{-Y}$ with 1.8 weight % H_2O

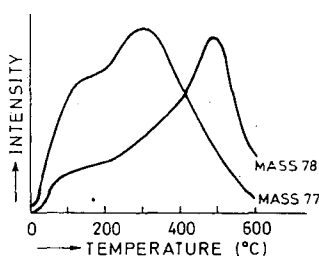


Fig. 2a. TPD spectra on anhydrous $\text{Ca}_{58}\text{-Y}$

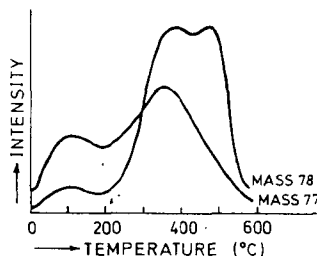


Fig. 2b. TPD spectra on $\text{Ca}_{58}\text{-Y}$ with 6.5 weight % H_2O

water, but a second maximum should not appear. Provided there are no Ca^{2+} ions on SII sites until all SI sites are occupied, the occupation of SII sites in CaY should begin at an exchange of 57%. Hence in anhydrous $\text{Ca}_{58}\text{-Y}$, only a few Ca^{2+} ions should be on SII sites. The cracking activity may be ascribed to them, *i.e.* the maximum at 480°C is due to the interaction of SBB with waterfree cations in accessible sites.

The "catalytic" function of water would be to enable the cations to migrate [3] from the SI sites (where they are located in the anhydrous zeolite without displaying activity) to the SI' and SII' sites or even SII sites, where they exhibit activity, rather than originate Brönsted sites (equation 1). Thus, the 480°C maximum could be ascribed to the desorption of benzene, previously formed from SBB, from an anhydrous cation. A hydrated cation is less strong an adsorption site, but is still active for cracking. So benzene is desorbed at 375°C .

It would be difficult to explain this result with OH groups. It is true, the number of OH groups should increase, when water is added (equation 1). But this should enhance the maximum or bring about a continuous shift to somewhat lower temperatures rather than lower the temperature by 100°C . It would be difficult to assign the two maxima to two types of OH groups, in the same way as we assign it to anhydrous and hydrated cations.

In $\text{Mg}_{32}\text{-Y}$, 9 of 16 SI sites are occupied. The anhydrous zeolite had a small maximum of benzene at 380°C (Fig. 3). When water was added a strong well marked maximum of benzene appeared at 360°C . $\text{Mg}_{62}\text{-Y}$ was similar to $\text{Mg}_{32}\text{-Y}$.

The maximum found with the Mg-Y was close to the low temperature maximum of Ca-Y. There was no second maximum. Mg^{2+} is known to be considerably more active than Ca^{2+} in comparable catalysts [4]. On the other hand, it retains more water. The reason for the activity and the retention of water is the same, *i.e.* its high EPA strength. So it is possible that the high temperature maximum observed with Ca-Y

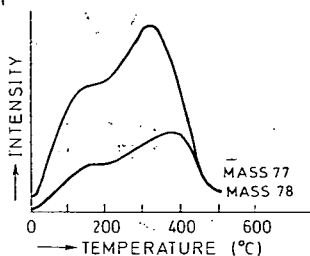


Fig. 3a. TPD spectra on anhydrous $Mg_{32}\text{-Y}$

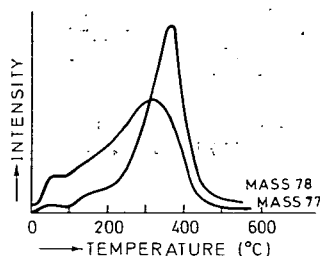


Fig. 3b. TPD spectra on $Mg_{32}\text{-Y}$ with 3.1 weight % H_2O

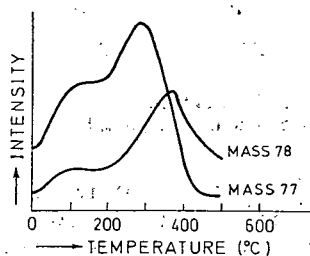


Fig. 4a. TPD spectra on anhydrous $Mg_{62}\text{-Y}$

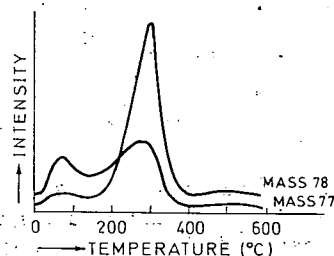


Fig. 4b. TPD spectra on $Mg_{62}\text{-Y}$ with 4.0 weight % H_2O

cannot be seen with Mg-Y, because it is impossible to remove the water to as high an extent as in Ca-Y.

With higher content of water the desorption maxima of benzene were shifted to lower temperatures.

Microcatalytic technique, Dealkylation

SBB was studied on $Ca_{100}\text{-Y}$ and $Ba_{64}\text{-Y}$ (Tables I and II). The cracking activity of $Ba_{64}\text{-Y}$ was nearly as high as that of $Ca_{100}\text{-Y}$. In our opinion, there is no possibility to interpret this finding with Brönsted sites, since Ba-Y is known to have fewer Brönsted sites than Ca-Y [5]. Thus, ascribing the activity to Brönsted sites, we should expect $Ca_{100}\text{-Y}$ to be more active than $Ba_{64}\text{-Y}$. However, the result can be explained if cations are assumed to be active sites. As Ba^{2+} tends to occupy SI' and SII' sites rather than SI sites [6], Ba-Y samples with a lower degree of exchange can have a higher activity than Ca^{2+} exchanged samples.

Table I

Dealkylation of SBB on Ca₁₀₀-Y as a function of content of water and temperature

Temperature of reaction °C	Water injected weight %	Aliphatic hydrocarbons % _a)	Benzene % _a)	SBB % _a)
500	0	28	22	50
	0.41	33	23	44
	2.07	35	30	35
420	0	23	11	66
	0.41	33	20	47
	2.07	38	12	50
330	0	23	13	64
	0.83	22	14	64
	4.15	27	19	54

a) The peak areas are given so that the sum of them is equal to 100%. No correction for sensitivity of different species was applied.

Table II

Dealkylation of SBB on Ba₆₄-Y as a function of water content and temperature

Temperature of reaction °C	Water injected weight %	Aliphatic hydrocarbons % _a)	Benzene % _a)	SBB % _a)
500	0	29	24	47
	2.22	30	26	44
440	0	20	16	64
	2.22	19	18	63
350	0	20	13	67

a) The peak areas are given so that the sum of them is equal to 100%. No correction for sensitivity of different species was applied.

Microcatalytic technique, Dehydration of 2-butanol

Mg₃₂-Y was studied between 330 and 540° C (Table III). Only a small alteration of the conversion was observed in that temperature range (of 210° C).

This may again be related to the migration under the influence of water of Mg²⁺ from inactive SI sites in the prisms to the (active) SI' and SIH' sites in the cubooctahedrons. A higher temperature implies a higher rate of reaction. If one (invariable) active center (one cation) is considered only the highest conversion should be expected at 540° C. However, in the reaction water is produced and that varies the number of Mg²⁺ in accessible positions, i.e. the number of active sites. Since less water is retained on the zeolite at higher than at lower temperatures, the number of the cations in active sites decreases with increasing temperature.

Table III

Dehydration of 2-butanol on Mg₃₂-Y as a function of content of water and temperature

Temperature of reaction °C.	Water injected weight %	Aliphatic hydrocarbons % _{a)}	2-butanol % _{a)}
540	0	64	36
400	0	67	33
	1.81	66	34
	3.62	68	32
330	0	69	31
	1.81	69	31
	3.62	68	32

a) The peak areas are given so that the sum of them is equal to 100%. No correction for sensitivity of different species was applied.

Consequently, there are two opposite effects: the increase of the rate of reaction on one hand and the decrease of the number of active sites, because of the lower water content on the other hand. This may be the reason for the reaction rate found to be independent of temperature.

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DECOMPOSITION OF ALCOHOLS OVER DIFFERENT FORMS OF GERMANIUM SUBSTITUTED FAUJASITE AND PHILLIPSITE

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Several cation forms of germanium substituted X zeolite and phillipsite are tested for their dehydration/dehydrogenation properties of alcohols. Both types of sites are present and act independently, excluding E_1cB type mechanism. No secondary reactions occur in striking contrast to their silicium homologues. Isotope effects measured on different samples indicate the mechanism is in between E_1 and E_2 , depending on the zeolite and the cation.

Upon ion exchange with polyvalent cations, the same behavior is observed as for other zeolites and other proton catalysed reactions. Dehydrogenation seems to occur at exposed surface germanium atoms.

Very weak acid sites related to the presence of residual surface carbonate are shown to dehydrate only tertiary alcohols.

Introduction

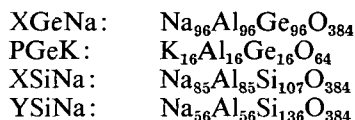
The catalytic decomposition of alcohols is strongly dependent upon the alcohol structure but also on the nature of the catalyst and, therefore, may provide information on the general way a catalyst functions in elimination and even other reactions. Practically, the use of alcohols as source of fuels and basic chemicals nowadays is being considered very seriously.

The dehydration/dehydrogenation capability of silicic zeolites was investigated intensively and the knowledge was reviewed several times [1—3]. The dehydration reaction was found to be catalysed by very weak acid sites [1, 2, 4] and is therefore a measure of the overall Brønsted acidity, although for polyvalent ion exchanged zeolites the direct influence of cations cannot be excluded experimentally [3, 5]. The dehydrogenation reaction of alcohols was related to the presence of cations, even at the impurity level [6].

It is the aim of the present work to test these ideas about reaction mechanism and active sites on the germanium homologues of faujasite and phillipsite zeolites.

Experimental

The synthesis and physico-chemical characterization of germanium substituted faujasite and phillipsite were described in detail [7—10]. The samples are denoted as follows. The first capital indicates the type zeolite (X, Y or P, phillipsite). This is followed by the indication whether the zeolite is silicic (Si) or germanic (Ge). Then is given the parent cation (Na or K) followed by the exchanged cation and its degree of exchange in %. The parent zeolites have the following anhydrous unit cell composition:



Other cations were exchanged into these zeolites, using diluted solutions and low solid to liquid ratios [4, 10]. The reactants were of analytical grade and deuterated alcohols were prepared according to a procedure found in literature [11].

Decomposition of alcohols was studied either in a conventional recirculation reactor or in a continuous flow reactor operating in the differential mode. Analysis of the products was done *in situ* using gas chromatography. *In situ* infrared spectra were recorded on a BECKMAN IR—12 double beam grating spectrometer.

Results

Reaction selectivity for isopropanol decomposition

Under the experimental conditions, the main reaction products from isopropanol were acetone and propylene. At the relatively high reaction temperatures ($>200^{\circ}\text{C}$), only traces of di-isopropylether were found. They will be neglected further on. In Table I, it is shown that neither the reaction time in the recirculation reactor, the alcohol pressure, nor the reaction temperature have a pronounced influence on the reaction selectivity. This is confirmed in the flow reactor for a wide range of contact times (0.5—3.5 s). The data therefore indicate that the sites responsible for dehydration and dehydrogenation act independently.

Fig. 1 shows the evolution of the amount of secondary products formed at increasing degree of isopropanol conversion in comparable conditions and for several catalysts. In the silicic faujasites (X and Y) they are of major importance, while on the germanic X and P zeolites, they are found in negligible amounts. This allows to state that in a wide range of reaction conditions, the germanium zeolites are highly selective towards primary products. Dehydrogenation is favored on PGe zeolite while the XGe zeolite has more pronounced dehydration power (see Table I).

Influence of the degree of cation exchange

Fig. 2 shows the relative rates of isopropanol dehydration and dehydrogenation for XGe in which Ca^{2+} was exchanged for Na^{+} , Ni^{2+} for Na^{+} , and Ni^{2+} for Ca^{2+} . In each case, there is a more than proportional increase of the dehydration activity.

Table I
Influence of reactant pressure and reaction temperature on selectivity of isopropanol decomposition

Catalyst	Reaction temp. °C	P kNm ⁻²	Selectivity ⁽¹⁾ in % for		S ⁽²⁾
			propylene	acetone	
XGeNaNi (60)	250	3.733	76.5	23.5	2.3
	280	3.733	76.9	23.1	2.5
	300	3.733	77.0	23.0	1.8
	300	1.333	78.9	21.1	1.2
XGeCaNi (60)	230	3.733	88.4	11.6	1.1
	270	3.733	88.3	11.7	0.5
	300	3.733	89.3	10.7	1.2
	300	1.333	91.3	8.7	2.2
	350	3.733	85.1	14.9	2.4
PGeKNi (60)	230	3.733	4.9	95.1	0.8
	300	1.333	11.4	88.6	1.1
	300	3.600	10.6	89.4	1.3

⁽¹⁾ Calculated on the basis of primary products.

⁽²⁾ Standard deviation of selectivity during reaction.

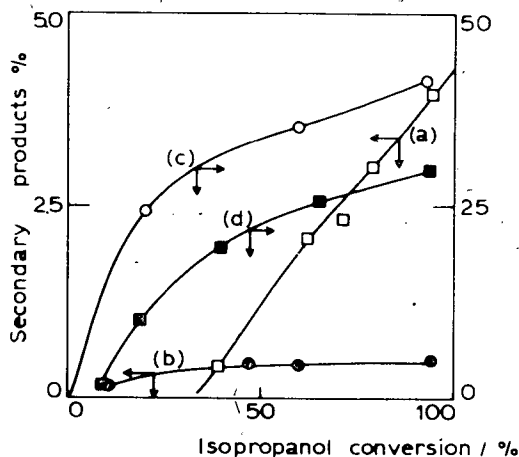


Fig. 1. Amount of secondary products formed against the degree of isopropanol conversion over: a) PGeNaNi (46) at 300° C; b) XGeCaNi (56) at 350° C; c) YSiNaCa (67) at 300° C; d) XSiNaCa (50) at 300° C

at exchange levels exceeding 50%. A very similar relation has been observed for the silicic analogues X and Y, and also for many other reactions (for a review, see ref. [2]). In the case of nickel exchanged zeolites, the behavior during dehydrogenation is similar, indicating the participation of nickel. For the XGeNaCa catalysts, dehydrogenating sites with different nature are present.

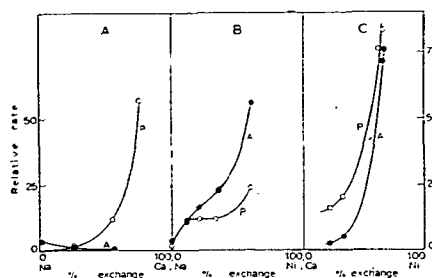


Fig. 2. Influence of the degree of cation exchange of XGeNa (A, B) or XGeCa (C) zeolites on the relative rate of propylene (P) and acetone (A) formation from isopropanol

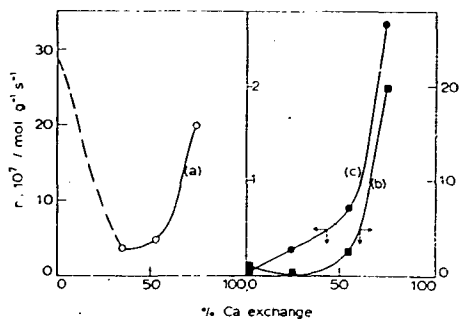


Fig. 3. Initial rate of alcohol dehydration (r) on Ca-exchanged XGeNa; a) $(\text{CH}_3)_3\text{COH}$ at 200°C ; b) $(\text{CH}_3)_2\text{CHOH}$ at 300°C ; c) $\text{CH}_3\text{CH}_2\text{OH}$ at 300°C

Influence of the nature of the alcohol

The initial rate of alcohol dehydration over XGeNaCa catalysts is given in Fig. 3. The activity decreases in the following sequence: tert. butanol $\gg$ isopropanol $\gg$ ethanol. This general order of reactivity parallels the generally observed order of stability of the corresponding carbonium ions [13]: tertiary $\gg$ secondary $\gg$ primary.

Surprisingly, the parent sodium form of XGe is more active than the Ca exchanged forms in the case of dehydration of the tertiary alcohol. In the case of isopropanol dehydration, the Na form is only slightly more active than the samples with low Ca content. This effect does no longer exist for the primary alcohol. This indicates that weak acid sites exist on XGeNa, which still catalyze the dehydration of tertiary and to a minor extent of secondary alcohols. Fig. 4 shows that these sites exist on the

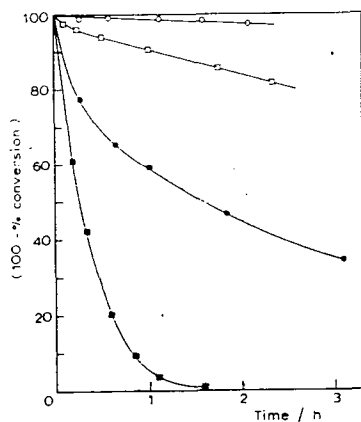


Fig. 4. Dehydration of tertiary-butanol on sodium X zeolites: XSiNa at 200°C (○) and 230°C (□); XGeNa at 200°C (●), and 230°C (■)

Table II

Initial rate of isopropanol decomposition on Ge substituted faujasite and phillipsite at 300°C

Catalyst	$r_p \times 10^8$ $\text{mol g}^{-1} \text{s}^{-1}$	$r_A \times 10^8$
PGeNa	3.4	4.8
XGeNa	3.7	5.6
PGeNi	2.5	23.7
PGeZn	2.2	196.0

germanium form, but not on the silicium homologue. Indeed, the dehydration activity of $(\text{CH}_3)_3\text{COH}$ is highest on the germanium form compared to the silicium X zeolite. The latter effect has to be related to the existence of residual carbonate species on the germanium sieve.

Influence of nature of cation and of zeolite

It was already pointed out that the parent germanium forms of phillipsite have stronger dehydrogenating properties than the faujasite. This is confirmed in Table II. From this table it is further clear that upon exchange with Ni and Zn, the dehydrogenating properties increase drastically. This is indicative of two kinds of dehydrogenating sites, one set being present on the parent zeolite, another appearing upon exchange with Ni^{2+} or Zn^{2+} .

The dehydrogenation properties of the germanium zeolites could be poisoned gradually with carbon monoxide (Fig. 5). At the same time an IR band at 2190 cm^{-1} with increasing intensity was observed. This band is due to chemisorbed CO.

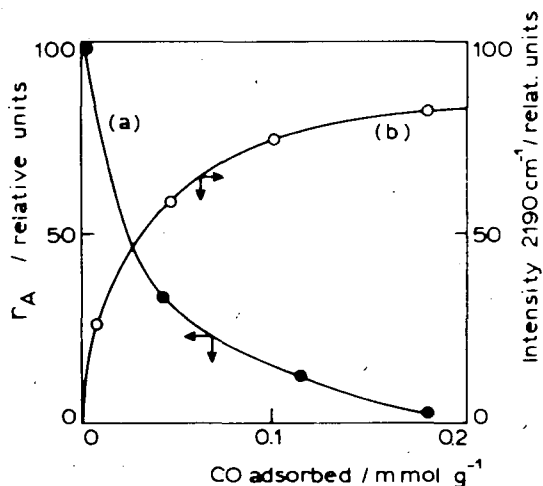


Fig. 5. Carbon monoxide poisoning on rate of acetone formation (a) on XGeNa at 275°C and intensity changes of the IR band (b) of adsorbed carbon monoxide at 200°C

Isotope effects

In Table III are given the isotope effects in the dehydration of 2-butanol. A significant effect is observed in the case of deuteration of the alcohol H atom over XSiNa, XGeCa and PGeNaCa. On the other zeolites this primary isotope effect is much less important, while a significant effect is observed when deuteration of the H atoms on a carbon atom in β position has occurred.

Table III
Dehydration of 2-butanol over zeolite

Zeolite	Temperature °C	$\alpha^{(1)}$	$\beta^{(2)}$
XSiNa ⁽³⁾	200	2.9	1.10
XGeNa	275	1.8	1.90
XGeCa	250	2.4	1.25
PGeNa	300	1.4	2.10
PGeNaCa (60)	300	2.0	1.75

(1) Isotope effect for $\text{CH}_3\text{—CH}_2\text{—CHOD—CH}_3$.

(2) Isotope effect for $\text{CD}_3\text{—CD}_2\text{—CHOH—CH}_3$.

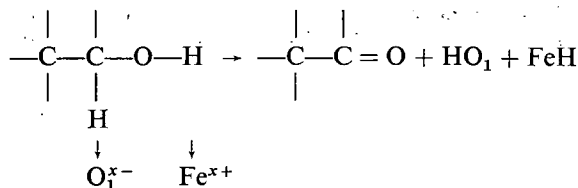
(3) From ref. [4].

Discussion

Reaction mechanism

Dehydration of alcohols may occur *via* a continuous sequence of possibilities, E_1 , E_2 and E_1cB eliminations being limiting cases [5]. In case of elimination near the E_1cB side, reaction starts with rupture of the most acidic C—H bond and dehydrogenation is occurring as well as dehydration [3, 5]. In the present case, there is strong evidence that distinct sites exist for dehydration and dehydrogenation (see Table I). This means necessarily that the alcohol dehydration mechanism is between E_1 and E_2 on the germanium zeolites. For the silicic X and Y zeolites, it has been proved that the reaction is on the E_1 side for most alcohols, methanol not taken into account [4]. When a primary isotope effect exists, the reaction has to shift to the E_1 side. When the mechanism is concerted (E_2 side) an isotope effect in H at C_β should exist. In this respect, Table III allows to conclude that: (i) upon germanium incorporation in the structure, the mechanism tends to shift more to the E_2 side, this being more pronounced for the germanium phillipsite; (ii) exchange with polyvalent cations (Ca^{2+}) shifts the mechanism again to the E_1 side, due to an increase of the electron pair acceptor properties of the structure [5], regardless whether the cations or protons act as active sites.

The dehydrogenation over Y and XSi was found to occur over an acid-base pair of sites, the impurity iron species playing a dominant role:



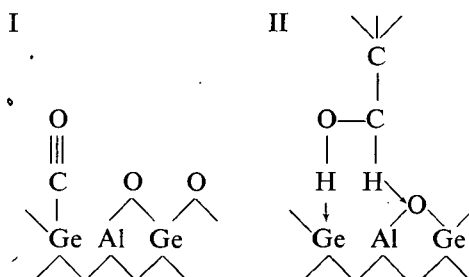
O_1 represents lattice oxygen. In the case of Ni^{2+} and Zn^{2+} exchanged samples, a similar mechanism may exist. The same mechanism can be invoked to explain the dehydrogenating activity of the parent unexchanged germanium sieves. The nature of the active site will be discussed later.

