

# 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  $\pi$  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 $\alpha$ , where spontaneous isomerization occurs, and zeolite NaA, which is inactive, isomerization is induced by addition of SO<sub>2</sub>. Fitting the reaction data by first order laws with respect to *n*-butene and SO<sub>2</sub> 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 $\alpha$ .

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 NaZn<sub>11</sub>A. Zeolite  $\alpha$  (Si/Al=2.47) synthesized by KACIREK [3] was ion exchanged with Ca<sup>2+</sup> 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 Brønsted acid sites are observed except on zeolite Ca $\alpha$ . 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  $1200\text{ cm}^{-1}$  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 <sup>-1</sup> ]	Cis-but-2-ene [cm <sup>-1</sup> ]	Trans-but-2-ene [cm <sup>-1</sup> ]
Na <sup>+</sup>	15.16	-10	-15	-17
Li <sup>+</sup>	24.00	-16	-18	-17
Ca <sup>2+</sup>	29.09	-25	-25	-32
Mg <sup>2+</sup>	44.36	-28	-33	-47
Ag <sup>+</sup>	11.44	-50		
Zn <sup>n+</sup>	38.97	-40	-48	-54

Because of cluster formation the real charge of Zn<sup>n+</sup> 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 $\alpha$ , 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 <  $10\text{ cm}^{-1}$  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  $\pi$  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  $\pi$ -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  $\pi$ -sp donor bonds with additional back-donation into  $\pi^*$  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 Ca $\alpha$ . 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.

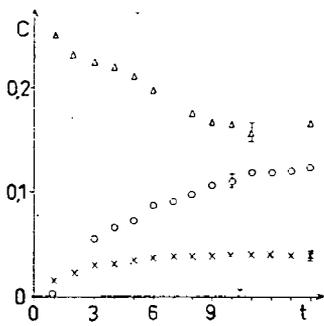


Fig. 1. Isomerization of *trans*-but-2-ene on CaA, composition of reaction mixture, C in arb. un., t in min.  $\Delta$  *trans*-but-2-ene;  $\circ$  *cis*-but-2-ene;  $\times$  but-1-ene.

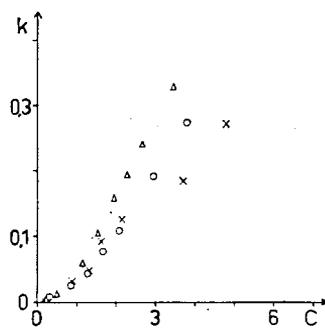


Fig. 2. Isomerization of but-1-ene on CaA, ZnA, MgA rate constant  $k$  ( $\text{sec}^{-1} \cdot \text{g}^{-1}$ ) versus  $\text{SO}_2$  concentration ( $10^{-3}$  Mol/g).  $\times$  CaA;  $\circ$  ZnA;  $\Delta$  MgA.

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 Ca $\alpha$ , 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  $\text{SO}_2$  the reac-

tion data fit a reversible first order equation (1)

$$\ln(x - x_e) = \ln(x_0 - x_e) - kx_0 t / (x_0 - x_e) \quad (1)$$

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 SO<sub>2</sub> content, except the small initial range. Upon coadsorption different SO<sub>2</sub> 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-SO<sub>2</sub>-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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