BASIC PRINCIPLES AND RECENT RESULTS OF $^1$H MAGIC-ANGLE-SPINNING AND PULSED FIELD GRADIENT NUCLEAR MAGNETIC RESONANCE STUDIES ON ZEOLITES

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ABSTRACT

In the first part it is shown both experimentally and theoretically that the $^1$H NMR chemical shift of surface hydroxyl groups as measured for strongly dehydrated zeolites by the MAS technique is a suitable parameter to characterize their strength of acidity. Moreover, this method allows a direct and unambiguous determination of the concentration and accessibility of the various OH groups. In contrast, for hydrated zeolites a superposition of several effects (e.g. Plank's mechanism, formation of hydroxonium ions, adsorption of water molecules on Lewis acid sites) may occur which requires a more detailed analysis of the spectra and additional information for an unambiguous interpretation.

In the second part recent results of pulsed field gradient (PFG) NMR studies of self-diffusion in zeolites are presented which include xenon self-diffusion, the anisotropy of diffusion in zeolites, NMR tracer exchange experiments and a critical comparison of PFG NMR diffusivities with results of other techniques.

$^1$H MAS NMR STUDIES ON DEHYDRATED ZEOLITES

The elementary step of catalysis by Brönsted acidic sites is the proton transfer from the surface hydroxyl group ZOH to the adsorbed molecule M:

$$ZOH + M = ZO^- + MH^+$$

(1)

Hence, the catalytic activity of a catalyst will be determined by at least three independent parameters for each sort of surface hydroxyl groups (Brönsted acidic sites):

(i) The strength of acidity as defined by the rate constant of the proton transfer to the adsorbed molecule,

(ii) the concentration and

(iii) the accessibility of the acidic sites.
Strength of Brønsted Acidity

According to eq. (1) the rate constant of the proton transfer depends both on the properties of the acidic site $\text{ZOH}$ and of the particular molecule $\text{M}$. In order to define a parameter which characterizes the protonating ability of the ZOH group but does not depend on the particular molecule we decompose reaction (1) into two processes:

\[
\text{ZOH} = \text{ZO}^- + \text{H}^+ \\
\text{H}^+ + \text{M} = \text{MH}^+
\] (2) (3)

which leads to the definition of the strengths of gas phase acidity and basicity as the standard Gibbs free energy change of processes (2) and (3), respectively (ref. 1).

In the following we shall use "strength of acidity" as a synonym for the standard Gibbs free energy change of process (2) since it is exactly this parameter which describes quantitatively the protonating ability of the Brønsted acidic site. To compare the strength of acidity with the deprotonation energy of the ZOH group $\Delta E_{\text{DP}}$, a quantity which follows from quantum chemical calculations, one must take into consideration that the standard Gibbs free energy $\Delta G_{\text{DP}}^0$ is the sum of the deprotonation energy $\Delta E_{\text{DP}}$, of the zero-point energy change $\Delta E_{\text{DP}}^0$ and of the Gibbs free energy change $\Delta G_{\text{DP}}^\text{therm}$ which results from the conversion of the three vibrational degrees of freedom of the proton as part of the ZOH group into its three translational degrees of freedom after leaving this group. Assuming that the zero-point energy change $\Delta E_{\text{DP}}^0$ is a constant and that the contribution of $\Delta G_{\text{DP}}^\text{therm}$ is negligible (ref. 2), the deprotonation energy $\Delta E_{\text{DP}}$, i.e. the energy difference of ZO$^-$ and ZOH, can be taken as a suitable measure for the strength of acidity.

With regard to the position of the $^1\text{H}$ MAS NMR signal of the ZOH group which is generally described by the so-called chemical shift $\delta_H$, i.e. the shift of the resonance relative to a standard (tetramethylsilane) in ppm, the following qualitative argument may be taken as a hint, that there is a direct relation between $\delta_H$ and the strength of acidity: A higher value of $\delta_H$ corresponds per definition to a reduced shielding of the external magnetic field and hence to a larger value for the net atomic charge of the hydrogen. On the other hand an enhancement of the net atomic
charge will lead to a reduction of the deprotonation energy. In agreement with this suggestion experimental values for $\delta_H$ and for the absolute gas phase acidities $\Delta G_{DP}^O$ measured for hydroxyl groups of various organic compounds in the gaseous state which are plotted in Fig. 1 show in fact a good correlation (cf. ref. 3).