Active sites for dehydration

The activity sequence: tertiary > secondary > primary alcohols indicates a proton catalyzed E_1 type reaction, since it parallels the stability of the corresponding carbo-nium ions. The behaviour upon Ca^{2+} exchange (more than linear increase above 50% exchange) tends to favor this interpretation. Indeed, this is a common behavior observed for most zeolites and for most proton catalyzed reactions in zeolites. However, since at this degree of exchange, Ca^{2+} ions become available in the supercage, it cannot be excluded that they act as active sites, since they have electron pair acceptor properties [3, 5]. At the moment, no direct experimental evidence is present, that could reject the generally accepted views in zeolite catalysis and favor the second hypothesis. The remarkable selectivities for primary reaction products observed on the present zeolites, are also observed for olefin isomerization on XGeNaNH_4 zeolites [13]. This suggests that in both cases protons may be the active sites. The parent XGeNa contains weak sites, not present on XSiNa and strong enough to catalyze the dehydration of tertiary alcohols (Figs 3 and 4). This has to do with the presence of residual surface carbonate species in the germanic sieve [7, 10]. Upon addition of water under reaction conditions bidentate carbonate species (bands at $1580\text{--}1250\text{ cm}^{-1}$) are replaced by monodentate species ($1660\text{--}1375\text{--}1175\text{ cm}^{-1}$) [14]. A similar observation was reported on MgO [15] and carbon dioxide was also found to enhance the dehydration properties of silicic zeolites by similar surface reactions [2].

Active sites for dehydrogenation

Besides the dehydrogenation sites on Ni and Zn exchanged germanium zeolites associated with a cation—lattice oxygen pair of sites, the parent germanium zeolites have dehydrogenating sites of distinct nature (Table II) which can be poisoned with CO (Fig. 5). This form of chemisorbed CO (2190 cm^{-1}) never observed on the silicium zeolites, is most probably bonded to germanium at oxygen deficient sites, and can be schematized as follows (I)



The reaction can occur over an acid-base pair of sites as illustrated in II.

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DEHYDRATION OF PROPAN-2-OL ON Y ZEOLITES

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Studies of propan-2-ol dehydration made in a flow system operating at a total pressure of one atmosphere, show that propene and di-isopropyl ether are readily produced by parallel reactions occurring at BRØNSTED acid centres within Y zeolites. In addition to HY; MgY, CaY, NiY, CuY, AgY and LaY were found to be active catalysts. Treatment with H₂S greatly increased the activities of NiY and CuY, had smaller effects on AgY and LaY, and none on MgY and CaY. A reaction mechanism involving carbonium and oxonium ion intermediates is discussed.

Introduction

Variations in alcohol structure, the nature and extent of cation exchange, and the susceptibility to base poisons show that carbonium ion intermediates are involved in alcohol dehydration on faujasitic zeolites [1—3]. Dehydration of propan-2-ol on X and Y zeolites in microreactors [4] and recirculatory-flow reactors [5] yields propene and water, whereas di-isopropyl ether is also produced in continuous-flow reactors [6, 7]. From a study of propan-2-ol dehydration on a series of HX zeolites, GENTRY and RUDHAM [6] proposed an ionic mechanism involving one O1H group for propene formation and two O1H groups for di-isopropyl ether formation. JACOBS *et al.* [7] investigated alkali cation exchanged X and Y zeolites, and showed that propene and di-isopropyl ether were formed by parallel reactions catalysed by weakly acidic OH groups. The OH groups were formed either by interaction of water with cations and the zeolite lattice, or by hydrolysis of polyvalent cation impurities. The generation of acidic OH groups through cation hydrolysis is also considered to be the source of activity for propan-2-ol dehydration on a number of di- and trivalent cation exchanged X and Y zeolites [4, 8—10].

Experimental

Propan-2-ol dehydration was studied in a continuous-flow system in which the total pressure of alcohol and nitrogen diluent was one atmosphere [6]. A small number of infra-red measurements were made using a cell which could take the place of the reaction vessel, and had provisions for dehydrating samples at elevated temperatures.

The catalysts were prepared from binder-free NaX (B. D. H./Linde 13X, lot 0003940) or NaY (Linde SK-40, lot 3606-150) by cation exchange with aqueous solutions of analytical grade salts. Catalysts are designated MX- n or MY- n , where n represents the extent of exchange in terms of the number of exchange cations M per unit cell.

Results and Discussion

Catalysis on HX and HY Zeolites

Catalysts were prepared by calcination of either 10 mg or 100 mg samples of NH_4X and NH_4Y for 16 hr at 623 K in a $1.67 \text{ cm}^3 \text{ s}^{-1}$ flow of cylinder N_2 . Infra-red examination of $\sim 50 \text{ mg}$, 2.5 cm pressed disc of $\text{NH}_4\text{Y-14.0}$ subjected to identical calcination showed deammoniation to be complete. A band at 3640 cm^{-1} superimposed on a broad band between $3700\text{--}3250 \text{ cm}^{-1}$ and a band at 1642 cm^{-1} indicated the presence of molecular water in addition to OH groups. Under these circumstances it is unlikely that any dehydroxylation occurs during calcination.

A series of comparative experiments between X and Y zeolites were made with samples of HX-8.6 and HY-8.4. It was found that the rate of formation of both diisopropyl ether (r_e , molecules $\text{g}^{-1} \text{ s}^{-1}$) and propene (r_p , molecules $\text{g}^{-1} \text{ s}^{-1}$) on HY-8.4 between 372 and 400 K obeyed zero-order kinetics with respect to propan-2-ol pressure between $2.8 \cdot 10^2$ and $4.2 \cdot 10^3 \text{ Pa}$. Similar experiments with HX-8.6 confirmed the small pressure dependencies previously observed [6]. Negligible error is introduced

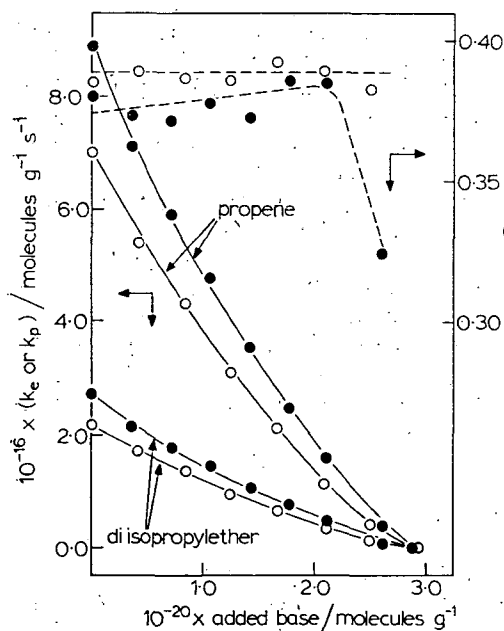


Fig. 1. Progressive poisoning of HY-8.4 with: ● — pyridine at 381 K, ○ — piperidine at 379 K.

in assuming zero-order kinetics for both catalysts at low extents of reaction, when r_e and r_p become the zero-order rate constants k_e and k_p . The effect of temperature on k_e and k_p was investigated with both catalysts under conditions where extent of dehydration was $< 10\%$ of $1.11 \cdot 10^3 \text{ Pa}$ of alcohol in a total flow of $0.5 \text{ cm}^3 \text{ s}^{-1}$. Measurements covering ~ 35 degrees gave excellent Arrhenius plots, and values of the activation energies E_e , E_p , pre-exponential factors k_e^0 , k_p^0 , and k_e and k_p at 377 K are given in Table I. The data clearly indicate that differences in activity between HX-8.6 and HY-8.4 are controlled by energetic considerations rather than by differences in the concentration of active sites. The concentration of active Brönsted acid sites was thus determined by titrating working catalysts by the progressive adsorption of pyridine or piperidine. Figure 1 shows plots obtained with HY-8.4,

where, for each base, the curves for k_e and k_p intersect on the zero activity axis. Similar results were obtained for HX-8.6, and values for the concentration of active sites, taken to be the amount of base necessary for complete poisoning, are given

Table I
Comparison of HX and HY catalysts

		HX-8.6	HY-8.4
Di-isopropyl ether formation	k_e at 377 K/molecules $\text{g}^{-1} \text{s}^{-1}$	$3.98 \cdot 10^{14}$	$2.24 \cdot 10^{16}$
	k_e^0 /molecules $\text{g}^{-1} \text{s}^{-1}$	$1.8 \cdot 10^{30}$	$1.6 \cdot 10^{30}$
	E_e /kJ mol^{-1}	113	100
Propene formation	k_p at 377 K/molecules $\text{g}^{-1} \text{s}^{-1}$	$2.82 \cdot 10^{15}$	$6.17 \cdot 10^{16}$
	k_p^0 /molecules $\text{g}^{-1} \text{s}^{-1}$	$1.6 \cdot 10^{32}$	$1.5 \cdot 10^{32}$
	E_p /kJ mol^{-1}	121	111
Brönsted acid site concentration/ $10^{-20} \cdot x$ sites g^{-1}	from NH_4^+ exchange	2.91	2.89
	from pyridine poisoning	2.61	2.88
	from piperidine poisoning	2.97	2.93

in Table I. The values obtained from the bases of different strength, and that calculated from the NH_4^+ content of the catalyst precursors, are closely similar. We conclude that all the hydroxyl groups produced by deammoniation are available, and are of sufficient acid strength, to catalyse the dehydration of propan-2-ol to di-isopropyl ether and propene. The selectivities for ether formation on HY-8.4, shown in Fig. 1 and defined as $S_e = 2k_e/(2k_e + k_p)$ remain effectively constant with increasing base adsorption until very high coverages are achieved. This, together with the observation that wide variations in reactant space velocity could not achieve a condition where $k_e > k_p$, show that propene and di-isopropyl ether are formed by parallel reaction paths.

The effects of varying the extent of ion exchange have been investigated with a series of HY catalysts using $1.11 \cdot 10^3$ Pa of propan-2-ol in a total flow of $0.5 \text{ cm}^3 \text{ s}^{-1}$ (a reactant mixture and flow rate used in all further experiments). Since values of E_e and E_p were all within 4 kJ mol^{-1} of the respective mean values of 99 and 111 kJ mol^{-1} , catalytic activities can be directly compared. Values of k_e and k_p at 377 K, an experimental temperature common to all catalysts, are plotted against the extent of exchange in Fig. 2. Linear plots are obtained for both products on catalysts containing more than 4 OH groups per unit cell, with values of S_e showing a monotonic increase from 0.36 for HY-4.3 to 0.47 for HY-16.6. This indicates that both propene and di-isopropyl ether formation involve a single OH group.

To account for our observations we propose the reaction sequence shown in Fig. 3. Since water is present after deammoniation, OH groups are ionised (1) to form H_3O^+ ions associated with structural O^- ions in the α -cages. At high propan-2-ol concentrations, proton transfer (2) gives an oxonium ion, which yields a carbonium ion by the E_1 elimination of H_2O (3). Subsequently, proton transfer (4) yields propene and H_3O^+ . Alternatively, interaction with propan-2-ol (5) results in an oxonium ion which, on proton transfer (6) yields di-isopropyl ether and H_3O^+ . In view of the partial pressure of propan-2-ol being relatively high to that of the water produced,

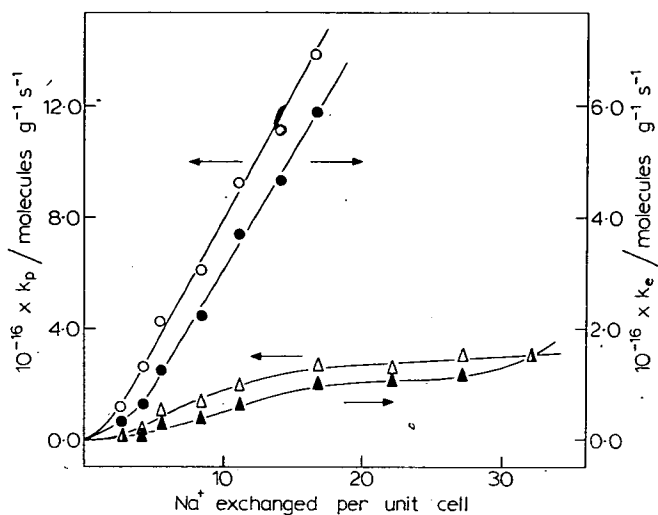


Fig. 2. Activity for di-isopropyl ether and propene formation at 377 K as a function of the extent of ion exchange: ● — k_e on HY, ○ — k_p on HY, ▲ — k_e on CuY, △ — k_p on CuY.

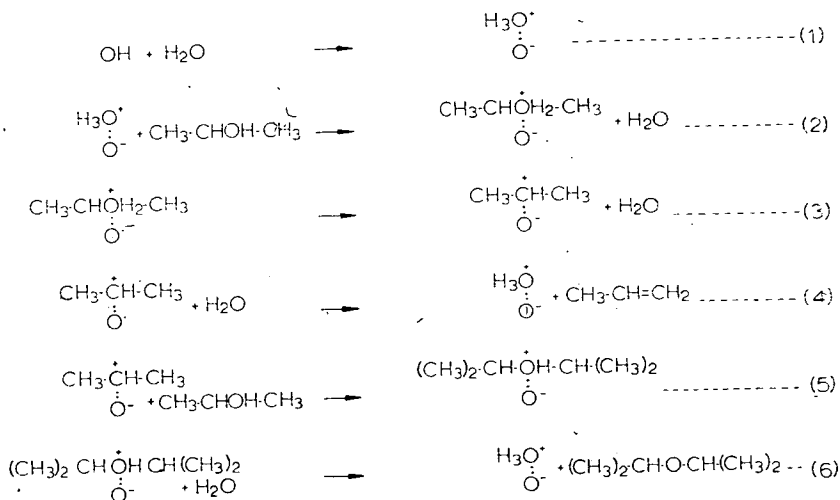
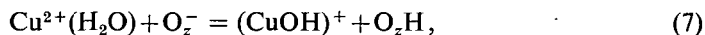


Fig. 3. Reaction sequence for di-isopropyl ether and propene formation on HY catalysts.

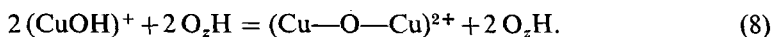
possible alternatives to (4) and (6) may be proton transfer to propan-2-ol to give the oxonium ion produced in (2). Presumably, the water elimination (3) makes the largest contribution to the overall activation energy, and this accounts for the similarity in E_e and E_p . This mechanism, although basically similar to those previously suggested [6, 7], differs in that only a single site is involved in ether production. Furthermore, it obviates the interaction of positively charged carbonium and oxonium ions [6].

Catalysis on CuY Zeolites

CuY zeolites catalyse propan-2-ol dehydration, but, in contrast to HY, they took an appreciable time to achieve constant activity following changes in the reaction conditions. The activity also depended on the initial dehydration conditions, but the chosen pretreatment of 2 hr in flowing N_2 ($0.67 \text{ cm}^3 \text{ s}^{-1}$) at 523 K gave the optimum activity most rapidly. Infra-red examination of CuY-8.4 given this pretreatment indicated the presence of molecular water. Values of k_e and k_p at 377 K obtained at nine Cu^{2+} contents are shown in Fig. 2, where the activity consistently falls below that suggested by the hydrolysis of *all* Cu^{2+} according to:



possibly followed by



Although zero-order kinetics were obeyed, E_e increased from 82 to 122 kJ mol^{-1} and E_p increased from 98 to 132 kJ mol^{-1} with increasing Cu content. The experimental findings show that the concentration of Brönsted acid centres is critically dependent on cation distribution and the extent of cation hydrolysis. In addition to concentration effects with water and other molecules on k_e and k_p , E_e and E_p vary from those on HY by contributions from the ΔH values associated with changes of cation location and hydrolysis.

Catalysis on Other Y Zeolites and the Effects of H_2S Treatment

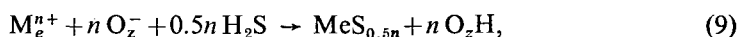
Catalytic activities at 377 K have been determined for a number of Y zeolites in which the extents of exchange of Na^+ for other cations were approximately equivalent. In all cases the catalysts were dehydrated as with CuY, and no dehydrogenating activity to acetone was observed. Values of k_e and k_p given in Table II show

Table II
Effect of H_2S treatment on dehydration activity at 377 K
(values of k_e and k_p in 10^{-14} molecules $\text{g}^{-1} \text{s}^{-1}$)

		HY-11.1	AgY-11.5	MgY-5.5	CaY-5.5	NiY-5.1	CuY-5.6	LaY-3.8
Before H_2S	k_e	370	330	0.68	0.076	4.5	60	230
	k_p	930	790	2.2	0.71	25	190	490
	S_e	0.44	0.46	0.38	0.18	0.27	0.39	0.48
After H_2S	k_e	—	420	0.68	0.096	220	450	200
	k_p	—	910	2.2	0.93	680	1000	450
	S_e	—	0.48	0.38	0.17	0.39	0.47	0.47

a wide spread of activities, with only that of AgY-11.5 approaching HY-11.1. This most probably occurred through a substantial reduction of $\text{Ag}^+ \rightarrow \text{Ag}^0$ accompanied by O_zH formation in the initial stages of reaction. The S_e values, apart from those of low activity catalysts which are subject to appreciable error, suggest the same mechanism as on HY zeolites.

In view of the increase in cumene cracking activity observed following H_2S treatment of certain ion-exchanged Y zeolites [11], we have determined activities following treatment of the catalysts with $\sim 20\text{ cm}^3 H_2S$ for 15 min. The data in Table II show a large increase in the activities of NiY-5.1 and CuY-5.6, a smaller effect with AgY-11.5, no effect with MgY-5.5 and Ca-5.5, and even slight poisoning with LaY-3.8. Additional experiments also showed that there was no effect with NaY and HY-14. Such observations are in accord with those of SUGIOKA *et al.* [11]. A series of experiments with H_2S treated CuY-4.2 confirmed that the activity increase was associated with Brönsted acidity, since complete poisoning with pyridine readily occurred at 377 K. In addition, the source of the additional activity possessed similar stability to that of untreated CuY zeolites, since there was no diminution in activity following heating at 523 K for 2 hr in flowing nitrogen. We believe the increases in activity arise from hydroxyl groups generated in the reaction:



and that the neutral $MeS_{0.5n}$ entity resists hydrolysis in the cases of AgY-11.5, NiY-5.1 and CuY-5.6. With AgY-11.5 both Ag^0 and Ag^+ probably react with H_2S , but only the Ag^+ will generate additional O_zH groups, so accounting for the smaller H_2S effect with this catalyst.

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ESR- AND SUSCEPTIBILITY MEASUREMENTS ON PALLADIUM PARTICLES SUPPORTED ON Y-ZEOLITES

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Pd(II)-ion exchanged zeolites have been dehydrated with flowing oxygen at 900 K. The dehydrated zeolites have been reduced with flowing hydrogen at 77 K and at 300 K and have been outgassed at 300 K and at 700 K respectively. Particle size and the size distribution of the Pd particles have been determined by electron microscopy and X-ray diffractometry. The results indicate that not all the palladium particles are atomically dispersed. A new resonant absorption at $g=2.16$ has been observed for the reduced samples. The temperature dependence of this line has been shown to give a maximum at significant temperatures depending on the particle size. Analogous results have been obtained by static magnetic measurements.

Introduction

Zeolites containing palladium belong to the most investigated metal loaded molecular sieves. The dispersion of the metal depends on the cation content, treatment before reduction and the condition of reduction. In recent years a number of papers dealt with the state of the metal in equally pretreated and equally reduced PdY-zeolites of the same composition. As was shown by GALLEZOT ET AL. [1] by crystal structure analysis, reduced palladium remains atomically dispersed inside the sodalite cage up to about 500 K. Between 500 K and 600 K the Pd(0) atoms migrate towards the outer surface of the zeolite, where they agglomerate into 2 nm diameter particles. NACCACHE ET AL. [2] demonstrated by ESR and IR spectrometry that the electron density of the Pd(0) is low because of its strong interaction with Lewis acid sites of the zeolite network due to the pretreatment conditions: actually 8% palladium was shown to be in the Pd(1) state. The electron deficient character of the isolated metal atoms was also evidenced by pyridine adsorption as reported by PRIMET ET AL. [3].

In the present study we are mainly interested in the magnetic properties of small metallic palladium clusters. Most of these particles are likely formed within the zeolite cavities; their diameters will be limited by the supercage size. In order to achieve this, we employed the same pretreatment conditions reported by the authors mentioned above; however, the conditions for the reduction have been modified.

Experimental Section

The starting material was the LINDE Na-Y-form (SK 40), the Mn(II)- and Fe(III)-impurities of which were less than 5 ppm. The desired exchange level was readily obtained by stirring a suspension of the zeolite at room temperature for 24 h in a tetramminepalladium ion solution containing a suitable amount of palladium. The zeolite was filtered and then washed with ammonia solution to eliminate Cl^- ions. The sample was analysed by neutron activation analysis. The palladium content was 12 wt% on a dry weight basis.

First, the sample, being in a shallow bed geometry, was slowly heated at a rate of 5 K/min in flowing oxygen followed by an overnight calcination in oxygen at 900 K. Then the zeolite was evacuated at the same temperature at a pressure of $1.3 \cdot 10^{-3}$ Pa for 15 h.

Secondly, the dehydrated zeolite was reduced by hydrogen, dried over activated molecular sieves at 77 K. Hydrogen gas at a pressure of $1.33 \cdot 10^4$ Pa was introduced through a breakseal into the vessel at 77 K and at 300 K respectively during 15 h.

Thirdly, the sample, reduced at 77 K was evacuated at 300 K for 12 h at a pressure of $1.3 \cdot 10^{-3}$ Pa. This sample will be referred to as PdY77/300/72. The zeolite reduced at 300 K followed by evacuation at 700 K for 36 h or 48 h at $1.3 \cdot 10^{-3}$ Pa will be referred to as PdY300/700/36 and PdY300/700/48 respectively. After reduction all samples were handled under argon atmosphere.

Magnetic susceptibility data were obtained using a Foner vibrating sample magnetometer at temperatures between 4 K and 300 K and fields up to 1.6 T. The ESR spectra were taken on a Bruker X-band spectrometer at temperatures between 4 K and 300 K. Electron micrographs and electron diffraction patterns were obtained of ultramicrotomed samples after embedding the samples in Spurr without exposure to air. Final magnification up to 300 000 times was carried out on a Philips EM 301.

