Influence of Molecular Shape on Probing Mass Transfer Resistances on Zeolites

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Mass transfer resistances in zeolite NaCaA after different hydrothermal pretreatment are probed by NMR tracer desorption studies with the short-chain-length hydrocarbons from methane to *n*-butane and with xenon. In all cases, the measurements lead to the coinciding result of forming surface barriers, which differ only slightly depending on the pretreatment modes, but lead to a retardation of molecular mass transfer more dramatically than the starting material. The dramatic retardation of mass transfer after hydrothermal pretreatment is confirmed by supplementary uptake measurements with *n*-decane.

Introduction

In contrast to conventional pulsed field gradient measurements (Pfeifer, 1976), the introduction of the nuclear magnetic resonance (NMR) tracer desorption technique (Kärger, 1982) has led to the direct observation and quantification of mass transfer resistances on the external surfaces of micoporous adsorbent particles. Applying methane as a probe molecule, the origin of the deterioration of granulated zeolite NaCaA under the conditions of industrial use could be attributed to the formation of such "surface barriers" (Kärger et al., 1988). Though it was produced by structural changes in or on the outer surface of the crystallites, the strength of the surface barrier is clearly also a function of the probe molecule under study. Due to a number of its advantages, in most previous NMR tracer desorption studies methane has been applied as a probe molecule (Kärger and Pfeifer, 1987).

It is the aim of this paper to probe the transport properties of a series of adsorbate molecules in NaCaA-type zeolites. In order to test the sensitivity of the molecules with respect to the formation of surface resistances, a set of specimens with surface barriers of different strength was produced by subjecting the starting material to various steaming sequences. It turns out that the information provided by applying methane as a probe molecule does, in fact, coincide with the results of NMR tracer desorption studies with hydrocarbons of larger chain lengths (ethane to butane), as well as with xenon. In addition, the observed sequence of transport resistances could even be reproduced with *n*-decane in uptake studies. One has to conclude, therefore, that the information on mass transfer in zeolite NaCaA as provided by NMR tracer desorption studies with methane is, in fact, typical of the whole series of *n*-paraffins. Thus, methane self-diffusion studies may serve as a valuable tool for characterizing and optimizing NaCaA-type zeolites in the field of paraffin extraction, for which they are mainly used (Seidel et al., 1979; Ruthven, 1984).

Experimental Studies

We have used a NaCaA zeolite powder with a calcium content of 67%, provided by the VEB Chemiekombinat Bitterfeld. The mean crystallite radius is 1 μm. For generating the surface barriers, the starting material (sample 0) was subjected to the following sequences of hydrothermal treatment:

Sample 1.1. The hydrated zeolite powder with a bed height of about 2 to 3 mm is introduced into an oven at the temperature of 600°C and is kept there for a period of 4 hours.

Sample 1.2. It is treated like sample 1.1 and then steamed at 180°C for 8 hours.

Sample 2.1. The same treatment as sample 1.1 is offered, but with a bed height of more than 20 mm instead 2 to 3 mm.

Sample 2.2. It is treated the same as for sample 2.1 and then steamed at 180°C for 8 hours.

In none of the above cases, the pretreatment has led to a change in the particle size distribution. For the NMR experiments, the zeolite samples were heated under continuous pumping, at a heating rate of 10 K/h to a final temperature of 400°C and then kept there for about 8 hours. In this way, previously adsorbed molecules have been removed from the intracrystalline pore system. Then the desired amount of a probe molecule was introduced into the samples by freezing them from a well-defined volume in a liquid-nitrogen bath. Finally, the loaded zeolite material was transferred into the NMR sample tubes which subsequently were sealed under flame.