Another experimental proof of our suggestion that $\delta_H$ is a suitable and sensitive measure for the strength of acidity is given by Fig. 2. In this figure Sanderson's intermediate electronegativity $S_m$, computed for zeolites of composition $\text{HAlO}_2(\text{SiO}_2)_n$ according to the equation

$$S_m = (S_H \cdot S_{Al} \cdot S_{O}^{2n+2} \cdot S_{Si})^{1/(3n+4)} \tag{4}$$

with $S_H = 3.55$; $S_{Al} = 2.22$; $S_{O} = 5.21$; $S_{Si} = 2.84$ (cf. ref. 4), is plotted together with experimental values of $\delta_H$ in dependence on the silicon-to-aluminium ratio $n$. The nearly identical functional dependence of both quantities provides ample evidence for the usefulness of $\delta_H$ as a measure for the strength of acidity. In this connection it should be mentioned that due to the use of CH$_4$ as an inner standard (ref. 3) the absolute values of $\delta_H$ plotted in Fig. 2 are reduced by about 0.3 ppm with respect to ref. 5 and that the accuracy of the absolute values of $\delta_H$ has been enhanced considerably so that the present error does not exceed $\pm 0.05$ ppm. Moreover it was possible to show by a thorough investigation that the residual linewidths which limit the accuracy for a determination of the values of $\delta_H$ for bridging OH groups on zeolites are not controlled by artefacts or imperfections rather than by the distribution width of the strength of acidity (ref. 6).
Fig. 2. Values for the intermediate electronegativity $S_m$ and the chemical shift $\delta_H$ of the (accessible) bridging OH groups in dependence on the silicon-to-aluminium ratio $n$ for various zeolites (HX: zeolite H-X; HY: zeolite H-Y; HM: mordenite; HE: erionite; HZ: H-ZSM-5).

For bridging OH groups of a zeolite H-Y with a silicon-to-aluminium ratio $n = 2.6$ the residual linewidth which can be reduced in the MAS NMR spectra after partial deuteration of the sample or by using multiple pulse sequences to reduce the dipolar proton proton interaction is of the order of 0.3 ppm (ref. 7). Taking into consideration the empirical formula (ref. 3)

$$f/cm^{-1} = 3906 - 74.5 \delta_H/ppm \quad (5)$$

which connects $\delta_H$ with the stretching vibration frequency $f$ of the OH groups, the residual MAS NMR linewidth of 0.3 ppm corresponds to a residual linewidth of the IR band of the bridging OH groups of ca. 20 cm$^{-1}$. This value agrees quite well with experimental results published recently in literature (ref. 8).

As a third argument which supports our suggestion that $\delta_H$ can serve as a measure for the strength of acidity we refer to non-empirical quantum chemical calculations (ref. 2) although due to the approximations inherent in such a treatment it is not such a conclusive proof as the above mentioned experimental results.

In Fig. 3 calculated shielding constants $\sigma_H$ (connected to the chemical shifts $\delta_H$ by the equation $\sigma_H = \delta_{\text{bare proton}} - \delta_H$) taken from ref. 2 are plotted in dependence on calculated deprotonation energies $\Delta E_{\text{DP}}$. Once more one observes a good correlation between both quantities.
Fig. 3. Dependence of calculated values for the chemical shielding $\delta_H$ on calculated values for the deprotonation energy (ref. 2).

Summarized, Figs. 1-3 demonstrate clearly that $\delta_H$ is a suitable and sensitive spectroscopic quantity to measure the strength of acidity as defined by eq. (2). In principle however, one should take into account that in these figures isolated hydroxyls of similar type are compared so that it is not clear whether there exists a generally valid correlation between $\delta_H$ and $\Delta E_{DP}$. Further experiments and calculations are necessary to answer this question which is of basic interest.

