NMR-STUDIES OF THE MOBILITY OF AROMATICS IN FAUJASITES

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The inter- and intramolecular part of the second moment of the proton resonance of C_6H_6 in NaX at about 100 K show four molecules above the S_2-sites rotating around their hexagonal axis. Other possible sites seem to be the windows between the large cavities. With increasing temperature tipping motions can be shown between these sites by relaxation measurements. Above 300 K translation is the predominating mobility mechanism, the characteristic parameters of which are drawn from T_1-measurements on C_6H_6, C_6H_5F and C_4H_4S in NaX and NaY. For cavities with almost no ions in the zeolites LaY, HY and "Ultrastable"-Y for benzene two regions with different mobility can be observed, the relative amount of which and the exchange rate of the molecules between them depend on temperature and the zeolite type.

Informations on the mechanism of molecular mobility in zeolite pores are important for an explanation of the catalytic properties of these substances. We have studied the mobility of benzene and related aromatics with NMR-methods in a variety of faujasites with low paramagnetic impurity between 77 and 450 K.

In NMR theory, the mobility is described usually in terms of correlation time τ_c, which can be regarded as the inverse of the jump frequency. τ_c is directly related to the nuclear relaxation times T_1 and T_2, where the exact relation depends on the special motional mechanism. The temperature function of T_1 shows a minimum for each kind of motion, T_2 usually decreases with decreasing temperature and becomes constant for molecules in fixed positions possibly, with a definite state of reorientation [1]. At the minima of T_1 holds $\tau_c \omega_L \approx 0.6$, from which τ_c can be obtained. ω_L is the frequency of the NMR-experiment. Further is there $T_1/T_2 = 1.6$ if motion of the molecules is isotropic with only one τ_c [2, 3]. Any deviation from this situation leads to an increase of this ratio. Usually τ_c is assumed to obey an Arrhennius law. The respective activation energy can be obtained by a measurement of the T_1-minimum for different ω_L. For molecules in fixed positions, the second moment M_2 of a wideline spectrum will give valuable information of the adsorbed phase. For nuclear dipole-dipole interaction and molecules undergoing rotational reorientations, M_2 obeys a relation [4].

$$M_2 = \sum_i K_i (3 \cos^2 \theta - 1)^2 (3 \cos^2 \gamma_i - 1)^2 r_i^{-6} \tag{1}$$

where the K_i contains the magnetic moments of the interacting nuclei, r_i is their distance and γ_i the angle of the internuclear vector and the axis of the rotation. θ is the angle of this axis with the applied magnetic field. For powders, the term containing

θ must be averaged over all possible θ. The K_i of the ^1H—^1D interaction is much less than that of the ^1H—^1H interaction. Therefore, from a comparison of the M_2, measured on C_6H_6 and 1,3,5-$C_6H_3D_3$, the contributions of the protons in the same and in different molecules can be separated [5]. Measurements on samples with 4 and 5.2 molecules in a large cavity show below 150 K and intramolecular M_2 of 0.84 Gauss² which is exactly the value obtained from Eq. 1. for a benzene molecule rotating around its sixfold axis. For lower coverages the M_2 indicate additional freedoms of motion. The intermolecular M_2 for 4 molecules in a large cavity is 0.28 Gauss². It can be assumed, that the molecules lie flat on the walls above the S_2-sites [6]. To simulate the rotation, four circles with the diameter of a benzene molecule have been arranged in the described position. In steps of one degree, the distances, r_i of the points of one circle to all points of the other circles have been calculated as well as the angles γ_i of the vectors r_i with the axis of the first circles. These values have been inserted into Eq. 1 and averaged for different distances of the benzene molecules. The measured value of 0.28 Gauss² is explained best by a distance of 3.1 Å of the benzene from the S_2-ion, which is in good agreement with the value obtained by GESCHKE [6] from CNDO-calculations.

The intermolecular M_2 for 5.2 molecules in a cavity is 0.4 Gauss². Because of the strong dependence of M_2 on the r_i of the interacting nuclei, from the explanation of this value a sensitive check of the possible positions of this molecule can be expected. We have carried out calculations with the fifth molecule in the center of the large cavity and in the window between the two cavities perpendicular and parallel to the window plane. Only the position parallel to the window can explain the measured intermolecular M_2. The values for the other situations are two to five times too large. This result allows conclusions on the sorption mechanism.