Results and Discussion

Before reduction the Pd(II)-ions are mainly located on SI' sites (GALLEZOT ET AL. [1]). Furthermore, about 1 % of the palladium is found in the Pd(III)-form as was shown by NACCACHE [4]. Our pretreated samples show a reddish-brown colour and an ESR signal assigned to Pd(III) in agreement with the samples of [1] and [2].

All the reduced and evacuated samples were characterized by X-ray diffractometry line broadening analysis and electron microscopy. The results are summarized in Table I.

Table I
Particle sizes of the reduced and evacuated samples

Sample	X-ray Mean diameter nm	Electron Microscopy Diameters nm
PdY77/300/72	7.6	.6—1.8 many 5—8 few
PdY300/700/36	20	.6—2.4 less 4—22 more
PdY300/700/48	35	.6—2.5 few 4—36 many

The sample PdY77/300/72 contains larger crystallites on the outer surface of the zeolite. This result, which is in contrast to the 100% dispersion found by other authors, should be due to the low reaction temperature or/and to the additional evacuation procedure. GALLEZOT ET AL. [1] found that, after room temperature reduction, 40% of the Pd atoms are distributed inside the sodalite units. Only after reduction at 500 K and 600 K larger Pd crystallites were found on the outer surface. This result shows that a high energy of activation is needed for the Pd to migrate into the large cages and then out of the pores. Since we find particles in the supercage as well as on the external surface when applying the same pretreatment conditions without rising the temperature above 300 K, some Pd atoms should be removed from the sodalite unit during reduction at 77 K. From the supercage the atoms can migrate to the external surface during evacuation. With our conditions most of the Pd particles were found to be in the large cage. This was our goal.

Upon reduction of the first few Pd ions, water molecules are converted to structural hydroxyl groups, [3]. These groups behave in a similar way to those of decationated zeolites. However, $O_{(3)}H$ groups appear to have a more pronounced acid character than those of H-Y zeolites. The Pd atoms in reduced Y-zeolites are situated close to the acid centers formed by the pretreatment. These withdraw electrons from palladium and as a result, some Pd(0) atoms are oxidized to Pd(I). This was demonstrated by ESR [3].

Recently, however, atomically dispersed Pd(0) was shown to give XPS positive chemical shift [5]. But these shifts were assigned to smaller electron relaxation energies and not to reducing properties of the zeolite surface. In addition, Pd(0) aggregates supported on zeolites, were shown by ESR not to give rise to significant electron transfer [5]. On the other hand, Pt microcrystals on zeolite supports form charge transfer complexes with Lewis acid sites.

Similar results were obtained for iron [6]. For the 250 atom cluster inside Y-type zeolites and even for the 13 atom cluster inside mordenite, prepared by sodium vapour reduction, we found nearly the same electronic configuration as in bulk iron. In A-type zeolites, however, which were reduced by sodium vapour, Lewis acid sites are present after dehydration, caused by a hydrolysis mechanism during ion exchange, producing on the metal cluster, an inner and an outer shell of different electron density, as was evidenced by NGR spectroscopy.

The X-ray patterns of our larger f.c.c. palladium particles show a slight lattice contraction. This should make quite sure, that the Pd on the outer surface does not contain any hydrogen, because this would cause a lattice expansion. A lattice contraction in microcrystals has been frequently observed. It should be a function of $1/(\text{particle size})$. As an example, a_0 -values of 10 nm gold particles on a substrate (KARIOS [7]) decrease by 0.3%, or 0.1% (20 nm microcrystals) and 0.07% (35 nm), respectively. This effect sometimes is called internal pressure. In Pd and Pt particles on zeolites no such observations are reported (GALLEZOT [8]). From the measured lattice contraction we should expect different magnetic properties of the palladium particles.

The results of the ESR spectra of the reduced samples are summarized in Table II. All samples show signals due to Pd(I), $g_{\parallel}(1)$, $g_{\parallel}(2)$. Only in the reduced samples we observed an additional intensive resonance absorption at $g=2.16$. The ESR absorption of Pd(I) $g_{\perp}(1)$, $g_{\perp}(2)$ overlaps with the Pd(0) signal. The temperature dependence of the peak to peak height of the differentiated absorption curve for the

Table II
g-values of the reduced and evacuated Pd-zeolites

Sample	Pd(I), $g_{\parallel}$	Pd(I), $g_{\perp}$	Pd (0) and Pd(I), $g_{\perp}$
PdY77/300/72	2.52	2.31	2.16
PdY300/700/36	2.53	2.31	2.16
PdY300/700/48	2.53	2.31	2.16

PdY77/300/72 is shown in Fig. 1 and for PdY300/700/36 and PdY300/700/48 in Fig. 2. Fig. 1 exhibits a maximum at $12 \text{ K} \pm 3 \text{ K}$ whereas the maxima in Fig. 2 are to be found at $72 \text{ K} \pm 10 \text{ K}$ and $110 \text{ K} \pm 10 \text{ K}$, respectively. For bulk palladium, the susceptibility has a broad maximum at $100 \text{ K} \pm 10 \text{ K}$.

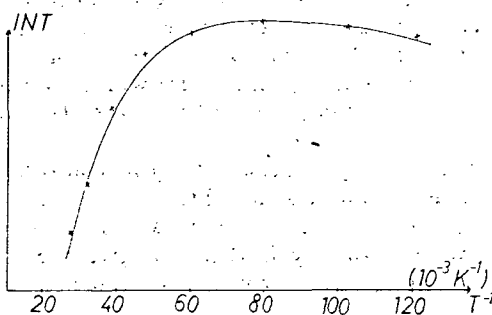


Fig. 1. Temperature dependence of the ESR-absorption at $g=2.16$ of the PdY77/300/72 sample.

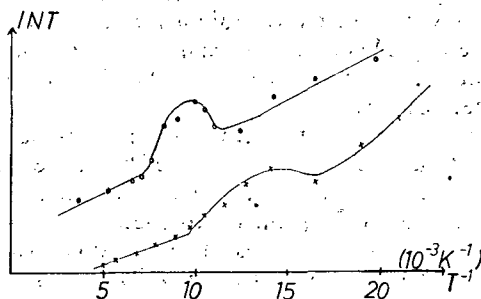


Fig. 2. Temperature dependence of the ESR-absorption at $g=2.16$ of the PdY300/700/36 (x) and PdY300/700/48 (O) samples.

Similar results were obtained from the susceptibility measurements. In Fig. 3 we illustrate, as an example, the relative susceptibility as a function of temperature of the PdY77/300/72 and PdY300/700/36 samples. The respective maxima lie at 82 K and 44 K. The slight difference with respect to the ESR results can be explained by

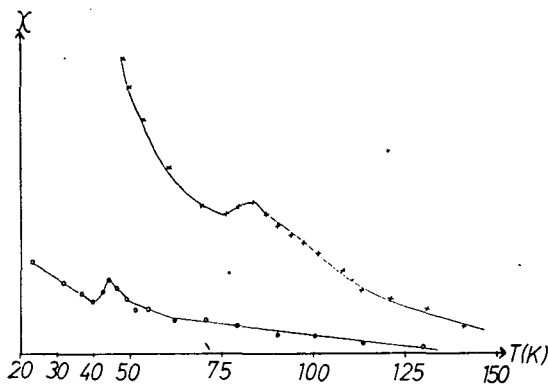


Fig. 3. Temperature dependence of the susceptibility (arbitrary units) of the PdY77/300/72 (○) and PdY300/700/36 (x) samples

the partial overlap of the Pd(0) and Pd(I) $g_{\perp}$ signals in the ESR spectrum and the restriction caused by the fact that we only employed the peak to peak height of the differentiated absorption curve as a relative measure of the susceptibility.

Another important result is the ratio of ESR signals due to Pd(0) and Pd(I) (*cf.* Table III). The amount of Pd(I) decreases as the temperature and the evacuation time increases. This behaviour is in contrast to the expected increase of Pd(I) caused by an increase in acidity at elevated temperatures. A possible explanation is a disproportionation of Pd(I) to Pd(0) and Pd(II) at higher temperatures.

Table III
Pd(0)/Pd(I) ratio of the reduced
and evacuated samples

Sample	Temperature	
	50 K	35 K
PdY77/300/72	2.6	2.2
PdY300/700/36	4.2	3.5
PdY300/700/48	4.9	4.3

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EXAMINATION OF THE MOBILITY OF MONOVALENT CATIONS IN A-, X- AND Y-ZEOLITES

By

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The arrangement and mobility of Li^+ -ions in dehydrated cation modified A-, X- and Y-zeolites were studied by NMR-line-width measurements. We determined the relative values of mobility of blocked up Na^+ -cations in dehydrated cation modified A-zeolites by means of an irreversible GC method.

Many publications appeared in the last few years on the determination of the structure of cation exchanged A-, X- and Y-zeolites. TUNG [1] has shown, that also the mobility of cations has an important influence on the catalytic and adsorptive properties of zeolites. A great variety of research methods (e.g. IR-spectroscopy, X-ray techniques, electrical conductivity measurements, sorption investigations, calorimetric measurements, NMR-method etc.) has been used for the determination of the arrangement of cations and their mobility in zeolites. In this work we give some information about our ^7Li -NMR measurements on cation modified X- and Y-zeolites and results about the mobility of monovalent cations on NaMeA-zeolites by means of the gaschromatographic method of irreversible adsorption of substance pulse [2].

Mobility of Li^+ -ions

Experimental and Discussion

The ion exchange was carried out by means of the chloride solutions. We used NaA, NaX ($\text{Si}/\text{Al}=1.35$) and NaY ($\text{Si}/\text{Al}=2.6$) without binder. The degree of ion exchange was determined by chemical analysis. The zeolites were activated at 673 K for 20 hrs in vacuum (pressure about 0.0133 Pa). ^7Li -NMR-spectra were measured using a wide-line-spectrometer KRB 35/62 at 21 MHz. The line width δH_p of the peak to peak distance of the NMR-signal was (1.8 ± 0.1) G at room temperature. We can't observe a small component analogue LECHERT [3], VUČELIĆ [4] at these degrees of exchange. The second moment of all samples was (0.73 ± 0.07) G² at room temperature. The frequencies from 21 to 9 MHz have no influence on the second moment as shown in [5].

That means, that the quadrupolar interaction is negligible. For determining the activation energy E_A and the correlation time τ_c of thermal motion we measured the temperature dependence of the line width. The results are shown in Table I.

Table I
Correlation time τ_c and activation energy E_A

Unit cell composition	Activation energy (kJ/mol)	Correlation times at 473 K (μ s)
$\text{Na}_{8,2}\text{Li}_{3,8}\text{A}$	30	110
Li_{12}A	30	110
$\text{Na}_{3,1}\text{Li}_{9,1}\text{Ca}_{0,4}\text{A}$	58	490
$\text{Na}_{5,4}\text{Li}_{5,6}\text{Mg}_{0,5}\text{A}$	58	460
$\text{Na}_{5,4}\text{Li}_{5,6}\text{Sr}_{0,5}\text{A}$	54	330
$\text{Na}_{4,4}\text{Li}_{5,2}\text{Ag}_{2,4}\text{A}$	34	180
$\text{Na}_{4,2}\text{Li}_{5,4}\text{Ti}_{2,4}\text{A}$	46	200
$\text{Na}_{3,8}\text{Li}_{5,5}\text{K}_{2,7}\text{A}$	44	200
$\text{Na}_{4,0}\text{Li}_{5,3}(\text{NH}_4)_{2,7}\text{A}$	45	200
$\text{Na}_{28,6}\text{Li}_{53,4}\text{X}$	13	120
$\text{Na}_{36,6}\text{Li}_{45,4}\text{X}$	13	120
$\text{Na}_{24,9}\text{Li}_{28,1}\text{Y}$	15	145
$\text{Na}_{30,4}\text{Li}_{45,5}\text{Ca}_{3,3}\text{X}$	19	160
$\text{Na}_{30,4}\text{Li}_{45,5}\text{Zn}_{3,3}\text{X}$	20	165

The second moment for ^7Li -NMR spectra in NaLiA -, NaLiX - and NaLiY -zeolites is the same. With the equation of VAN VLECK [6] we can calculate a mean Li-Al-distance of (2.35 ± 0.03) Å. If we set the Li-ions on SI- or SII-positions in X- and Y-zeolites we get a Li-Al-distance of $\text{Li}_\text{I}\text{-Al} = 3.57$ Å and $\text{Li}_\text{II}\text{-Al} = 3.1$ Å. The position SI should not be occupied by Li-ions [7]. In earlier works [8] we proposed, that all Li-ions are more displaced in the direction of the Al-ion. We assume the same arrangement in the case of X- and Y-zeolites.

The correlation times of Li-ions in A-zeolites are nearly the same as in X- and Y-zeolites, as shown in Table I. The activation energy is in the case of A-zeolite (30 ± 3) kJ/Mol and X- and Y-zeolites (13 ± 3) kJ/Mol. We have shown [8] that the magnetic correlation time of the Li-ions can be set equal the mean life time on a cation position. Consequently the Li-ions must make in all zeolites an isotropic diffusion process in the large cavity.

Different monovalent cations in A-zeolite reduce slightly the motion of the Li-ions; the activation energy decreases.

The activation energy of the mobility of protons [9] in NaHA has been reported to be 42 kJ/Mol and that of the Ti -ions in TIA [10] to be 38 kJ/Mol. These values are nearly in agreement with those of Li-motion in NaLiHA and NaLiTIA . Thus the less mobile cations cause a smaller mobility of the Li-ions. Divalent cations already reduce the mobility of Li-ions in the A-zeolite at lower M^{2+} -degrees of exchange as can be seen from Table I. The position of the Li-ions is not changed by the divalent cations. An exact determination of E_A and τ_c for M^{2+} -content larger than 8% is not possible yet. In contrast to the A-zeolite we find at the X- and Y-zeolite no influence of divalent cations on the Li-ion mobility at these degrees of cation exchange. We

attribute this fact to the positions of divalent cations. ANGELL [11] has shown that these divalent cations occupy firstly the positions inside the hexagonal prism. The field of the cations is screened in this position. Consequently they have no influence on the mobility of Li-ions in the large cavity.

Mobility of Na^+ -ions

Experimental and discussions

Although in 4A-zeolites all windows between the supercages are blocked up by Na^+ -cations ($\text{Na}(2)$) still *trans*-butene-2 from all butene isomers can diffuse into the micropores. Therefore *trans*-butene-2 is a good tracer molecule for our examinations. Its rate of diffusion is dependent on the mobility of $\text{Na}(2)$ -ions. In a column filled with zeolite we gave by a constant rate of H_2 -stream a pulse series of *trans*-butene-2. Through comparison of the peak height or peak area of the input and output signals of the pulse series we obtained informations about the amount of adsorbed molecules per pulse diffusing into the micropores dependent on the load with *trans*-butene-2 [2]. The peak heights after 15 pulses on $\text{Na}_{11}\text{Me}_1^+\text{A}$ -zeolites are shown in

Table II
Peak heights (ph) of 4A-zeolites after 15 pulses
(70 ml/h H_2 -stream, experimental conditions see Fig. 1)

Composition inert material	ph (cm) 25.0	Composition NaA	ph (cm) 0
$\text{Na}_{11}\text{K}_1\text{A}$	22.1	$\text{Na}_{10}\text{K}_2\text{A}$	23.0
$\text{Na}_{11}\text{Rb}_1\text{A}$	23.0	$\text{Na}_{11}\text{Cs}_1\text{A}$	22.0
$\text{Na}_{11}\text{Ag}_1\text{A}$	15.5	$\text{Na}_{11}\text{Ti}_1\text{A}$	14.5
$\text{Na}_{11}\text{Li}_1\text{A}$	15.0	$\text{Na}_8\text{Li}_4\text{A}$	16.0
$\text{Na}_{8.5}\text{Li}_{4.5}\text{Mg}_1\text{A}$	17.0	$\text{Na}_{2.5}\text{Li}_{7.5}\text{Ca}_1\text{A}$	15.0
$\text{Na}_{10}\text{Mg}_1\text{A}$	0	$\text{Na}_{10}\text{Ca}_1\text{A}$	9.0

Table II. The behaviour of *trans*-butene-2 diffusion changes depending on the mobility of exchanged monovalent cation and its position. The exchange of only one K^+ -, Rb^+ - and Cs^+ -ion per supercage nearly completely stops the diffusion of *trans*-butene-2. The exchanged monovalent cation occupy position type II [12] and the peak heights show that only one cation checks the mobility of all blocked up cations. This special behaviour is called ensemble effect by reason of a complex concerted way of motion of the cations. We explain the diffusion of *trans*-butene-2 through the windows as follows.

An adsorbed *trans*-butene-2 molecule mainly jumps from cation to cation and in NaA -zeolites especially from delocalized cation to another one. Independent of the movements of adsorbed molecules the delocalized cations have their own mechanism of motion within a supercage and also an oscillatory motion between the equivalent positions on each side of the eight membered oxygen rings. Only at the moment when a blocked up cation jumps from position type II to another position can jump

trans-butene-2 from one side to the other side of the eight membered oxygen ring to the new blocked up cation on that side. In the moment, when a change of blocked up cations takes place at a window only *trans*-butene-2 and no other butene isomer overcomes the barrier, because only the complex *trans*-butene-2/ Na^+ has the same equivalent position of each side of the eight membered oxygen ring. The higher the mobility of blocked up cations, the more often the change of cations, the higher the possibility of jumps of *trans*-butene-2 through the windows, the higher the rate of *trans*-butene-2 diffusion into micropores of zeolites.

The exchange of one Ag-, Tl- or Li-ion also brings a decrease of *trans*-butene-2 diffusion. The checking influence of this cations is smaller, caused by other cation positions. The first Ag- and Tl-ions mainly occupy positions of type III and Li^+ has its own position [13]. In each case no significant dependence of the mobility on the degree of exchange of slower cations has been found.

As has been shown by RUTHVEN [14] the exchange of one divalent cation per supercage is followed by the removal of one Na(1) and one Na(3)-cation, but all there blocked up Na(2)-cations remain at place. By each further exchange of divalent cations the blocked up Na(2)-cations disappear one by one and in $\text{Na}_4\text{Me}_4^{2+}$ -A-zeolites all windows are free of Na-ions. These cation distribution explains the role of divalent cations by opening of windows but not the special dependence on the kind of divalent cation. By exchange of one divalent cation per supercage the mobility of blocked up Na-cations decreased or increased depending on kind of cation [15]. The behaviour of *trans*-butene-2 in such zeolites is shown in Fig. 1. The higher the

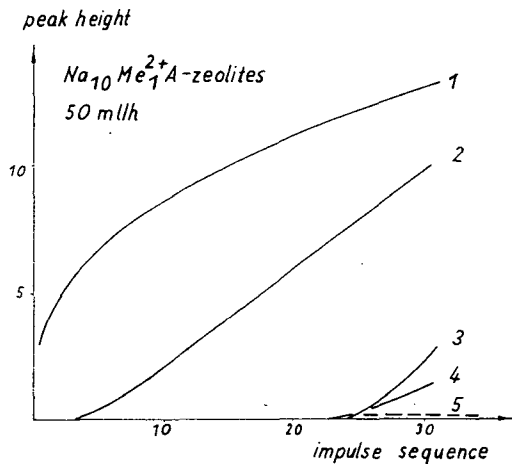


Fig. 1. Peak heights of $\text{Na}_{10}\text{Me}_4^{2+}$ A-zeolites in dependence on the impulse sequence. Zeolites: 1 $\text{Na}_{10}\text{Sr}_1\text{A}$; 2 $\text{Na}_{10}\text{Ca}_1\text{A}$; 3 Na_{12}A ; 4 $\text{Na}_{10}\text{Zn}_1\text{A}$; 5 $\text{Na}_{10}\text{Mg}_1\text{A}$. Experimental conditions: length of column 20 cm; diameter of column 0.3 cm; height of filling 14.6 cm; temperature of column 293 K; carrier gas velocity 50 ml/h; initial pressure $5.05 \cdot 10^4$ Pa; grain size 0.2, —0.25 μm ; impulse sequence 1 min; press power $8.1 \cdot 10^7$ Pa.

rate of *trans*-butene-2 diffusion in dependence on load, the steeper are the curves. At constant experimental conditions we found for $\text{Na}_{10}\text{Me}_1^{2+}\text{A}$ -zeolites independently of the rate of H_2 -stream the following sequence in the rate of *trans*-butene-2 diffusion:



The different course of curves is caused by two effects:

1. The divalent cations influencing the mobility of blocked up Na-cations in dependence on their locations and their electric field.
2. Each divalent cation has a different interaction with *trans*-butene-2 in dependence on its location and ionic radius.

The smaller the interaction of *trans*-butene-2 with the divalent cation, the higher the adsorption of *trans*-butene-2 at the Na(2) cations, the higher the obstruction for following diffusing *trans*-butene-2 molecules. The Na(3) ion has the highest interaction with *trans*-butene-2. Therefore the obstruction for diffusion of *trans*-butene-2 begins later (in the case of Fig. 1 after 25 pulses or 1.02 molecules per supercage). In the first part of this report it has been shown that one divalent cation in a 4 A-zeolite has a very high influence on the Li-ion mobility. How are the properties in $\text{NaLiMe}^{2+}\text{A}$ -zeolites in relation to the mobility of blocked up Na(2) cations (see Table II)? There is no significant influence on the mobility of Na(2) cations when one divalent cation is present, because the Li-ions exert the main influence on the mobility of blocked up Na^+ -cation.

Conclusions

The most mobile monovalent cations are Na(2) Na(3) in A- and Na^+ at site III in X-zeolites. Other exchanged monovalent cations in delocalized positions are checking the mobility of Na-cations. The checking of mobility by uniform positions is independent of the number of slower cations. The slowest cation forces the checking of mobility of all other monovalent delocalized cations.

The Li-cation has its own position without a difference between localized and delocalized positions, the correlation time of Li^+ is independent of the number of exchanged Li-ions, and of Si/Al-ratio.

Divalent cations in 4 A-zeolites influence the mobility of delocalized monovalent cations by means of their electric fields and as centre of adsorption in dependence on their positions. Divalent or monovalent cations in X- or Y-zeolites in localized position in the hexagonal prism have no influence on the mobility of Li-cations. The Li-ion can serve as a tracer cation to determine the localized positions of cations in X- and Y-zeolites.

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A STUDY OF CATALYTIC CRACKING OF *n*-HEPTANE OVER CHROMIUM-EXCHANGED ZEOLITES

By

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N-heptane cracking over a chromium-exchanged Y-zeolite was studied in a flow system at 400°, 450° and 470 °C. The initial catalytic activity increases with the extent of chromium-exchange. The primary product distributions obtained suggest the occurrence of cracking through the classical carbonium ion mechanism, accompanied by a bimolecular disproportionation reaction. The relative contribution of these two reaction pathways seems to depend on reaction temperature.

