NMR Study of Mass Transfer in Granulated Molecular Sieves

Nuclear magnetic resonance (NMR) tracer desorption technique in combination with the traditional pulsed field gradient technique is applied to measure directly intracrystalline and long-range molecular transport, as well as molecular exchange rates, between the individual crystallites in granulated molecular sieves. It is found that the granulation process leads to the formation of transport resistances on the external surface of the crystallites, which may be dramatically enhanced during their technical application. As an example, for granulated zeolite NaCaA the enhancement of such surface barriers under hydrothermal conditions and under the influence of a hydrocarbon atmosphere is studied. Since both intra- and intercrystalline transport are found to remain practically unaffected by this treatment, changes in the overall transport behavior are caused by the enhanced transport resistance on the external surface of the zeolite crystallites.

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Introduction

Adsorption and desorption dynamics of molecular sieve batches is characterized by the superposition of a variety of elementary processes that are ongoing in both the intra- and intercrystalline space and at the interface between them. Since the dynamic adsorption capacity is one of the most decisive quantities determining the efficiency of adsorption columns, the investigation of the individual steps of molecular transport has become a major goal of applied research in adsorption science and technology (Ruthven, 1984). It is only by the study of each of the constituent processes of molecular migration that macroscopically observed deterioration of the adsorption capacity may be attributed to the processes generating them during molecular sieve production and/or application. With the introduction of the nuclear magnetic resonance (NMR) tracer desorption technique (Kärger, 1982; Ruthven, 1984) in addition to the standard NMR techniques of measuring intracrystalline and intercrystalline coefficients of molecular diffusion (Kärger and Pfeifer, 1987), a direct observation of the molecular exchange rates between different crystallites has for the first time become possible. We have applied these NMR techniques to characterize the transport properties of commercially available molecular sieves NaCaA after different modes of pretreatment and application.

Comparing the assembly of zeolite NaCaA in its crystalline form with the granulated species, the process of granulation is found to slow down the long-range self-diffusion (i.e., the molecular transport over distances considerably exceeding the crystallite diameter) while the intracrystalline self-diffusion remains practically unaffected. Moreover, as a consequence of the granulation process the formation or enhancement of a transport resistance at the outer surface of the crystallites (a "surface barrier") is observed. Depending on the mode of industrial application (hydrothermal conditions, contact with hydrocarbons at elevated temperatures) the surface barrier may be dramatically enhanced, leading to a steep decrease in the dynamic adsorption capacity of the molecular sieve. Comparing the granulated form with a simply pressure-compacted molecular sieve, hydrothermal stability is found to be reduced by the granulation process. Changes in both the long-range and intracrystalline mobility of the investigated systems are negligibly small in comparison with the retardation effect imposed by the surface barriers.

In view of the numerous factors possibly influencing the dynamic adsorption capacity, the proposed method may serve as a valuable guide in the search for the critical steps in adsorption dynamics and hence for the elucidation of the mechanisms and conditions affecting them during molecular sieve production and application.

Method

The principles of the NMR technique for measuring the elementary processes of molecular migration in molecular sieves are presented in the literature (Kärger, 1982; Ruthven, 1984; Kärger and Pfeifer, 1987). It is sufficient therefore to recall the

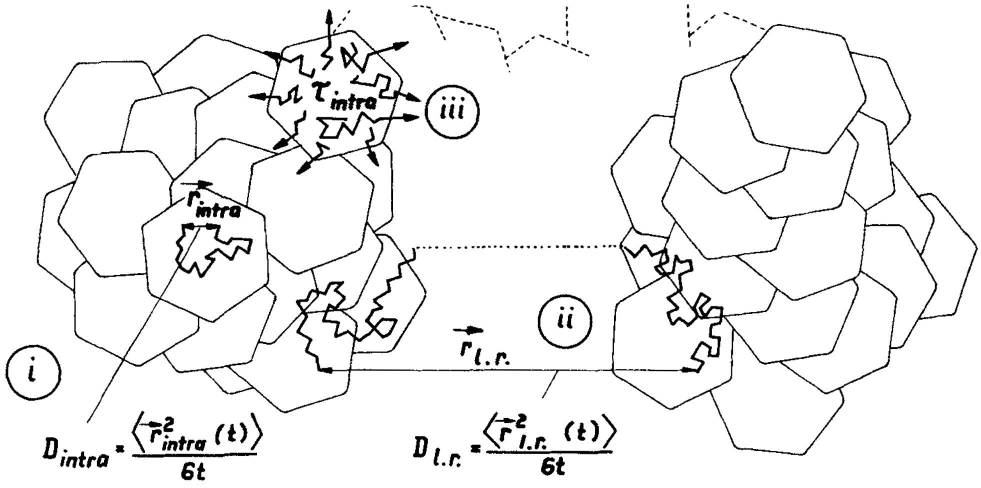

Figure 1. Elementary processes of molecular migration in molecular sieves and their determination by NMR.

main quantities accessible by this technique, shown schematically in Figure 1.

