ϵ = reactor point effectiveness defined by Eq. 14
ϵ_p = pellet effectiveness
$(\eta_{in})_d$ = effectiveness factor for fresh inner core of deactivated catalyst pellet
η = effectiveness factor for fresh catalyst pellet
λ = thermal conductivity
ρ = density
ϕ_p = Thiele modulus for chemisorption reaction, $L\sqrt{k_p/D_p}$
$(\phi_p)_c$ = $L\sqrt{(k_p)_c/D_p}$
$(\phi_p)_o$ = $L\sqrt{(k_p)_o/D_p}$
τ = residence time, Z/U
τ_c = residence time of coolant
ξ = equilibrium constant in rate expression

Subscripts

c = at $x = x_c$, coolant side
L = at pellet center
p = poisoning species
s = at pellet surface
o = bulk fluid
in = reactor inlet
out = reactor outlet

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A Study of Fast Tracer Desorption in Molecular Sieve Crystals

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A modification of the customary NMR (Nuclear Magnetic Resonance) pulsed field gradient technique is shown to allow the observation of tracer desorption phenomena in a time interval of 4 . . . 1 000 ms. The processes observed are only limited by molecular transport in the individual crystallites. Other influences, such as intercrystalline transport resistances and the finite rate of adsorbate supply or adsorption heat dissipation, as known from traditional sorption experiments, can be excluded.

The method is applied to several zeolitic adsorbate-adsorbent systems: methane . . . hexane/NaX; ethane/NaCaA. The tracer desorption curves show the expected dependences on paraffin chain length, sorbate concentration and crystallite size. Comparison with the coefficients of intracrystalline diffusion shows that desorption is limited by intracrystalline transport, excluding the existence of structural surface resistances for these systems. Application of the technique to small zeolite crystallites allows the observation of molecular transport phenomena considerably slower than accessible until now by customary NMR techniques.

SCOPE

The classical method of studying ad- and de-sorption kinetics involves following the transient sorption curve generated when the adsorbent is exposed to a change in ambient sorbate concentration. Besides molecular transport in the individual crystallites, the overall process thus observed may be limited by a number of additional phenomena, such as the intercrystalline transport or the finite rates of adsorbate supply and adsorption heat dissipation. Especially with short sorption times being of the order of or less than 1 s, the latter processes in general completely mask the influence of the microscopic transport. Presented here is a method for recording tracer desorption from

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the individual crystallites in a time interval of ≈4 . . . 1 000 ms. The method is based on the nmr pulsed field gradient technique by which it can be decided, whether during a fixed time interval a molecule has remained in some crystallite or whether it has covered some larger distance in the intercrystalline space.

The method is used to investigate the desorption of some light paraffins from NaX and NaCaA zeolite crystallites. The results are compared with the coefficients of intracrystalline diffusion in order to decide whether there might exist some additional transport resistance on the zeolite crystallite surfaces.

Application of the method to small adsorbent particles allows the observation of transport phenomena considerably slower than accessible until now by customary NMR techniques. This is demonstrated by ethane desorption studies on differently pretreated NaCaA zeolites with a mean crystallite radius of 0.5 μm.

CONCLUSIONS AND SIGNIFICANCE

By a modified analysis of nmr pulsed field gradient experiments, tracer desorption curves in a time scale of 4 . . . 1 000 ms can be determined. In this way, the lower limit for the sorption time constants, confined until now to a minimum value of 1 s, has been reduced to considerably smaller values.

Comparison between the diffusivities derived from the desorption curves and intracrystalline diffusivities for methane, ethane, n-butane and n-hexane in NaX and for ethane in NaCaA shows that desorption is exclusively determined by intracrystalline transport. The existence of structural transport resistances at the crystallite surface must, therefore, be excluded.

On applying this technique to small crystallites, desorption curves with apparent diffusivities down to 10^{-15} m^2·s^{-1} can be observed. Such values are by more than three orders of magnitude smaller than the lower limit of diffusivities accessible by the customary application of the NMR-pulsed field gradient technique. With this new technique, the basis for a reliable comparison between equilibrium and non-equilibrium diffusivities over at least a few orders of magnitude has been developed.

INTRODUCTION

The traditional method of studying sorption kinetics is to measure the transient sorption curve generated when a sample of the adsorbent is exposed to a change in ambient sorbate concentration. The time constant of the overall process thus observed may be determined by numerous mechanisms, such as the rates of adsorbate supply (Struve et al., 1980) and of adsorption heat dissipation (Doelle and Riekert, 1977; Lee and Ruthven, 1979; Kočiřík et al., 1979; Ruthven et al., 1980) and the transport resistances of intercrystalline and intracrystalline diffusion (Ruthven and Loughlin, 1972; Kočiřík and Zikánová, 1972, 1974; Dubinin et al., 1975; Barrer, 1979a). Due to its practical and theoretical significance, in general one is interested in the velocity of the intracrystalline molecular transport. However, it is just this process which is masked by the other mechanisms in many cases. This is true especially for rapid sorption processes. Traditional sorption experiments with time constants of the order of 1 s therefore contain—if at all—rather limited information about the molecular transport within the individual crystallites. In the following it will be shown that a modified analysis of NMR pulsed field gradient experiments (Stejskal and Tanner, 1965; Pfeifer, 1972, 1976) provides direct information about tracer desorption behavior. In contrast to traditional tracer techniques, this method is directly sensitive to molecular transport in the individual crystallite, covering time constants in the region of ≈4 . . . 1 000 ms.

