

EXAMINATION OF THE MOBILITY OF MONOVALENT CATIONS IN A-, X- AND Y-ZEOLITES

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The arrangement and mobility of Li^+ -ions in dehydrated cation modified A-, X- and Y-zeolites were studied by NMR-line-width measurements. We determined the relative values of mobility of blocked up Na^+ -cations in dehydrated cation modified A-zeolites by means of an irreversible GC method.

Many publications appeared in the last few years on the determination of the structure of cation exchanged A-, X- and Y-zeolites. TUNG [1] has shown, that also the mobility of cations has an important influence on the catalytic and adsorptive properties of zeolites. A great variety of research methods (e.g. IR-spectroscopy, X-ray techniques, electrical conductivity measurements, sorption investigations, calorimetric measurements, NMR-method etc.) has been used for the determination of the arrangement of cations and their mobility in zeolites. In this work we give some information about our ^7Li -NMR measurements on cation modified X- and Y-zeolites and results about the mobility of monovalent cations on NaMeA-zeolites by means of the gaschromatographic method of irreversible adsorption of substance pulse [2].

Mobility of Li^+ -ions

Experimental and Discussion

The ion exchange was carried out by means of the chloride solutions. We used NaA, NaX ($\text{Si}/\text{Al}=1.35$) and NaY ($\text{Si}/\text{Al}=2.6$) without binder. The degree of ion exchange was determined by chemical analysis. The zeolites were activated at 673 K for 20 hrs in vacuum (pressure about 0.0133 Pa). ^7Li -NMR-spectra were measured using a wide-line-spectrometer KRB 35/62 at 21 MHz. The line width δH_p of the peak to peak distance of the NMR-signal was (1.8 ± 0.1) G at room temperature. We can't observe a small component analogue LECHERT [3], VUČELIĆ [4] at these degrees of exchange. The second moment of all samples was (0.73 ± 0.07) G^2 at room temperature. The frequencies from 21 to 9 MHz have no influence on the second moment as shown in [5].

That means, that the quadrupolar interaction is negligible. For determining the activation energy E_A and the correlation time τ_c of thermal motion we measured the temperature dependence of the line width. The results are shown in Table I.

Table I.
Correlation time τ_c and activation energy E_A

Unit cell composition	Activation energy (kJ/mol)	Correlation times at 473 K (μ s)
$\text{Na}_{8,2}\text{Li}_{3,8}\text{A}$	30	110
Li_{12}A	30	110
$\text{Na}_{3,1}\text{Li}_{9,1}\text{Ca}_{0,4}\text{A}$	58	490
$\text{Na}_{5,4}\text{Li}_{5,6}\text{Mg}_{0,5}\text{A}$	58	460
$\text{Na}_{5,4}\text{Li}_{5,6}\text{Sr}_{0,5}\text{A}$	54	330
$\text{Na}_{4,4}\text{Li}_{5,2}\text{Ag}_{2,4}\text{A}$	34	180
$\text{Na}_{4,2}\text{Li}_{5,4}\text{Tl}_{2,4}\text{A}$	46	200
$\text{Na}_{3,8}\text{Li}_{5,3}\text{K}_{2,7}\text{A}$	44	200
$\text{Na}_{4,0}\text{Li}_{5,3}(\text{NH}_4)_{2,7}\text{A}$	45	200
$\text{Na}_{28,6}\text{Li}_{53,4}\text{X}$	13	120
$\text{Na}_{36,6}\text{Li}_{45,4}\text{X}$	13	120
$\text{Na}_{24,9}\text{Li}_{28,1}\text{Y}$	15	145
$\text{Na}_{30,4}\text{Li}_{45,5}\text{Ca}_{3,3}\text{X}$	19	160
$\text{Na}_{30,4}\text{Li}_{45,5}\text{Zn}_{3,3}\text{X}$	20	165

The second moment for ^7Li -NMR spectra in NaLiA-, NaLiX- and NaLiY-zeolites is the same. With the equation of VAN VLECK [6] we can calculate a mean Li-Al-distance of (2.35 ± 0.03) Å. If we set the Li-ions on SI- or SII-positions in X- and Y-zeolites we get a Li-Al-distance of $\text{Li}_\text{I}\text{-Al}=3.57$ Å and $\text{Li}_\text{II}\text{-Al}=3.1$ Å. The position SI should not be occupied by Li-ions [7]. In earlier works [8] we proposed, that all Li-ions are more displaced in the direction of the Al-ion. We assume the same arrangement in the case of X- and Y-zeolites.

