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

By
P. FEJES, I. HANNUS, I. KIRICSI, K. VARGA
Department of Applied Chemistry, József Attila University, Szeged, Hungary

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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 ($k = 10^{-2}\ s^{-1}$ 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 oder 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 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 mol dm^{-3} sodium acetate solution. After ion exchange the catalyst was carefully washed using slightly alkaline water (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 synthetized 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 $2 \cdot 10^{-2}$ dm^3 NaN_3 solution in water (concentration of $NaN_3 = 5 \cdot 10^{-2}$ 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 $4 \cdot 10^{-2}$ 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 dm^3; from this the volume of the system at the reactor temperature 0,0707 dm^3, at room temperature: 0,1257 dm^3), 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 NaN_3. As it is well-known from elementary chemistry NaN_3 decomposes into Na and N_2 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 H_2O and N_2 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 N_2 at 650 and 690 are supposed to be the decomposition of NaN_3 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 NaN_3 in- and outside of the NaY crystallites is very dependent on the method of preparation of samples containing NaN_3 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 NaN_3, its distribution, temperature programming,

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

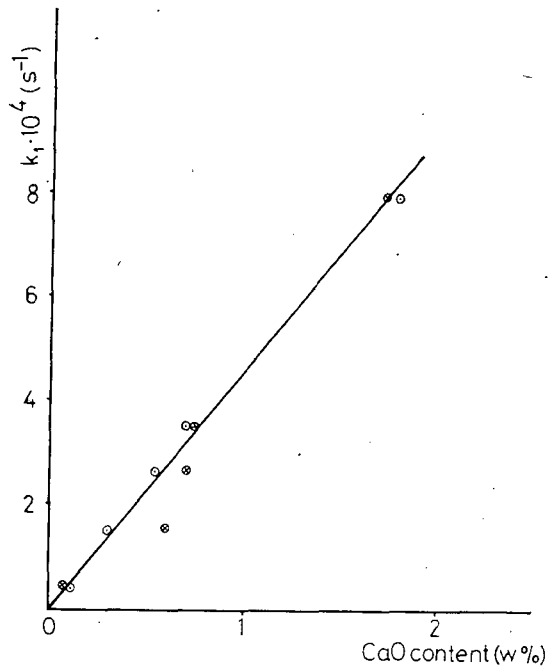

Fig. 1. Measured apparent rate constants as function of the CaO content of NaY zeolites (determined by EDAX: ⊙ and XFLA ⊗)

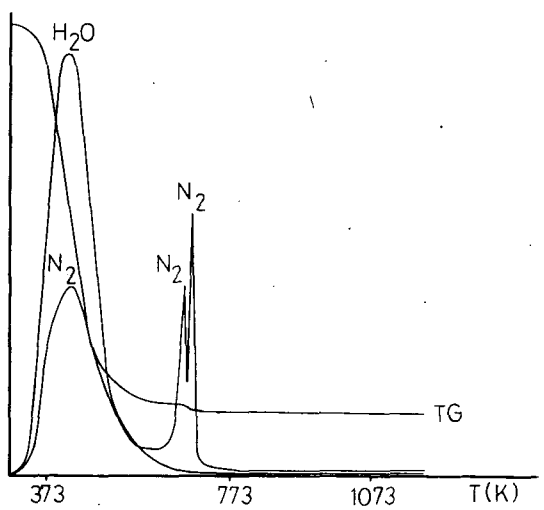

Fig. 2. Thermogravimetry combined with MS product analysis of a NaY zeolite sample containing NaN_3

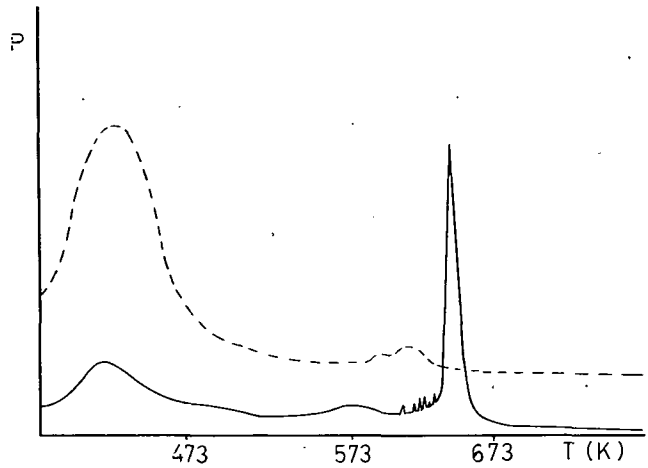

Fig. 3. Monitoring of loss of water and decomposition of NaN_3 by the pressure change in the reactor at constant pumping speed during heat treatment. Continuous line: for catalyst No. 6; dashed line: for No. 7 (shifted upwards)

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:

$$—OH + Na \rightarrow —ONa + H \tag{1}$$

the other to the neutralization reaction:

$$NaOH + H^+ \rightarrow Na^+ + H_2O \tag{2}$$

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 disappearence 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].