Introduction

The cracking of paraffinic hydrocarbons has been extensively studied on zeolites containing ammonium, alkaline earth and rare earth cations [1—7], but on transition metal cation-exchanged zeolites the literature is scarce. It is generally accepted that the catalytic activity of zeolites is strongly associated with surface protons and that the reaction proceeds by a carbonium ion mechanism [8—9]. However, in those cases in which the selectivity to cracking products was examined in detail, significant differences between the experimental results and the products predicted by the conventional carbonium ion mechanism were found. In an earlier work [10] we reported some preliminary data showing that in the decomposition of *n*-heptane over CrY zeolites, cracking is the major reaction while isomerization and dehydrocyclization only occur to a minor extent. In this study we present a more detailed investigation of *n*-heptane cracking over the same series of catalysts. The composition of the cracking products and the variation of the selectivities with the extent of cation exchange are examined with respect to the mechanism of the reaction.

Experimental methods

Materials

The catalysts used were prepared from a NaY zeolite (SK—40) obtained from Linde (lot. no. 3607-411). The original zeolite was previously purified by treatment with 0.1 M sodium acetate solution followed by the necessary washings with deionized water. A series of four samples with different chromium content were prepared by repeated exchange of the purified zeolite with 0.2 M aqueous solution of chromium

acetate at 55 °C. During the exchange the pH of the slurry was fixed at 4.5 by adding 0.1 M HNO_3 solution. In following this procedure all the zeolite samples suffered an approximately similar degree of decationation (1–13%) in addition to the chromium exchange. After the exchange, the samples were thoroughly washed with deionized water until no acetate or nitrate ions were detected in the filtrate. They were later dried at 110 °C, pelleted, crushed and sized to 80–120 mesh.

The degree of exchange was determined by analysis of the remaining sodium and exchanged chromium in the solid zeolite, and by measuring the extracted sodium in the filtrate. Table I shows the composition of the catalyst samples. All chemicals were at least of reagent grade purity.

Table I
Composition of Catalysts

Catalyst	Cations			
	per unit cell		% Na^+ replaced by:	
	Na^+	Cr^{3+}	H^{++}	Cr^{+3}
CrHNaY-24	35.9	4.4	12	24
CrHNaY-32	30.7	6.0	13	32
CrHNaY-52	19.4	9.7	13	52
CrHNaY-58	18.2	10.8	9	58

* Calculated from the difference of Na^+ in the parent NaY zeolite and $\text{Na}^+ + \text{Cr}^{3+}$ in the solid after the exchange.

Procedure

The catalytic activity was measured in a flow reactor at atmospheric pressure and temperatures of 400° to 470 °C. For each experiment a fresh portion of hydrous-form catalyst (1–3 g) was placed in a Pyrex tube (12 mm i.d.) between two plugs of quartz wool. Prior to use, the catalysts were pretreated under a flow of dry helium as follows: raising the temperature up to 350 °C over a period of 1 h period, and holding at that temperature for 2.5 h. The reactor was then cooled to the reaction temperature while maintaining the helium stream. Liquid *n*-heptane was introduced into the system by a small displacement pump at a feed rate varying from 2.7 to 11.0 ml/h. Samples of both liquid and gas products were taken at 30 min intervals during 3 to 4 h runs.

The liquid products were analyzed by GLC, using a 4.3 m column with silicone gum rubber (SE-30) on Chromosorb P at a temperature program of 35°–150 °C, and the gas products with a 2 m column of silica gel and Porapak Q at a temperature program of 35°–180 °C.

Results and discussion

Some blank experiments were performed in order to evaluate the thermal decomposition of *n*-heptane. At the higher reaction temperature, 470°C, and the smaller flow rate of *n*-heptane, 2.7 ml/h, used in this study, the conversion was ~3%. Since the contribution of thermal cracking was usually less than 10% of the total conversion, we have not attempted to make any corrections when reporting the catalytic data.

Additional experiments were carried out to look at the catalyst deactivation. On samples with a high chromium content we found a linear decay of the activity [10]. However, on samples with less chromium the activity was almost constant over a period of several hours. Thus, the initial values of the activity and product selectivity were determined by extrapolation back to zero reaction time. The results were satisfactorily reproduced and the material balance was generally greater than 94%.

Measurements were performed at different reaction temperatures over a wide range of conversions on the CrHNaY-32 sample. The results obtained are shown

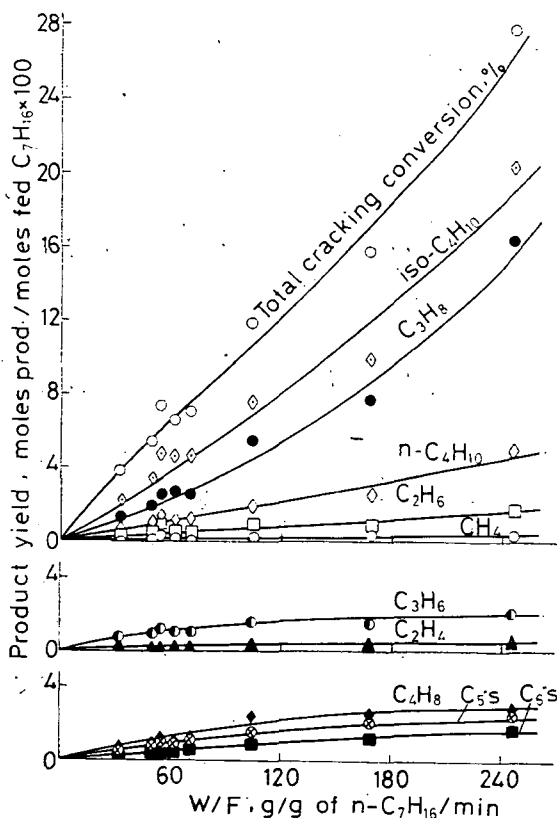


Fig. 1. Dependence of cracking conversion and product yield of CrHNaY-32 zeolite on contact time at 400°C.

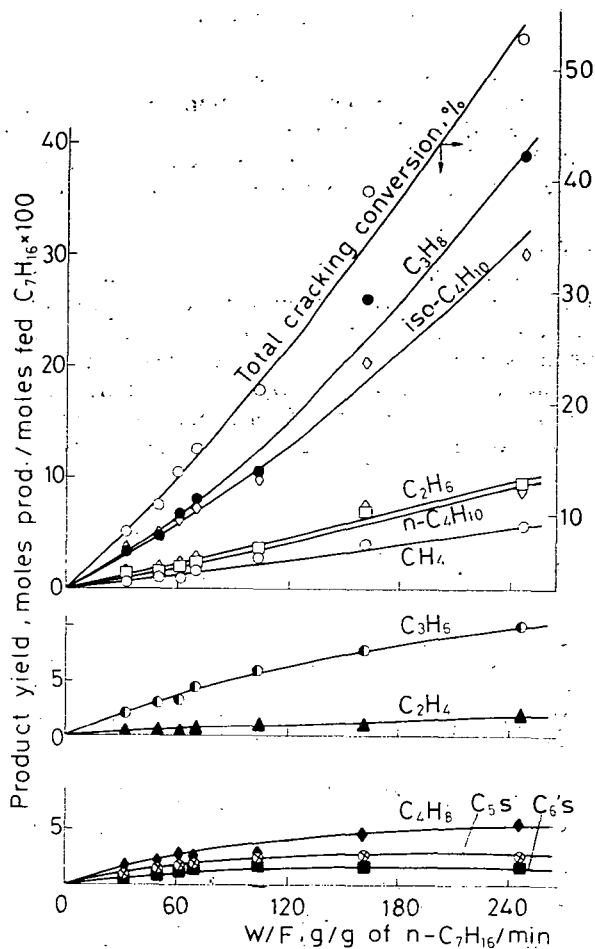


Fig. 2. Dependence of cracking conversion and product yield of CrHNaY-32 zeolite on contact time at 450 °C.

in Figs. 1, 2 and 3. The total cracking conversion has been calculated on the basis of a carbon balance in the products, by referring to the number of carbon atoms in the *n*-heptane feed. We can see that the yields to the different products increase continuously with increasing contact time and that all of them appear to be primary products of the reaction. This is confirmed in Fig. 4, where a typical plot of product selectivities versus cracking conversion at 450 °C shows positive values for the different selectivities at zero conversion. Using similar plots for the other temperatures, we have determined the corresponding initial product distribution, which are summarized in Table II. The large production of C_3 's and C_4 's and the relatively small quantities of CH_4 and C_2 's observed, specially at 400 °C, together with iso/normal ratios of the C_4 , C_5 and C_6 alkanes higher than 1, are typical characteristics of *n*-

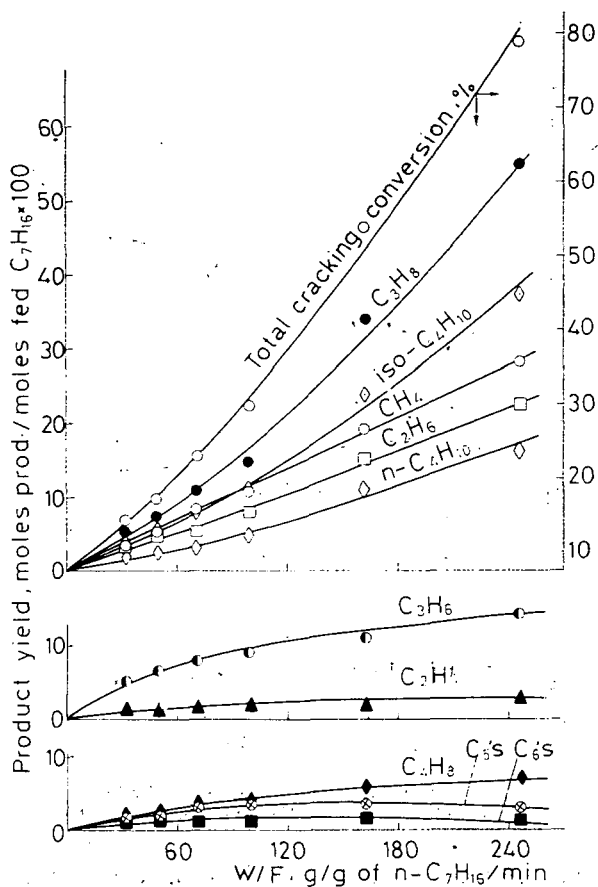
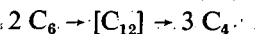
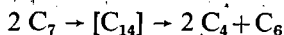


Fig. 3. Dependence of cracking conversion and product yield of CrHNaY-32 zeolite on contact time at 470 °C.

heptane cracking by carbonium ion intermediates. However, other reaction features noted in Table II, e.g., C₁, C₂ and C₃ fractions not equal to C₆, C₅ and C₄, respectively, and saturate-to-unsaturate ratio in each fraction generally greater than one, can not be easily explained by a carbonium ion mechanism.

These results suggest therefore, that the cracking of *n*-heptane over chromium zeolites partially follows a different mechanism from the classical one involving carbonium ion intermediates. In our opinion such an additional mechanism would involve the following disproportionation reactions:



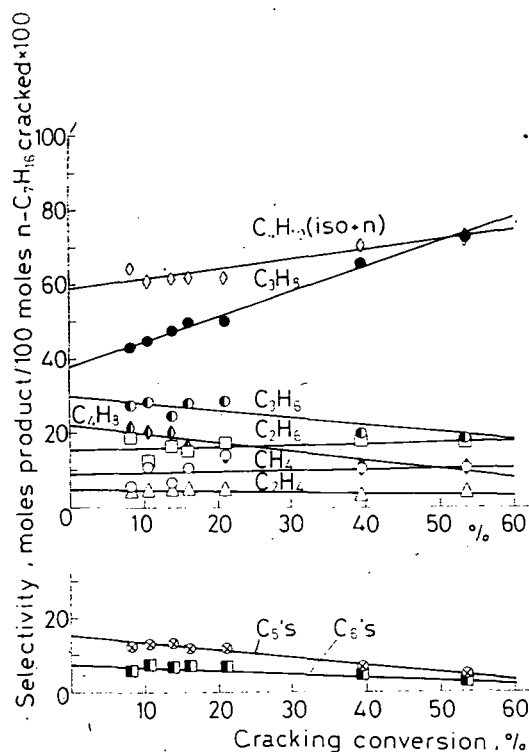


Fig. 4. Typical plot of product selectivity vs. cracking conversion with CrHNaY-32 zeolite at 450 °C

which would explain the great amount of C_4 's formed. A similar disproportionation mechanism has been put forward for *n*-heptane cracking on ammonium-exchanged Y zeolites [6]. The suggestion of radical and carbonium ion mechanism taking place simultaneously [7] does not seem very probable in our case, because the results obtained, particularly at 400 °C, show a high relative concentration of *isobutane* to C_1 and C_2 hydrocarbons. However, the proposal of a monomolecular mechanism of direct scission of carbon-carbon bond simultaneously with a bimolecular disproportionation [6] seems to be more consistent with the results of Table II, particularly at 400 °C.

At a higher temperature it seems necessary to accept a decrease in the relative contribution of the disproportionation mechanism to the overall reaction, in order to explain the decrease of the C_4/C_3 , C_4/C_2 and C_4/C_1 ratios. On the other hand, the decrease of paraffins to olefins ratio in the products with reaction temperature may well result from the lower contribution of the disproportionation reactions mentioned above, together with a greater facility of the olefins to desorb from the catalyst and the fewer hydrogen transfer reactions.

The effect of the extent of cation exchange on the cracking activity and on the product distribution has been studied at three different temperatures. The results

Table II

Initial Product Distribution for the Cracking of n-heptane on HNaYCr-32 zeolite at Different Reaction Temperatures (mole of cracked products per 100 moles of C₇ cracked)

Product	400 °C	450 °C	470 °C
Methane	1	9	34
Ethane	14	15	26
Ethylene	3	5	11
Total C ₂ 's	17	20	37
Propane	29	38	36
Propylene	20	30	43
Total C ₃ 's	49	68	79
Iso-Butane	66	42	27
n-Butane	18	17	13
Butenes	18	22	18
Total C ₄ 's	102	81	58
Total C ₅ 's*	13	15	15
Total C ₆ 's**	8	7	7
C ₄ /C ₃	2.1	1.2	0.7
C ₄ /C ₁	102.0	9.0	1.7
C ₄ /C ₂	6.0	4.0	1.6
Paraf./Olef.***	3.3	2.0	1.4

* Predominantly isopentane and decreasing amounts of n-pentane and 2-methyl 2-butene.

** Predominantly 2-methyl pentane and 3-methyl pentane, followed in decreasing order of n-hexane and 1-hexane.

*** In fractions C₂ to C₄.

Table III

Distribution of Cracked Products on Several Catalysts at Different Reaction Temperatures. (Moles of cracked products per 100 moles of C₇ cracked)

Catalyst Temp. °C	CrHNaY-24			CrHNaY-32			CrNHAY-52			CrHNaY-58		
	400	450	470	400	450	470	400	450	470	400	450	470
Conversion, %												
cracking	2.4	7.6	12.7	5.4	10.6	16.9	10.7	23.6	37.0	12.2	32.8	49.2
Methane	+	15.3	27.5	1.1	10.9	32.5	7.0	25.4	46.0	7.4	39.6	50.8
Ethane	21	16.4	23.5	11.6	13.1	29.0	9.9	13.9	21.6	11.1	14.1	26.4
Ethylene	+	7.9	7.1	2.2	4.3	8.8	1.9	3.9	4.1	2.7	4.5	4.5
Propane	39.6	49.7	47.2	35.8	44.8	44.0	49.5	52.2	51.7	46.3	58.2	54.4
Propylene	21.0	41.2	43.3	18.5	28.5	38.7	15.9	26.0	31.6	20.5	28.5	30.0
Isobutane	55.4	31.7	29.9	63.7	44.8	33.4	68.4	52.3	43.9	66.9	46.5	40.1
n-Butane	17.5	15.7	15.0	21.9	16.5	13.9	17.6	16.9	15.7	16.7	12.9	13.9
Butenes	34.6	26.3	21.2	14.9	20.7	16.1	6.0	12.7	13.5	8.0	13.7	14.2
Total C ₅ 's	16.6	9.7	10.6	12.7	13.1	10.7	11.7	9.5	7.3	12.3	9.5	6.8
Total C ₆ 's	5.0	3.9	4.4	8.0	7.6	6.4	8.2	5.1	4.1	9.0	4.9	4.5

obtained, summarized in Table III, show firstly that the cracking activity of the zeolites increase with the degree of chromium exchange and, secondly that all catalysts present similar product distribution patterns, which resemble the one obtained with the CrHNaY-32 sample. Although some gradual changes in the selectivities are noted as the chromium content in the zeolite increases, that may be due to differences in conversion level. Comparison of the product selectivities for CrHNaY-24, CrHNaY-52 and CrHNaY-58 zeolites with the corresponding values of CrHNaY-32 at equal conversion, obtained from Fig. 4 and similar figures for 400° and 470 °C (not included here), reveals that the selectivities do not sensibly change with the percentage of chromium exchange, suggesting a similar cracking mechanism for all the CrHNaY samples.

In conclusion, the results obtained in *n*-heptane cracking on chromium-exchanged Y zeolite show that the activity increases as chromium content is increased. The cracking product distributions obtained suggest, in accordance with other studies [5—7], that the reaction takes place by two types of mechanisms, which involve carbonium ion intermediates and disproportionation reaction, and that their relative contributions to the overall reaction depend on temperature.

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REACTIONS OF METHANOL OVER HIGHLY SILICEOUS ZEOLITES

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A family of novel zeolites with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios between 45 and 120 has been designated Nu—1. Sorption studies indicate a pore size of about 0.60 nm. HN—1 resembles HZSM-5 in catalysing the conversion of methanol to aromatics, but the activity decays rapidly.

Introduction

In the 1960's and early 1970's there were high hopes that crystalline zeolites would yield fundamental insights into heterogeneous catalysis. We now know that this view was too optimistic, and that even zeolites have active sites with a spectrum of activities. However, in our view, catalysts based on radically different zeolite framework still offer the best chance of major advances in catalysis, especially in the petroleum field.

Recently new families of highly siliceous zeolites have been discovered *e.g.* ZSM—5 [1], and these offer the possibility of new catalytic processes.

In this work we compare methanol conversion over our novel zeolite Nu—1 with conversion over ZSM—5 and mordenite.

Experimental

Zeolite Nu—1

Zeolite Nu—1 has been synthesized from mixtures low in aluminium, and with tetramethyl ammonium (TMA) as major cation. It is readily distinguished from other highly siliceous zeolites by its very characteristic X ray diffraction data and infrared data. Detailed information on Nu—1 synthesis has been published only in patent form [2]. Table I gives typical X-ray data obtained on a Phillips diffractometer using copper K α radiation. Five different varieties of Nu—1 have been found as indicated by small but subtle variation in X ray data.

In as-made Nu—1 up to 2.5 moles of TMA can be occluded in the lattice, and this can only be removed by thermal/oxidative breakdown. Reproducible manufacture of Nu—1 catalysts is extremely difficult. From DTA studies it is clear that above 180 °C, even with low oxygen levels, runaway burn off can occur. Large exotherms

Table I
Zeolite Nu—1 in hydrogen form

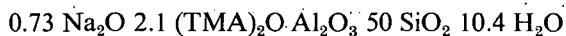
d (Å)	100 I/10	d (Å)	100 I/10	d (Å)	100 I/10
8.87	18	4.30	51	3.81	22
8.28	69	4.08	37	3.687	16
6.53	43	4.03	100	3.508	29
6.19	75	3.965	73	3.256	27
4.45	52	3.845	74	2.858	15

have been observed and local temperatures as high as 750 °C have been recorded. Significant lattice damage can occur at temperature exceeding 550 °C.

Unlike ZSM—5 and other highly siliceous zeolites Nu—1 does not show marked hydrophobic tendencies *i.e.* the ratio water sorption/*n*-hexane sorption is more typical of the hydrophilic zeolites such as A or X. The Nu—1 samples used in this work were prepared in a pyrex 25 litre lined autoclave under quiescent conditions at 180 °C for 72 hours, from reaction mixtures of composition

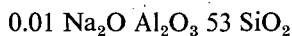


After filtration, washing and drying for 17 hours at 120 °C the as-made Nu—1 had a composition



Nu—1 catalyst preparation

The Nu—1 was exchanged twice with 2 mls of 5% w HCl per g. After filtering, washing and drying at 120 °C the product was calcined in a stepwise manner from 150→450 °C (in air previously saturated at 25 °C with water). After 1 hour at each temperature a 50° step was taken. At 450 °C the temperature was held for 17 hours and then taken slowly up to 550 °C which was held for 3 hours. The product was



and contained 0.3% w carbon and <0.05% w nitrogen.

Sorption studies on Nu—1

In order to obtain reproducible sorption results it was necessary to thoroughly "clean up" the Nu—1. This was achieved by calcining in ammonia at 450 °C for 24 hours to break the TMA, mainly to carbonaceous residues, which could be burnt off fairly readily at 450 °C in air over a 24 hour period. The product contained <0.1% carbon.

Sorption data, obtained on McBain silica spring balances, is presented as kinetic curves in Figs. 1 and 2. All experiments were carried out at 25 °C and $P/p_0 \approx 0.5$.

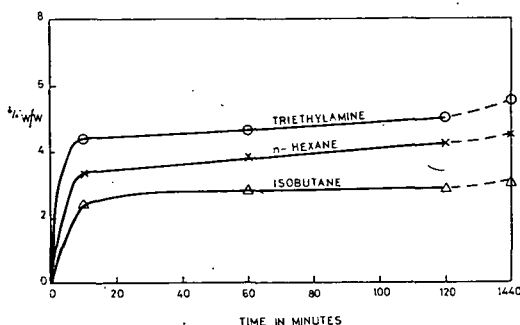


Fig. 1. Sorption rates for triethylamine, *n*-hexane and isobutane at $P/P_0=0.5$, 25°C

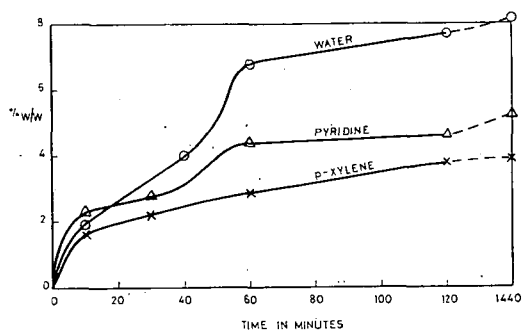


Fig. 2. Sorption rates for water, pyridine and *p*-xylene at $P/P_0=0.5$, 25°C

Catalytic reactions

A conventional pulse microreactor system was used to obtain the initial catalytic activity of Nu—1 in methanol conversion to hydrocarbon products. 1 or 2 μl injections of methanol were vapourised in a nitrogen stream, passed over 0.3–0.4 g catalyst pellets and the reaction products analysed on a GC column (3 m of 15% OV 101 silicone on Chromosorb, programmed for 60° – 360°C). A flow reactor (10 ml catalyst bed) with off-line analysis was used to find steady-state catalytic activity. On-line activation/regeneration of catalysts was possible in both units (typically 18 hours at 450°C under fast air flow).