The maximum sorption capacity, observed for benzene in NaX, lies at 5.2—5.4 molecules in a large cavity [7]. The limit of our model is at 6 molecules. Further, the rather good mobility observed above 250 K, can be easily explained to take place via a tipping from the sites above the S_2-ions into the sites in the window or vice versa, or from an occupied S_2-site to an unoccupied one. The mobility at higher temperatures has been studied by relaxation measurements. The analysis of the temperature functions of T_1 for C_6H_6, 1,3,5-$C_6H_3D_3$ and mixtures of C_6H_6—C_6D_6 shows for about 4 molecules in a large cavity a distinct maximum of the intermolecular relaxation rate at about 200 K, which is in good agreement with the discussed tipping motions (Fig. 1). The behaviour for full loading is somewhat difficult to survey, but not in
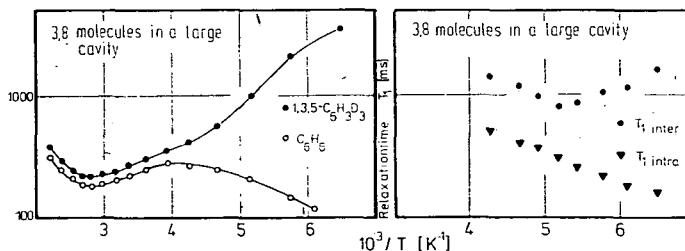

Fig. 1. Temperature behaviour of T_1 for samples with about four molecules benzene in a large cavity of NaX in different deuteration states, and separation of the inter- and the intramolecular contribution to T_1.

contradiction with the suggested model. A striking effect of these measurements is, that the T_1 of the protons does not depend on deuteration near and above the T_1-minimum. According to PFEIFER's [2] "relaxation analysis" scheme this means that the relaxation occurs via an interaction with the residual paramagnetic impurities of the zeolite, being about 5 ppm Fe^{3+}. Because of the large distances of these Fe^{3+} ions, translational diffusion must be the predominating mobility mechanism in this temperature region. From the average distance of the Fe^{3+} and the value of T_1 at 300 K an approximate self diffusion coefficient 10^{-8} cm² sec⁻¹ can be estimated. For a more exact analysis of the temperature function of T_1, the theory of TORREY [8] and KRÜGER [9] has been used, describing the dipolar relaxation caused by translational diffusion. In this theory, the relaxation times are given by rather complicated functions of τ_c, the concentration of the paramagnetic centers, the mean jump distance and the shortest possible distance of the molecule to the paramagnetic centers. Using the τ_c from the temperature function of T_1 and the activation energy of the motion, obtained from the T_1-minima at different ω_L, the measured temperature behaviour of T_1 has been fitted, varying the mentioned parameters of the theory. The results for . NaX are summarized in the Table I. The self diffusion coefficient D, included in this

Table I

Parameters of the Translation-Relaxation-Model for Benzene in NaX-Zeolite

Coverage Molecules /Cavity	Temp. in K	D in cm²/s		$\sqrt{\langle r^2 \rangle}$ in Å	E_{act}		Temp. of T_{1min} for 60 Mc
		direct	Model		kJ/mol		
					direct	Model	
5.3	374	$1.4 \cdot 10^{-7}$	$8.8 \cdot 10^{-8}$	4.9	—	35	391
3.7	374	$1.8 \cdot 10^{-7}$	$1.1 \cdot 10^{-7}$	4.4	16	14	382
	364	$1.6 \cdot 10^{-7}$	$1.1 \cdot 10^{-7}$				
	354	$1.3 \cdot 10^{-7}$	$1.0 \cdot 10^{-7}$				

D Self-Diffusion-Coefficient.
$\sqrt{\langle r^2 \rangle}$ Mean Jump Distance.
E_{act} Activation Energy.

table, has been obtained from the jump distance and the correlation time by the Einstein relation. Additionally it has been measured directly on especially synthesized large crystals using the method of TANNER and STEIJSKAL [10], as shown in the Table I. The agreement between these values of D and those obtained from the fit of the temperature function of T_1 is fairly good.

For benzene in NaY, the minima of T_1 lie at temperatures, where the benzene desorbs already from the sample. A fit of the described kind is, therefore, not possible. An estimation shows, that the mobility is distinctly restricted compared with NaX, which has been observed already in earlier studies [11, 12].

The respective values for thiophene and fluorobenzene are summarized in Table II. Both adsorbates show an increased mobility, which is best demonstrated by the lower temperatures of the T_1-minima. The self diffusion coefficient usually increases with decreasing coverage. For C_6H_6 and C_6H_5F the activation energy from full to

Table II

Parameters of the Translation-Relaxation Model for
C_6H_5F *and* C_4H_4S *on* NaX *and* NaY

Sample	Coverage Molecules /Cavity	D for 320 K cm²/s	$\sqrt{\langle r^2 \rangle}$ in Å	E_{act} kJ/mol	Temp. of T_{1min} for 60 Mc
C_6H_5F	4.2	$2.2 \cdot 10^{-8}$	2.7	34	336
in NaX	3.0	$9.5 \cdot 10^{-8}$	3.5	20	309
	1.2	$3.5 \cdot 10^{-7}$	3.6	27	279
C_6H_5F	4.6	$1.8 \cdot 10^{-8}$	2.9	24	369
in NaY	3.2	$5.8 \cdot 10^{-8}$	3.7	13	345
	1.3	$1.7 \cdot 10^{-7}$	3.8	30	303
C_4H_4S	5.1	$5.2 \cdot 10^{-8}$	2.9	12	323
in NaX	3.5	$9.8 \cdot 10^{-8}$	3.3	13	296
	2.0	$1.7 \cdot 10^{-7}$	3.5	17	286
	1.0	$1.6 \cdot 10^{-7}$	3.8	16	294
C_4H_2S	5.3	no T_1-minimum			
in NaY	3.7	no T_1-minimum			
	2.0	$1.1 \cdot 10^{-7}$	4.2	14	323
	1.2	$1.3 \cdot 10^{-7}$	4.2	17	313

D Self diffusion-Coefficient.
$\sqrt{\langle r^2 \rangle}$ Mean Jump Distance.
E_{act} Activation Energy.

half coverage decreases, whereas the activation energy for C_4H_4S remains rather constant over the observed range of coverages. It can be concluded that the small dipole moment of C_6H_5F and C_4H_4S leads to a partial orientation of the molecules in the strong fields of the S_2-ions which disturbs the strong interaction of the π-electrons with these ions as it is observed for the benzene molecules.

