

# SPECTROSCOPIC AND KINETIC STUDIES ON THE CYCLOPROPANE ISOMERIZATION OVER MORDENITES OF DIFFERENT ACIDITY

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## ABSTRACT

Isomerization of cyclopropane over mordenites of different acidity has been studied by UV-VIS-IR spectroscopy and reactor kinetic measurements.

Apart from the beginning and at high degrees of conversion the kinetics follows the law of a first order irreversible reaction. With increasing proton content of the zeolite the rate of isomerization is enhanced and the activation energy is decreased. The formation of allylic and polyenylic carbocations in Bronsted acidic mordenites responsible for the production of oligomers can be proved by UV-VIS as well as by IR spectroscopy. By-products of this kind are missing on the Na-form, although there is evidence for a low residual surface acidity, the confirmation of which seems to be more likely by kinetic experiments or conversion of selected probe molecules than by vibrational spectroscopy.

## INTRODUCTION

In spite of the spectacular transformation of coal or organic waste to hydrocarbons over silica-rich zeolites, there is still much industrial interest and effort in isomerization, which runs parallel to cat-cracking and upgrades the benzine fraction. As this type of reaction is known to be catalyzed by strong acids in homogeneous media, the intermediacy of carbonium ions also with zeolites should be established and their role in parallel or consecutive reaction steps should be explored.

Due to its higher module, mordenite is of greater stability compared to faujasites and seems to be well-suited in the H-exchanged form for fundamental investigations. As the test reaction isomerization of cyclopropane was chosen, details of which are well-established in the literature /1/, stating the rate determining step

being the formation of the non-classical protonated cyclopropane intermediate. The objective of this paper was to examine the dependence of the kinetic parameters for the isomerization of cyclopropane upon the proton content of the zeolite and the influence of other compounds enhancing the allylic ion generation.

## EXPERIMENTAL

Materials. The base material was synthetic mordenite Zeolon 100-Na (Norton) designated as Zeolon. A part of this sample was stirred for 16 hours at 350 K in an excess of 1 molar NaCl solution in order to achieve the homo-ionoc Na-form, named NaM. Starting from Zeolon, mordenites of different ammonium content were prepared by stirring with stoichiometric amounts of 0.1 molar solutions of ammonium chloride at 350 K for 16 hours. The compositions were determined by atomic absorption spectrophotometry (AAS) and neutron activation analysis. Samples will be designated as  $\text{Na}_x\text{HyM}$ , where M denotes  $\text{Al}_8\text{Si}_{40}\text{O}_{96}$ .

Cyclopropane (Merck, stated purity 99.998%), allene (Matheson, 97%), ammonia (Matheson, 99.998%) and propene (Messer-Griesheim, 99.98%) were used without further purification.

Apparatus. A stainless steel recirculatory flow reactor was used for the kinetic experiments, a more detailed description of which will be given elsewhere /2/. For product analysis the system was connected via a motor-driven sampling valve to a gas chromatograph (VARIAN AEROGRAPH 1520). The FID (flame ionization detector) signal is controlled by an 8-bit microcomputer (COMMODORE CBM 8032) and was stored for further processing on a disk. The FID response was calibrated by known amounts of cyclopropane and propene, respectively. Baseline correction, determination of the rate constants by linear regression and calculation of the apparent activation energies were performed by the aid of computer programs.

The spectra were recorded on a CARY 17, DIGILAB FTS 14 or DIGILAB FTS 20 spectrometer, respectively. Details of the instruments and procedures employed have been described previously /3,4/.

Pretreatment. For reactor measurements 0.5 g of the 0.3-0.5 mm sieve fraction of pelletized zeolites were used and activated in a helium stream of 0.58 ccm/s at 750 K for 13 hours.

For the spectroscopic studies, thin self-supporting wafers were applied and outgassed at 750 K under high vacuum conditions (see also /3,4/).

## RESULTS AND DISCUSSION

UV-VIS spectroscopic studies. Isomerization of cyclopropane over Y-type zeolites has been studied by Fejes et al. by means of reactor kinetic measurements /5/. Their kinetic curves showed a pronounced induction period indicating the formation of a reactive intermediate on the catalyst prior to isomerization. Upon pre-adsorption of traces of propene or allene this induction period decreased or disappeared, respectively. Allylic cations were assumed to be these intermediates.