Several different samples of HNu—1 were tested in the pulse microreactor at 375° and 450°C . Differences in activity for the conversion of methanol to hydrocarbons were found, but these could not be correlated with variations in either preparative method or physical properties (e.g. crystallite size, X-ray diffraction pattern) of the catalyst. Nevertheless the yields of aromatics were consistent over a range of conversions, and a similar product distribution was obtained from dimethyl ether feed. Aromatic product distribution for two samples of HNu—1 are shown in Table II. Very fast decay of hydrocarbonforming activity was found: the injection of 20 μl

Table II
Aromatic product distribution (% wt)

Microreactor unit zeolite catalyst	Pulse, 450 °C			Flow, 371 °C [4]
	-HNu-1 A*	HNu-1 B*	HZSM-5	HZSM-5
Benzene	1	8	14	4.1
Toluene	17	12	33	25.6
Ethylbenzene	33	20	24	34.7
m-, p-Xylene, o-Xylene	10	5	8	9.0
C ₉	21	23	9	19.1
C ₁₀	14	26	6	7.0
C ₁₁ ⁺	4	6	6	0.4

* Activity of sample A about 10 x activity of Sample B.

CH₃OH (10x initial pulse) was found to decrease total aromatics (from a subsequent 2 μ l CH₃OH) by about 60% and after 60 μ l CH₃OH aromatics formation was negligible. Calcination in air restored the original activity.

A sample of the same batch B of HNu-1 was used with CH₃OH feed in the flow reactor at 375° and 450 °C, LHSV 1-2 hr⁻¹. Dimethyl ether was the only gaseous product and no hydrocarbons were found.

Discussion

Sorption

The sorption results suggest that Nu-1 has ports close to 6A because molecules such as xylenes enter somewhat sluggishly and large molecules *e.g.* symmetrical trimethylbenzene are only adsorbed on the external surface. Sorption in zeolites always occurs by activated surface diffusion because the inter-crystalline channels are so narrow that real gas phases cannot exist. The results for sorption of isobutane, *n*-hexane and triethylamine (Fig. 1) are typical of sorption on zeolites where the molecules are significantly smaller than the zeolite ports. However triethylamine has a Lennard Jones minimum kinetic diameter of 7.8 Å [2]. The rate curves for water, *p*-xylene and benzene suggest there is a significant barrier to entry of the Nu-1 lattice and that after a significant time delay activated diffusion occurs in an autocatalytic manner. The results for water $\sigma=2.8$ Å are puzzling, but may be related to the high silica content of Nu-1, the barrier here may be hydrophobic siloxane rings which perhaps eventually hydrate and then allow access of further water. In the truly hydrophobic zeolites *e.g.* ZSM-5 this does not occur, water only has access to a limited portion of the voidage which is available to hydrocarbons.

Catalysis

The formation of aromatics from methanol over Nu-1 is evidence that some catalytic sites in Nu-1 are strongly acidic. Both the carbon-carbon bond formation and the hydrogen transfer reactions necessary to give aromatics from the intermediate products of methanol conversion are probably carbonium-ion reactions. The distri-

bution of aromatics (Table II) is broadly similar to that found with HZSM—5 catalysts [4, 5] with toluene and xylene as main products, but little benzene is found with NHu—1. The product end-point at about C₁₀ aromatics, as with HZSM—5, is probably due to steric constraints. The small proportion of C₉, C₁₀ aromatics arise from their low diffusivity in NHu—1 at 375°—450 °C. No measurable sorption of these compounds was found at 25 °C.

The rapid decay of hydrocarbon formation over Nu—1 is in contrast to the stability of ZSM—5 [4], but shows similarities to mordenite in hydrocarbon formation at 400 °C [6] and in CH₃OCH₃ formation at 155°—240 °C [7]. Complete deactivation of Nu—I needed about 5 molecules CH₃OH/Al atom. Even if no volatile products were formed there was insufficient polymeric material to block all acid sites. Deactivation by pore-mouth blocking, as probably occurs in mordenite [6, 7], and catalysis by only a small fraction of acid sites are possible explanations. The continued formation of dimethyl ether probably occurs on unpoisoned weak acid sites, including any on the crystal exterior.

After the initial formation of C₂H₄ from CH₃OH over strongly acidic zeolites, conventional carbonium ion reactions can explain, qualitatively at least, the formation of aromatic or non-aromatic [6] hydrocarbons. Strong acidity of the high-silica zeolites, mordenite, ZSM—5 and Nu—1, is needed for a fast initial step, which therefore involves cationic intermediates. However, neither CH₃⁺ nor oxonium ions (CH₃OH₂⁺, etc) are plausible intermediates, so the mechanism remains obscure.

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INFLUENCE OF ZEOLITE STRUCTURES ON THEIR DEHYDRATION CATALYTIC PROPERTIES

By

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The present study deals with the investigation of relationship of crystalline structure of zeolites to their catalytic activity.

Study of the character of dehydration reaction of *isopropyl* alcohol over synthetic type faujasite, L, erionite zeolites and on the natural clinoptilolites and their hydrogen forms, high-temperature-adsorption of compounds of the base character, and application of isotopic heterogeneous exchange and microcalorimetric methods enabled the authors to find a relation between a structure and catalytic activity of zeolites.

Study of the catalytic activity and selectivity, the nature of the active sites and the influence of zeolite structure on the given properties deserves thorough consideration of investigators.

In papers [1—6] dehydration of *isopropyl* alcohol was investigated over synthetic zeolites. The role of cation nature and the degree of exchange of a monovalent cation by a polyvalent one on the catalytic activity of zeolites were studied. Notwithstanding the fact that the overwhelming majority of the authors relate catalytic activity of zeolites to the acidic nature of active sites, in certain cases direct relationship between the activity and the degree of acidity of zeolites is not clearly established [7].

In the present study catalytic activity of highly siliceous zeolites of different structure (NaY, KL, NaKE and natural clinoptilolites and their hydrogen forms) was investigated using the decomposition of *isopropyl* alcohol as a model reaction.

Experimental

The catalytic activity of zeolites was studied by the flow method. Experiments were carried out in a quartz reactor at atmospheric pressure. The analysis of the gaseous reaction products was made by GC.

Initial zeolites were washed to pH=9. X-ray diffraction studies of the treated samples, as well as of the zeolites used testify the preservation of crystalline lattice. The amount of the zeolite loaded into the reactor was 25 cm³. Experimental points were taken when constant activity of the catalyst has been reached. Ammonium zeolites were obtained by the treatment of initial zeolites with 0.25—0.50 and 1.0 N solutions of ammonium chloride with an addition of small amount of NH₄OH.

Hydrogen forms of zeolites were obtained by calcinating the ammonium forms up to 300–350°C in nitrogen flow. All samples were preheated in a reactor under the flow of pure nitrogen, for 5 hr. High-temperature adsorption of the compounds of basic character was carried out at 210°C. After each experiment careful regeneration of catalyst was conducted, returning the sample to its initial activity.

Investigation of the possibilities of isotopic heterogeneous exchange of oxygen atoms in order to study oxidic catalysts, conducted by G. K. BORESKOV, was developed further in the studies of K. H. M. MINACHEV, where a novel approach of determination of absolute concentration and mobility of hydrogen of heterogeneous catalysts was applied for the reaction of heteroexchange of deuterium. We have used one of the versions of the method [8] described in a series of papers. Differential heats of adsorption were determined at 25°C by using a microcalorimeter type Calve of the French firm "Cetaram".

Results and Discussion

Synthetic faujasite type NaY zeolite is not characterized by high dehydration capacity. Substitution of Na cations by ammonium ions and subsequent decomposition of the latter according to a conventional scheme leads to the formation of hydrogen (decationized) forms of zeolite. The experimental data obtained show that a rise in the degree of exchange causes sharp increase of catalytic activity of faujasite type zeolite (Fig. 1). Decationization of Y type zeolites up to 30% decreases temperature values corresponding to the minimal and maximal values of conversion by more than 100°. Exchange of Na ions by NH_4^+ ions up to 47% with the subsequent

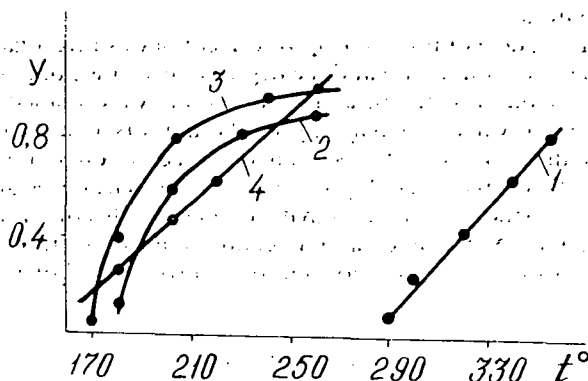


Fig. 1. Dehydration of isopropyl alcohol over faujasites: 1. NaY, 2. 0.30 HNaY, 3. 0.47 HNaY, 4. 0.69 HNaY.

decationization, significantly enhances the catalytic properties of zeolites. Further decationization causes no appreciable change in dehydration activity.

Synthetic type L zeolite exhibits low catalytic activity (Fig. 2). Decationization of initial zeolite NH_4KL causes considerable increase of catalytic activity.

NaKL type zeolite is also characterized by a low catalytic activity. Very low conversion ($y=0.056$) of isopropyl alcohol occurs at 300°C, and reaches its maxi-

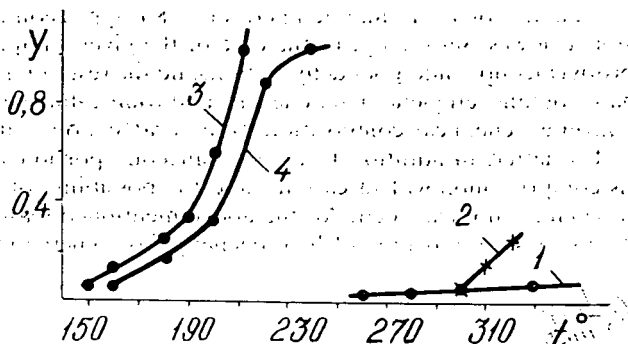


Fig. 2. Dehydration of isopropyl alcohol over zeolite L, erionite and their hydrogen forms: 1. KL, 2. NaKE, 3. HKL, 4. HNaKE

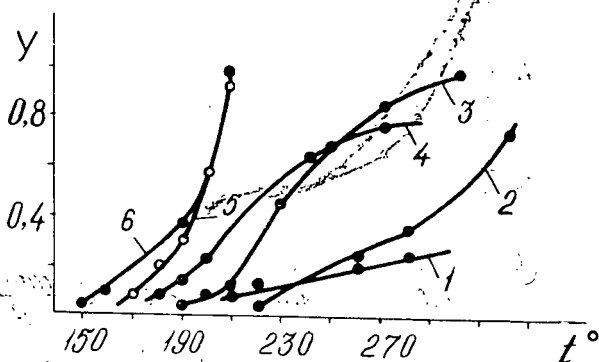


Fig. 3. Dehydration of isopropyl alcohol over natural clinoptilolites: 1. KI(2), 2. KI(3), 3. KI(1), 4. HKI(2), 5. HKI(3), 6. HKI(1)

mum at 320 °C ($y=0.21$). Conversion of the erionite type zeolite into its hydrogen form essentially increases its catalytic activity enabling complete conversion of *iso*-propyl alcohol — at a temperature as low as 240 °C.

Natural clinoptilolites of Boga (1), Dzegvi (2) and Khekordzula (3) origin (Georgian SSR) proved to be of special interest from catalytic point of view. As seen from Fig. 3 initial clinoptilolite of Boga origin provides complete conversion of *isopropyl* alcohol at 300 °C, that is, significantly exceeds in its catalytic activity synthetic monovalent cation forms of type faujasite, erionite and L zeolites. Conversion of the given clinoptilolite into its hydrogen form improves its catalytic properties (190 °C — $y=0.38$; 210 °C — $y=1.00$).

Natural clinoptilolites of Dzegvi and Khekordzula origin are also characterized by high activity. An advantage of clinoptilolites is expressed in their high selectivity; in all experiments water and propylene were the end products of the conversion of *isopropyl* alcohol. In the case of synthetic zeolites and their hydrogen forms selectivity of the process was not always achieved: samples of HNaKE and HNaY showed

traces of hydrogen and propane at high temperatures. KL type zeolite and its hydrogen forms exhibited lowest selectivity. In the case of the given samples more than a half of the *isopropyl* alcohol undergoes dehydration, and the rest of it forms hydrogen, propane, methane, butane, ethylene, 1-butene, *cis*- and *trans*-2-butenes. As compared with synthetic zeolites, chemical composition of natural clinoptilolites is far more heterogeneous. The latter, in addition to aluminosiliceous portion and the cations of alkali metals comprise monovalent cations, and the possibility of the presence of amorphous phase *etc.* is not excluded. All the above-mentioned reasons may be responsible for the increase of a degree of heterogeneity from energetic point of view.

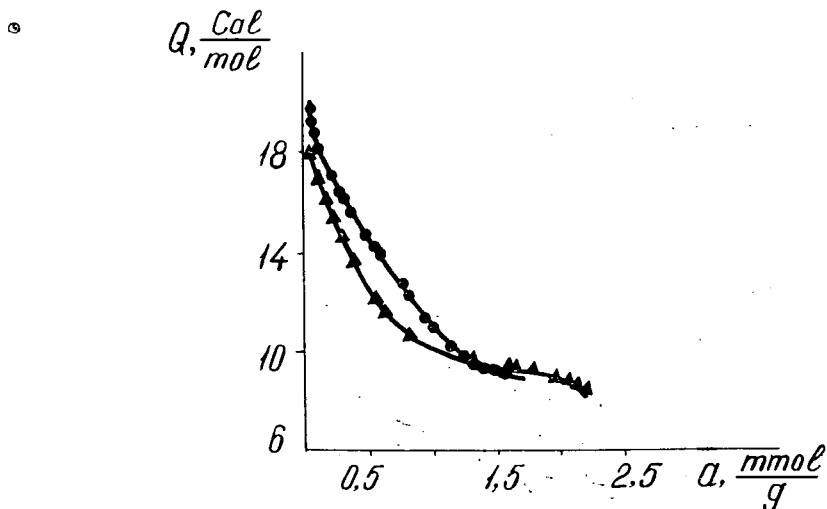


Fig. 4. Dependence of differential heats on adsorption values $Q_a = f(\bar{a})$ for the systems CO_2 — HKI(3) (●), CO_2 — K1(3) sample — 0.25N HCl (▲)

In order to elucidate the character of the above-mentioned degree of energetic heterogeneity, microcalorimetric method was used to determine the differential heats of adsorption of carbon dioxide over clinoptilolites of Khekordzula origin and their hydrogen forms. Consideration of the dependence of $Q_a = f(\bar{a})$ has shown that the zeolites under investigation manifest clearly expressed heterogeneity (Fig. 4). In contrast to the synthetic zeolites, curves of $Q_a = f(\bar{a})$ are not characterized by certain plateaus, they manifest specific sharp slopes. Similar results were obtained for clinoptilolites [9]. Choosing adsorption of ammonia as a model system, the authors [9] offer multi-stepped curve of $Q_a = f(\bar{a})$. Thus, the increased order of energetic heterogeneity of clinoptilolites is beyond doubt. In the case of the zeolites under study, several kinds of coordinatively unsaturated polyvalent cations and hydroxyl groups unequally polarized by them, $\text{Me}(\text{OH})^+$ complexes, imperfections of different nature, admixed amorphous phase *etc.* may serve as active sites. It must be taken into account that heterogeneity of the possible catalytic active sites does not affect the selectivity of clinoptilolites, it is always maximum and appreciably exceeds the selectivity of synthetic zeolites.

With the view to elucidate the nature of the active sites responsible for decomposition of *isopropyl* alcohol, we have conducted high-temperature (210 °C) adsorption of bases over zeolites. Experimental data have shown that the addition of ammonia causes complete deactivation of catalysts, and poisoning by pyridine suppresses the greater part of activity. Decrease of catalytic activity due to the addition of compounds of basic character enables us to suggest, that catalytic activity of the zeolites studied by us is conditioned by acid sites. High selectivity of clinoptilolites at an evident abundance of a variety of active sites increases the necessity of a further thorough examination of the views on the narrowness of the band of acidic spectrum, conditioning the process of dehydration. Deviation from selectivity, observed in the case of L type zeolite, may be ascribed to the specific nature of zeolite structure, but not to the variety of hydroxyl groups.

With the view to investigate kinetic properties of hydrogen atoms isotopic heterogeneous exchange method was used.

Studies of KL zeolites show that hydrogen atoms enter the isotopic heteroexchange only at high temperatures ($t > 250$ °C). KL zeolites consist only of one type of hydrogen atoms, mobility of which significantly increases with the rise of temperature (at 300 °C, $w_2 \cdot 10^3 = 4.2 \text{ min}^{-1}$; 400 °C—7.3; 500 °C—10.6). Neither the hydrogen atoms of 0.35 HKL decationized zeolites participate in the exchange of D_2 at 250 °C. Exchange of atoms of protium by deuterium is observed at high temperatures. Decationization of KL zeolites causes marked increase of a total concentration of hydrogen atoms — proportionate to decationization degree (for KL (H_s)=0.47 mmol/g; for 0.35 HKL (H_s)=1.24 mmol/g). At the given temperature all hydrogen atoms are characterized by similar kinetic properties.

Already at 250 °C hydrogen atoms of erionite show the ability of participating in isotopic exchange. Hydrogen atoms in the zeolite KNaE are represented into two H_A and H_B varieties. The amount of atoms of the type H_B exceeds that of H_A almost by an order of magnitude (H_A =0.05 mmol/g, H_B =0.45 mmol/g). Inversion of this ratio with increasing temperature is of special interest.

The results obtained by the method of heteroexchange of deuterium show that for the type L zeolites hydrogen atoms enter heteroexchange at temperatures significantly exceeding the temperature interval of dehydration process, for erionite the temperatures partly overlap. Hence, it may be supposed that hydrogen atoms are not dominating in the process of dehydration, but the possibility is not excluded that these atoms may play significant role in the other processes proceeding by carbonium-ion mechanism at high temperatures.

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MAGNETIC STUDY OF ZEOLITE-SUPPORTED NICKEL CATALYSTS

By

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The magnetic and catalytic properties of Ni supported on LINDE 4A, 5A, 10X, 13X, NaY and NORTON mordenite-type zeolites have been studied. A chemical method has been used to determine the Ni content of ion-exchanged catalysts. The rate of reduction has been investigated at different temperatures by a magnetic method. The reduced catalysts were freed of hydrogen, and their saturation magnetizations and Curie temperatures were determined by thermomagnetic analysis. To compare the activities of the catalysts, they were used for the hydrogenation of benzene. Infrared spectra of zeolites and ion-exchanged and reduced catalysts were recorded. It was found that besides the ion-exchanged Ni the nickel salt too is irreversibly sorbed on the zeolites; the zeolite supported Ni catalysts are reduced only at higher temperature, and even then only partially, and so coarse-grained Ni is formed (characterized by a Curie temperature close to that of compact Ni). On the surface of the A-type molecular sieves finely dispersed Ni is formed; the catalytic activity and hydrogen content of this are higher than the values for X-type supported catalysts.

Introduction

Zeolite-supported nickel catalysts are generally prepared by ion-exchange [1—5] or impregnation [6—7] followed by drying or calcination and finally reduction with hydrogen at 300—600 °C.

The metal content of zeolite-supported Ni catalysts may be anything from a few per thousand to 30—40 w/w%. Depending on the metal content, the catalyst can be suited to various purposes.

The structures of zeolite-supported Ni catalysts were investigated by various methods, first of all by magnetic measurements and X-ray diffraction [8—18].

On the basis of review of the literature dealing with zeolite-supported nickel catalysts it can be stated that these catalysts have been relatively little investigated and there is some contradiction about the reducibility and dispersity of nickel.

Some authors found both large and small nickel particles [12], but others only large nickel crystals [13]. It can be found such a date that nickel has atomic dispersion on the surface of X-type zeolite [9]. The reason of this contradictory results may be that differences in catalyst preparation and in the methods of examination exist and the authors investigated only one of some type of zeolite supported nickel. Therefore it is difficult to compare the results.

Our aim was to study catalysts employed in industrial processes, *i.e.* containing a larger amount of catalytically active metal and supported by different types of

zeolites. Thereby we tried to establish a correlation between special properties of the zeolite supports, the structure of the nickel found on the surface (determined from magnetic measurements), and the catalytic properties.

Investigations were carried out with LINDE 4A, 5A, 10X, 13X, Y and NORTON mordenite zeolite-supported Ni catalysts. The stoichiometric compositions of the supports are listed in Table I. The rate of nickel reduction, the amount of metallic

Table I
Composition of zeolite supports and catalysts

Support	Overall formula + n H ₂ O	Ni (w/w %) theoretical, stoichio- metrically exchanged	Ni (w/w %) measured, unreduced	Metallic Ni (w/w %) in reduced catalyst, calcd. from magnetization
LINDE 4A	Na ₂ O·Al ₂ O ₃ ·1.92 SiO ₂	20.1	28.0	5.7
5A	0.25 Na ₂ O·0.75 CaO·Al ₂ O ₃ · ·1.92 SiO ₂	20.1	25.8	4.2
10X	0.21 Na ₂ O·0.62 CaO·Al ₂ O ₃ · ·2.48 SiO ₂	18.2	25.0	2.6
13X	0.83 Na ₂ O·Al ₂ O ₃ ·2.48 SiO ₂	18.2	23.5	4.2
LINDE Y	Na ₂ O·Al ₂ O ₃ ·5.02 SiO ₂	16.8	20.3 ¹	2.2
LINDE Y			22.7 ²	3.2
NORTON mordenite	Na ₂ O·Al ₂ O ₃ ·10.60 SiO ₂	13.4	15.1 ¹	3.2
NORTON mordenite			21.9 ²	4.3

¹ Ion exchange at 25 °C.