To study the influence of the S_2-ions samples of LaY, HY and "Ultrastable"-Y have been prepared. The temperature functions of T_1 and T_2 of these samples have been summarized in the Figure 2. The distributions of correlation times are considerably broadened compared with the NaX and NaY. In LaY, two regions of different T_2 are observed, the relative amounts of which vary almost over the whole range of temperatures. T_1 shows only one component. Here from an average life time of the molecules in the state with the lower mobility of 10 ms can be estimated for 300 K. HY shows two regions in T_1 and T_2 indicating rather low exchange rate between the two states of a strong bonding of the fixed molecules. The "Ultrastable"-Y shows the rare case of a T_2 minimum, indicating the presence of a small region with a short correlation-time and a variety of states with long τ_c which are in a rapid molecular exchange. Summarizing, the removal of the cations result in an increased mobility of the regions with good mobility which can be seen from the decreased temperatures of the T_1-minima compared with NaY. In all three types sorption sites with varying strength and ability to exchange molecules with the more mobile phase can be observed, which seem to be characteristic for the type of the modified zeolite. The nature of these sites may be best characterized by definite lattice defects created by the sample preparation.
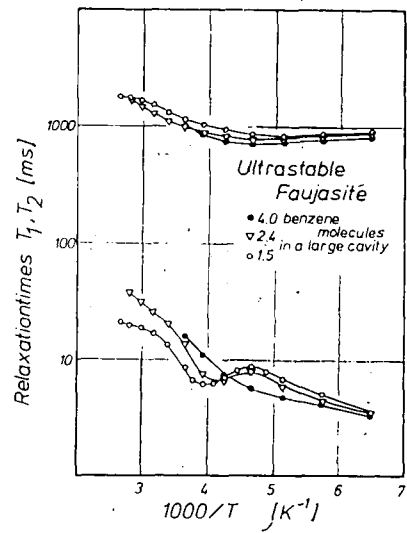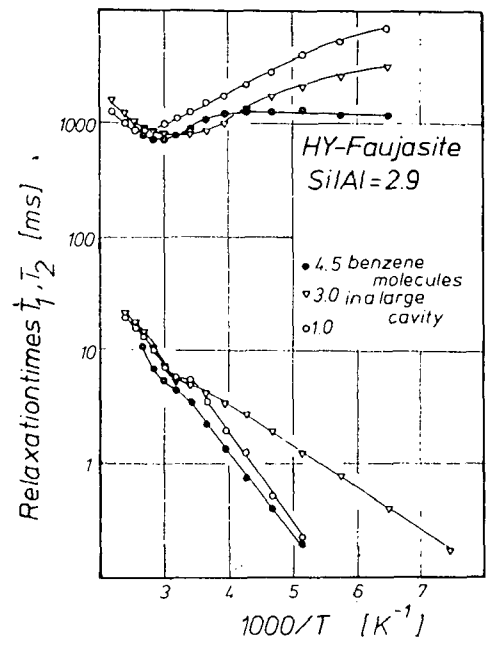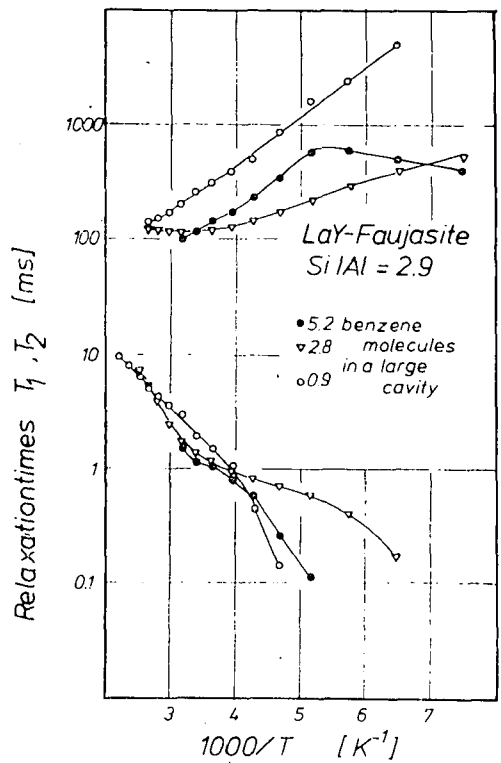
Fig. 2. Temperature behaviour of the relaxation times T_1 and T_2 for benzene in LaY, HY and "Ultrastable"-Y.

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