By co-operation, we have studied the formation of carbocations in mordenites of different Bronsted acidity using UV-VIS-NIR spectroscopy. The results are summarized as follows /4/: Upon adsorption of allene, propene, cyclopropane, isopropanol, and acetone, respectively, similar electronic bands in the region 200-600 nm were observed. Their development with time or upon heating up to 370 K decreased in the sequence given above (allene being exceptionally reactive) as well as with decreasing proton content of the zeolites. The bands were divided into four groups and assigned to the  $\pi-\pi^*$  transitions of mono-, di-, tri-, and tetraenylic carbenium ions. Mechanistically, their formation can be explained by the following steps (see /4/): (i) protonation (and dehydration) of the adsorbates leads to the propyl or allyl ion, respectively; (ii) hydride ion abstraction (by a propyl ion, e.g.) from propene produces the allyl ion; (iii) dienylic carbenium ions are formed by reaction of the allyl ion with allene directly, whereas the reaction of the allyl ion with a mono- or diene to a di- or trienylic carbocation requires consecutive deprotonation and hydride ion abstraction.

In addition to the published results, we recently investigated the adsorption of allene and cyclopropane on the base material, Zeolon, expecting no formation of carbenium ions, due to the lack of Bronsted acidity. In case of cyclopropane this expectation was proved; no bands were detected even after heating up to 500 K. Surprisingly, upon admission of allene at room temperature very weak absorptions arose immediately, increasing in intensity upon short heating to 400 K. Analysis of this sample by AAS indicated a slight deficiency of Na. Therefore, we assume that this gap is balanced by OH groups, even though they were not detectable by IR spectroscopy. This conclusion agrees with the results and the proposed mechanism of carbocation formation and is supported by further IR spectroscopic and kinetic studies discussed later.

In conclusion, the formation of allylic carbenium ions - even upon adsorption of cyclopropane - in Bronsted acidic mordenites was proved by UV-VIS spectroscopy. But nevertheless, an important question is still open: Is the allylic ion involved in the cyclopropane isomerization or does it produce oligomers via the observed polyenylic carbocations only ?

IR spectroscopic studies. Unfortunately, using the transmission technique, strong lattice vibrational modes of the zeolites obscure bands of adsorbed species in the range below  $1300\text{ cm}^{-1}$ . Furthermore, the sharp increase of light scattering at higher wavenumbers leads to spectra of poorer quality in the region above  $3000\text{ cm}^{-1}$ . Therefore, and for shortening the discussion, the spectra presented here will be restricted to the region  $2300\text{-}1300\text{ cm}^{-1}$ . Nevertheless, our conclusions are confirmed by the bands in the range up to  $4000\text{ cm}^{-1}$  as well !

The positions and intensities of the bands of propene adsorbed in NaM at room temperature are very similar to those observed on A-type zeolites /3/. The absorptions at  $1455\text{ (CH}_3\text{ asym. def.)}$  and  $1635\text{ (C=C stretch)}$  are the most intense (very strong) followed by those at  $1435, 1382\text{ (strong)}$  and  $1417\text{ (medium)}$  ( $\text{CH def. modes}$ ). As the C=C stretching mode shows a cation-sensitive downscale shift on A-type zeolites /3/ and its position on NaM is identical to that on NaA, sorption of the propene molecules in front of sodium ions is concluded. The spectrum does neither change with time nor does it indicate the formation of any other species.

The spectra of cyclopropane adsorbed in Zeolon at room temperature (Figure 1) prove the slow isomerization on this zeolite, confirmed by the increase of the bands of propene with time and upon short heating of the loaded sample. In the spectral region shown, cyclopropane exhibits only two bands, one of them accidentally at the same position as propene ( $1435\text{ cm}^{-1}$ ) and the other one ( $1462\text{ cm}^{-1}$ ), being a doubly degenerate and only raman active mode of the free molecule, becomes IR active due to symmetry lowering upon

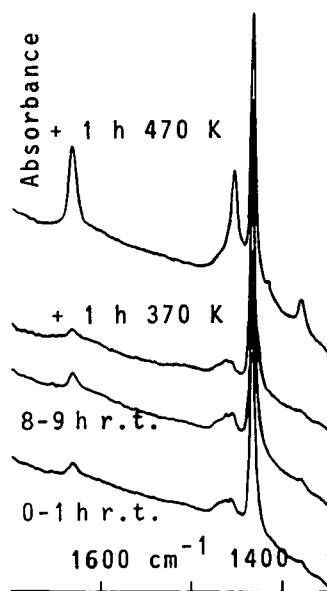


Fig. 1. IR spectra of cyclopropane adsorbed in Zeolon. (r.t. = room temp.)

adsorption. As this mode does not split into two bands (parallel to the corresponding absorptions in the CH stretch region) a "face on" interaction of the cyclopropane molecules with sodium ions has to be assumed (compare /3/).