Nuclear magnetic resonance spectroscopy with pulsed field gradients (PFG NMR) (Kärger and Pfeifer, 1987) allows the measurement of mean displacements of the adsorbed molecules within the sample tube over an observation time t of some milliseconds. In this way, it is possible to determine both the intracrystalline self-diffusivity D of the adsorbed molecule and their intracrystalline mean life time τ_{intra} (Kärger et al., 1988). Combining these two quantities yields direct information about the existence of surface barrier, since additional surface resistances in molecular mass transfer will affect only τ_{intra}, not D (Kärger, 1982).

The NMR self-diffusion and tracer desorption measurements have been carried out as previously described by monitoring the dependence of the NMR signal intensity (the "spin echo") on the applied magnetic field gradients (Kärger, 1982; Kärger and Pfeifer, 1987). The intensity of the field gradients was typically of the order of 5 T/m, the field gradient pulse lengths were varied between 0.1 and 2 ms, and the observation time (i.e., the separation between the two field gradient pulses) was varied between 1 and 200 ms. The short-chain-length paraffins, methane to butane, have been observed by means of ^{1}H NMR spectrometry using the home-built spectrometer FEGRIS (Fleischer et al., 1985) at a resonance frequency of 60 MHz.

The ^{129}Xe NMR diffusion measurements have been carried out with another home-built spectrometer UDRIS (Heink et al., 1989) at a resonance frequency of 24.9 MHz, corresponding to a proton resonance frequency of 90 MHz. The outer diameters of the NMR sample tubes were 8 and 10 mm, respectively. For both spectrometers, the filling height of the zeolite powder within the sample tubes was about 15 mm. For the ^{1}H NMR measurements, a probe head with a range of temperature control between −100°C and +200°C was used. The xenon self-diffusion measurements were carried out only at room temperature.

The mean error in the absolute values for the intracrystalline mean life times depends on the time interval over which the tracer desorption curve may be followed in the NMR experiments. It is typically of the order of 30%. Applying the same NMR pulse sequence to different samples, the uncertainty in the measurement of the intracrystalline mean life may be as low as 10%.

The *n*-decane uptake measurements were carried out using a home-built constant-volume, variable-pressure device with a pressure sensor head and a 170-6c-type electronics unit from MKS Instruments, Inc., Burlington, MA.

By using an ultra-high vacuum valve connecting the dosing volume and the sorption vessel, time delays caused by opening the valve could be reduced to less than 0.1 s. Since the response time of the Baratron capacitance monometer was in the ms range (better than 25 ms) and the dead time delay of the device is in the region up to 10^{-2} s, response curves of the adsorbate uptake with time constants of seconds could unambiguously be measured.

Data evaluation was based on the conventional model of diffusion-controlled uptake for a linear sorption isotherm and for negligible heat effects (Bülow et al., 1983). The linearity of the adsorption isotherm during the uptake could be guaranteed by using sufficiently small pressure steps (<0.1 Pa). Isothermicity could be proven to exist by applying Ruthven's criterion (Lee and Ruthven, 1979; Ruthven, 1983), as well as by realizing that for uptake measurements with the untreated samples (i.e., in the fastest uptake measurements where, if at all, nonisothermicity is most likely to occur) the diffusivities determined agreed satisfactorily with previous data, obtained with larger zeolite crystallites, where heat effects were definitely excluded (Ruthven, 1984; Bülow et al., 1984, 1986).

In the measurements, an amount of 10 mg zeolite was used, spread over an area of 15 cm^2. The samples were activated in an analogous way to that described in the NMR experiments. The final pressure before starting the adsorption sequences was less than 10^{-2} Pa. Because the mean error in the pressure measurements was less than 0.08%, the relative amount adsorbed during the final uptake process was determined with an uncertainty of less than 0.1%.

