# ISOMERIZATION OF CYCLOPROPANE OVER Co(II)-EXCHANGED A-TYPE ZEOLITES

P. FEJES, I. Kiricsi, Gy. Tasi, K. Varga
Department of Applied Chemistry, József Attila University, Szeged,
Hungary

## ABSTRACT

Study of the skeletal isomerization of cyclopropane over Co(Na)A
zeolites exchanged to different levels reveals that the reaction takes
place irreversibly and follows first-order kinetics. The rate is pro-
portional to the number of accessible $Co^{2+}$ ions in the large cavities.
This value is the same as the number of adsorbed propylene molecules
at full coverage. In contrast to the situation with Brönsted acids as
catalysts, the reaction intermediate is a $\pi$-adsorbed complex produced
by the interaction of cyclopropane adsorbed "face-on" over $Co^{2+}$ ions.
As $Co^{2+}$ ions are inactive in side-reactions such as oligomerization
and cracking, the kinetics of isomerization can be studied under
"clean" conditions.

## INTRODUCTION

It is widely accepted that the skeletal isomerization of cyclo-
propane on solid acids is one of the most simple catalytic transforma-
tions. The reaction takes place irreversibly, following apparent
first-order kinetics, and edge-protonated cyclopropane is regarded as
the reaction intermediate [1-5]. The product propylene is not stable
in contact with Brönsted acids, as it undergoes further reactions
leading to different oligomeric and cracking products [6-8]. These un-
desired side-reactions can be avoided and the kinetic picture is accord-
ingly simplified if alkaline earth or transition metal ion-exchanged
zeolites, as Lewis acids, are used as catalysts [9]. With Co(Na)A
zeolites, for example, it was possible to follow the kinetics by i.r.
spectroscopy, measurements in a static reactor permitting estimation
of the relevant rate coefficients of the surface reaction [10]. The
i.r. spectroscopic studies revealed that the active centres are $Co^{2+}$
ions interacting with cyclopropane adsorbed in a "face-on" mode [11].
The reactor experiments resulted in a strict correlation between the
true kinetic parameters and the number of accessible $Co^{2+}$ ions in the

zeolitic framework.

This paper is intended to shed light on some details of the kinetics of cyclopropane isomerization over Co(Na)A zeolites exchanged to various extents.

## EXPERIMENTAL

The Co(Na)A specimens were obtained from binderless Linde 4A zeolite by exchange with $Co(NO_3)_2$ solution. Their compositions are given in Table 1.

Table 1

Unit cell compositions of catalysts used

| No | Composition |
|----|-------------|
| 1 | $Na_{12} - A \quad (A = Al_{12}Si_{12}O_{48})$ |
| 2 | $Co_{0.24}Na_{11.52} - A$ |
| 3 | $Co_{0.85}Na_{10.2} - A$ |
| 4 | $Co_{1.38}Na_{9.24} - A$ |
| 5 | $Co_{3.6} Na_{4.8} - A$ |
| 6 | $Co_{3.7} Na_{4.6} - A$ |
| 7 | $Co_{4.02}Na_{3.96} - A$ |
| 8 | $Co_{4.55}Na_{1.9} - A$ |

The zeolite samples were characterized by XRD, IR spectroscopy and TG.

For adsorption and kinetic studies, the catalyst samples were heat-treated at 673 K, in vacuo, for 4 h. (The final pressure attained was better than $10^{-2}$ Pa.) A description of the kinetic equipment used and the product GC analysis is to be found in [12].

## RESULTS

Adsorption experiments with cyclopropane run into difficulties. because the kinetic diameter of the cyclopropane molecule (around 0.52 nm) is larger than the pore openings in NaA. On the other hand, cyclopropane undergoes a quite fast transformation over Co(Na)A, even at ambient temperature. These obstacles are not encountered with propylene as adsorptive.