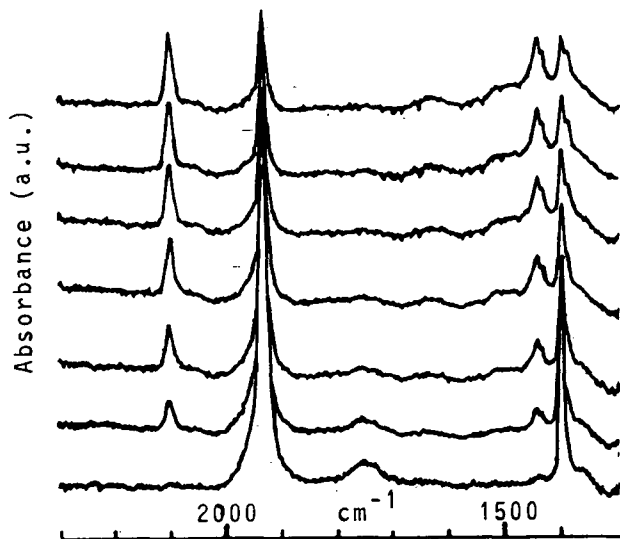


Fig. 2. Dynamic IR spectra of allene adsorbed in Zeolon at room temperature. Sequence from bottom to top (0-10 h after admission).

As allene turned out to be the most reactive substrate concerning the formation of carbenium ions, its adsorption in Zeolon at room temperature was investigated by IR spectroscopy as well (Figure 2). Most of the bands observed in the region 1300-4000  $\text{cm}^{-1}$  are unambiguously assigned to allene and its isomer, propine. Concerning Figure 2 this is mainly confirmed by the decreasing intensities of the absorptions at 1935, 1750, and 1400  $\text{cm}^{-1}$  (C=C stretch, combination of bending modes, and CH def. of allene) and by the increase of the bands at 2102, 1442, and 1388  $\text{cm}^{-1}$  ( $\text{C}\equiv\text{C}$  stretch and CH def. of propine). But in addition a broad absorption at 1510  $\text{cm}^{-1}$  arises with time. In agreement with our UV-VIS results and published IR data we assign this band to the CCC stretch of allyl type cations. Deno /6/ and Evans /7/ reported this absorption of monoenylic ions to appear around 1530  $\text{cm}^{-1}$ , shifting downscale upon further alkylation and / or conjugation. Furthermore it is generally observed that most of the CH and especially C=C bands of hydrocarbons are shifted to lower wavenumbers upon adsorption in zeolites. So, we conclude that allene isomerizes to propine via the allylic

cation, even though Bronsted acidic hydroxyl groups are not detectable on this sample by IR spectroscopy. But kinetic studies (see below) and recent IR studies on the acidity of our zeolites by adsorption of ammonia /8/ revealed that even the Zeolon exhibits a low residual Bronsted acidity.

The spectra of propene adsorbed in HM ( $\text{Na}_{0.2}\text{H}_{7.8}\text{M}$ ) indicate fast oligomerization. Only during the first 10 minutes after admission propene bands at 1455, 1435 (shoulders, CH def.), and  $1613\text{ cm}^{-1}$  (C=C stretch of propene interacting with OH groups) are visible. The assignment of the latter is confirmed by the large shift of the OH stretching band from  $3610$  to  $3480\text{ cm}^{-1}$ . The most intense bands are those of oligomers at  $1465$ ,  $1385$ , and  $1370\text{ cm}^{-1}$ , which do not vanish upon heat treatment under vacuum. Immediately after adsorption of propene, the CCC stretching mode of allylic cations at  $1535\text{ cm}^{-1}$  is present and that of dienyllic carbenium ions arises at  $1505\text{ cm}^{-1}$  with time. So, the spectra prove the fast oligomerization of propene in HM via allylic and dienyllic carbenium ions in agreement with the UV-VIS results.

Upon adsorption of cyclopropane in HM at room temperature (Figure 3) bands of propene at  $1635$ ,  $1613$ ,  $1455$ , and  $1435\text{ cm}^{-1}$  are detectable only during the first few minutes after admission. In course of time new absorptions at  $1535$ ,  $1505\text{ cm}^{-1}$  (CCC stretches of mono- and dienyllic carbenium ions), and of oligomers in the region below  $1450\text{ cm}^{-1}$  arise. After heating the loaded sample to  $370\text{ K}$  for one hour even the intense C=C stretching bands of propene totally disappeared and those of the carbocations and the oligomers became the most intense ones. Thus, a fast isomerization of cyclopropane to propene in HM and consecutive (or parallel) oligomerization of propene via allylic and dienyllic carbocations is concluded.