In the $^1$H MAS NMR spectra of dehydrated zeolites containing only oxygen, silicon and aluminium in the framework, in general five lines can be separated which have been denoted (refs. 3 and 9) as a, b, c, d, and e:

**Line a** at 1.8 to 2.3 ppm is caused by non-acidic (silanol) OH groups. In the case of carefully dehydrated (200 °C, 10 K/h, 10$^{-2}$ Pa, 24 h) silica this line appears at somewhat lower values (1.65 ppm for aerosil 200/Degussa). A distinction between single and geminal OH groups however is not possible since from the single line shown in Fig. 4 (dehydrated sample) we must conclude

$$|\delta_{H\text{single}} - \delta_{H\text{geminal}}| \leq 0.1 \text{ ppm}$$  \hspace{1cm} (6)

which is in agreement with infrared studies

$$|f_{\text{single}} - f_{\text{geminal}}| \leq 7 \text{ cm}^{-1}$$  \hspace{1cm} (7)

but at variance with a former interpretation of Lippmaa et al. (ref. 10).
The adsorption of water which interacts with SiOH groups gives rise to a shift of ca. 0.4 ppm to higher values of $\delta_H$ as can be seen from Fig. 4 (ref. 11). The $^1H$ MAS NMR signal of silanol groups in molecular sieves of SAPO-type may also appear at lower values of $\delta_H$ (cf. Fig. 5).
Line b at 3.8 to 4.4 ppm is ascribed to acidic OH groups which are known to be of bridging type (SiOHAl). The value of $\delta_H$ increases with increasing silicon-to-aluminium ratio of the zeolite (cf. Fig. 2).

Line c at 4.8 to 5.6 ppm is also ascribed to acidic OH groups of the bridging type but influenced by an additional electrostatic interaction of the hydroxyl proton presumably with neighbouring oxygen atoms of the six-membered ring (corresponding to the shift of the so-called LF-band in infrared spectroscopy). The fact that for the bridging OH groups pointing into the large cavities (HF-band) and into the small cavities (LF-band) separate lines appear in the $^1$H MAS NMR spectra (lines b and c, respectively) excludes the possibility of a fast proton exchange among the four oxygens around an aluminium atom of the zeolite framework.

Line d at 6.5 to 7.0 ppm is due to residual ammonium ions.

Line e at 2.5 to 3.6 ppm represents hydroxyl groups associated with extra-framework aluminium species. Due to the limited space available for these OH groups their $\delta_H$-value will be determined at least to a certain degree by an additional electrostatic interaction of the hydroxyl proton with other oxygen atoms. In accordance with this suggestion, for isolated AlOH groups the chemical shift is much lower and in the interval $-0.5 \text{ ppm} \leq \delta_H \leq 1 \text{ ppm}$ (cf. Fig. 5 and ref. 12).

For POH groups the value of $\delta_H$ is between 1.5 ppm and 4 ppm depending among others on interactions mentioned for line c.

**Concentration of Brönsted Acidic Sites**

With respect to a measurement of the concentration of hydroxyl groups (Brönsted acidic and non-acidic sites) nuclear magnetic resonance spectroscopy has an extremely important advantage compared with infrared spectroscopy since the area of an $^1$H MAS NMR signal is directly proportional to the concentration of the hydrogen nuclei contributing to this signal irrespective of their bonding state so that any compound with a known concentration of hydrogen atoms can be used as a reference (mostly water). In Fig. 5 $^1$H MAS NMR (Bruker MSL 300) and infrared stretching vibration spectra (Digilab FTS-20) are shown for two differently synthesized specimens of SAPO-5 (ref. 13). While the positions of the various signals in the NMR and IR spectra correspond to each other quite well and are in agreement with IR results published recently (ref. 14), there are dramatic differences in the
relative intensities. Hence, even the relative intensity of an OH stretching vibration band cannot be taken as a measure for the concentration of the respective hydroxyl group in contrast to the NMR signal.

**Accessibility of Brønsted Acidic Sites**

The accessibility of hydroxyl groups can be easily determined through a study of the $^1$H MAS NMR spectra after loading the adsorbent with a suitable molecule which however must be fully deuterated in order to avoid an unwanted additional $^1$H NMR signal. Using deuterated pyridine the concentrations of accessible and non-accessible silanol groups of silica could be determined (ref. 15). With the same probe molecule it was also possible to show unambiguously that line (b) in the $^1$H MAS NMR spectra of zeolites H-Y is due to OH groups which are easily accessible to pyridine (ref. 16) and that line (c) is caused by OH groups pointing into the small cavities (LF-band in infrared spectroscopy). Through this direct method it was possible to correct the formerly (ref. 17) postulated wrong correlation (LF-band and line (b)). In Fig. 6 results are shown for a shallow-bed (400 °C) pretreated SAPO-5 unloaded, and after keeping it loaded with deuterated n-hexane for 1 hour at 50 °C. There is no doubt that the 3.9 ppm signal is caused by bridging OH groups which are easily accessible to n-hexane in contrast to the 4.9 ppm signal.