1. The coefficient of intracrystalline self-diffusion, *Dintra*, is a measure of intracrystalline molecular mobility, and may be introduced via Fick's first law

$$\vec{j}^* = -D \operatorname{grad} c^* \qquad (1)$$

relating the flux density $\vec{j}^*$ to the concentration gradient c^* of labeled molecules under the conditions of overall equilibrium, or by Einstein's formula

$$\langle r^2(t) \rangle = 6\,D\,t \qquad (2)$$

for the molecular mean square displacement during the observation time t.

2. The coefficient of long-range self-diffusion, D_{lr}, is a measure of the molecular transfer rate through an assemblage of zeolite crystallites. The relations by which D_{lr} may be introduced are formally identical with Eqs. 1 and 2. However, while for intracrystalline self-diffusion the space scale considered is much smaller than the diameter of the crystallites, and hence a significant interference between the crystallite boundary and the diffusing molecules is excluded, long-range self-diffusion is considered with respect to a space scale considerably exceeding the crystallite diameters, Figure 1.

3. The molecular mean lifetime, τ_{intra}, in the interior of the individual crystallites ("tracer desorption time").

Since for gas phase adsorption the molecular concentration in the intercrystalline space can be neglected in comparison with the intracrystalline concentration, τ_{intra} coincides with the mean time of molecular exchange between the individual crystallites. Under the assumptions that the crystallites can be approximated by spheres of radius R, and that molecular desorption is controlled only by intracrystalline diffusion, one has (Kärger, 1982; Bülow, 1985)

$$\tau_{intra} = \tau_{intra}^{diff} = R^2/15\,D_{intra} \qquad (3)$$

Any enhancement of τ_{intra} in comparison with τ_{intra}^{diff} directly indicates the existence of additional transport resistances at the outer surface of the individual crystallites.

The determination of τ_{intra} by the NMR tracer desorption technique implies the inequality $D_{intra} \ll D_{lr}$ (Kärger, 1982) which is clearly fulfilled in the present investigations; see Figures 2c and 2d.

Experimental Procedure

The NMR self-diffusion and tracer desorption experiments have been carried out by means of the NMR pulse spectrometer FEGRIS built in our laboratory (Kärger et al., 1987b). A detailed description of the experimental procedure is given by Kärger (1982). With commercial samples, the range of measurement may be considerably enhanced by applying a large constant field gradient in addition to the pulsed field gradients. It has been shown (Richter et al., 1986a) that in this case, by NMR tracer desorption technique a time constant τ'_{intra} is obtained which in the limit of small values coincides with the intracrystalline lifetime τ_{intra} (under the chosen experimental conditions practically for $\tau'_{intra} \leq 5$ ms), and which increases faster than only linearly with increasing values of τ_{intra}. Hence, apart from a simplification of the experimental procedure, differences in the kinetics of intercrystalline molecular exchange in different samples may more easily be determined.

We have studied granulated molecular sieves NaCaA purchased from VEB Chemiekombinat Bitterfeld (5A Z) and from Union Carbide Corporation (5A UCC), as well as a 5A zeolite crystallite powder that is used as the starting material for the granulated 5A Z. In both cases the mean crystallite diameters are of the order of 4 μm. These specimens were subjected to different treatments both in the laboratory and during their industrial application, as described below.

For the NMR measurements, the zeolite materials were heated to 637 K over a time interval of 4 h in open glass tubes of about 8 mm OD with a filling height of 15 mm. After evacuation to a pressure of about 10^{-2} Pa the samples were loaded via vacuum distillation with six molecules of methane per large cavity.

Coarse information about the deterioration of the zeolite material was obtained by conventional chromatographic and breakthrough measurements (Lederer and Lederer, 1957). In

Table 1. Influence of Compaction and Granulation on Molecular Transport of Methane in Zeolite NaCaA

NaCaA Form	D_{intra} $10^{-10}\,m^2/s$	τ_{intra} ms	D_{lr} $10^{-7}\,m^2/s$
Powder	9 ± 2	2.5 ± 0.5	21 ± 8
Compacted	9 ± 2	2.3 ± 0.5	2.2 ± 0.9
Granule	9 ± 2	5.6 ± 1.1	2.8 ± 1.1

the former measurements hydrogen was used as a carrier gas and the retention volume V_R was determined for *n*-pentane at 523 K. The breakthrough capacity K_D was determined with a hydroraffinate in the boiling range 461–594 K in an adsorption column under atmospheric pressure and at a temperature of 653 K.