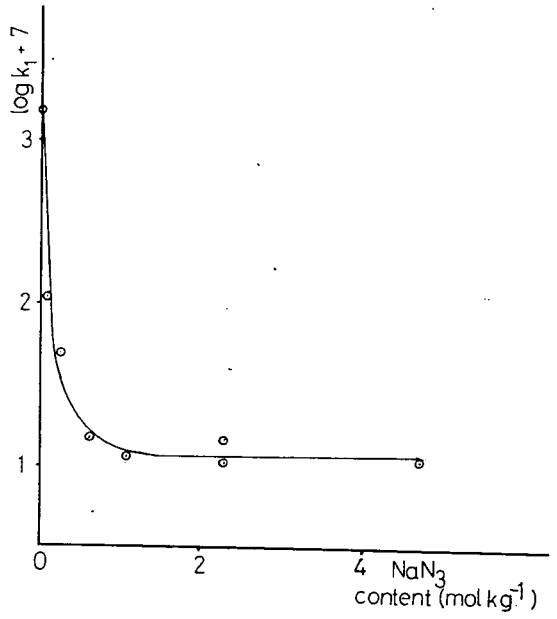

Fig. 4. Catalytic activity as function of the initial NaN_3 content.

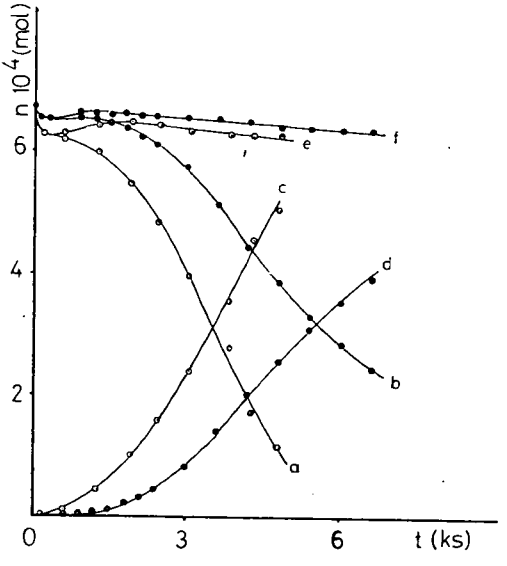

Fig. 5. Kinetic curves for two catalysts containing different amounts of calcium.

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.*

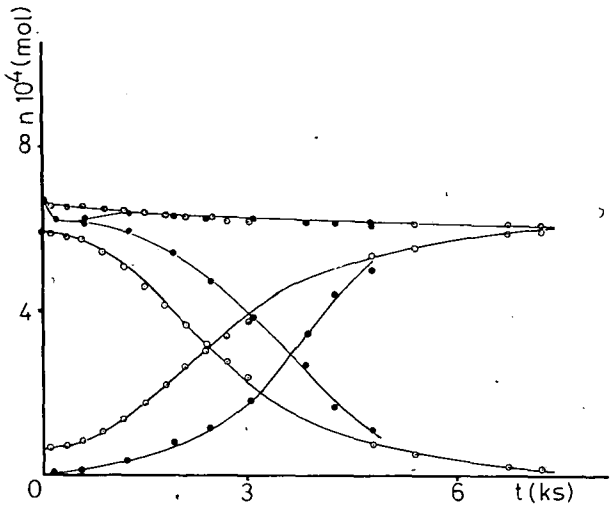

Fig. 6. Kinetic curves showing the effect of added propylene.

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:

$$-\frac{dP}{dt} = k_1 P \tag{3}$$

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:

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

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:

$$\bar{v} \equiv v_1 + v_2 \cdot \frac{T_1}{T_2} \tag{5}$$

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:*

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

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 $O^{2-}_{(2)}$, $O^{2-}_{(3)}$ and $O^{2-}_{(4)}$ 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

$$q \equiv \frac{M}{S} \cdot \frac{a}{c}. \tag{7}$$

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

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

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 $T_2 = 573$ K [16, 17] $k^* = 2.1 \cdot 10^{-10}\ \mathrm{s}^{-1}$. In an empty reactor (*i.e.* in a reactor without catalyst) the measured value of k_1 at 573 K was $1.2 \cdot 10^{-6}\ \mathrm{s}^{-1}$ (and because $k_2 = 0$ in this case it means by equ. (4) that $k^* = 3.3 \cdot 10^{-6}\ \mathrm{s}^{-1}$) 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, $k_1 = 1.53 \cdot 10^{-4}\ \mathrm{s}^{-1}$; from the Ca^{+2} content (providing that $Ca^{2+}/H^+ \approx 1$ and all H^+ ions are active [which is probably by far not the case!]) $\lambda/N \leqq 5.5 \cdot 10^{-2}$ mol kg^{-1}; an estimate for the equilibrium constant of sorption is $K = 211\ \mathrm{dm}^3\ \mathrm{mol}^{-1}$ and for the bulk density $\sigma = 0.375\ \mathrm{kg\ dm}^{-3}$. From all these follows the true rate constant of the heterogeneous cyclopropane transformation: $k = 10^{-2}\ \mathrm{s}^{-1}$. 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:

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

These data are in excellent agreement with the k_2 value *computed* from our experiments: $k_2 = 4.4 \cdot 10^{-2}\ \mathrm{s}^{-1}$, 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 □) according to the equations:

$$\{—SiO_2\}+2\,Na \rightarrow \{—SiO\,□\}+Na_2O$$

or (9)

$$\{—AlO_2^-\}+2\,Na \rightarrow \{—AlO\,□^-\}+Na_2O$$

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:

$$H^+ + C{=}C{—}C \rightarrow C{—}\overset{+}{C}{—}C \quad \text{(propyl cation)}$$

$$C{—}\overset{+}{C}{—}C + \underset{C—C}{\overset{C}{\diagup\!\diagdown}} \rightarrow C{—}C{—}C + C{\cdots}\overset{+}{C}{—}C \quad \text{(propenyl cation)}$$

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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