NEW METHOD

A synopsis of the application of NMR to adsorbate-adsorbent systems including diffusion studies is given in the review articles by Pfeifer (1972, 1976). For the description of the new method, we have to recall a few items only: The quantity measured in nmr experiments is the vector sum of the magnetic moments of the nuclei under consideration in a plane perpendicular to the direction of a magnetic field $\vec{B}$. Each of these "elementary magnets" is carrying out a precessional motion around the direction of $\vec{B}$ with the Larmor frequency

$$\omega = \gamma_g B, \tag{1}$$

where the gyromagnetic ratio γ_g is a characteristic parameter for each kind of nuclei. For protons, which we will exclusively refer to in the following, $\gamma_g = 2.675 \cdot 10^8$ T^{-1}s^{-1}. In the NMR-pulsed gradient technique, two inhomogeneous pulsed fields

$$B_1 = gz \tag{2}$$

of duration δ and separation Δ between each other are superimposed on a constant, homogeneous field B_o. For convenience, δ is assumed to be much less than Δ. By Eq. 2, we have chosen the z-axis of our coordinate system to coincide with the direction of the field gradient g.

By means of appropriate radio frequency pulses, an nmr signal is produced. The phase φ of the precessional motion of the elementary magnets at the time of this "spin echo" is the difference

$$\varphi = \int_{2^{nd}\ \mathrm{pulse}} \omega dt - \int_{1^{st}\ \mathrm{pulse}} \omega dt \tag{3}$$

between the phases accumulated during the gradient pulses. Combining Eqs. 2, 1 and 3 we obtain

$$\varphi = \delta \gamma_g g (z_2 - z_1), \tag{4}$$

where z_i denotes the z coordinate of a particle at the time of the i-th gradient pulse. The contribution of this particle to the total magnetization is attenuated by the cosine of this angle, since due to symmetry, the total magnetization will appear in the direction $\varphi = 0$. We get the total signal intensity Ψ by integrating over all possible particle positions z_1 and z_2:

$$\Psi(\Delta, g\delta) = \int p(z_1) P(z_2, z_1 | \Delta) \cos[\delta \gamma_g g (z_2 - z_1)] dz_2 dz_1. \tag{5}$$

$p(z_1)dz_1$ is the probability of finding a molecule with the z coordinates $z_1 \ldots z_1 + dz_1$ at the time of the first gradient pulse. $P(z_2, z_1|\Delta)$ denotes the (conditional) probability that a molecule initially located at the space coordinate $z = z_1$ will have moved to position $z_2 \ldots z_2 + dz_2$ after time interval Δ. For homogeneous media, $P(z_2, z_1|\Delta)$ depends only on the difference $z_2 - z_1$. It is the solution of the diffusion equation for an instantaneous point source in an infinite medium:

$$P(z_2, z_1|\Delta) = \frac{1}{[2\pi \langle (z_2 - z_1)^2 \rangle]^{1/2}} \exp\left\{ - \frac{(z_2 - z_1)^2}{2 \langle (z_2 - z_1)^2 \rangle} \right\}. \tag{6}$$

where the mean square displacement in the z direction is related to the self-diffusion coefficient by Einstein's equation

$$\langle (z_2 - z_1)^2 \rangle = 2D\Delta. \tag{7}$$

Inserting Eq. 6 into 5 one obtains the familiar relation (Pfeifer 1972, 1976; Barrer, 1979a)

$$\Psi(\Delta, g\delta) = \exp\left\{ - \gamma_g^2 \delta^2 g^2 \frac{\langle (z_2 - z_1)^2 \rangle}{2} \right\}. \tag{8}$$

This equation shows that the slopes in the usual $ln\,\Psi$ vs. $(\delta g)^2$ plots are largest for the largest displacements.

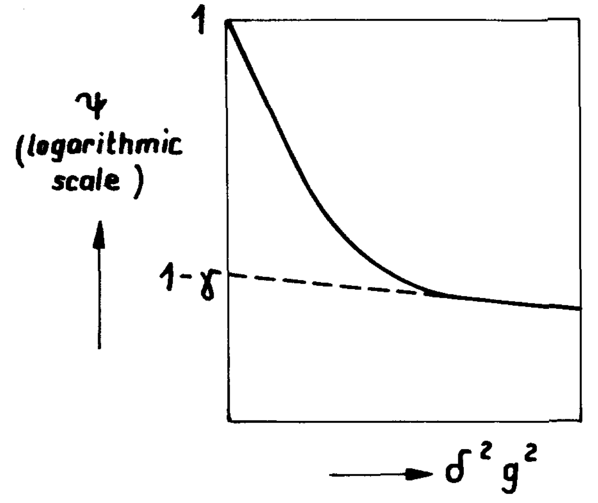

Figure 1. Determination of the amount desorbed (γ) during the time interval of the nmr experiment from the dependence of the spin echo attenuation Ψ on the pulsed field gradient intensities δg. The slopes of the two branches of this plot are proportional to the mean square displacement in the inter- and intra-crystalline spaces.