Figure 1 shows the adsorption isotherms of propylene on NaA zeolite. The isotherms cannot be described correctly by either the Langmuir or the Freundlich isotherm equation: at low temperatures they are rather of the Langmuir type, while at higher temperatures

the Freundlich isotherm equation seems to be valid, with a continuous transition between the two types at intermediate temperatures. Similar results have been obtained with samples with low $Co^{2+}$ contents.
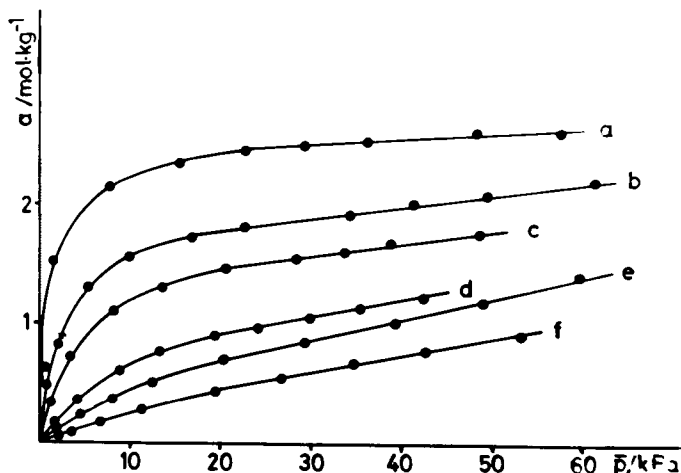


Fig. 1. Adsorption isotherms of propylene on NaA zeolite. (Temperatures: a 332 K; b 377 K; c 398 K; d 438 K; e 453 K; f 473 K.)

Figure 2 depicts the isosteric heats of adsorption at different coverages, as obtained from the isotherms for NaA and a low-level exchanged specimen (No. 2). It is clearly seen that, after some decrease, near $a_s = 0$, the curves level off at the same value ($Q_{st}$ = 47 kJ $mol^{-1}$) for the two adsorbents. The quite high value of $Q_{st}$ implies weak chemisorption, as found by Schirmer in the case of Ca(Na)A [13].

With ethylene as adsorptive the character of the curves for a specimen containing 1 $Co^{2+}$ ion/u.c. is similar; nevertheless, the levelling-off occurs at a lower isosteric heat of adsorption ($Q_{st}$ = 42 kJ $mol^{-1}$ [14]).

At high $Co^{2+}$ ion-exchange levels (see specimens No. 6 and No. 7), the isosteric heat curves are similar to each other (see Fig. 3), but differ markedly from those seen in Fig. 2. At higher coverages a constant value of $Q_{st}$ = 75 kJ $mol^{-1}$ is reached here too.

The adsorption heat curves in Fig. 2 and 3 clearly demonstrate that no simple adsorption model can be valid for the adsorption of propylene on $Co^{2+}$-exchanged NaA zeolites.

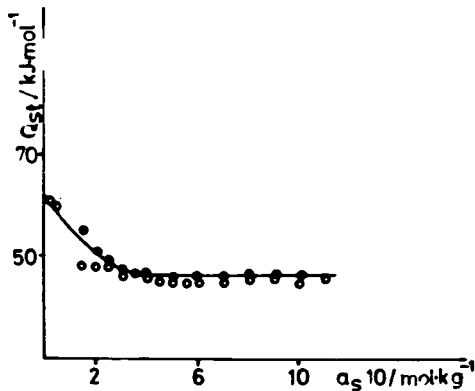The kinetic curves of cyclopropane isomerization, as measured

Fig. 2. Isosteric heat of ad-
sorption at different cov-
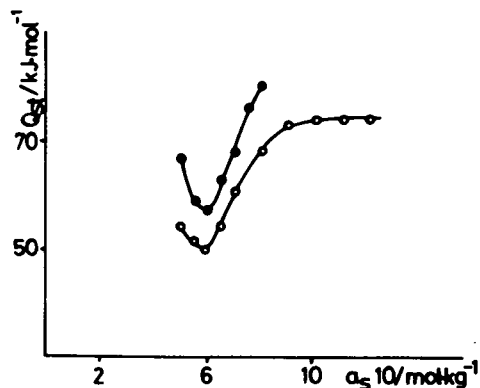erages for NaA (o) and sample
No. 2 (●).