² Ion exchange at 100 °C.

nickel and its magnetic characteristics were measured with a FARADAY-type magnetic balance [19—20].

The amount of Ni taken up on the zeolite was determined by chemical analysis. The activities of the catalysts were studied in benzene hydrogenation. Infrared spectra were recorded on the pure and ion-exchanged zeolites, and on the reduced catalysts.

Experimental

5 g LINDE 4A, 5A, 10X and 13X zeolites were boiled for 4 hours with 800 ml 0.5 N Ni(NO₃)₂ solution under reflux.

1 g LINDE NaY and NORTON mordenite zeolites were boiled for 1 hour with 400 ml 0.1 N Ni(NO₃)₂ and 0.1 g Na-acetate.

1 g LINDE NaY and NORTON mordenite zeolites were shaken for 10 hours with 200 ml 0.1 N Ni(NO₃)₂ and 0.1 g Na-acetate. The ion-exchanged zeolite was filtered off and washed with distilled water until Ni²⁺ could no longer be detected in the filtrate with dimethylglyoxime. The zeolite thus washed free of unbound nickel ions was dried in vacuum at 100—120 °C and stored in air.

Before the various tests, the samples were dried to constant weight in vacuum at 120 °C, and the dry, impregnated or unimpregnated zeolite was then weighed accurately.

The amount of Ni taken up by ion-exchange was determined gravimetrically. 100 ml 1 N NaCl solution was acidified with 1 drop of concentrated HCl, and about 0.3 g catalyst (with an accuracy of 0.1 mg) was added. The solution was refluxed for 4 hours, filtered, and the support remaining on the filter washed with 3×5 ml 1 N NaCl solution. The Ni^{2+} in the filtrate was determined with dimethyl-glyoxime [21]. The results are given in Table I.

The catalysts were reduced with hydrogen at 375, 400 and 425 °C in the measuring compartment of a FARADAY-type magnetic balance [19]. Following the cooling of the samples to 100 °C from the reduction temperature, the magnetization of the samples was measured as a function of the duration of reduction. The results are listed in Table II.

Table II
Change of magnetization on reduction of the catalysts

Support		Temp. (°C)	Time (hrs)			
			2	4	6	8
			magnetization ($\text{emu g}^{-1} \text{cm}^3$) ¹			
LINDE	4A	375	0.38	0.70	0.97	1.13
		400	0.77	1.15	1.37	1.48
		425	1.50	1.96	2.25	2.50
	5A	375	0.16	0.42	0.52	0.60
		400	0.33	0.76	1.08	1.15
		425	0.52	1.16	1.45	1.50
	10X	375	0.16	0.24	0.30	0.37
		400	0.20	0.30	0.42	0.52
		425	0.59	0.86	1.19	1.30
	13X	375	0.10	0.17	0.25	0.31
		400	0.33	0.54	0.79	0.95
		425	1.07	1.50	1.95	2.01

¹ 1 $\text{emu g}^{-1} \text{cm} = 10^3/4 \text{ Am}^{-1}$.

Table II (continued)
Change of magnetization on reduction of the catalysts

Support	Temp. (°C)	Time (hrs)								
		0.25	1	2	3	4	5	6	7	8
		magnetization ($\text{emu g}^{-1} \text{cm}^3$) ¹								
Linde Y ²	400	0.20	0.32	0.44	0.57	0.62	0.89	0.96	1.04	1.08
Linde Y ³	400	0.11	0.40	1.08	1.32	1.39	1.41	1.63	1.70	—
Norton mord.	400	1.25	1.49	1.59	1.63	1.64	—	—	—	—
Norton mord.	400	1.88	2.10	2.11	2.16	2.20	2.21	—	—	—

¹ 1 $\text{emu g}^{-1} \text{cm}^3 = 10^3/4 \text{ Am}^{-1}$.

² Ion exchange 25 °C.

³ Ion exchange 100 °C.

The catalysts reduced for 8 hours at 425 °C were degassed for 2 hours in argon at the reduction temperature. The magnetization of the catalysts thus pretreated was measured as a function of temperature and field strength (25–400 °C, 5–10 kOe). The thermomagnetic curves are shown in Figs. 1, 2, 3 and 4.

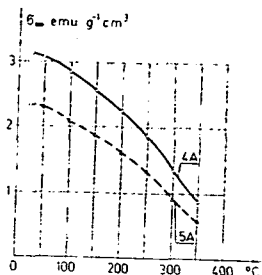


Fig. 1. Thermomagnetic curves of LINDE 4A and 5A-type zeolite-supported Ni catalysts. Saturation magnetization as a function of temperature

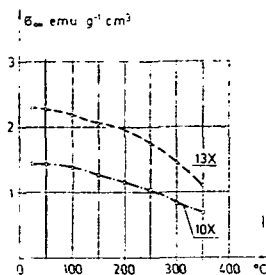


Fig. 2. Thermomagnetic curves of LINDE 10X and 13X-type zeolite-supported Ni catalysts. Saturation magnetization as a function of temperature

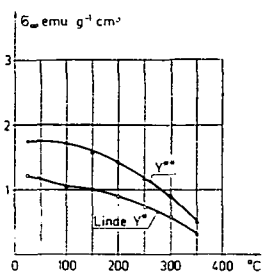


Fig. 3. Thermomagnetic curves of LINDE Y** (ion exchange at 100 °C) and Linde Y* (ion exchange at 25 °C) type zeolite-supported Ni catalysts. Saturation magnetization as a function of temperature

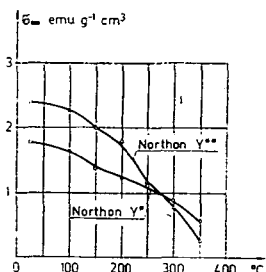


Fig. 4. Thermomagnetic curves of NORTON mordenite** (ion exchange at 100 °C) and NORTON mordenite* (ion exchange at 25 °C) type zeolite-supported Ni catalysts. Saturation magnetization as a function of temperature

The results of the magnetic measurements were evaluated by computer as reported earlier [18], *i.e.* the saturation magnetization (σ_{∞}^0) and CURIE temperature (θ) was determined for the LINDE A and X catalysts (Table III).

The activities of the catalysts were compared in benzene hydrogenation. 5 g granulated zeolite was subjected to ion-exchange as described above, and then placed in a reactor 22 mm of internal diameter and reduced. Hydrogenations were carried out with the activated catalysts at 150, 170 and 190 °C, with a H₂: benzene mol ratio of 6:1, and a benzene feed rate of 0.065 mol/h. The conversion was established by gas-chromatographic analysis of the reaction mixtures (Table III). This measure-

Table III
Magnetic properties and catalytic activities of catalysts

Support	Saturation magnetization (emu g ⁻¹ cm ³)	CURIE temp. (K) ¹	Magnezation change on freeing from hydrogen (%)	Benzene conversion %, 0.065 mol/hr benzene per 5 g catalyst		
				150	170	190
4A	3.28	500	9.8	—	—	—
5A	2.42	566	34.8	90	96	99
10X	1.50	587	6.2	49	72	84
13X	2.42	628	6.3	2	5	10

¹ Curie temperature of compact Ni: 631 K.

ment could not be made with the LINDE 4A zeolite, for in the course of ion-exchange the granulated material disintegrated. This was to be expected, since it is known that the structure of the 4A-type molecular sieve is damaged during Ni ion-exchange.

Infrared spectra of the zeolites and the ion-exchanged and reduced catalysts were recorded in KBr pellets with a Perkin-Elmer 237 spectrophotometer.

Discussion

On ion-exchange under the conditions employed here the exchange is presumably complete (Table I), with, at the same time, a considerable amount of nickel salt and/or hydroxide is irreversibly sorbed, which cannot be removed by washing with distilled water. The Ni(NO₃)₂ decomposes on the reduction of the catalyst, and the NiO formed from it, or possibly already present, and the Ni²⁺ incorporated into the zeolite lattice may be reduced in parallel.

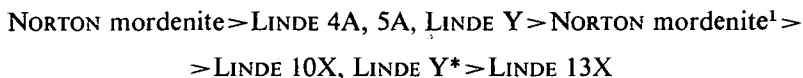
The absorption bands indicative of zeolitic water (1650 cm⁻¹) and also of surface hydroxyls (3500 cm⁻¹) decrease considerably in the infrared spectra after ion-exchange. Together with the results of the determinations of the nickel content, this suggests that a large part of the surface is covered by irreversibly sorbed nickel salt or hydroxide.

The rate of formation of metallic nickel on hydrogen reduction can be measured only above 350 °C, but even at higher temperature it is very low (Table II). Exception is the NORTON mordenite-type catalyst only (reduction time at 400 °C 1 hour). This is surprising, as Al₂O₃ and SiO₂-supported Ni (NiO) catalysts had been found to be reduced at an appreciable rate even at around 300 °C [22].

The chemical determination of the nickel content indicated that NiO was formed from the Ni(NO₃)₂ present at the reduction temperature, and this should be reduced at an appreciable rate. A further surprising result was that only a fraction of the nickel was reduced even after treatment with hydrogen for 8 hours at 425 °C.

This can be explained by the presence of a significant proportion of Ni in the channels and cavities of the zeolites. The metallic nickel formed on the reduction of NiO or Ni²⁺ on the surface blocks this off from access by H₂. In the interior of the aluminosilicate skeleton the inwards diffusion of H₂ and the outwards diffusion of the products of decomposition and reduction of the nickel salt are strongly inhibited.

From the shapes and slopes of the thermomagnetic curves (Figs. 1—4) and from the CURIE temperatures obtained by computer evaluation of the thermomagnetic analysis (Table III) the following sequence of nickel-dispersity on the different zeolites could be concluded:



(¹ ion exchange at 25 °C).

Finely dispersed nickel is found on the NORTON mordenite and LINDE A type zeolites, with coarser grains on the X-type. The thermomagnetic curves and Curie temperatures for the latter more closely resembled those for compact nickel.

There was a significant difference between the dispersity of nickel on Y type zeolites ion exchanged at 100 °C and at 25 °C. In the first case the nickel content was higher and so the irreversibly sorbed nickel content also. We suppose that the reduction of this is easier and gives the finely dispersed metal.

The correlation between the hydrogen content of the Ni catalysts and the difference of the magnetizations of the hydrogen-saturated and hydrogen-free catalysts is almost linear: lesser the amount of sorbed hydrogen, the smaller the difference between the magnetizations of these two states. Thus, the hydrogen content of the catalysts is characterized by the per cent magnetization change shown in column 4 of Table III, which is the results of thermal treatment in argon at 425 °C [17—18]. On this basis the catalysts on the different types of support can be arranged in a sequence. It can be seen that the hydrogen content of the 5A-type molecular sieve-supported Ni is substantially higher than those of the catalysts on X-type supports.

A picture in accord with this is also provided by the measurements on the benzene hydrogenation activity (Table III): the activity of the 5A-supported Ni is higher than those of the 10X and 13X-supported catalysts, though the metallic Ni content of the 10X-supported catalyst is also smaller.

In the course of the magnetic measurements, a study was made of whether the magnetization of the catalysts changes on the action of atmospheric O₂, *i.e.* whether their metallic Ni content is oxidized. In contrast with the Al₂O₃ and SiO₂-supported Ni catalysts already mentioned, the zeolite-supported catalysts cannot be oxidized in air up to 100 °C, *i.e.* their magnetization does not vary in air at 100 °C. This too confirms that the Ni in them is not finely dispersed, and not pyrophoric.

The 4A and 5A and the 10X and 13X-type zeolite supported catalysts have different properties, in spite of the fact that when their cations are exchanged completely for Ni, uniformly NiA or NiX-type materials should be obtained. The probable explanation of the differences is that the Ni salt or Ni hydroxide irreversibly sorbed on the zeolites have different structures, depending on the nature of the cations in the initial zeolites, and thus the properties of the reduced catalysts differ also.

In summary it can be stated that the zeolite-type Ni catalysts examined differ in many respects from the Al₂O₃ and SiO₂-supported Ni catalysts. The Ni²⁺ and NiO in them can be reduced at an appreciable rate only at higher temperatures (400 °C), but even under these conditions only partially, and as a consequence the metallic nickel forms larger particles. This is clearly indicated by the magnetic and catalytic measurements. On the other hand, the Ni formed, which is more stable as a result of the crystalline structure of the zeolite, is less readily oxidized.

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ISOMERIZATION OF THE METHYLNONANES AND 2-METHYLOCTANE ON A BIFUNCTIONAL ZEOLITE CATALYST

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2-Methyl-, 3-methyl-, 4-methyl-, 5-methylnonane, and 2-methyloctane were hydroisomerized on a Pt/Ca-Y-zeolite catalyst at a total pressure of 4.1 MPa and temperatures ranging from 210 to 230 °C. No hydrocracking occurred under these conditions. The product distributions were determined by temperature programmed capillary GLC using different stationary phases. The mechanism is discussed in terms of nonbranching (type *A*) and branching (type *B*) carbenium ion rearrangements. Unknown selectivities in the rearrangement behaviour of long chain alkyl carbenium ions are revealed.

Introduction

Catalytic isomerization of alkanes is of considerable importance in petroleum refining. Commercial objectives are improvement of octane rating of light gasoline components or the production of *isobutane*. Another potential application is pour point lowering of heavier petroleum fractions, *e.g.*, of jet fuel or diesel fuel [1, 2].

Whereas there is a vast number of publications dealing with product distributions, kinetics and possible mechanisms of isomerization of *light* hydrocarbons containing up to six or seven carbon atoms, hardly any information is available concerning the isomerization of *long chain* alkanes. Such informations are desirable both for a better understanding of potential processes for pour point lowering and for a more detailed insight into the mechanisms of hydrocracking and catalytic cracking where cleavage is preceded by skeletal rearrangement. The existing gap in our knowledge on isomerization of long chain alkanes is due to both the difficulties encountered in product analysis and the fact that cracking reactions often interfere if the feed hydrocarbon contains more than six carbon atoms.

Recently it has been shown [3] that long chain alkanes may be hydroisomerized in high yields if special bifunctional catalysts, *e.g.*, of the noble metal/zeolite type are used. With the *n*-alkanes of 13 to 16 carbon atoms remarkable selectivities were encountered which are not observable with light *n*-alkanes [4]. The present paper reports on the hydroisomerization of long chain alkanes containing one methyl branching.

Experimental

Principally, the apparatus consisted of a high pressure saturator for loading the hydrogen with hydrocarbon vapor, and a downflow fixed bed reactor. Details are given elsewhere [5]. 0.45 g of the Union Carbide SK 200 catalyst, *i.e.*, 0.5% Pt/Ca-Y-zeolite were used. Drying and activation of the catalyst were carried out *in situ* by purging with nitrogen and hydrogen, respectively, at 0.1 MPa and a maximum temperature of 400 °C.

Purities of the feed hydrocarbons as determined by capillary GLC were as follows: 2-methylnonane 99.7%, 3-methylnonane 99.95%, 4-methylnonane 97.4%, 5-methylnonane 99.95%, and 2-methyloctane 98.2%. Product distributions were corrected under the assumption that the feed impurities underwent no reaction. All experiments were conducted at a hydrogen partial pressure of 4.0 MPa and a hydrocarbon partial pressure of 0.1 MPa.

The required high resolution analyses of the products could be achieved by capillary GLC with squalane and polypropylene glycol as stationary phases. Length and internal diameter of the capillaries were 100 m and 0.25 mm, respectively. Starting at ambient temperature the column oven was heated with 1 °C/min. A flame ionization detector and an electronic integrator were used.

As a whole the resolution of the peaks either on squalane or polypropylene glycol was good. The only major analytical problem was the separation of 3-ethyloctane from 2-methylnonane when the latter was the feed. For assignment of the peaks the experience from earlier work on hydrocracking [3, 6] was available. In addition to this, use was made of retention index values reported in the literature [7, 8]. 4-Propylheptane was purchased as a reference substance from Roth, Karlsruhe and its structure ascertained by mass spectrometry. Its retention index reported in [8] for Apiezon L was found to be approximately valid for polypropylene glycol while that given in [7] did not agree with the experimental value.

Results

Hydrocarbons with a carbon number exceeding that of the feed were never observed. Undesired hydrocracking reactions were absent or negligible under the conditions applied. The highest degree of cracking conversion was 0.3%. In this case the distribution of the cracked products showed all features of an ionic hydrocracking rather than those of hydrogenolysis over platinum [3].

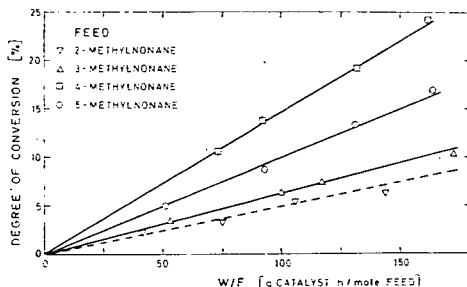


Fig. 1. Hydroisomerization of the methylnonanes on Pt/Ca-Y-zeolite ($T = 210$ °C)

Table I

Distributions of the Products (mole-%) Formed from the Methylnonanes at Low Degrees of Conversion X (T=210 °C)

Feed $W/F \left[\frac{\text{g catalyst} \cdot \text{h}}{\text{mol feed}} \right]$ $X [\%]$	2-ME-Nonane	3-ME-Nonane	4-ME-Nonane	5-ME-Nonane
	41	53	74	51
	2.4	3.4	10.7	4.9
2-ME-Nonane	—	27.3	0.8	0.4
3-ME-Nonane	77.5	—	27.4	9.3
4-ME-Nonane	6.9	36.6	—	52.7
5-ME-Nonane	0.9	5.1	31.8	—
3-ET-Octane	(1)	13.7	14.5	6.2
4-ET-Octane	0.5	8.4	20.5	28.0
4-PR-Heptane	0	0.1	1.6	2.4
n-Decane + DM-Octanes	14.2	8.8	3.4	1.0
	100.0	100.0	100.0	100.0

(1) Not determined

Table II

Distributions of the Products (mole-%) Formed from the Methylnonanes at Medium Degrees of Conversion X (T=230 °C)

Feed $W/F \left[\frac{\text{g catalyst} \cdot \text{h}}{\text{mol feed}} \right]$ $X [\%]$	2-ME-Nonane	3-ME-Nonane	4-Me-Nonane	5-ME-Nonane
	127	168	95	91
	31	39	38	37
2-ME-Nonane	—	26.2	2.9	1.6
3-ME-Nonane	55.0	—	30.9	13.1
4-ME-Nonane	14.0	34.6	—	46.7
5-ME-Nonane	4.5	9.1	26.8	—
3-ET-Octane	(1)	10.0	12.8	7.3
4-ET-Octane	4.1	9.2	17.8	23.0
4-PR-Heptane	0.1	0.6	1.8	2.1
n-Decane + DM-Octanes	22.3	10.3	7.0	6.2
	100.0	100.0	100.0	100.0
n-Decane	9	13	15	18
2,3-DM-Octane	13	6	15	13
2,4-DM-Octane	17	10	12	15
2,5-DM-Octane + 3,5-DM-Octane	24	26	28	24
2,6-DM-Octane	14	8	3	3
2,7-DM-Octane	9	6	4	3
3,4-DM-Octanes ⁽²⁾	3	7	5	7
3,6-DM-Octanes ⁽²⁾	4	13	5	5
4,5-DM-Octanes ⁽²⁾	1	2	5	3
Others ⁽³⁾	6	9	8	9
	100	100	100	100

⁽¹⁾ Not determined.

⁽²⁾ Both diastereomers.

⁽³⁾ Essentially 4 unidentified peaks; possibly including 2,2-DM- and 3,3-DM-octane.

(1) Both diastereomers.

branching in the carbon skeleton is not changed whereas in type *B* rearrangements a ramification is created or vanished. Type *A* rearrangements are considered to proceed *via* a classical sequence of hydride and alkyl shifts. Type *B* rearrangements of light alkanes were shown to be best interpreted in terms of protonated cyclopropane intermediates [10, 11].

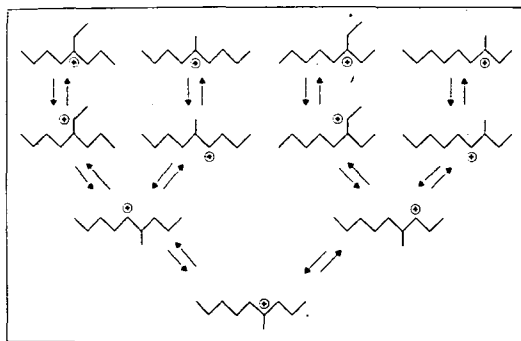
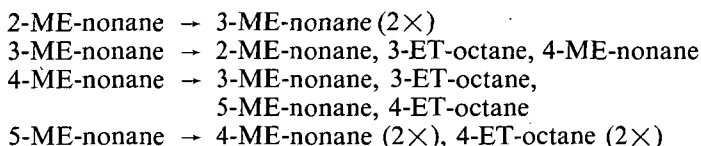


Fig. 2. Reaction sequences in type *A* rearrangements of the tertiary carbenium ion derived from 4-methylnonane.

In Fig. 2 the type *A* mechanism is applied, as an example, to the tertiary carbenium ion derived from 4-methylnonane. Applying the same procedure to all positional isomers results in the following prediction of primary products (relative statistical probabilities other than unity are given in brackets):



The actual product distributions at low degrees of conversion (Table I) essentially confirm the assumed mechanism. In particular, the methyloctanes are formed as predicted. As expected 4-propylheptane occurs as a secondary product of 4-ethyloctane. A more subtle consideration, however, reveals two systematic deviations from the simple statistic prediction of primary products: A methyl shift is always faster than a competing shift of a bulkier alkyl group. As a consequence, *e.g.*, the rate of formation of 4-methylnonane from 5-methylnonane is *ca.* twice that of 4-ethyloctane. Furthermore, competing methyl shifts do not proceed at equal rates. The preferred methyl shift is the one towards the center of the main chain. *E.g.*, 3-methylnonane yields 4-methylnonane with a higher rate than 2-methylnonane.

At higher degrees of conversion the selectivities are still visible though less pronounced due to secondary reactions, *cf.* Table II. At $X=38\%$ 4-methylnonane yields somewhat more 3-methylnonane than 5-methylnonane. This is due to the higher thermodynamic equilibrium concentration of 3-methylnonane. The behaviour of

2-methyloctane (Table III) in type *A* rearrangement is quite analogous to 2-methylnonane.