An adequate description of molecular transport in heterogeneous media is more complicated (Barrer, 1968; Crank, 1975; Jury, 1967, 1977) and, with it, the determination of convenient theoretical patterns for the nmr signal intensity in microparticle adsorbents becomes similarly difficult.

In the following we will restrict ourselves to the special case:

(i) During the "measuring time" Δ only a part $\gamma(\Delta)$ of the molecules is leaving the microparticles (crystallites) where they were located during the first gradient pulse

(ii) The displacements $z_2 - z_1$ of these molecules are much larger than those for the remaining molecules

Under these conditions, the conditional probability $P(z_2,z_1|\Delta)$ can be split into two terms:

$$P(z_2 z_1|\Delta) = \gamma(\Delta)P_{\mathrm{inter}}(z_2,z_1|\Delta) + (1-\gamma(\Delta))P_{\mathrm{intra}}(z_2,z_1|\Delta). \tag{9}$$

where the quantities $P_{\mathrm{inter(intra)}}(z_2,z_1|\Delta)$ again denote probability functions as defined in connection with Eq. 5, but now refering only to the fraction of the molecules which leaves (remains in) the crystallites. According to condition (ii)

$$\begin{aligned}\langle (z_2 - z_1)^2\rangle_{\mathrm{intra}} &= \int p(z_1)P_{\mathrm{intra}}(z_2,z_1|\Delta)(z_2 - z_1)^2 dz_1 dz_2 \\ \ll \langle (z_2 - z_1)^2\rangle_{\mathrm{inter}} &= \int p(z_1)P_{\mathrm{inter}}(z_2,z_1|\Delta)(z_2 - z_1)^2 dz_1 dz_2.\end{aligned} \tag{10}$$

From Eq. 7, the intracrystalline molecular displacement can be derived to be

$$\langle (z_2 - z_1)^2\rangle^{1/2} = (2D_{\mathrm{intra}}\Delta)^{1/2}. \tag{11}$$

provided this value does not exceed the characteristic dimension (radius R) of the crystallites. According to our starting condition, in this case instead of Eq. 11 one would have

$$\langle (z_2 - z_1)^2\rangle^{1/2}_{\mathrm{intra}} \approx R. \tag{12}$$

For visualizing the main idea of the new method, we assume at first that $P_{\mathrm{inter}}(z_2,z_1|\Delta)$ and $P_{\mathrm{intra}}(z_2,z_1|\Delta)$ can also be approximated by Eq. 6, with corresponding mean square displacements as discussed in Relations 10–12. In analogy with Eq. 8 one obtains

$$\begin{aligned}\Psi(\Delta,g\delta) \approx\ & \gamma(\Delta)\exp\left\{-\gamma_g^2\delta^2 g^2 \frac{\langle (z_2 - z_1)^2\rangle_{\mathrm{inter}}}{2}\right\} \\ &+ (1-\gamma(\Delta))\exp\left\{-\gamma_g^2\delta^2 g^2 \frac{\langle (z_2 - z_1)^2\rangle_{\mathrm{intra}}}{2}\right\}.\end{aligned} \tag{13}$$

As illustrated in Figure 1, the relative number $\gamma(\Delta)$ of the molecules having left the crystallites during Δ can easily be determined from the $ln\Psi$ vs. $(\delta g)^2$ plots via Eq. 13. If the above condition (ii) is strictly fulfilled, in any case the second branch in this representation will be practically parallel to the abscissa, so that the determination of $(1-\gamma)$ is possible without any assumption concerning the functional dependences of $P_{\mathrm{inter}}(z_2,z_1|\Delta)$ and $P_{\mathrm{intra}}(z_2,z_1|\Delta)$.

