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, SiO_2/Al_2O_3 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 dm^3 solution, solution concentrations were varied from $10^{-3} - 1\ mol \cdot dm^{-3}$, 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 KNO_3 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 $dm^3 \cdot h^{-1}$ carrier gas (H_2), 100 mg catalyst sample, reaction temperature 673 K, $6 \cdot 10^{-3}$ 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 $mol \cdot Pa^{-1} \cdot g^{-1} \cdot h^{-1}$.

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

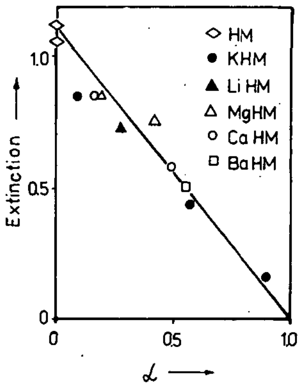

Fig. 1. Extinction of NH_4^+ absorption band in the i.r. spectra at 1450 cm^{-1} after adsorption of NH_3 ($4 \cdot 10^3$ Pa) at 370 K on some mordenite sample as a function of the exchange degree α (α=0 in case of the HM).

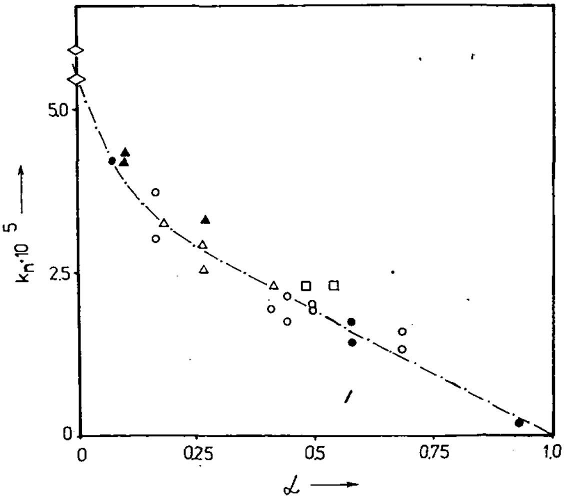

Fig. 2. Correlation between reaction rate constant of *n*-octane cracking k_n, and exchange degree α. (For the meaning of the points see Figure 1).

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 expecially high at lower exchange degree.

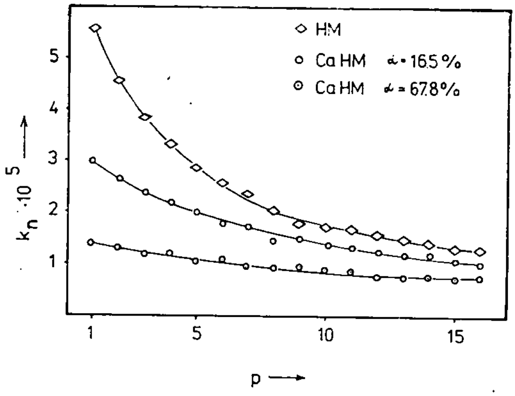

Fig. 3. Aging properties of HM and two CaHM samples: k_n as a function of pulse number p

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 activation energy of $-49\ \mathrm{kJ \cdot mol^{-1}}$. This negative value reflects the adsorption strength of the olefins.

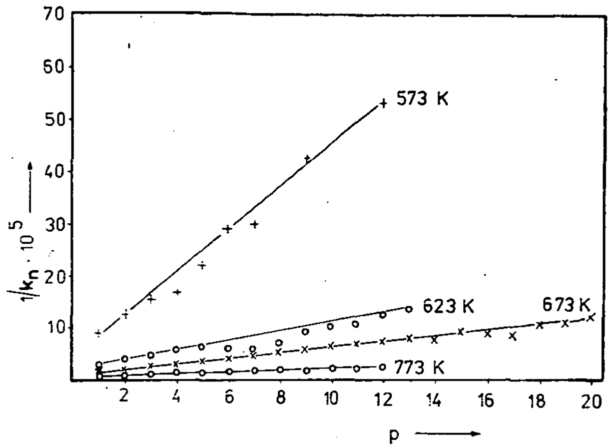

Fig. 4. Aging properties of HM: Reciprocal value of the reaction rate constant as a function of pulse number and reaction temperature as parameter

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 ($B \simeq 4 \cdot 10^4\ \mathrm{Pa \cdot h \cdot g \cdot mol^{-1}}$). 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 simmultaneous 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 $\frac{D_n}{D_{iso}} \simeq 100$. 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 SiO_2/Al_2O_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).