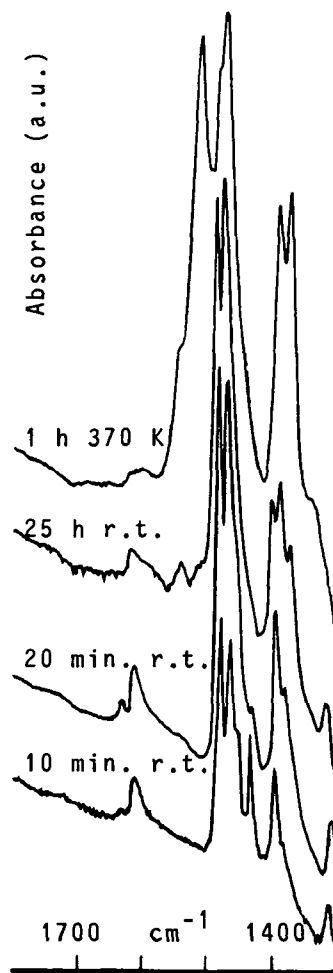


Fig. 3. IR spectra of cyclopropane adsorbed in HM.

Concerning the adsorption of cyclopropane or propene in morde-nites of lower proton content, the generation of the bands discussed above is comparable, but the rate of formation of oligomers diminishes with decreasing Bronsted acidity. On samples of small proton content (e.g Na<sub>7</sub>H<sub>1</sub>M) carbocations are not detectable by IR spectroscopy. Here the bands of the adsorbed species are more clearly assigned to cyclopropane or propene as they are very similar to those observed on NaM.

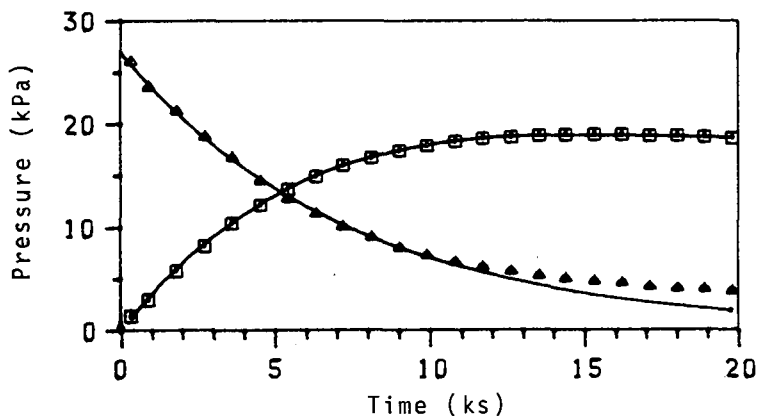


Fig. 4. Kinetic curves (partial pressure vs. time) of the cyclopropane isomerization over Zeolon. (Triangles / squares = experimental cyclopropane / propene data; mass of catalyst 0.5 g)

Kinetic Studies. In Figure 4 a typical set of kinetic curves of the cyclopropane isomerization over Zeolon (reaction temperature: 473 K) is presented. (The cyclopropane curve is calculated by converting  $\ln p(\text{cp})$  vs. time, obtained by linear regression, to the exponential function, whereas the propene data were fitted by a polynomial). In contrast to studies of Fejes et al. on Y-type zeolites /5/ our curves do not indicate any induction period. Deviations from the law of a first order irreversible reaction are detectable at high degrees of conversion only (compare Figure 4: 9 ks = 70% conversion), due to blocking of the active sites by adsorbed propene. At lower reaction temperatures, further small deviations (experimental cyclopropane data higher than the calculated ones) at the very beginning of the reaction (up to 15 minutes) are due to the process of approaching the sorption equilibrium. These features were obtained on A-type zeolites as well /9/.

For convenience all samples were activated overnight (13 hours, exactly) at 750 K. But as the UV-VIS spectra proved the formation of carbenium ions upon adsorption of allene on the starting material, Zeolon, which can be interpreted by Bronsted acidic groups only, the influence of different activation times was investigated. The rate constants of the isomerization measured at 473 K reaction temperature decreased linearly with increasing the activation time from 3 to 18 hours, and a further small decrease was observed upon extending this time to 40 hours. Thus we conclude, that the low residual Bronsted acidity of this sample was reduced by dehydroxylation, even though acidic OH groups were not detectable by IR spectroscopy.