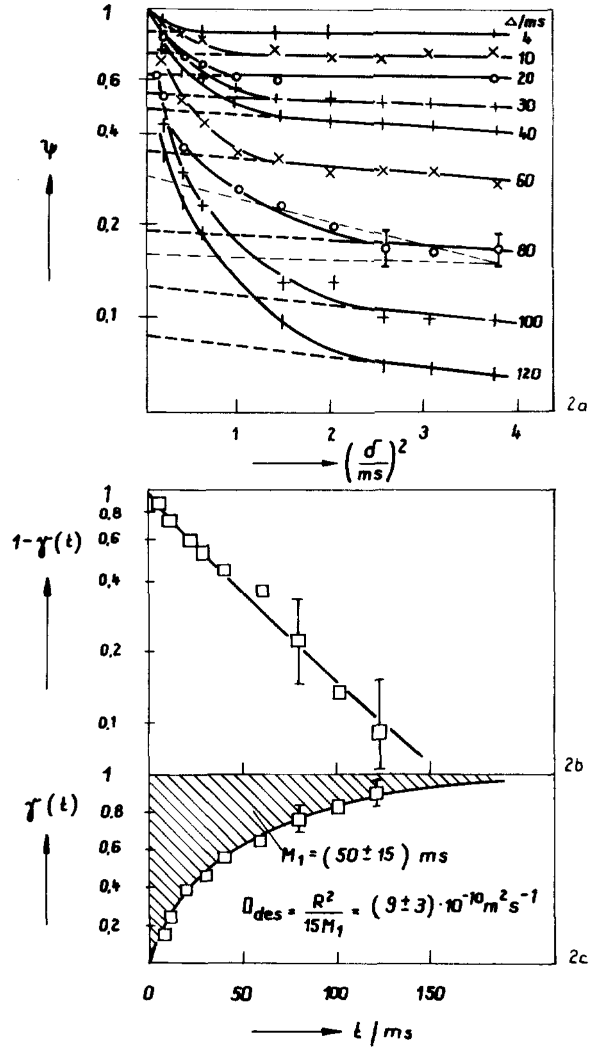

Figure 2. Analysis of the NMR data for tracer desorption studies (in the example: butane/NaX, 165 mgg^{-1}, R = 25 μm, 353 K). 2a: The dependence of echo attenuation Ψ on the gradient pulse width δ (g has been kept constant during the experiment) for different observation times Δ. The extrapolation of the second branch to the ordinate (dashed lines) provides the values for 1 − γ(Δ) (□ in Figure 2b). As an example, the uncertainty in these values is indicated for the observation time Δ = 80 ms. 2b: Tracer desorption curve as determined from Figure 2a (t = observation time Δ). 2c: Determination of D_{des} from the first statistical moment of the desorption curve (= shaded area) by Eq. 15.

Repeating the experiments with different time intervals between the gradient pulses, the complete time dependence can be determined. It contains just the information of tracer desorption experiments for the individual crystallites. While traditional tracer experiments do not provide any possibility for labelling on a microscopic scale, in nmr techniques this labelling is realized in a straightforward way via the phase of the precessional motion of the magnetization of the individual nuclei (Eqs. 1–4).

The region of accessible observation times Δ is determined by the rise and fall times of the gradient pulses (lower limit) and by the nuclear magnetic relaxation times T_1 and T_2 of the sample and by the sensitivity of the spectrometer (upper limit). We realized observation times of 4 . . . 1 000 ms. The drastic increase in the observation times in comparison with previous investigations (e.g.,

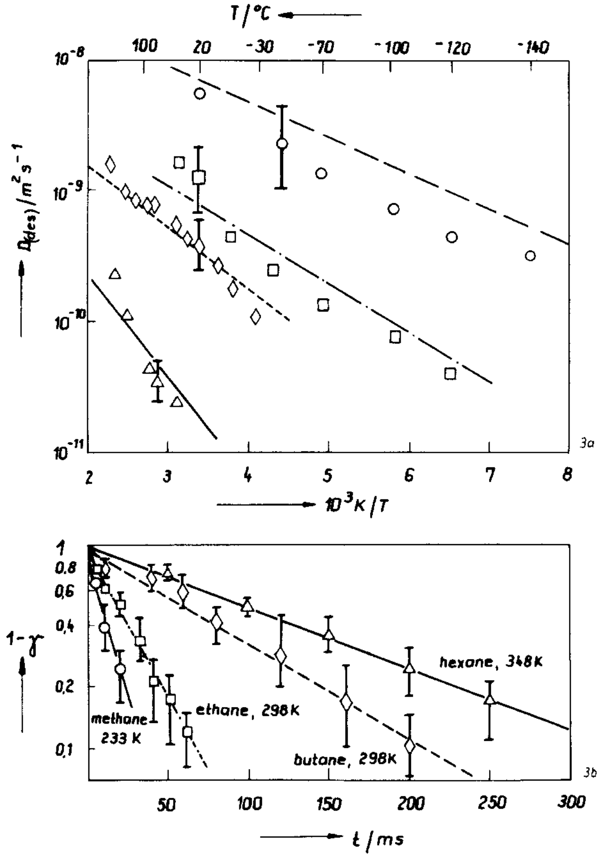

Figure 3. Tracer desorption with paraffins of different chain length:
○ methane/NaX, 94 mgg^{-1}, R = 25 μm
□ ethane/NaX, 113 mgg^{-1}, R = 25 μm
◇ n-butane/NaX, 165 mgg^{-1}, R = 25 μm
△ n-hexane/NaX, 165 mgg^{-1}, R = 10 μm
3a: Temperature dependence of the effective diffusivities D_{des}; the corresponding coefficients of intracrystalline self-diffusion (Walter, 1980; Kärger et al., 1980) as determined by the traditional nmr pulsed field gradient technique are indicated by the various lines through the data. 3b: Tracer desorption curves for selected temperatures.