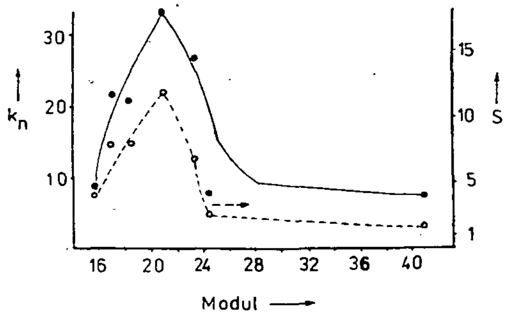

Fig. 5. Activity and selectivity of acid leached HM with different modul (SiO_2/Al_2O_3 mole ratio). Solid line k_n, dashed line S

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).

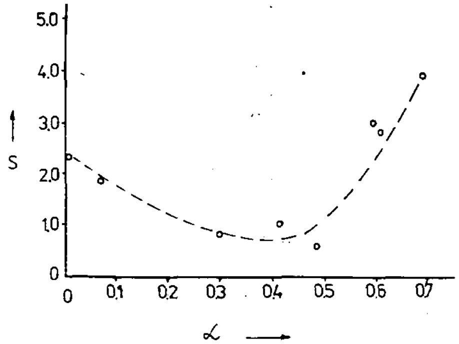

Fig. 6. Selectivity S in the cracking of *n*-octane/*iso*-octane on CaHM with different exchange degrees

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%), Ca^{2+} ions increase the selectivity in spite of decreasing activity. In connection with the results presented by MORTIER ET AL. [8] on the position of Ca^{2+} 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 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 Cu^{2+} and Ni^{2+} 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 satte, exert no effect on selectivity.

Table I

Catalytic properties of Co^{2+}, Cr^{3+}, Cu^{2+} *and* Ni^{2+} *exchanged sodium mordenites*

Catalytic activity (k_n, $\mathrm{mol \cdot g^{-1} \cdot h^{-1} \cdot Pa^{-1}}$), deactivation constant (B, $\mathrm{Pa \cdot h \cdot g \cdot mol^{-1} \cdot pulse^{-1}}$), 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

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ZEOLITE CATALYZED LIQUID PHASE DEHYDRATION OF α-PHENYLETHANOLS

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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*-toly)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(%) = (moles of A produced/moles of alcohol reacted) × 100. First several zeolites were tested in the dehydration of α-(*p*-tolyl)ethanol. The order of activity found was CaL, H-ZSM—5 < HL, H-mordenite, CaX < NH_4Y, MgY, CaY, CeY, LaY, 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.

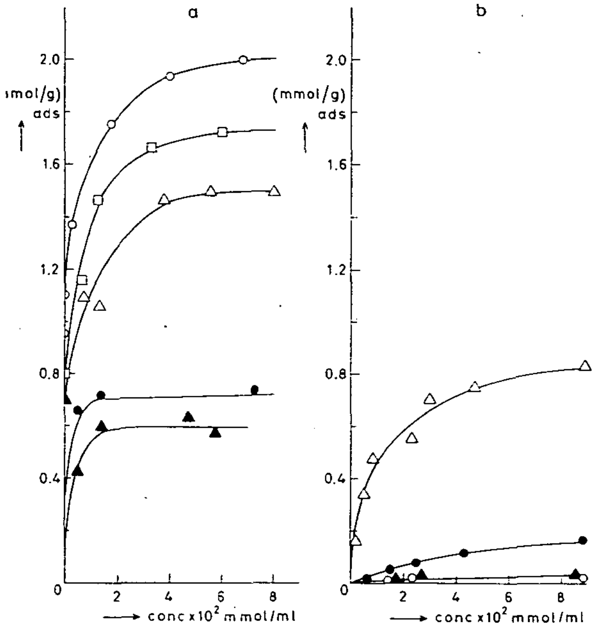


Fig. 1. Adsorption isotherms at 22° of △ alcohol (I), ○ styrene (II), □ p-ethyltoluene (V), ▲ ether (III) and ● dimer (IV) from hexane (a) and diethyl ether (b)

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 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.