Some kinetic data of the cyclopropane isomerization over mordenites of different Bronsted acidity are summarized in table 1.

Table 1

Rate constants (k) and apparent activation energies (Ea)

Sample	k (443 K) (s <sup>-1</sup> )	Ea (kJ/mol)	temp. range (K)	number of data
Na <sub>4</sub> H <sub>4</sub> M	1.04 10 <sup>-3</sup>	72 ± 4	383 - 443	4
Na <sub>6</sub> H <sub>2</sub> M	5.00 10 <sup>-4</sup>	74 ± 10	286 - 443	3
Zeolon	2.28 10 <sup>-5</sup>	102 ± 2	443 - 473	4
NaM	1.90 10 <sup>-6</sup>	111 ± 3	443 - 523	5

k values are given for using 0.5 g of zeolite.

Temp. range and number of data refer to calculation of Ea

Table 1 shows that the rate constants are enhanced with increasing Bronsted acidity of the samples whereas the apparent activation energies decrease. Whether the rate constants are proportional to the proton content cannot be decided clearly, due to the limitations of the analysis of the samples exhibiting very low acidity, i.e. Zeolon and NaM. Nevertheless, we conclude that the rate determining step of the cyclopropane isomerization over acidic mordenites is the protonation of the adsorbate, leading to a non-classical carbonium ion intermediate.



As UV-VIS and IR spectroscopy prove the formation of oligomers inside the framework of the zeolites, their formation was studied by gas chromatography as well. At a reaction temperature of 403 K in case of NaM there are no by-products detectable even after complete conversion of cyclopropane to propene, whereas in case of  $\text{Na}_6\text{H}_2\text{M}$  weak peaks of by-products were detected in the gas phase even at the very beginning of the isomerization, i.e. about 20% conversion. Nevertheless they amount only to less than 0.1% of propene and cyclopropane, respectively. Only after full conversion their amount is remarkably enhanced. So, they do not affect the accuracy of the kinetic measurements.

#### SUMMARY AND CONCLUSIONS

Isomerization of cyclopropane to propene over mordenites is proved by IR spectroscopy and reactor kinetic measurements. On samples of negligible Bronsted acidity no by-products are detectable by IR spectroscopic and gas chromatographic measurements. The kinetics follows the law of a first order irreversible reaction without any indication of an induction period. On acidic mordenites the rate constants are enhanced and apparent activation energies decrease with increasing proton content of the samples, indicating the rate determining step to be the protonation of cyclopropane to a non-classical carbonium ion. The formation of oligomeric by-products via allylic and polyenylic carbenium ions on acidic mordenites is proved by UV-VIS and IR spectroscopy. Both IR spectroscopy as well as gas chromatographic studies show their generation during isomerization, the rate of their formation being very small compared to the rate of isomerization. Thus, the formation of the by-products is concluded to be a negligible side reaction. The question, whether the proven allylic cation is involved in cyclopropane isomerization is still open, as its formation can be rationalized via small amounts of propene, formed at the very beginning of the isomerization, as well.

#### ACKNOWLEDGEMENT

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## REFERENCES

1. Jacobs, P.A.: Carboniogenic Activity of Zeolites. Elsevier Sci. Publ. Co., Amsterdam, 1977, p. 97
2. Förster, H., Seebode, J., to be published
3. Förster, H., Seebode, J., Zeolites 3, 1983, 63
4. Fejes, P., Förster, H., Kiricsi, I., Seebode, J. in: Structure and Reactivity of Modified Zeolites, Jacobs, P.A. et al. (Eds.), Elsevier Sci. Publ. B.V., Amsterdam, 1984, p. 91
5. Fejes, P., Hannus, I., Kiricsi, I., Varga, K., Acta Phys. Chem. Szeged 24, 1970, 119
6. Deno, N.C. in: Carbonium Ions; Olah, G.A., Schleyer, R.P. (Eds.) Wiley-Interscience, New York, 1970, Vol. II, p. 783
7. Evans, J.C. in: Carbonium Ions; Olah, G.A., Schleyer, R.P., (Eds.), Wiley-Interscience, New York, 1968, Vol. I, p. 223
8. Förster, H., Jacobasch, H., to be published
9. Fejes, P., Kiricsi, I., Förster, H., Seebode, J., Zeolites 4, 1984, 259