$\Delta \leqq 10$ ms in Pfeifer, 1972) is due to the application of the stimulated echo technique (Tanner 1970).

EXPERIMENTAL

We investigated zeolites synthesized by S. P. Ždanov and N. N. Samulevič, Leningrad, with mean crystallite radii between 0.5 and 25 μm. The measurements were carried out in 7 mm diameter sealed sample tubes, containing the adsorbate-adsorbent systems. In general, activation of the zeolite material in the sample tubes was accomplished by evacuating the samples at 400°C and 5.10^{-3} Pa for 20 h. Subsequently, the adsorbate was introduced by vacuum distillation. The amount sorbed was determined gravimetrically and volumetrically and checked afterwards by the intensity of the nmr signal of the sealed samples (Heink et al., 1978).

We used a pulse spectrometer built in our laboratory (Heink, 1974) which works at a proton resonance frequency of $\omega/2\pi$ = 60 MHz. We applied the 90°-τ_1-90°-τ_2-90°-τ_1-echo sequence (stimulated echo technique) with gradient pulses immediately after the first and third radio-frequency 90°-pulses, and recorded the dependence of the spin echo intensity Ψ on the gradient intensity δg for different pulse separations $(\tau_1 + \tau_2) = \Delta$.

The examples given in Figures 2a–c visualize our way of analyzing the primary data in the nmr experiments. Following a plot like that in Figure 1, the spin echo attenuations give the relative numbers of molecules having left the crystallites (Figure 2a). In Figure 2b these values are shown in the customary $ln[1 - \gamma(\Delta)]$ representation. The uncertainty in these values is due to the uncertainty in determining echo attenuations and in extrapolating the second branch to the ordinate as indicated in Figure 2a. The corresponding error bars of Figure 2b obviously show that an analysis of the functional dependence of $\gamma(\Delta)$ cannot provide reliable information. It should be sufficient, therefore, to characterize the desorption curves by one convenient parameter. For this purpose we have chosen the first statistical moment (Kočiřík and Zikánová, 1972, 1974; Dubinin et al., 1975; Barrer, 1979a)

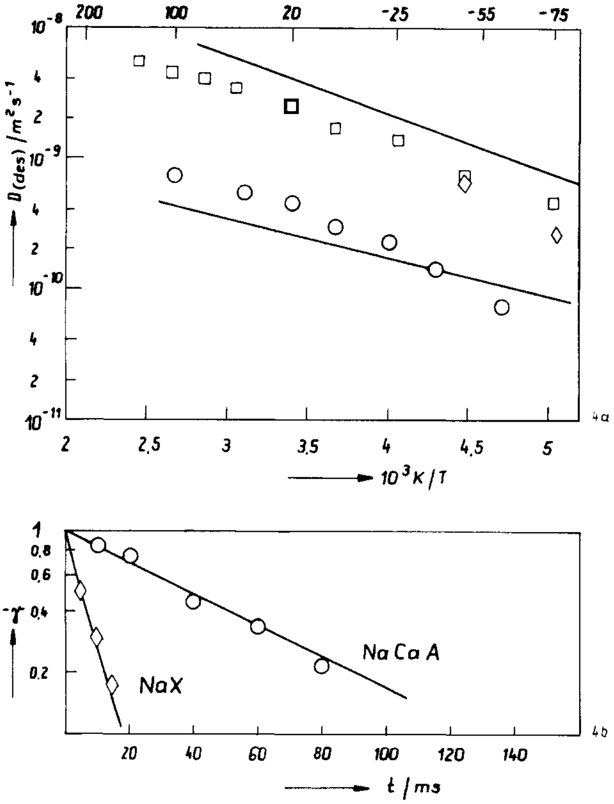

Figure 4. Tracer desorption with ethane from NaX (□: R = 25 μm; ◇: R = 10 μm) and NaCaA (○: R = 8 μm) zeolites for sorbate concentrations of about 80 mgg^{-1}: 4a: Temperature dependence of the effective diffusivities D_{des}. The corresponding coefficients of intracrystalline self-diffusion (Walter, 1980; Kärger et al., 1980; Kärger and Caro, 1977) are indicated by the various lines. 4b: "Tracer desorption" curves for comparable temperatures and crystal radii (NaX: 223 K, 10 μm; NaCaA: 213 K, 8 μm).

$$M_1 = \int_0^\infty (1 - \gamma(\Delta))d\Delta, \tag{14}$$

which can easily be obtained by determining the area between $\gamma(\Delta)$ and 1 (shaded area in Figure 2c). This moment takes account of the whole desorption curve. With this parameter and the mean crystallite radius R, we introduced the quantity

$$D_{des} = \frac{R^2}{15M_1}. \tag{15}$$

Under the condition that molecular desorption is limited by intracrystalline diffusion, D_{des} coincides with the intracrystalline self-diffusion coefficient (Dubinin et al., 1975).