Results and Discussion

Probing with methane

It is well known (Breck, 1974) that NaCaA-type zeolites are unstable under hydrothermal conditions. By probing the properties of the hydrothermally deteriorated zeolite crystallites by NMR self-diffusion measurements with methane as a probe molecule, it has been found that lattice distortions are predominantly in the vicinity of the crystallite surface, since the desorption rates (i.e., $1/\tau_{\text{intra}}$), not the intracrystalline diffusivities, were dramatically reduced (Kärger et al., 1988). In this paper, we concentrated on the application of the NMR tracer desorption measurements for determining the intracrystalline mean life, since the general measurement of the intracrystalline diffusivities was prohibited due to the small sizes of crystallites (Kärger and Pfeifer, 1987). Table 1 shows intracrystalline mean life of methane in the various NaCaA samples, as determined by the NMR tracer desorption technique, for a sorbate concentration of six molecules per cavity at −80°C. The results obtained may be summarized as follows:

1. In all cases, the hydrothermally treated samples exhibit a more dramatic retardation in their tracer desorption rates than the starting material.
2. In contrast to this effect, the differences for the various modes of hydrothermal pretreatment are much smaller.
3. The strength of the surface barriers is (slightly) enhanced by an increase of the bed height during the thermal pretreatment (enhanced "self-steaming") and by subsequent steaming.

The formation of surface barriers under hydrothermal conditions may be explained by a deposition of nonframework aluminum species in the vicinity of the crystallite surface, as previously determined by means of X-ray photoelectron spectros-

Table 1. Intracrystalline Mean Life of Short-Chain Paraffins in NaCaA-Type Zeolite Crystallites after Hydrothermal Pretreatment

Probe Molec.	Conc./Molec. per Cavity	$\frac{T}{K}$	Sample Mode	$\frac{\tau_{intra}}{ms}$	$\frac{\tau_{intra}}{\tau_{intra}(0)}$
Methane	6	193	0	0.5 ± 0.2	1
			1.1	40 ± 10	80
			1.2	45 ± 10	90
			2.1	50 ± 15	100
			2.2	60 ± 20	120
Ethane	4	343	0	1 ± 0.3	1
			1.1	15 ± 5	15
			1.2	25 ± 8	25
			2.1	19 ± 6	19
			2.2	35 ± 10	35
Propane	3	483	0	28 ± 9	1
			1.1	360 ± 120	13
			1.2	400 ± 130	14
			2.1	380 ± 125	15
			2.2	600 ± 200	20
n-Butane	3	483	0	42 ± 6	1
			1.1	320 ± 110	8
			1.2	420 ± 140	10
			2.1	380 ± 130	9
			2.2	540 ± 180	13

copy (Kärger et al., 1987). Item 2 is evidently brought about by the fact that, under the given conditions, all pretreatments lead to a collapse of the zeolite framework in the vicinity of the crystallite surface, which is modified only slightly depending on the modes of pretreatment. It was the aim of this paper to evaluate the validity of the above results 1 to 3 by examining the situation with different probe molecules.

NMR tracer desorption with paraffins of varying chain lengths

For the application of the NMR tracer desorption technique, the long-range diffusivity, i.e., the mass transfer rate through the bed of zeolite crystallites needs to be larger than the intracrystalline diffusivity (Kärger, 1982). Since the activation energy of long-range self-diffusion is larger than that of intracrystalline diffusion, this condition in any case may be fulfilled for sufficiently high temperatures. On the other hand, definite values for the molecular intracrystalline mean life are attainable only if during the shortest observation time (≈ 1 ms) at least a certain fraction of the adsorbed molecules ($\gtrsim 25\%$) does not leave their crystallites. This, in turn, requires that the temperature cannot be chosen to be too high. Therefore, the measurement of all five samples necessitated the application of different measuring temperatures for the different probe molecules. Table 1 summarizes the chosen temperatures and the measured intracrystalline mean life for the paraffin homologues from methane to butane. Measurement with still larger *n*-paraffins would have required higher measuring temperatures, which were not attainable with the given spectrometer.