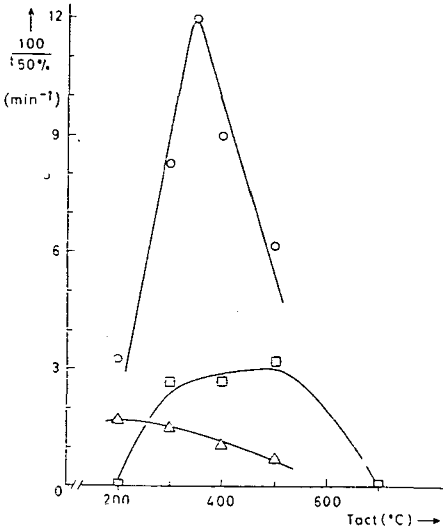


Fig. 2. Effect of the activation temperature on the activity for dehydration ($100/t_{50\%}$). ○ NaCeY-62%, △ NaCaY-82% and □ $NaNH_4Y$-50%

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].

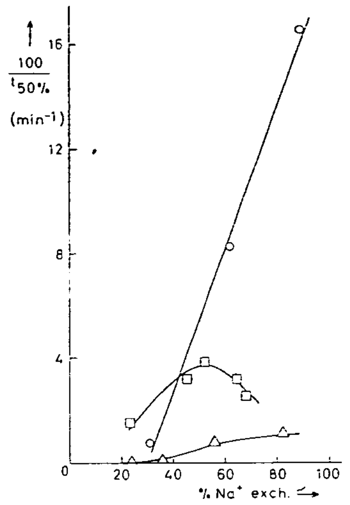


Fig. 3. Effect of the degree of cation exchange on the activity for dehydration (100/$t_{50\%}$). ○ NaCeY, △ NaCaY and □ NaNH$_4$Y. (T_{act} 400°)

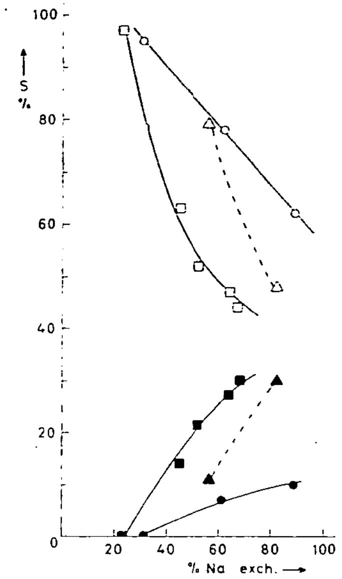


Fig. 4. Effect of the degree of cation exchange on the selectivity after 90% conversion, ○, △, □ styrene (II) and ●, ▲, ■ ether (III). ○ NaCeY, △ NaCaY and □ NaNH$_4$Y. (T_{act} 400°)

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 NaNH$_4$Y 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 NaNH$_4$Y-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

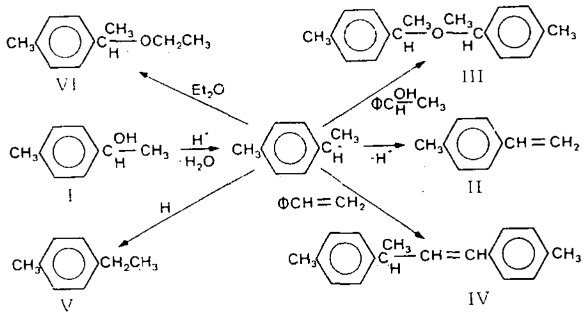
Substituent effects[a]

Para-substituent	CH_3O	CH_3	H	Br
$t_{50\%}$ (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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