RESULTS AND DISCUSSION

Some Characteristic Dependences

In the following, a few examples of the application of this new technique are given. Comparative studies of the dependence of tracer desorption kinetics on the chain length of n-paraffins in NaX zeolites (Figure 3) and on the free apertures of the micropores in the zeolites (Figure 4) show the expected behavior (Barrer, 1979a,b; Ruthven, 1977; Walter, 1980): desorption kinetics are slowed down with increasing chain length and with decreasing diameter of the "windows" in the micropore system. Figure 5 gives a few examples of the influence of the sorbate concentration on tracer desorption kinetics. In this case, the expected decrease with increasing sorbate concentration (Pfeifer and Kärger, 1979) is also observed. The results for tracer desorption at zeolite crystallites of different size,

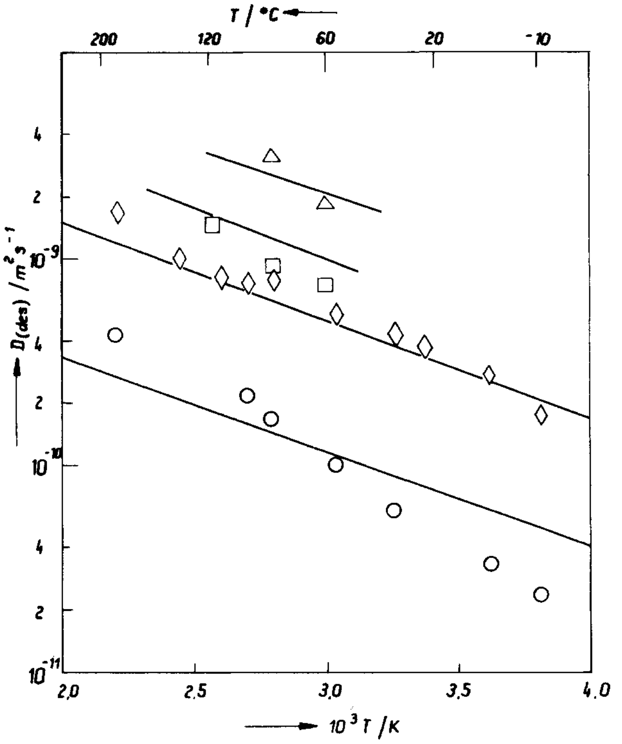

Figure 5. Temperature dependence of the effective diffusivities for tracer desorption of n-butane on NaX-zeolites for different sorbate concentrations (△: 105 mgg^{-1}, □: 137 mgg^{-1}, ◇: 165 mgg^{-1}, ○: 195 mgg^{-1}); intracrystalline diffusivities (Walter, 1980; Pfeifer and Kärger, 1979; Kärger et al., 1980) are indicated by the full lines.

but at comparable sorbate concentrations, are shown in Fig. 6: As expected, tracer desorption from the larger crystallites proceeds more slowly. However, the quantities D_{des} as obtained on the basis of Eq. 15 are in reasonable agreement with each other.

Limiting Step in Tracer Desorption

Traditional adsorption and desorption experiments can be limited by macroscopic as well as microscopic processes. In the technique described here, the influence of all macroscopic effects such as the finite velocity of adsorbate supply (Struve et al., 1980) and of adsorption heat dissipation (Doelle and Riekert, 1977; Kočiřík et al., 1979; Ruthven et al., 1980) can be excluded. Any influence of macropore diffusion (Ruthven, 1972) can be estimated from the slope of the second part in the $\ln \Psi$ vs. $(\delta g)^2$ plot as discussed in connection with Figure 1. This influence is completely negligible if the slope is much less than the initial slope of the representation. The observed desorption kinetics must therefore be limited by processes inherent to the individual crystallites, such as intracrystalline diffusion or overcoming some transport resistances at the crystalline surface.

First information about the nature of limiting processes relevant in our experiments can be deduced from the study of the dependence of M_1 on the radius. For barrier limited desorption, the first statistical moment is related to the surface resistance α^{-1} by the equation (Zolotarev, 1975)

$$M_1^{\text{barrier}} = R/3\alpha. \tag{16}$$

Therefore, the quantity D_{des} as introduced by Eq. 15 should be proportional to the radius of the crystallites according to the equation

$$D_{\text{des.}}^{\text{bar.}} = \frac{\alpha R}{5}. \tag{17}$$

Our experimental findings (cf., Figure 6) are in contrast to this dependence, thus suggesting that the observed desorption processes are limited by intracrystalline diffusion. However, since we had to assume that α is radius independent, in view of the possibility of a radius dependent surface resistance (Bülow, 1978), such an argument is not completely convincing. Direct information about the limiting processes can be obtained by comparison of our results with coefficients of intracrystalline self-diffusion as obtained by the customary application of nmr pulsed field gradient technique (Pfeifer 1972, 1976).