The above-mentioned statements 1 to 3 are confirmed by measurements with all probe molecules considered. Due to the small size of the crystallites, the conditions for measuring unrestricted intracrystalline self-diffusion improved with decreasing mobility. Thus, for *n*-butane, in addition to τ_{intra}, in the starting material (sample 0) and in sample 1.2, the coefficients of intracrystalline diffusion have been determined. The values obtained are presented in Figure 1 and compared with NMR self-diffusion data previously determined with larger zeolite crystallites for propane and *n*-butane (Kärger and Ruthven, 1981). It appears from Figure 1 that the butane data agree closely with the previous measurements, being about half an order of magnitude below the values of propane. It is remarkable that, as a result of the hydrothermal pretreatment, the intracrystalline mobility is reduced by not more than a factor of two, while the tracer desorption time is enhanced by one order of magnitude. This is just the situation encountered in the previous studies with methane (Kärger et al., 1988), and unambiguously indicates that reduction in the desorption rate can be explained only by the formation of surface barriers. Thus the surface distortion probed by the methane self-diffusion studies has likewise been found to lead to surface resistances for the mass transfer of the longer *n*-paraffins. Since the critical diameter of propane and butane is already that of the homologous series of the *n*-paraffins, there is little indication that with further increasing chain lengths this situation should change.

Uptake measurements with n-decane

To study the influence of the hydrothermal pretreatment on the transport properties of long-chain paraffins, we have followed the molecular uptake of *n*-decane. Characteristic uptake curves for the various zeolite specimens measured at a temperature of 350°C are presented in Figure 2. In agreement with the observations for short-chain paraffins, molecular uptake on the hydrothermally pretreated samples is retarded more significantly than on the starting material. In principle, the origin of this retardation may be determined based on an analysis of the

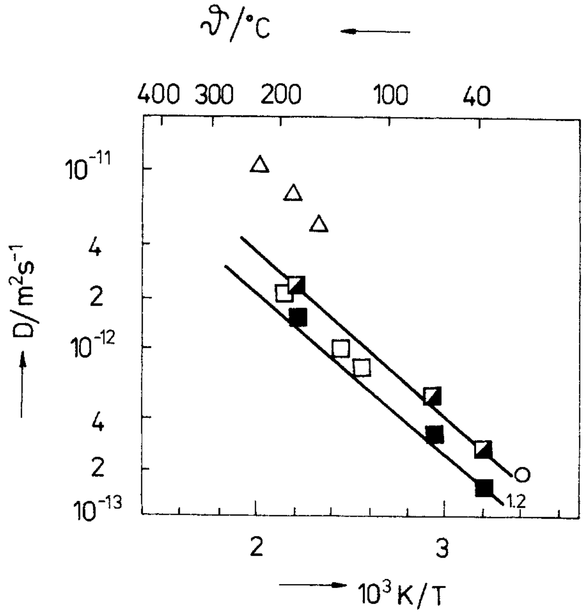

Figure 1. Self-diffusion coefficients of *n*-butane adsorbed on zeolite NaCaA.

Sample 0 (◪) and sample 1.2 (■) at a sorbate concentration of 3 molecules per cavity; compared with previous NMR self-diffusion measurements with *n*-butane (□) and propane (△) on NaCaA-type zeolites with large crystallites uptake curve shape (Ruthven, 1984; Bülow et al., 1984) since barrier-limited adsorption should lead to a sigmoidic shape of the γ vs. $\sqrt{t}$ plots.

In practice, however, such a discrimination is very insensitive since the shape of the uptake curve may be influenced by numerous additional influences such as the finite rates of adsorbate supply (Struve et al., 1983) and adsorption heat dissipation (Ruthven, 1984), or the particle size distribution. Thus, also in the present case no clear evidence of a sigmoidic shape is provided, and for a quantitative analysis it is sufficient to consider the uptake curves as if being controlled by intracrystalline diffusion with an apparent diffusivity D_d^{eff}.