Possible type *B* rearrangements of carbenium ions derived from 2-methyloctane are represented in Fig. 3. For the sake of brevity the protonated cyclopropane intermediates are written in a face-protonated form although corner- or edge-protonated entities appear to be more likely [10, 12]. If the branching is assumed to start from the most stable ion, *i.e.*, the tertiary 2-methyl-(2)octyl-cation then 2,2-DM- and 2,3-DM-heptane are expected as the only primary products.

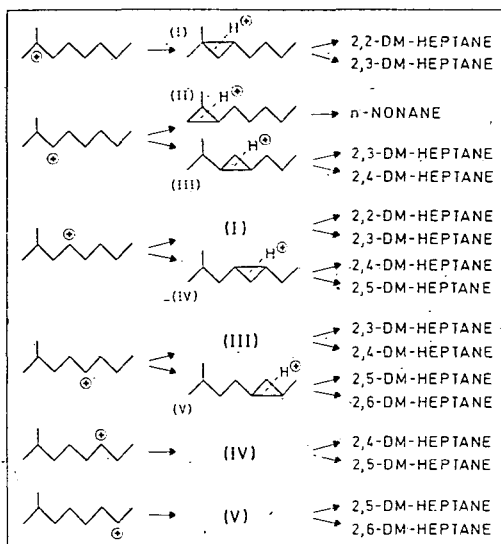


Fig. 3. Possible pathways for type *B* rearrangement of carbenium ions derived from 2-methyloctane

Table III unambiguously shows that such a mechanism is not consistent with the experimental result. If, on the other hand, branching is assumed to start from the mixture of secondary carbenium ions and to be governed by mere statistics, then the expected distribution is:

n-nonane:	$100/15 \approx 6.5\%$
2,2-DM-heptane:	$100/15 \approx 6.5\%$
2,3-DM-heptane:	$300/15 = 20\%$
2,4-DM-heptane:	$400/15 \approx 26.5\%$
2,5-DM-heptane:	$400/15 \approx 26.5\%$
2,6-DM-heptane:	$200/15 \approx 13\%$

which is in rather good agreement with the actual distribution shown in Table III. In particular, the relatively low rates of formation of *n*-nonane, 2,2-DM-heptane, and 2,6-DM-heptane are correctly predicted.

Application of the same formalism to the methylnonanes is less straightforward. One reason for this is the incomplete analysis of individual dimethyloctanes. It is

interesting to note, however, that 2-methylnonane is the most reactive isomer for type *B* rearrangement while it is the least reactive for type *A* rearrangement, cf. Tables I and II. Additional systematic investigations are required to arrive at a full understanding of the selectivities encountered in ionic rearrangement of long chain alkanes containing one methyl branching.

Conclusions

Hydroisomerization of higher alkanes on properly balanced bifunctional catalysts is a powerful tool for studying the details of rearrangement of long chain alkyl carbenium ions. Both the non-branching and the branching rearrangements exhibit distinct features which are not observable with C₆ or lower molecules. In a sense the latter are special cases which do not contain enough carbon atoms to reveal the detailed information on the most favorable rearrangement routes.

Acknowledgement

The authors thank PROF. DR. K. HEDDEN, Head of the Division of Gas, Oil, and Coal of the Engler-Bunte-Institute, who generously supported this work. H. FARAG acknowledges a post-doctoral scholarship granted by International Seminar for Research and Education in Chemical Engineering and Physical Chemistry at the University of Karlsruhe.

Abbreviations

DM = dimethyl-, ET = ethyl-, ME = methyl-, PR = propyl-.

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CATALYTIC PROPERTIES OF MODIFIED MORDENITES IN THE CRACKING OF *n*-OCTANE AND *iso*-OCTANE

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Introduction of alkaline and alkaline earth cations into H-mordenite effects catalytic activity, shape selectivity and deactivation of mordenite in the cracking of *n*- and *iso*-octane. The changes in cracking activity correspond to the changes of BRÖNSTED acidity of the mordenite. Deactivation rate depends to a much higher degree on BRÖNSTED acidity than activity. Changes in selectivity are explained by slow diffusion of the *iso*-octane.

Introduction

The high catalytic activity of modified mordenites, especially H-mordenites, in the cracking of paraffins is well known [1]. Mordenite may also act as shape selective catalyst. This subject has been surveyed in a recent review by CSICSERY [2]. The rapid activity decline by coking during the reaction limits the use of the mordenite as catalyst. Several authors have studied the aging properties of mordenite [1, 3]. The present work reports a study of the effect of introducing alkaline and alkaline earth cations into the H-mordenite on the catalytic activity, on the shape selectivity and on the aging properties in the cracking of *n*- and *iso*-octane.

Experimental part

MeH-mordenites (Me=Li, K, Mg, Ca, Ba) were prepared by ion exchange starting from H-mordenite (prepared by acid treatment of a synthetic mordenite, SiO₂/Al₂O₃ mole ratio=14) with the solutions of the nitrates. Care was taken that the pH of the exchange solution was always >3, thus avoiding uncontrolled dealumination. Exchange condition: 298 K, 4 g mordenite per dm³ solution, solution concentrations were varied from 10⁻³–1 mol·dm⁻³, resulting in different degrees of exchange. Exchange degree is calculated from the exchange amount related to the exchange capacity as determined by exhausted ion exchange with KNO₃ solution. HM of various moduli were prepared by repeated acid leaching with conc. HCl.

Catalytic studies were performed using the usual micropulse technique. If not stated otherwise, reaction conditions were as follows: $3 \text{ dm}^3 \cdot \text{h}^{-1}$ carrier gas (H_2), 100 mg catalyst sample, reaction temperature 673 K, $6 \cdot 10^{-3} \text{ cm}^3$ pulse volume (*n*-octane liquid was used in the case of activity test, for the determination of selectivity, a mixture *n*-octane: *iso*-octane = 1:1 was injected). Variation of carrier gas velocity and catalyst weight showed that the reaction rate constant k can (formally) be calculated after BASSETT and HABGOOD: $k = \frac{F}{W \cdot R \cdot T} \ln \frac{1}{1-x}$. The reaction rate constant of *n*-octane cracking, k_n , is given as a measure for catalytic activity, selectivity S is calculated as $S = k_n/k_{iso}$ (k_{iso} = rate constant of *iso*-octane cracking). k_n is given in $\text{mol} \cdot \text{Pa}^{-1} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$.

Brönsted acidity was determined by i.r. investigation of chemisorbed ammonia. The extinction of the ammonia ion absorption band at 1450 cm^{-1} was taken as a measure for acidity. For sample preparation and i.r. characterization of surface OH groups see [4].

Results and discussion

The introduced cations effect the i.r. spectra within the OH (respectively OD) region of the mordenite only in one aspect: The extinction of the OH vibration band at 3610 cm^{-1} is reduced proportionally to the amount of cation. The Brönsted acidity of the mordenite decreases linearly with increasing content of the incorporated cation independent of the kind of investigated cation (Figure 1). The behaviour of

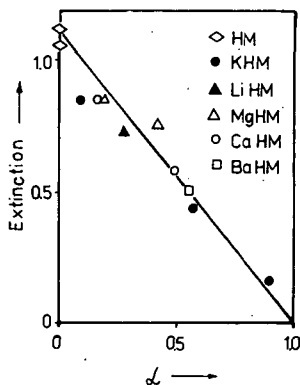


Fig. 1. Extinction of NH_4^+ absorption band in the i.r. spectra at 1450 cm^{-1} after adsorption of NH_3 ($4 \cdot 10^3 \text{ Pa}$) at 370 K on some mordenite sample as a function of the exchange degree α ($\alpha=0$ in case of the HM).

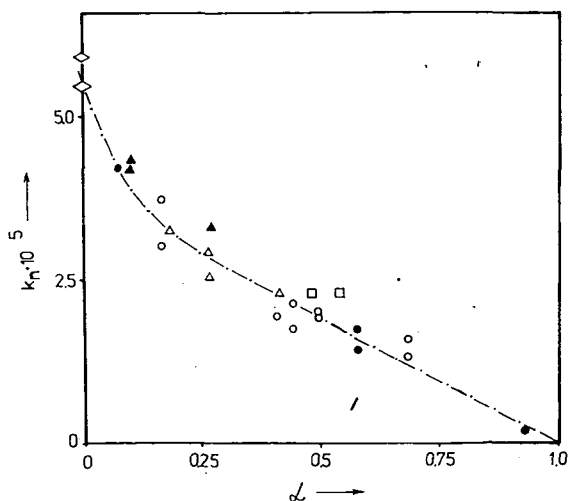


Fig. 2. Correlation between reaction rate constant of *n*-octane cracking k_n , and exchange degree α . (For the meaning of the points see Figure 1).

the MeH-mordenites closely resembles to partially poisoned H-mordenites. This is also seen from the variation of *catalytic activity* shown in Fig. 2. The catalytic activity of all samples can be given by a common function of the exchange degree, there is no specific cation influence. In the region of 40–100% cation exchange the activity decreases linearly with increasing exchange. Therefore a direct linear relation exists between activity and Brönsted acidity (e.g. extinction of NH_4^+ — band at 1450 cm^{-1}), as may be expected in the case of a reaction following a 1-center mechanisms. At lower exchange level, however, activity depends much stronger on the exchange degree (and on the acidity as defined above). Such behaviour might be explained principally by a diffusion hindrance caused by the cation. In this case, however, a specific cation effect should be expected and the greater *iso*-octane molecule should be effected much more than the *n*-octane, leading to an increase in selectivity which was not observed. Therefore a distribution of acid centers strength within the mordenite must be supposed, the influence of cation incorporation on the acidity being especially high at lower exchange degree.

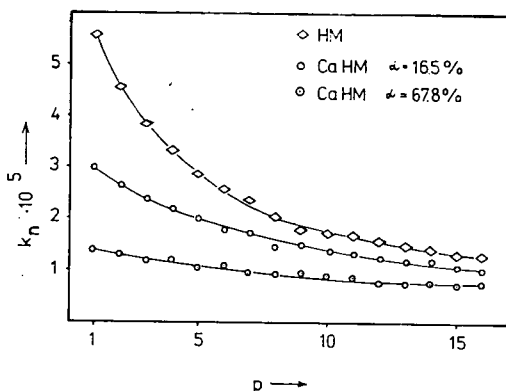


Fig. 3. Aging properties of HM and two CaHM samples: k_n as a function of pulse number p

The introduction of cations results in an obvious improvement of the *activity time dependence* as demonstrated by Fig. 3 with calcium as the incorporated cation. The curves in Fig. 3 can be reproduced by the equation:

$$\frac{1}{k_n} - \frac{1}{k_{n,1}} = B(P-1)$$

$k_{n,1}$ = rate constant of *n*-octane cracking, calculated from the first pulse

B = constant for deactivation process

P = pulse number

(This equation can be derived [5] from the relations given by WOJCIECHOWSKI [6] and assuming a 1-center mechanism for the cracking reaction and a 2-center mechanism for the oligomerization of product olefins as the rate determining step for deactivation [7]).

Fig. 4 gives the value $1/k$ as a function of the pulse number P for the starting H-mordenite with the reaction temperature as parameter. It is seen that the above given equation is appropriate to describe the deactivation process. The temperature dependence of the constant B , calculated from the slope of the curves obtained at different reaction temperatures, follows the Arrhenius equation with an apparent

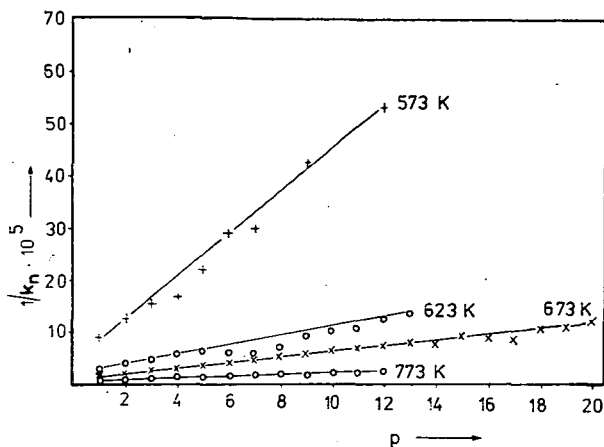


Fig. 4. Aging properties of HM: Reciprocal value of the reaction rate constant as a function of pulse number and reaction temperature as parameter

activation energy of $-49 \text{ kJ} \cdot \text{mol}^{-1}$. This negative value reflects the adsorption strength of the olefins.

Increasing reaction temperature favours desorption of olefins which appear more and more in the reaction products. The value of the constant B for all MeH-mordenite samples, independent of the kind of cation and exchange degree, scatters around a common value ($B \approx 4 \cdot 10^4 \text{ Pa} \cdot \text{h} \cdot \text{g} \cdot \text{mol}^{-1}$). Consequently may be concluded that the improvement of the activity time behaviour by cation introduction is based on a kinetic effect: The rate of "coking", following a multi-site mechanism, depends more strongly on Brönsted acidity than does the rate of the cracking reaction.

All factors governing *shape selectivity* of mordenite in the simultaneous cracking of *n*- and *iso*-octane can be explained by slow diffusion of the branched hydrocarbon. For the ratio of the diffusion coefficients of *n*-octane (D_n) and *iso*-octane (D_{iso}) we found on HM from static adsorption experiments in the precatalytic region

a value $\frac{D_n}{D_{iso}} \approx 100$. The ratio of the reaction rate of *n*- and *iso*-octane under our reaction conditions being about 2–5, the cracking of *n*-octane should proceed under kinetic control, while the cracking of *iso*-octane is supposed to be diffusion limited.

In accordance with this model we found that the selectivity parameter $S = \frac{k_n}{k_{iso}}$ strongly increases with increasing reaction temperature. This model also corresponds to the catalytic results found on HM with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (Fig. 5).

The existence of a maximum in the activity-modul-curve is a well known fact: in addition it can be stated that selectivity is directly correlated to activity (those possessing the highest activity exhibit the highest selectivity, as would have been expected in the case of simultaneous reactions with one reaction being diffusion limited).

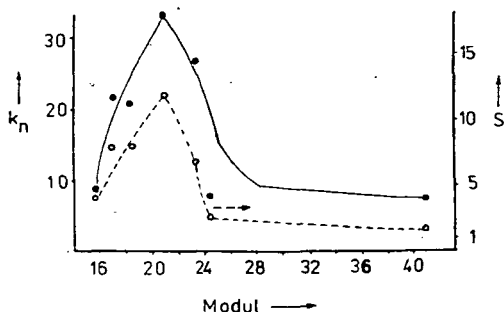


Fig. 5. Activity and selectivity of acid leached HM with different modul (SiO₂/Al₂O₃ mole ratio). Solid line k_n , dashed line S

In the case of introducing cations into the HM generally two factors can be expected to influence the selectivity: 1. Selectivity is influenced by changing activity (and therewith changing the extent of diffusion limitation) and 2., Cations may act as diffusion barrier. By these two effects the selectivity of CaHM samples given in Fig. 6 can be explained. Starting from HM the value S decreases with increasing amount of introduced calcium ions (and decreasing activity).

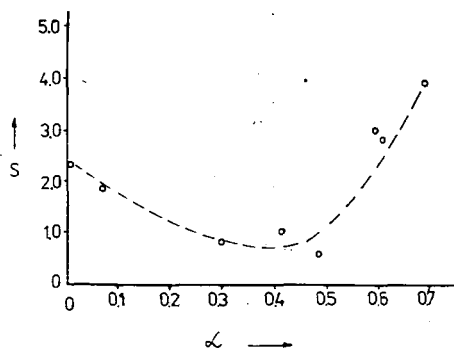


Fig. 6. Selectivity S in the cracking of *n*-octane/*iso*-octane on CaHM with different exchange degrees

Due to this effect even such results are achieved as are known from usual cracking catalysts: *iso*-octane is more readily cracked than *n*-octane. At higher exchange level ($>50\%$), Ca²⁺ ions increase the selectivity in spite of decreasing activity. In connection with the results presented by MORTIER ET AL. [8] on the position of Ca²⁺ ions in mordenite it may be concluded that calcium ions only at higher exchange degree occupy positions in the main channel (these positions being energetically less favoured).

It may be suggested that these calcium ions in the main channel act as diffusion barrier for the larger *iso*-octane molecule thus increasing selectivity.

The conclusions about the effect of alkaline and alkaline earth cations on activity, deactivation rate and selectivity can be extended to other cations. In Table I

Table I
*Catalytic properties of Co²⁺, Cr³⁺, Cu²⁺ and Ni²⁺
exchanged sodium mordenites*

Catalytic activity (k_n , mol·g⁻¹·h⁻¹·Pa⁻¹), deactivation constant (B , Pa·h·g·mol⁻¹·pulse⁻¹), shape selectivity (S) and extinction (E) of the i.r. OH adsorption band at 3610 cm⁻¹. Exchange degree α related to exchanged sodium.

Catalyst	α	$k_n \cdot 10^6$	$B \cdot 10^{-6}$	S	E
CoNaM	22	5.4	0.66	3.5	0.39
CrNaM	15	5.3	0.23	3.7	0.33
CuNaM	34	8.5	0.04	1.0	0.31
NiNaM	40	8.0	0.01	1.2	0.09

the results of the catalytic studies obtained with CoNaM, CrNaM, CuNaM and NiNaM are shown together with the extinction of the OH adsorption band in the i.r. spectra at 3610 cm⁻¹ (which in this special case serves as a measure for Brönsted acidity). Catalytic activity (k_n) corresponds to acidity. (The reduction of Cu²⁺ and Ni²⁺ ions under reaction conditions results in a further increase of acidity). The deactivation constant B possesses a higher value in the case of CoNaM and CrNaM than in the above reported case of HM and HMeM (Me = alkaline, alkaline earth). The high deactivation rate on these samples corresponds to the high catalytic activity of cobalt and chromium ions in the olefin oligomerization [9, 10], which is suggested to be rate determining step for deactivation. The higher selectivity of CoNaM and CrNaM in comparison to the selectivity of CuNaM and NiNaM samples is based on the effect of cobalt and chromium ions, resp., for which a position within the main channel is supposed. Nickel and copper, which during catalysis exist in reduced state, exert no effect on selectivity.

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ZEOLITE CATALYZED LIQUID PHASE DEHYDRATION OF α -PHENYLETHANOLS

By

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The dehydration of α -(*p*-tolyl)ethanol on NaNH_4Y , NaCeY and NaCaY was investigated. The reaction rate and the selectivity for styrene formation were found to depend on the degree of cation exchange, the activation temperature, the alcohol/zeolite ratio, the solvent used, and the nature of substituents.

Introduction

In the literature the formation of styrenes in high yields by gas phase catalytic dehydration of α -phenylethanols [1, 7] is described. The application of common liquid phase methods resulted in poor yields [2—5]. Here, the use of zeolites would seem attractive in view of the location of the catalytic acid sites inside a pore system which is expected to prefer the adsorption of the starting compounds. In this paper we report the use of Y-zeolites for the liquid phase dehydration of α -phenylethanols.

Experimental

Reagents

Pure grade reagents and solvents were used. Liquids were dried using zeolite KA. The zeolites NaY, SK—500, NaX and KA were obtained from Union Carbide, zeolite L from Alfa Products and H-mordenite from Norton. NH_4Y , CaY, and CeY, LaY, NH_4L , CaL and CaX were obtained by ion exchange of NaY. NaCaY-50% means that 50% of the Na ions were exchanged with Ca ions. Zeolite H-ZSM—5 was prepared according to a patented procedure [8]. The zeolites were activated at 400° [9], unless specified otherwise.

Standard procedure for dehydration

Alcohol (9 mmol), diethyl ether (30 ml) and catalyst (3 g) were stirred at 25°. As internal standard 1,3,5-tri-*t*-butylbenzene (3.7 mmol) was added. The reaction was followed by taking samples of the reaction mixture at suitable intervals. Diethylamine/methanol (1:3) was added to the samples to quench the reaction and to desorb reactant and products from the zeolite. After centrifuging a 0.1—0.5 μl portion of the solution was subjected to GC-analysis using SP 2250 (3% on Chrom. GHP) as stationary phase at 100—200°.

Results and discussion

The dehydration of α -(*p*-tolyl)ethanol (I) to yield *p*-methylstyrene (II) was used as a test reaction. Generally the dehydration resulted in the formation of *p*-methylstyrene (II) together with the ether, bis[α -(*p*-tolyl)ethyl]ether (III), the dimer 1,3-(*p*-tolyl)-1-butene (IV), and *p*-ethyltoluene (V). The selectivity for the formation of a product A during the reaction is expressed by: $S(\%) = (\text{moles of A produced} / \text{moles of alcohol reacted}) \times 100$. First several zeolites were tested in the dehydration of α -(*p*-tolyl)ethanol. The order of activity found was $\text{CaL}, \text{H-ZSM}-5 < \text{HL}, \text{H-mordenite}, \text{CaX} < \text{NH}_4\text{Y}, \text{MgY}, \text{CaY}, \text{CeY}, \text{LaY}, \text{SK}-500$. The zeolites NaNH_4Y , NaCaY and NaCeY were selected for a more detailed investigation.

Adsorption

NaY , being inactive in the dehydration reaction, was used as a model Y-zeolite to study the adsorption of reactant and products from solutions. The changes in concentration were followed by GC-analysis. As shown in Fig. 1 all compounds were rather well adsorbed from hexane. Ethereal solvents were found to compete much stronger for the inner surface. From tetrahydrofuran (THF) only the alcohol (I) was weakly adsorbed (0.03 mmole/g). In diethyl ether the compounds II–V were found to adsorb weakly whereas the adsorption of the alcohol (I) was substantial. These data suggest that during dehydration in diethyl ether initially all products, except water, formed in the zeolite will be replaced by the alcohol.