The correlation times of Li-ions in A-zeolites are nearly the same as in X- and Y-zeolites, as shown in Table I. The activation energy is in the case of A-zeolite (30 ± 3) kJ/Mol and X- and Y-zeolites (13 ± 3) kJ/Mol. We have shown [8] that the magnetic correlation time of the Li-ions can be set equal the mean life time on a cation position. Consequently the Li-ions must make in all zeolites an isotropic diffusion process in the large cavity.

Different monovalent cations in A-zeolite reduce slightly the motion of the Li-ions; the activation energy decreases.

The activation energy of the mobility of protons [9] in NaHA has been reported to be 42 kJ/Mol and that of the Tl-ions in TIA [10] to be 38 kJ/Mol. These values are nearly in agreement with those of Li-motion in NaLiHA and NaLiTIA. Thus the less mobile cations cause a smaller mobility of the Li-ions. Divalent cations already reduce the mobility of Li-ions in the A-zeolite at lower M^{2+} -degrees of exchange as can be seen from Table I. The position of the Li-ions is not changed by the divalent cations. An exact determination of E_A and τ_c for M^{2+} -content larger than 8% is not possible yet. In contrast to the A-zeolite we find at the X- and Y-zeolite no influence of divalent cations on the Li-ion mobility at these degrees of cation exchange. We

attribute this fact to the positions of divalent cations. ANGELL [11] has shown that these divalent cations occupy firstly the positions inside the hexagonal prism. The field of the cations is screened in this position. Consequently they have no influence on the mobility of Li-ions in the large cavity.

Mobility of Na⁺-ions

Experimental and discussions

Although in 4A-zeolites all windows between the supercages are blocked up by Na⁺-cations (Na(2)) still *trans*-butene-2 from all butene isomers can diffuse into the micropores. Therefore *trans*-butene-2 is a good tracer molecule for our examinations. Its rate of diffusion is dependent on the mobility of Na(2)-ions. In a column filled with zeolite we gave by a constant rate of H₂-stream a pulse series of *trans*-butene-2. Through comparison of the peak height or peak area of the input and output signals of the pulse series we obtained informations about the amount of adsorbed molecules per pulse diffusing into the micropores dependent on the load with *trans*-butene-2 [2]. The peak heights after 15 pulses on Na₁₁Me₁⁺A-zeolites are shown in

Table II

Peak heights (ph) of 4A-zeolites after 15 pulses
(70 ml/h H₂-stream, experimental conditions see Fig. 1)

Composition inert material	ph (cm) 25.0	Composition NaA	ph (cm) 0
Na ₁₁ K ₁ A	22.1	Na ₁₀ K ₂ A	23.0
Na ₁₁ Rb ₁ A	23.0	Na ₁₁ Cs ₁ A	22.0
Na ₁₁ Ag ₁ A	15.5	Na ₁₁ Tl ₁ A	14.5
Na ₁₁ Li ₁ A	15.0	Na ₈ Li ₄ A	16.0
Na _{5.5} Li _{4.5} Mg ₁ A	17.0	Na _{2.5} Li _{7.5} Ca ₁ A	15.0
Na ₁₀ Mg ₁ A	0	Na ₁₀ Ca ₁ A	9.0

Table II. The behaviour of *trans*-butene-2 diffusion changes depending on the mobility of exchanged monovalent cation and its position. The exchange of only one K⁺-, Rb⁺- and Cs⁺-ion per supercage nearly completely stops the diffusion of *trans*-butene-2. The exchanged monovalent cation occupy position type II [12] and the peak heights show that only one cation checks the mobility of all blocked up cations. This special behaviour is called ensemble effect by reason of a complex concerted way of motion of the cations. We explain the diffusion of *trans*-butene-2 through the windows as follows.

An adsorbed *trans*-butene-2 molecule mainly jumps from cation to cation and in NaA-zeolites especially from delocalized cation to another one. Independent of the movements of adsorbed molecules the delocalized cations have their own mechanism of motion within a supercage and also an oscillatory motion between the equivalent positions on each side of the eight membered oxygen rings. Only at the moment when a blocked up cation jumps from position type II to another position can jump

trans-butene-2 from one side to the other side of the eight membered oxygen ring to the new blocked up cation on that side. In the moment, when a change of blocked up cations takes place at a window only *trans*-butene-2 and no other butene isomer overcomes the barrier, because only the complex *trans*-butene-2/ Na^+ has the same equivalent position of each side of the eight membered oxygen ring. The higher the mobility of blocked up cations, the more often the change of cations, the higher the possibility of jumps of *trans*-butene-2 through the windows, the higher the rate of *trans*-butene-2 diffusion into micropores of zeolites.

The exchange of one Ag-, Tl- or Li-ion also brings a decrease of *trans*-butene-2 diffusion. The checking influence of this cations is smaller, caused by other cation positions. The first Ag- and Tl-ions mainly occupy positions of type III and Li^+ has its own position [13]. In each case no significant dependence of the mobility on the degree of exchange of slower cations has been found.