As a measure of the adsorption rate, we have determined the first statistical moments (Kočiřík and Zikánová, 1972; Barrer, 1979)

$$M_1 = \int_{t=0}^{\infty} [1 - \gamma(t)]\, dt \tag{1}$$

of the uptake curves $\gamma(t)$. They may be transformed to the effective diffusivities D_d^{eff}, using the relation (Struve et al., 1983; Ruthven, 1984)

$$D_d^{\text{eff}} = \frac{R^2}{15M_1} = \frac{p_\infty - p_v}{p_a - p_v} \tag{2}$$

where the quantities R^2, p_v, p_a, and p_∞ denote the mean square crystallite radius and the adsorbate pressure in the gas phase before the pressure step, immediately after the pressure step and at final equilibrium, respectively.

In the case of diffusion-limited uptake, D_d^{eff} coincides with the coefficient of intracrystalline diffusion D_d. To compare with the molecular transport parameters determined under equilibrium conditions, the diffusion coefficients are generally represented in terms of the so-called corrected diffusivities D_o defined by the relation (Ruthven, 1984)

$$D_o = D_d \frac{d \ln c(p)}{d \ln p}, \tag{3}$$

where $c(p)$ denotes the sorbate concentration in equilibrium with a sorbate atmosphere of pressure p.

Table 2 summarizes the first statistical moments of the uptake curves and the corrected apparent diffusivities calculated using Eqs. 2 and 3 for the various NaCaA zeolite specimens. All measurements refer to a temperature of 350°C and a sorbate concentration of 0.3 molecules per cavity. It should be mentioned that over the whole concentration range covered in the uptake experiments ($0 < c \leq 0.35$ molecules per cavity), the corrected apparent diffusivity remains constant within an interval of about ±15%.

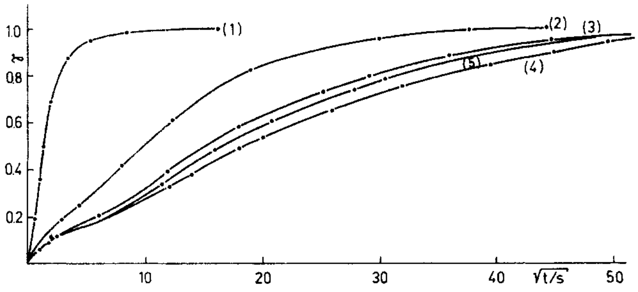

Figure 2. Typical uptake curves in the constant-volume variable-pressure experiments with *n*-decane.

At a sorbate concentration of 0.3 molecules per cavity on the various NaCaA specimens at a temperature of 350°C: curve (1) (sample 0); curve (2) (sample 1.1); curve (3) (sample 1.2); curve (4) (sample 2.1); and curve (5) (sample 2.2)

The corrected diffusivities for the starting material (sample 0, cf. curve 1 in Figure 2) are in satisfactory agreement with previous uptake studies of *n*-decane in zeolite NaCaA with larger crystallites (Bülow et al., 1980; Vavlitis et al., 1981). Hence, the value obtained surely is a correct measure of intracrystalline mobility, and surface barriers are not yet of any influence. In agreement with the finding of the NMR diffusion studies with the short-chain paraffins, in the hydrothermally pretreated zeolite samples molecular uptake is found to be significantly slowed down. This may unambiguously be referred to the formation of surface barriers. Consequently, the corrected apparent diffusivities obtained must be assumed to be determined by surface barriers rather than by the intracrystalline molecular mobility, so that the notation "apparent" is in fact justified. It is remarkable that, similar to the finding with the short-chain paraffins, the most dramatic difference is observed between the starting material and the treated specimens, while with the exception of sample 1.1 the relative differences between the individually treated samples are very small.

NMR tracer desorption with xenon

^{129}Xe NMR tracer desorption has been studied with the starting material and the samples 1.1 and 2.2, i.e., with those two specimens which showed the largest difference among the hydrothermally treated samples.