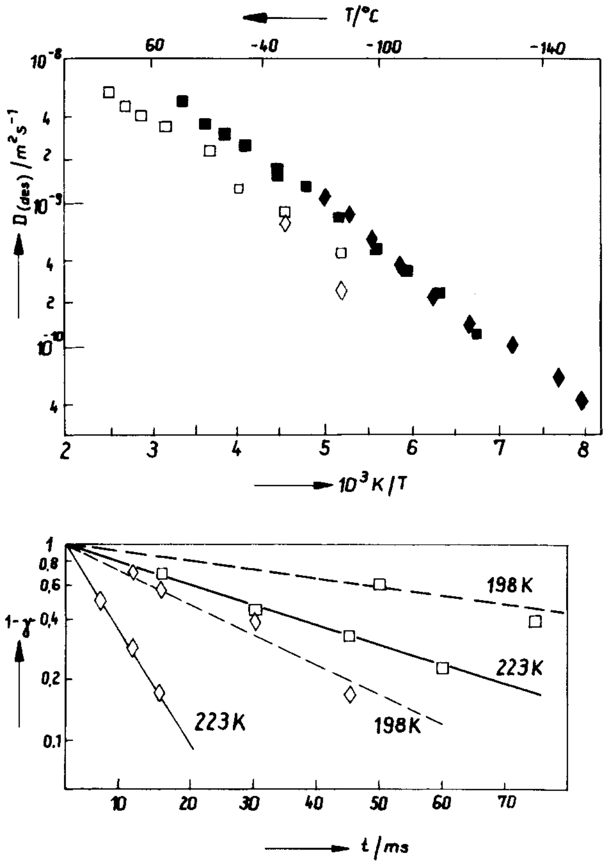

Figure 6. Diffusivity data for ethane on NaX zeolites with mean crystallite radii R = 10 μm (◇) and R = 25 μm (□) for sorbate concentrations of 80 mgg^{-1}. 6a: Temperature dependence of the tracer desorption data; (open symbols) and of the intracrystalline diffusivities (full symbols, from Walter, 1980). 6b: Tracer desoprtion curves for 198 K (dashed lines) and 223 K (full lines).

These values have been obtained in previous investigations of the same systems (Kärger and Caro, 1977; Walter, 1980; Pfeifer and Kärger, 1979; Kärger et al., 1980) and are indicated in our representations by thin lines. Taking account of the uncertainty in the values for D_{des}, the agreement is satisfactory. Desorption as observed under the given experimental conditions must therefore be limited by the intracrystalline molecular transport. In agreement with previous qualitative considerations for hexane diffusion in NaX zeolites (Kärger et al., 1976), it has been shown that for the adsorbate-adsorbent systems methane . . . hexane/NaX and ethane/NaCaA after the moderate sample pretreatment described above, there are no perceptible transport resistances at the crystallite surface under equilibrium conditions.

Therefore, among the explanations for the previously observed radius dependences of the apparent diffusivities of paraffin adsorption on NaCaA zeolites (Kärger et al., 1977), a general existence of structural surface barriers can be excluded. Some possibilities for non-equilibrium processes leading to the observed radius dependences are discussed in the literature (Bülow et al., 1979, 1980). It is evident that such processes cannot be observed by the new technique.

Tracer Desporption with Small Crystallites

While the lower limit for zeolitic diffusivities accessible at present by the customary nmr pulsed field gradient technique is of the order of $10^{-11} \ldots 10^{-12}$ m^{2}s^{-1}, for D_{des} considerably lower

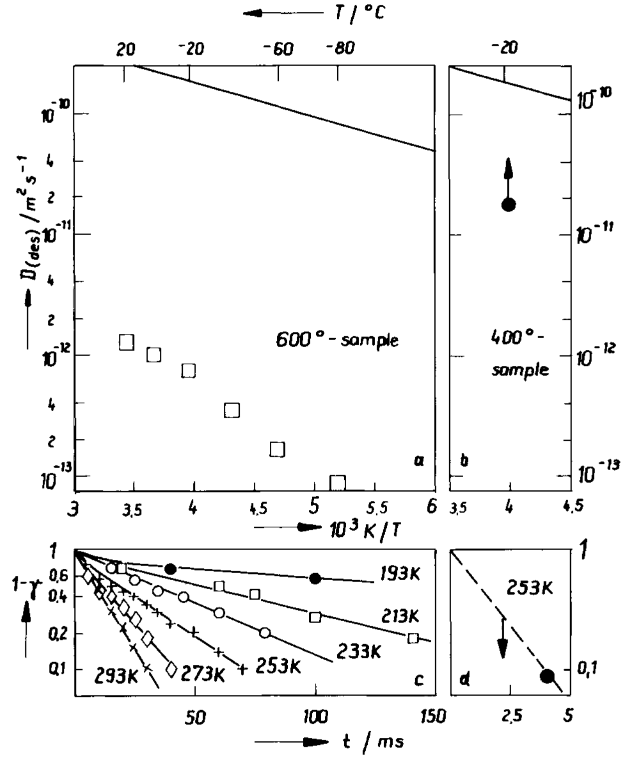

Figure 7. Tracer desorption of ethane from small NaCaA zeolite crystallites ($\approx$80 mgg^{-1}: $R \approx 0.5$ μm). 7a,b: Effective diffusivities D_{des} for tracer desorption from the 400°C-sample (a) and from the 600°C-sample (lower limit) (b). The coefficients of intracrystalline self-diffusion for ethane in 5A zeolites (Kärger and Caro, 1977) are represented by the full lines. 7c,d: Tracer desorption curves for the 400°C-sample (c) and for the 600°C-sample (majorant) (d).

values can be obtained. Inserting into Eq. 15 the realistic values $R = 0.1$ μm and $M_1 = 1$ s, the lower limit of D_{des} can be estimated to be at least of the order of 10^{-15} m^2·s^{-1}. This value is in the region of diffusivities readily accessible to traditional uptake techniques. Until now, comparative nmr and uptake studies were possible only in a very narrow interval of diffusivities (Barrer, 1979b).