As has been shown by RUTHVEN [14] the exchange of one divalent cation per supercage is followed by the removal of one Na(1) and one Na(3)-cation, but all there blocked up Na(2)-cations remain at place. By each further exchange of divalent cations the blocked up Na(2)-cations disappear one by one and in $\text{Na}_4\text{Me}_4^{2+}$ -A-zeolites all windows are free of Na-ions. These cation distribution explains the role of divalent cations by opening of windows but not the special dependence on the kind of divalent cation. By exchange of one divalent cation per supercage the mobility of blocked up Na-cations decreased or increased depending on kind of cation [15]. The behaviour of *trans*-butene-2 in such zeolites is shown in Fig. 1. The higher the

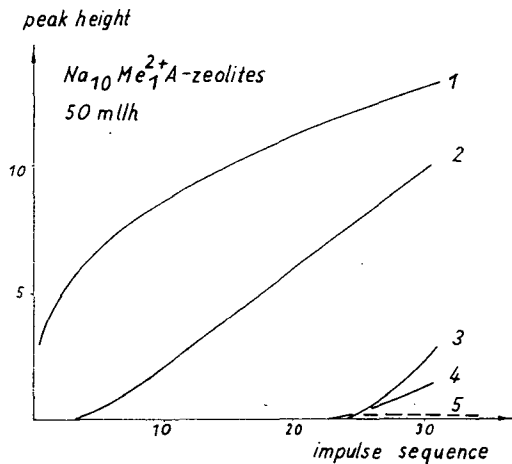


Fig. 1. Peak heights of $\text{Na}_{10}\text{Me}_{12}^+$ A-zeolites in dependence on the impulse sequence. Zeolites: 1 $\text{Na}_{10}\text{Sr}_1\text{A}$; 2 $\text{Na}_{10}\text{Ca}_1\text{A}$; 3 Na_{12}A ; 4 $\text{Na}_{10}\text{Zn}_1\text{A}$; 5 $\text{Na}_{10}\text{Mg}_1\text{A}$. Experimental conditions: length of column 20 cm; diameter of column 0.3 cm; height of filling 14.6 cm; temperature of column 293 K; carrier gas velocity 50 ml/h; initial pressure $5.05 \cdot 10^4$ Pa; grain size 0.2, —0.25 μm ; impulse sequence 1 min; press power $8.1 \cdot 10^7$ Pa.

rate of *trans*-butene-2 diffusion in dependence on load, the steeper are the curves. At constant experimental conditions we found for $\text{Na}_{10}\text{Me}_2^+\text{A}$ -zeolites independently of the rate of H_2 -stream the following sequence in the rate of *trans*-butene-2 diffusion:



The different course of curves is caused by two effects:

1. The divalent cations influencing the mobility of blocked up Na-cations in dependence on their locations and their electric field.
2. Each divalent cation has a different interaction with *trans*-butene-2 in dependence on its location and ionic radius.

The smaller the interaction of *trans*-butene-2 with the divalent cation, the higher the adsorption of *trans*-butene-2 at the Na(2) cations, the higher the obstruction for following diffusing *trans*-butene-2 molecules. The Na(3) ion has the highest interaction with *trans*-butene-2. Therefore the obstruction for diffusion of *trans*-butene-2 begins later (in the case of Fig. 1 after 25 pulses or 1.02 molecules per supercage). In the first part of this report it has been shown that one divalent cation in a 4 A-zeolite has a very high influence on the Li-ion mobility. How are the properties in $\text{NaLiMe}^{2+}\text{A}$ -zeolites in relation to the mobility of blocked up Na(2) cations (see Table II)? There is no significant influence on the mobility of Na(2) cations when one divalent cation is present, because the Li-ions exert the main influence on the mobility of blocked up Na^+ -cation.

Conclusions

The most mobile monovalent cations are Na(2) Na(3) in A- and Na^+ at site III in X-zeolites. Other exchanged monovalent cations in delocalized positions are checking the mobility of Na-cations. The checking of mobility by uniform positions is independent of the number of slower cations. The slowest cation forces the checking of mobility of all other monovalent delocalized cations.

The Li-cation has its own position without a difference between localized and delocalized positions, the correlation time of Li^+ is independent of the number of exchanged Li-ions, and of Si/Al-ratio.

Divalent cations in 4 A-zeolites influence the mobility of delocalized monovalent cations by means of their electric fields and as centre of adsorption in dependence on their positions. Divalent or monovalent cations in X- or Y-zeolites in localized position in the hexagonal prism have no influence on the mobility of Li-cations. The Li-ion can serve as a tracer cation to determine the localized positions of cations in X- and Y-zeolites.

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