Figure 3 shows the experimental points of ^{129}Xe NMR tracer desorption determined at room temperature for the three selected samples. The corresponding numerical data are summarized in Table 3. Again, it appears that the difference in the desorption behavior of the two treated samples is much less than that of one of the samples and the starting material.

In a previous ^{129}Xe NMR tracer desorption study with laboratory-synthesized zeolites NaCaA (Kärger et al., 1989), significant transport resistances on the crystallite surface have also been observed in the as-synthesized samples, while with methane as a probe molecule surface barriers were not observable. This experimental finding was explained by the larger kinetic diameter of the xenon atoms (0.49 nm) (Stuart, 1967)

Table 2. First Statistical Moments and Corrected Apparent Diffusivities Calculated from Eqs. 2 and 3 for the Uptake of *n*-Decane*

Sample Mode	M_1 s	D_o^{app} $10^{-16}\,\text{m}^2\cdot\text{s}^{-1}$	$D_o^{\text{app}}(0) / D_o^{\text{app}}$
0	3.1	88.00	1
1.1	83.5	2.20	40
1.2	297.0	0.65	135
2.1	248.0	0.80	110
2.2	270.0	0.70	125

*By NaCaA specimens after different hydrothermal pretreatment at 35°C and a sorbate concentration of 0.3 molecules per cavity

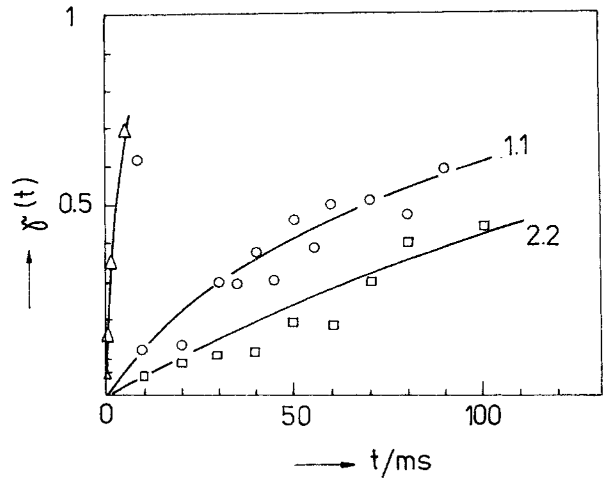

Figure 3. Experimental data for NMR tracer desorption of xenon in the NaCaA specimens.

0 (△), 1.1 (○), and 2.2 (□) at room temperature for a sorbate concentration of 3 atoms per cavity

compared with that of methane (0.42 nm) (Stuart 1967). One might have expected, therefore, that the slight differences between the desorption properties of the different treated samples for the paraffins should become more pronounced with xenon. The experiments show, however, that with xenon the surface barriers after hydrothermal pretreatment are also probed in a similar way to the short-chain hydrocarbons.

Comparing the data of Tables 1 and 3 one might be puzzled by the fact that apparently the larger molecules are not more affected by the steaming than the smaller molecules. However, one must be aware of the fact that as a consequence of the different activation energies (Kärger et al., 1986), the difference in the desorption rates will enhance with decreasing temperatures. As a necessary condition for the application of the NMR tracer desorption technique, the measuring temperature had to be raised with increasing molecular size.

Conclusion

The phenomenon of surface barriers is in fact typical for a certain group of adsorbate molecules. It seems most likely that a broader variety of probe molecules should yield more definite correlations between the nature of the probe molecules and the strength of the surface resistances, and thus contribute to a better understanding of the phenomenon of the surface barrier.

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Table 3. Intracrystalline Mean Life of Xenon in NaCaA-Type Zeolite Crystallites after Hydrothermal Pretreatment*

Sample Mode	τ_{intra} / ms	$\tau_{\text{intra}} / \tau_{\text{intra}}(0)$
0	7 ± 2	1
1.1	105 ± 30	15
2.2	210 ± 60	30

*For a sorbate concentration of 3 atoms per cavity at room temperature

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