Since with the present experimental level, nmr pulsed field gradient technique only registers molecular displacements of the order of at least 1 μm, the new method can be applied, if the diffusion paths of the molecules having left the crystallites during Δ are at least of this order of magnitude. However, this is also possible, when the intracrystalline displacements are beneath this limit and hence too small to allow the customary application of the pulsed field gradient technique for studying intracrystalline transport.

As an example of the application of this tracer desorption technique to small zeolite crystallites, Figure 7 shows the results for ethane desorption from NaCaA zeolites with a mean crystallite radius of about 0.5 μm. One sample was activated as described above. Prior to adsorption, the second sample was heated up to 600°C in continuous contact with air and subsequently activated. X-ray studies and the determination of the adsorption isotherms showed that after this procedure the crystallite structure has been preserved and that the adsorption capacity was only insignificantly reduced (Bülow and Rauscher, 1982).

The values of D_{des} for the 600°C-sample are considerably lower than the lower limit for the diffusivities of customary pulsed gradient experiments. Comparison with the estimated values of D_{des} for the 400°C-sample (here only the lower limits can be given) and with the intracrystalline self-diffusion coefficients obtained in previous investigations, shows that desorption kinetics in these zeolites is drastically slowed down. For traditional uptake experiments with the same system, the observed time constants are still at the lower limit of resolution, so that a rather complicated analysis of the experimental data becomes necessary (Bülow and Rauscher, 1980). Since due to the smallness of he zeolite crystallites, the unambiguous determination of the intracrystalline diffusivity in the 600°C-sample by the customary pulsed field gradient technique is not yet possible, it cannot be decided at present, whether this decrease in desorption kinetics is due to the formation of some surface resistance or due to some change in the total intracrystalline pore system.

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NOTATION

B = magnetic field vector
D = self-diffusion coefficient
D_{des} = parameter of the desorption curve ($\equiv R^2/15 M_1$), coincides with D for diffusion limited desorption
g = gradient of the magnetic field
M_1 = first statistical moment
$P(z_2, z_1|\Delta)$ = (conditional) probability density that a molecule initially located at $z = z_1$ will have moved to position z_2 after time interval Δ
$p(z_1)$ = probability density of finding a molecule at the space coordinate $z = z_1$
R = mean crystallite radius
t = time
z = space coordinate in the direction of the field gradient

Greek Letters

α = surface resistance parameter, defined by the relation $j_s = \alpha(a_s - a_{s\infty})$ between the particle flow j_s through the surface and the difference $(a_s - a_{s\infty})$ between the actual and the equilibrium concentrations at the crystallite boundary
γ_g = gyromagnetic ratio
$\gamma(\Delta)$ = relative number of molecules desorbed after time Δ
Δ = distance between the gradient pulses ("observation" time)
δ = duration of the gradient pulses
φ = difference between the precession phases of the nuclear magnetic moment, accumulated during the gradient pulses
Ψ = NMR spin echo attenuation due to diffusion
$\tau_{1,2}$ = time intervals between the high frequency pulses in the pulse sequence for the stimulated echo
ω = Larmor frequency ($\equiv \gamma_g B$)

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Analysis of Multicomponent Separation by Displacement Development

The separation of multicomponent mixtures by displacement development is fully analyzed by applying the theory of multicomponent chromatography. With Langmuir isotherms it is possible not only to elucidate all the characteristic features of the process but also to derive analytic expressions for the critical value of the developer concentration and the plateau concentration as well as the width of each pure component band attained at the ultimate stage. A specific example demonstrates that the actual solution at the ultimate stage is identical to that predicted *a priori* by using these expressions. The bed length required for complete separation is determined by examining the wave interactions involved. This procedure is clearly illustrated.

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SCOPE

Displacement development is well known in the field of chromatography. The characteristic feature is that, when a mixture of adsorbable species is displaced through a column of adsorbent by adding a solution of a species with higher adsorptivity than any of the species present, the species are gradually separated and form pure component bands. These bands maintain sharp boundaries at both ends and propagate side by side in sequence with the same speed.

The technique was first introduced by Tiselius (1943), who noticed that the plateau concentrations of pure component bands depend only upon the concentration of the development agent (to be called a "developer" in the following) and are independent of the concentrations in the original mixture. Glueckauf and Coates (1947) demonstrated experimentally that for a packing of good quality the boundaries of pure component

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