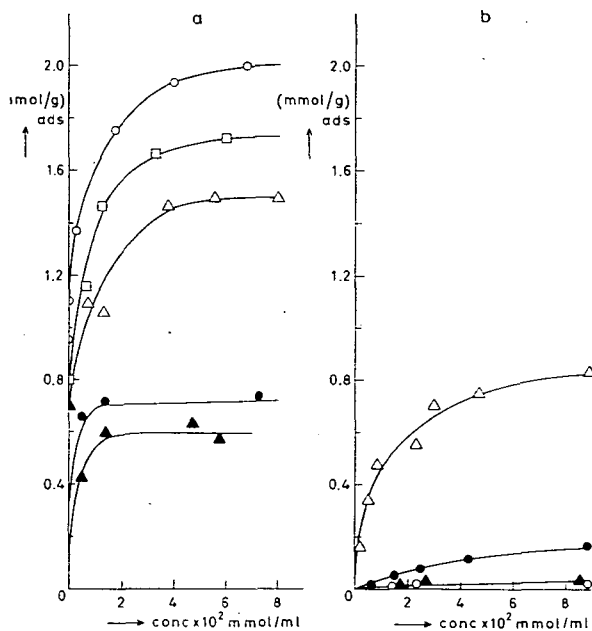


Fig. 1. Adsorption isotherms at 22° of Δ alcohol (I), $\circ$ styrene (II), $\square$ p-ethyltoluene (V), $\blacktriangle$ ether (III) and $\bullet$ dimer (IV) from hexane (a) and diethyl ether (b)

Effect of the activation temperature

As shown in Fig. 2 maximum activity of NaCeY and NaCaY is obtained at temperatures of 350° and 200° resp., which are rather close to those (resp. 300° and 250°) where a maximum amount of surface hydroxyl groups has been observed by IR spectroscopy [6, 10]. For NaNH_4Y the dehydration activity seems also related

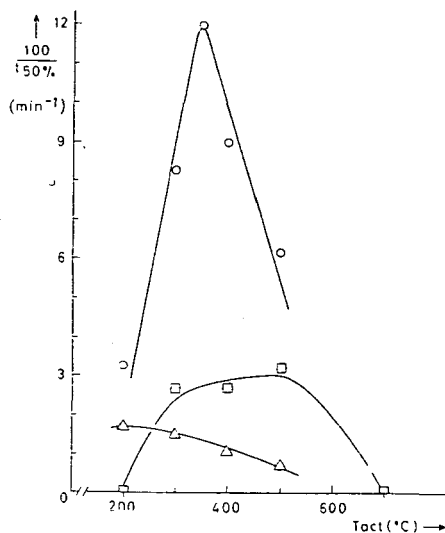


Fig. 2. Effect of the activation temperature on the activity for dehydration ($100/t_{50\%}$).
 ○ NaCeY-62%, △ NaCaY-82% and
 □ NaNH_4Y -50%

to the hydroxyl concentration [10]. The observed selectivities for styrene (II) formation were for NaNH_4Y 50—55%, for NaCaY 46—77%, for NaCeY 67—88%. Generally a decrease in styrene formation was accompanied by an increase in ether (III) formation. Compounds IV, V and VI were formed in minor amounts.

Influence of the extent of cation exchange

As shown in Fig. 3 the activity increased with increasing degree of cation exchange. For NaNH_4Y a maximum in activity was reached at 50—55% exchange, which is close to the reported [6] maximum value (60%) of Brönsted acidity of NaHY zeolites. For NaCeY and NaCaY the activity increased starting from about 30% exchange. A similar effect [12] has been reported for the dehydration of 2-propanol over NaCaY. At low exchange degrees the polyvalent cations occupy preferably site I, in the hexagonal prisms [13]. Here they are expected to be dehydrated and no new acid sites are created by dissociation of water of hydration.

As shown in Fig. 4 there is also a strong effect on the selectivity, the highest styrene selectivity being obtained at a low degree of exchange. It has been suggested that in ether formation a pair of hydroxyl groups is involved [11].

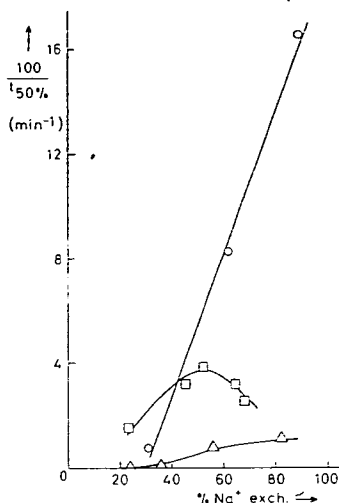


Fig. 3. Effect of the degree of cation exchange on the activity for dehydration ($100/t_{50\%}$). $\circ$ NaCeY, $\triangle$ NaCaY and $\square$ NaNH₄Y. (T_{act} 400°)

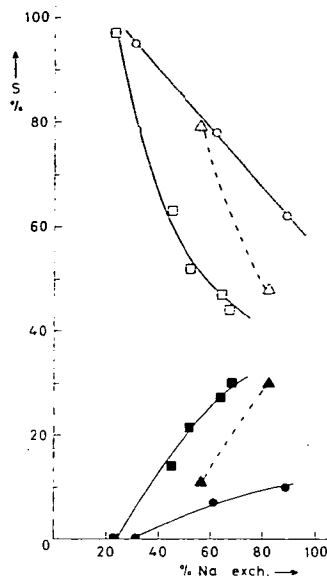


Fig. 4. Effect of the degree of cation exchange on the selectivity after 90% conversion, $\circ$, $\triangle$, $\square$ styrene (II) and $\bullet$, $\blacktriangle$, $\blacksquare$ ether (III). $\circ$ NaCeY, $\triangle$ NaCaY and $\square$ NaNH₄Y. (T_{act} 400°)

Effect of alcohol/zeolite ratio and solvent

Owing to the preference of water for the zeolite the generation of water will influence the reaction rate. Accordingly, an increase in the alcohol/zeolite ratio caused a disproportional increase in $t_{50\%}$. The self-poisoning due to the accumulation of water was confirmed by the application of a combination of zeolite NaNH₄Y to catalyse the reaction and a small pore zeolite KA to adsorb selectively the water formed in the reaction; a rapid and complete conversion of the alcohol was observed. An increase in the alcohol/catalyst ratio also resulted in an increase of ether formation due to a prolonged "saturation" of the zeolite with alcohol.

When the inner reactant and product concentrations were decreased by using THF a very slow reaction occurred at 25°. A reasonable rate was obtained when carrying out the dehydration at 50°. In both experiments the selectivity for styrene formation was over 99% which may be caused by a low concentration of reactant at the active sites; perhaps also by the increased proton acceptor character of THF.

Substituent effects and reaction mechanism

A series of para-substituted α -phenylethanols were subjected to dehydrations using NaNH₄Y-40% as the catalyst and THF as solvent (Table I). High selectivities for styrene were obtained. The only by-products detectable by GC analysis were the

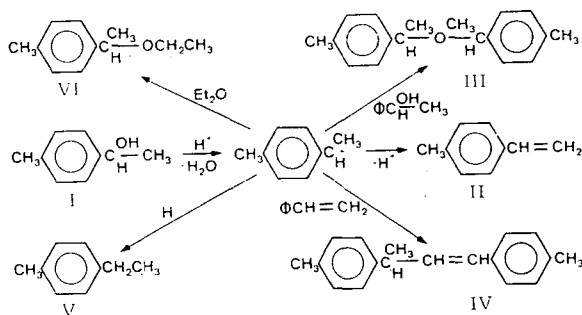
Table 1
Substituent effects^a

Para-substituent	CH ₃ O	CH ₃	H	Br
<i>t</i> _{50%} (min)	< 3	30	50	> 1000

^a Alcohol (1.8 mmol) and catalyst (3 g) were stirred in THF (30 ml) at 60°.

para-substituted ethylbenzenes (<1%). Reactions carried out in diethyl ether show the same order for *t*_{50%} but lower selectivities.

The data show that electron donating para-substituents, which stabilize the intermediate carbenium ion, increase the rate of dehydration whereas the reverse is true for electron withdrawing substituents. This proves that the fission of the protonated alcohol to yield water and the carbenium ion is the rate-determining step.



As shown by the influence of cation exchange and activation temperature, the catalytic zeolite surface serves to protonate the alcohol and to accommodate the protonated species at a hydrophilic surface. Probably the surface has also a proton-accepting function in the conversion of the carbenium ion into the styrene (II). Reaction of the carbenium ion with alcohol or styrene results in the formation of ether (III) or dimer (IV), respectively. In diethyl ether also the ethyl ether (VI) was formed. Hydride transfer to the carbenium ions can provide the para-substituted ethylbenzenes (V). For this process several donor C—H bonds can be imagined, the precise origin is not known, however.

In conclusion Y-zeolites are well suited for dehydration of α -phenylethanols; for obtaining high selectivity to styrene either a low density of Brönsted acid sites or a strongly competing solvent is required.

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CONVERSION OF METHANOL TO HYDROCARBONS OVER NATURAL MORDENITE

By

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The process of methanol conversion to hydrocarbons C_1 — C_8 over modified natural mordenites as catalysts was investigated. The catalysts applied show high activity but short life-time. A mechanism of the process, proceeding through methyl radical, has been proposed.

Introduction

The process of methanol conversion to hydrocarbons over zeolitic catalysts was investigated intensively in the last few years.

The development of methanol production technology from synthesis gas opens the real possibility to utilize methanol as a raw material for preparation of aliphatic and aromatic hydrocarbons.

The dehydration of methanol over zeolitic catalysts was first performed by VENUTO and LANDIS [1] ten years ago and later by TOPCHIEVA ET AL. [2]. These authors have found some amounts of light hydrocarbons in the reaction products.

H-mordenite was applied by WEBB and GATES [3] as a catalyst for methanol dehydration.

In the seventies the scientists from Mobile Research and Development Corp. [4—6] worked out the process of methanol (and other heteroorganic compounds) transformation into hydrocarbons over a new class of zeolites type ZSM. They claim high yields of C_2 — C_{10} hydrocarbons and a good stability of the catalysts.

The present work has been undertaken to check the possibility of the application of natural mordenite as catalyst for the investigated process.

Experimental

Materials

Starting material for preparation of catalysts was Hungarian natural mordenite (lot No 2/76). Methanol, reagent grade, and argon or hydrogen, technical grade, were used without further purification.

Catalysts

Raw natural mordenite was treated with 4N hydrochloric acid (50 °C, 5 hrs) and afterwards washed with distilled water. The chemical composition is shown in

Table I
*Chemical Composition of the Natural
Mordenite from Hungary*

Chemical composition wt %	Raw mordenite	Acid treated mordenite
SiO ₂	68.81	70.71
Al ₂ O ₃	10.79	11.07
Fe ₂ O ₃	0.82	0.51
TiO ₂	0.076	0.08
CaO	2.12	1.76
MgO	0.11	0.06
Na ₂ O	1.84	0.80
K ₂ O	4.56	4.49
H ₂ O (1000 °C)	10.51	11.66

Table I. The cation exchange was performed by mixing the acid treated zeolite with solutions of potassium, cerium, cobalt, indium, titanium or chromium chloride at 50 °C during 7—14 days. The dried catalysts were sieved and the fraction of 0.65—1.25 mm grains was used. So obtained modified mordenites were activated in dry argon stream at the temperatures 350—500 °C.

Apparatus and procedure

The catalysts were tested in static and flow systems. The measurements done in static system enabled us to preselect some more promising catalysts.

The main investigations were performed in flow system. The catalytic reactor was a double U shape tube (8 mm i. d., 200 mm long). The first part of the tube was used as a preheater. The catalyst bed (10 mm deep, about 400 mg of catalyst) was placed in the second part of the reactor. Methanol vapours were carried into the reactor by argon (or sometimes by hydrogen) stream. Samples of gases from the reactor were analysed by GLC. Two types of chromatographic columns were used: 6 m long (3 mm i. d.) with a mixture of dimethylsulpholane, propylene carbonate and silver nitrate on Chromosorb P (temp. 20 °C, p_{N_2} = 2,5 atm) and 2 m long with polyethylene glycol on chromosorb P (temp. 90 °C, p_{N_2} = 1 atm).

Results and discussion

The products of the investigated process are mainly C₁—C₅ hydrocarbons (paraffins and olefines) and water, in some cases dimethyl ether and unreacted methanol, too.

The reaction of methanol conversion was carried out on the starting (raw) natural mordenite and on several catalysts obtained by its modification. The percen-

tage of the conversion as well as the product composition depend upon the applied catalyst, the temperatures of catalyst activation and of the reaction and the space velocity.

The catalysts were activated at temperatures between 300—500 °C. The catalytic reaction was carried out between 250 and 500 °C.

At reaction temperatures below 300 °C the conversion of methanol was rather low and the only products were dimethyl ether and water. At temperatures over 350 °C for all applied catalysts, except raw mordenite, complete (100%) conversion of methanol was observed.

The period of time between the start of the reaction and the moment of methanol appearance in the product, corresponding the complete conversion, we name catalyst "life-time".

Changes of product composition with time on stream were observed for all catalysts as are shown in Fig. 1 for the potassium exchanged mordenite. The biggest

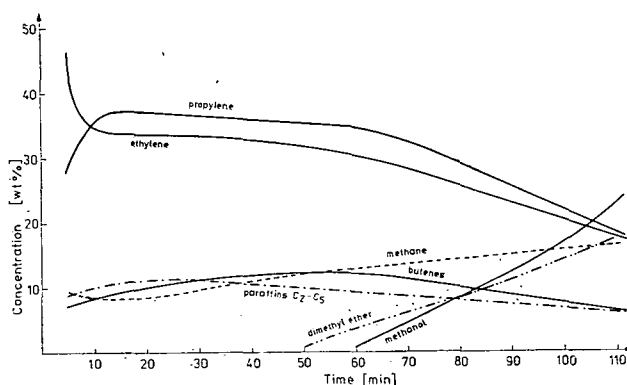


Fig. 1. Changes of product composition occurring with time on stream. Catalyst: potassium exchanged mordenite. Activation temperature: 500 °C. Reaction temperature: 450 °C. Space velocity: 0.25 g methanol/g catalyst/hr

changes of the composition take place during the first few minutes of the reaction. After that short time the catalyst activity is nearly stable. Dimethyl ether appears at the end of that period. Extending the reaction time over the value of the "life-time" one can observe the fast decrease of ethylene and propylene concentration and the rapid increase of dimethyl ether and methane contents. The "life-time" of the catalyst depends upon the type of modified mordenite. The values varied between 15 min. and 5 hrs (Table II).

The influence of reaction temperature on the process is evident. The increase of the temperature from 350 to 450 °C caused the rise of the olefine concentration and of the catalyst "life-time" (Fig. 2). Further increase to 500 °C was associated with the diminishing of the amounts of ethylene and propylene.

Table II
Natural Mordenite — Catalyzed Hydrocarbon Formation

Temperature of activation and reaction [°C]	Space velocity [g CH ₃ OH/g cat/hr]	Products**			
		Time of appearance [min]		Hydrocarbons [wt %] after 60 min reaction	
		Dimethyl ether	Methanol	Paraffins	Olefines
Raw natural mordenite					
350	0.31	at once	at once	18.5	35.1
400	0.31	at once	20	33.5	53.3
450	0.33	50	25	15*	84.2*
Acid treated					
350	0.24	15	60	31*	46*
400	0.34	90	100	30	70
450	0.26	150	170	26	74
Potassium exchanged					
350	0.26	110	210	41	59
400	0.29	40	20	23	60
450	0.26	300	300	22	78
Cerium exchanged					
350	0.24	60	120	39	60
400	0.30	110	120	32	68
450	0.30	150	190	22	78
Titanium exchanged					
350	0.31	20	30	30	33
400	0.35	90	150	48	52
450	0.25	135	140	40	60
Indium exchanged					
350	0.50	15	20	42*	49*
400	0.35	30	25	25	32
450	0.28	120	120	35	65
Cobalt exchanged					
350	0.27	15	15	36*	47*
400	0.29	15	30	21	48
450	0.23	40	45	26	48
Chromium exchanged					
350	0.28	15	—	30*	52
400	0.30	40	30	17	56
450	0.29	150	180	25	75

* After 30 min. of reaction.

** Without water and coke.

The temperature of catalyst activation has rather a small effect on the "life-time" of the catalyst as well as on the product composition. On the other hand, the space velocity of methanol has a great influence.

For the potassium-exchanged mordenite (Table III) the 4 times increase of space velocity decreased the "life-time" of the catalyst about 40 times. The influence was not so drastic in case of other catalysts applied. The changes of the space velocity have some effects on product composition too, especially on methane and olefine concentration (Table III).

Table III

Effect of Space Velocity on Methanol Conversion and Hydrocarbon Distributions over Potassium Exchanged Natural Mordenite

Space velocity [g CH ₃ OH/g catal/hr]	0.260	0.440	1.03	0.088	0.165	0.250
Temperature of activation [°C]	450	450	450	500	500	500
Temperature of reaction [°C]	450	450	450	450	450	450
Time of methanol appearance [min]	360	25	9	240	90	60
Hydrocarbon distribution [wt %] after 30 min. of the reaction						
Methane	11.0	10.3	9.7	23.0	11.0	9.8
Ethane	1.9	1.6	1.6	1.7	1.5	1.5
Ethylene	37.3	32.9	16.7	38.8	34.4	33.4
Propane	9.9	7.8	5.1	4.7	6.9	6.3
Propylene	29.5	34.3	16.1	26.0	33.2	35.9
<i>i</i> -Butane	2.4	1.2	0.6	1.3	1.3	1.6
<i>n</i> -Butane	—	0.9	0.8	0.5	1.2	0.8
Butenes	7.5	8.7	4.3	2.5	9.9	10.0
<i>i</i> -Pentane	0.6	0.4	0.6	0.5	0.7	0.6
Dimethyl ether	0.0	1.8	44.4	0.0	0.0	0.0

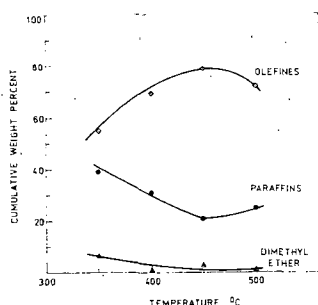


Fig. 2. Effect of the reaction temperature on the hydrocarbon distribution. Catalyst: potassium exchanged mordenite. Activation temperature: 500 °C. Space velocity: 0.26 g methanol/g catalyst/hr. Reaction time: 30 min

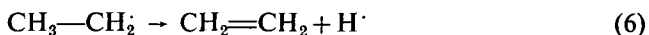
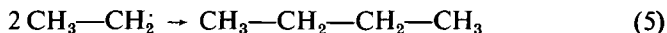
Mechanism

The mechanism of methanol-into-hydrocarbons transformation is still unknown [8]. It is obviously very complicated and proceeds *via* several steps.

We think, according to our results, that the initiating step of the process is the generation of methyl radicals occurring on radicogenic sites of the zeolite

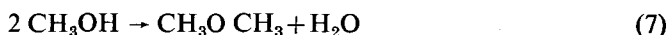


and that methyl radicals can be the precursors of a sequence of consecutive reactions, *e.g.*:



and so on.

So obtained hydrocarbons can undergo further reactions (*e.g.* cracking, isomerization, polymerization). Dimethyl ether is formed by methanol dehydration on acidic Brönsted sites of the catalysts:



The water molecules, generated in the process, can modify the catalyst by formation of new acidic centers accelerating the reaction (7), leading to a decrease of catalyst selectivity.

On the other hand it is well known [9] that coke deposit formation progressively deactivates the catalysts.

Conclusions

Modified natural mordenites show catalytic activity in the process of methanol-into-hydrocarbons conversion but they undergo fast deactivation. The potassium exchanged mordenite was found to be the most interesting catalyst among the investigated samples.

The most promising aspect of the investigated process is the possibility of producing olefines from methanol.

Acknowledgement

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Acta Physica et Chemica, Nova series	Tom.	VIII,	Fasc.	3—4,	1962.
Acta Physica et Chemica, Nova series	Tom.	IX,	Fasc.	1—2,	1963.
Acta Physica et Chemica, Nova series	Tom.	IX,	Fasc.	3—4,	1963.
Acta Physica et Chemica, Nova series	Tom.	IX,	Fasc.	3—4,	1963.
Acta Physica et Chemica, Nova series	Tom.	X,	Fasc.	1—2,	1964.
Acta Physica et Chemica, Nova series	Tom.	X,	Fasc.	3—4,	1964.
Acta Physica et Chemica, Nova series	Tom.	XI,	Fasc.	1—2,	1965.
Acta Physica et Chemica, Nova series	Tom.	XI,	Fasc.	3—4,	1965.
Acta Physica et Chemica, Nova series	Tom.	XII,	Fasc.	1—2,	1966.
Acta Physica et Chemica, Nova series	Tom.	XII,	Fasc.	3—4,	1966.
Acta Physica et Chemica, Nova series	Tom.	XIII,	Fasc.	1—2,	1967.
Acta Physica et Chemica, Nova series	Tom.	XIII,	Fasc.	3—4,	1967.
Acta Physica et Chemica, Nova series	Tom.	XIV,	Fasc.	1—2,	1968.
Acta Physica et Chemica, Nova series	Tom.	XIV,	Fasc.	3—4,	1968.
Acta Physica et Chemica, Nova series	Tom.	XV,	Fasc.	1—2,	1969.
Acta Physica et Chemica, Nova series	Tom.	XV,	Fasc.	3—4,	1969.
Acta Physica et Chemica, Nova series	Tom.	XVI,	Fasc.	1—2,	1970.
Acta Physica et Chemica, Nova series	Tom.	XVI,	Fasc.	3—4,	1970.
Acta Physica et Chemica, Nova series	Tom.	XVII,	Fasc.	1—2,	1971.
Acta Physica et Chemica, Nova series	Tom.	XVII,	Fasc.	3—4,	1971.
Acta Physica et Chemica, Nova series	Tom.	XVIII,	Fasc.	1—2,	1972.
Acta Physica et Chemica, Nova series	Tom.	XVIII,	Fasc.	3—4,	1972.
Acta Physica et Chemica, Nova series	Tom.	XIX,	Fasc.	1—2,	1973.
Acta Physica et Chemica, Nova series	Tom.	XIX,	Fasc.	3,	1973.
Acta Physica et Chemica, Nova series	Tom.	XIX,	Fasc.	4,	1973.
Acta Physica et Chemica, Nova series	Tom.	XX,	Fasc.	1—2,	1974.
Acta Physica et Chemica, Nova series	Tom.	XX,	Fasc.	3,	1974.
Acta Physica et Chemica, Nova series	Tom.	XX,	Fasc.	4,	1974.
Acta Physica et Chemica, Nova series	Tom.	XXI,	Fasc.	1—2,	1975.
Acta Physica et Chemica, Nova series	Tom.	XXI,	Fasc.	3—4,	1975.
Acta Physica et Chemica, Nova series	Tom.	XXII,	Fasc.	1—4,	1976.
Acta Physica et Chemica, Nova series	Tom.	XXIII,	Fasc.	1,	1977.
Acta Physica et Chemica, Nova series	Tom.	XXIII,	Fasc.	2—3,	1977.
Acta Physica et Chemica, Nova series	Tom.	XXIII,	Fasc.	4,	1977.