Fig. 3. Isosteric heat of ad-
sorption at different coverages
for samples No. 6 (o) and No. 7
(●).

in a recirculatory flow reactor using catalyst samples with varying
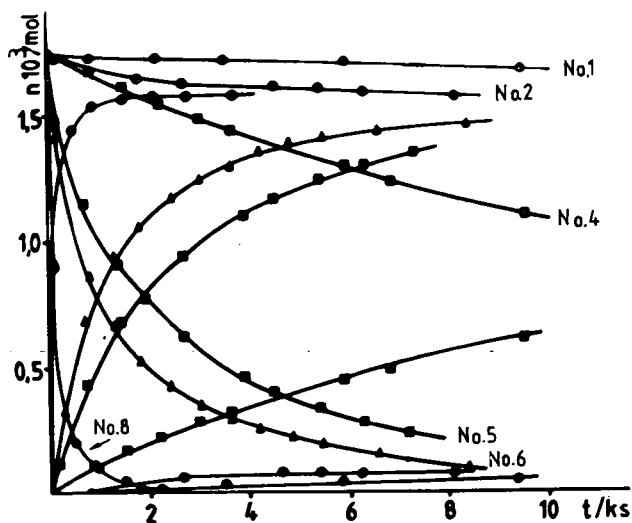$Co^{2+}$ contents, are shown in Fig. 4. NaA turns out to be a practically



Fig. 4. Kinetic curves of cyclopropane isomerization. (Reaction
temperature 473 K; mass of catalyst $2 \cdot 10^{-4}$ kg; reactor volume
0.14 $dm^3$.)

inactive catalyst, mainly due to sieving effects. The curves reflect
a similar change between specific activity and $Co^{2+}$ content. The ac-
tivation energies computed from the kinetic curves are listed in

Table 2.

Activation energies for cyclopropane isomerization

| Zeolite samples | No. 4 | No. 5 | No. 6 |
|---|---|---|---|
| Activation energies kJ mol$^{-1}$ | 47.2 | 64.3 | 65.7 |

DISCUSSION

The adsorption properties of NaA for different hydrocarbons have been investigated by several authors [15-17]. From the results it could be concluded that through exchange of the bulky Na$^+$ ions for ions of increasingly smaller size (e.g. Ca$^{2+}$, Mg$^{2+}$, Co$^{2+}$, etc.) the pore openings could be widened (the eight-ring windows are blocked by ions of smaller diameter), permitting the penetration of bulkier hydrocarbon molecules.

Though the amount of propylene adsorbed increases with the degree of Co$^{2+}$ ion-exchange, no direct proportionality can be observed (see Fig. 5). Breck came to a similar conclusion concerning ethylene adsorption on KNaA zeolites [16].

The first-order rate constants for the isomerization reaction can be seen in Fig. 5 too. The similarity of these two sets of data proves that in the chemisorption and in the catalytic reaction the same centres are involved, their number and distribution (accessibility) being identical.

The kinetic curves in Fig. 4 for both cyclopropane consumption and propylene production are apparently first order in the case of high-level exchange. No induction period whatsoever is discernible in the curves, in contrast to NaY and NaCaY zeolites [12], and no oligomeric species or cracking products could be identified by GC. The activation energy for these samples ($E_a^+ = 65$ kJ mol$^{-1}$) agrees well with that found previously [18].

At low exchange levels the character of the kinetic curves differs markedly from that found before. The activation energy (for sample No. 4) drops from 65 kJ mol$^{-1}$ to $E_a^+ = 47$ kJ mol$^{-1}$, this value being equal to the isosteric heat of adsorption for propylene at high coverages on the same samples.

Propylene preadsorbed on the activated catalyst does not influence the rate of cyclopropane skeletal isomerization. Allene, admit-

ted to the catalyst before commencement of the experiment, causes re-
tardation. This is probable due strong chemisorption, or else is caused
by its isomerization product, methylacetylene, rendering the active
sites inaccessible for cyclopropane and/or propylene.