The feed rate was 0.5 g/gh at a gas (H_2) to hydrocarbon mass ratio of 300:1. As a means of desorption we have applied ammonia. Both the retention volume V_R and the breakthrough capacity K_D reflect the dynamic adsorption capacity of the molecular sieve.

Results and Discussion

Process of granulation

Table 1 compares the transport characteristics of methane in NaCaA molecular sieves as a crystallite powder, in the compacted form (pressure of compaction ≃ 20 MPa) and after industrial granulation. It becomes evident that intracrystalline molecular self-diffusion remains practically unaffected by the different pretreatments of the zeolite crystallites.

Comparing the loose assembly of crystallites with their compacted and granulated forms, a significant loss in long-range mobility is observed. This may easily be explained by the reduction of the intracrystalline void space during the procedures of compaction and granulation, respectively.

The time constants τ'_{intra} indicate a retardation in the rate of intracrystalline molecular exchange in the granulated specimens. Since, on the other hand, intracrystalline self-diffusion remains unchanged, this effect can only be explained by the existence of additional transport resistances at the outer surfaces of the zeolite crystallites. One must conclude, therefore, that the process of granulation leads to the formation and/or the enhancement of surface barriers.

Molecular sieves under hydrothermal conditions

It is well known that zeolites are unstable under hydrothermal conditions. This holds especially true of NaCaA type zeolites, as demonstrated by Breck (1974) and by Semadeni (1969) with Linde 5A molecular sieves.

In order to investigate the mechanisms of molecular sieve deterioration under hydrothermal conditions, molecular sieves 5A Z were introduced into a column (45 mm dia., filling height 200 mm) and subjected to a nitrogen stream of extreme humidity ($p_{water} \simeq 90$ kPa) at different temperatures (373–873 K) and at atmospheric pressure (Richter et al., 1986b). Figure 2 gives a comparison between the macroscopically observed transport characteristics of these sieves with the parameters of molecular transport as determined by NMR. In addition we have included the corresponding quantities τ^{diff}_{intra} calculated by Eq. 3 from D_{intra} and the

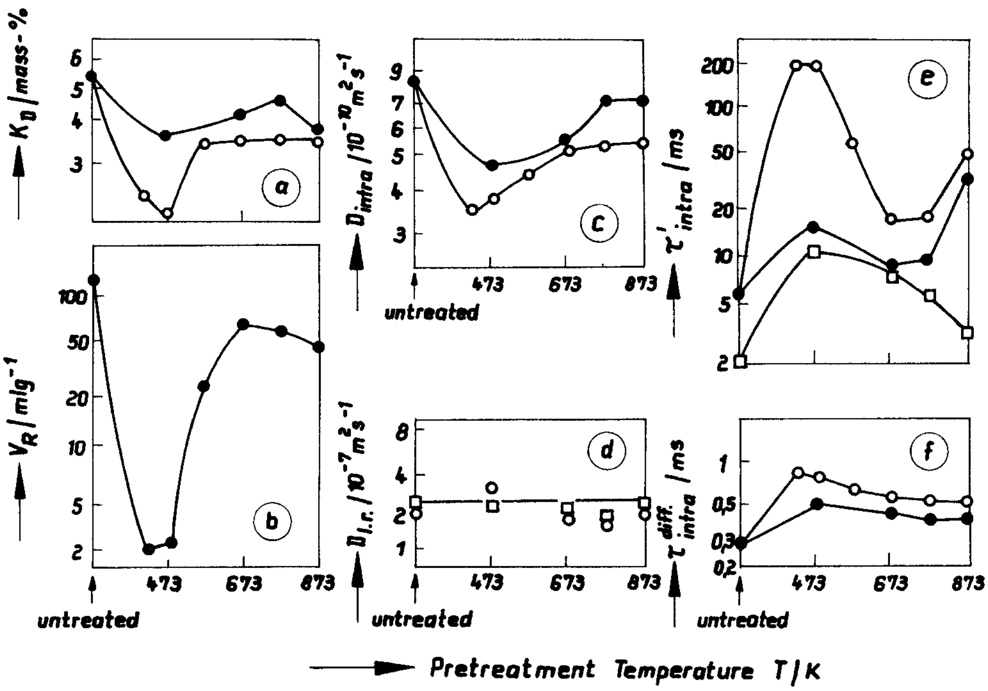

Figure 2. Effect of temperature of hydrothermal treatment on NaCaA zeolite granules.