These findings are opposite to those found earlier on NaCaY
zeolites exhibiting weak Brönsted acidity, where small amounts of pre-
sorbed propylene or allene reduced the length of the induction period
by creating $C_3H_5^+$ carbocations as ionic chain carriers. This behaviour
is characteristic for promoters.

Indirectly, this result suggests that the Co(Na)A samples are
free of any Brönsted acidity. Förster and co-workers came to a similar
conclusion from their investigation of the i.r. spectra of CoNaA
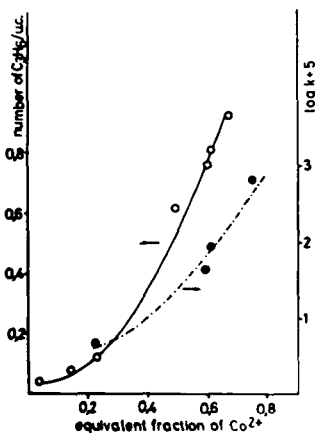zeolites in the OH region [19].



Fig. 5. Comparison of the adsorption and kinetic data

On the basis of what has been stated about the correlation found
between specific activity (expressed as the first-order rate constant
of the surface reaction) and $Co^{2+}$ content (see Fig. 5), it seems very
probable that, starting from NaA, with adsorption practically nil for
cyclopropane, the sieving effect diminishes progressively with in-
creasing levels of exchange, permitting access to active sites in the
zeolite cavities. This point is stressed, for there are a few cases in
the literature where a similar trend was observed with Brönsted acid
sites as active centres, which necessitates another explanation [20].

REFERENCES

1. Habgood, H.W., George, Z.M., Molecular Sieves, Soc. Chem. Ind. London, 1968. p. 130.

2. Bassett, D.W., Habgood, H.W., J. Phys. Chem. 64, 769 (1960).

3. George, Z.M., Habgood, H.W., J. Phys. Chem. 72, 1689 (1968), 74, 1502 (1970).

4. Hightower, J.W., Hall, W.K., J. Am. Chem. Soc. 90, 851 (1968), J. Phys. Chem. 72, 4555 (1968).

5. Hall, W.K., Larson, J.G., Gerberich, H.R., J. Am. Chem. Soc. 85, 3711 (1963), 87, 1880 (1965).

6. Kiricsi, I., Hannus, I., Varga, K., Fejes, P., J. Catal. 63, 501 (1980).

7. Tam, N.T., Cooney, R.P., Curthoys, G., J. Catal. 44, 81 (1976).

8. Õrhalmi, O., Fejes, P., Symp. on Mech. of Hydrocarbon Reactions, 1973 Siófok, Hungary, Akadémiai Kiadó, 1973., p. 475.

9. Förster, H., Seebode, J., Zeolites 3, 63 (1983).

10. Fejes, P., Förster, H., Kiricsi, I., Seebode, J., Varga K., Zeolites, to be published

11. Seebode, J., Diplomarbeit Universität Hamburg, 1981.

12. Fejes, P., Hannus, I., Kiricsi, I., Varga, K., Acta Phys. Chem. Szeged 24, 119 (1978).

13. Schirmer, W., Meinert, G., Grossmann, A., Monatsberichte 11, 886 (1969).

14. Klier, K., Kellerman, R., Hutta, P.J., J. Chem. Phys. 61, 4224 (1974).

15. Masahiro Nitta, Shigemi Matsumoto, Kazuo Aomura, J. Chem. Soc. Chem. Comm. 1974, p. 552.

16. Breck, D.W., Eversole, W.G., Milton, R.M., Reed, T.B., Thomas, T.L., J. Am. Chem. Soc. 78, 5963 (1956)

17. Schöllner, R., Ulber, G., Platzdasch, K., Chem. Techn. 34, 583 648 (1982)

18. Fejes, P., Förster, H., Kiricsi, I., Seebode J., Zeolites 4, 259 (1984)

19. Förster, H., Seelemann, R., J. Chem. Soc. Faraday I., 77, 1359 (1981)

20. Jacobs, P.A., "Carboniogenic Activity of Zeolites". Elsevier, Amsterdam, 1977, p. 128.