● = 7 h; ○ = 14 h; □ = values of compacted zeolite for 14-h period

a. breakthrough capacity

b. specific retention volume for *n*-pentane

c,d. intracrystalline (c) and long-range (d) self-diffusion coefficient of methane

e. intracrystalline mean life times τ'_{intra}

f. τ^{diff}_{intra}

Table 2. Parameters of Molecular Transport in Granulated Zeolite NaCaA (5AZ) after Deterioration by Contact with Hydrocarbons of Different Boiling Ranges

Boiling Range °C	τ'_{intra} ms	D_{intra} $10^{-10} \cdot m^2 \cdot s^{-1}$	τ^{diff}_{intra} ms	V_R $mL \cdot g^{-1}$
Starting material	2	9	0.3	115
190–290	3	9	0.3	85
190–320	5	7	0.4	70
260–320	17	5	0.5	64
290–320	19	5	0.5	52

crystal diameter. It refers to the limiting case where besides intracrystalline diffusion there are no other resistances of molecular transport. From Figure 2 the following conclusions may be drawn:

1. In comparison with the changes in τ'_{intra} and D_{intra}, long-range self-diffusion remains practically unaffected by hydrothermal treatment.
2. The hydrothermal treatment leads to slight changes in the intracrystalline mobility. Comparison between the observed (τ'_{intra}) and limiting (τ^{diff}_{intra}) tracer desorption times shows, however, that in any case intracrystalline diffusion is too fast to have any influence on molecular adsorption or desorption behavior. The rate of adsorption and desorption is controlled totally by surface barriers.
3. The macroscopically observed transport behavior (values of K_D and V_R) is adequately reflected by the tracer desorption time constants τ'_{intra}. The deterioration of the dynamic adsorption capacity must be attributed therefore to the increasing influence of surface barriers.

Studying the surface composition of A-type zeolite crystallites by X-ray photoelectron spectroscopy (Kärger et al., 1987a) the formation and enhancement of surface barriers due to hydrothermal pretreatment could be shown to be accompanied by a decrease of the cation content in the surface layer, indicating a structural collapse of the surface layer of the zeolite crystallites.

Molecular sieves in contact with hydrocarbons at elevated temperatures

In equipment similar to that of the preceding section, NaCaA molecular sieves were subjected alternately to a stream of hydrogen containing the paraffin distillate (0.3%; for about 15 min) and to an ammonia stream to displace the hydrocarbons (for about 10 min). After 10 cycles, the retention volume V_R, the NMR tracer desorption time constant τ'_{intra}, and the intracrystalline self-diffusion coefficient D_{intra} were measured. Table 2 shows the results obtained with hydrocarbons of different boiling ranges (Richter et al., 1986b). As in the case of hydrothermal deterioration, from the large difference in the values of τ'_{intra} and τ^{diff}_{intra} one has to conclude that molecular exchange is controlled by surface barriers rather than by the intracrystalline self-diffusion. It is found that the tracer desorption time constants τ'_{intra}, and consequently the intensity of the surface barriers, increase with increasing boiling range of the petrol distillate.

Table 3. Parameters of Molecular Transport in Granulated Zeolite NaCaA (5A UCC) after Different Times on Stream in a Petroleum Refinery

Time on Stream h	τ'_{intra} ms	D_{intra} $10^{-10} \cdot m^2 \cdot s$	τ^{diff}_{intra} ms	K_D Mass %
0	2	11	0.2	4.7
12,000	33	9	0.3	4.0
19,000	55	11	0.2	3.9
25,000	67	11	0.2	3.6
38,000	98	7	0.4	2.6

Again, the formation of surface barriers turns out to be the decisive process in the deterioration of the molecular sieves.

Table 3 gives a comparison of the dynamic adsorption capacities with the values of τ'_{intra} and D_{intra} (or τ^{diff}_{intra}) for the commercial zeolite 5A UCC after different times on stream in a petroleum refinery. The decreases in the dynamic adsorption capacities with increasing times on stream clearly indicate the continuing deterioration of the molecular sieve. The results of the NMR tracer desorption technique (τ'_{intra}) and their comparison with intracrystalline diffusivities, lead to the conclusion that the reduction of the dynamic capacity results from an increasing intensity of the surface resistances rather than, for example, from a deposition of reaction products in the intracrystalline pore system.

Notation

c^* = concentration of labeled molecules
D = self-diffusion coefficient
D_{intra} = coefficient of intracrystalline self-diffusion
D_{lr} = coefficient of long-range self-diffusion
$\overline{j}^*$ = flux density of labeled molecules
K_D = breakthrough capacity
r = molecular displacement
R = crystallite radius
t = time
V_R = retention volume

Greek letters

τ_{intra} = intracrystalline molecular lifetime
τ'_{intra} = time constant of NMR tracer desorption experiment ($\tau'_{intra} \geq \tau_{intra}$)
τ^{diff}_{intra} = intracrystalline molecular lifetime, calculated under the assumption that molecular exchange is exclusively limited by intracrystalline self-diffusion, Eq. 3

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Manuscript received June 29, 1987, and revision received Oct. 8, 1987.