![Fig. 6. $^1$H MAS NMR spectra of a shallow-bed (400 °C) pretreated SAPO-5. a) unloaded, (b) after keeping the sample loaded with deuterated n-hexane for 1 hour at 50 °C.](image-url)
So the higher value of $\delta_H$ must be due to the above mentioned additional electrostatic interaction and we ascribe the signals at 4.9 ppm and 3.9 ppm to bridging OH groups located in the 6- and 12-membered rings of the SAPO -5 structure.

$^1$H MAS NMR STUDIES ON HYDRATED ZEOLITES

$^1$H MAS NMR studies of hydrated zeolites may be complicated by a superposition of three effects:

(i) Plank's mechanism, i.e. the adsorption and dissociation of water molecules on extra-framework multivalent cations like Ca$^{2+}$ with a formation of bridging OH groups. The $^1$H MAS NMR signal of the latter hydroxyls appears at $\delta_H$ values of ca. 0 ppm and 2.8 ppm for calcium ions in the large and small cavities of zeolites Y, respectively (ref. 18). It seems to be noteworthy that for these OH groups eq. (5) is not fulfilled and that a simple interpretation cannot be given at present for this experimental finding.

(ii) Formation of hydroxonium ions at Brønsted acid sites which, however, take part in a fast proton exchange with physically adsorbed water molecules and OH groups. In general, it should be necessary to include in this exchange also water molecules hydrogen-bonded to Brønsted acid sites. These species for which the chemical shift $\delta_H$ is unknown could not be observed in the infrared spectra of rehydrated zeolites (ref. 19). It is possible to determine quantitatively the concentration of hydroxonium ions from the position of the $^1$H NMR signal. In shallow-bed (400 °C) treated zeolites H-Y the probability to find a water molecule in the state of a hydroxonium ion is ca. 0.2 - 0.3 for a rehydration corresponding to one water molecule per bridging OH group (ref. 20).

(iii) Adsorption of water molecules on Lewis acidic sites giving rise to a narrow line at $\delta_H = 6.5$ ppm. In the case of hydrothermally pretreated zeolites H-Y (540 °C, 20 h, 4 kPa water vapour pressure) a concentration of (2 ± 0.5) Lewis acid sites of this type per unit cell could be found. Surprisingly the MAS sideband pattern of the signal at 6.5 ppm could only be explained quantitatively if these Lewis acid sites are not connected with extra-framework aluminium ions. Therefore, we assume that the signal at 6.5 ppm is caused by water molecules adsorbed on threefold coordinated and positively charged silicon atoms of the zeolite framework (ref. 20), i.e. on sites which where proposed by
Kazansky (ref. 21) in order to explain an infrared band at 4035 cm\(^{-1}\) for H\(_2\) adsorbed on a zeolite H-Y activated at 400 °C under deep-bed conditions. Further experimental and theoretical work seems necessary to prove whether threefold coordinated and positively charged silicon atoms in the zeolite framework really exist.

PULSED FIELD GRADIENT (PFG) NMR SELF-DIFFUSION STUDIES

**Xenon Self-Diffusion**

In the last few years, xenon has turned out to be an efficient adsorbate for probing the pore structure and the internal surface of adsorbents by means of NMR spectroscopy (refs. 22-24). The advantage of xenon in comparison to other adsorbates is brought about by the large chemical shifts of \(^{129}\)Xe NMR as a consequence of the large electron shell, and by the fact that xenon as a noble gas leaves the adsorbent structure essentially unaffected. In particular, in zeolite research \(^{129}\)Xe NMR has been successfully applied for probing pore and channel dimensions (ref. 25), cation distributions (ref. 26), reaction sites (ref. 27) and structural peculiarities (ref. 28). Following the pioneering work of J. Fraissard and coworkers, it is now applied in various laboratories (refs. 29-31).

The advent of \(^{129}\)Xe NMR in zeolite research has been accompanied by some controversy in the interpretation of the obtained spectra. In particular, on observing separate lines in the NMR spectra and attributing them to certain states or regions of the xenon atoms within the adsorbate-adsorbent systems, one has to imply that the rate of exchange between these states or regions is less than the difference in the Larmor frequencies of these lines (ref. 32). If the spatial separation of the respective regions is known, an estimate of the diffusivities of the xenon atoms within the sample becomes possible (ref. 33). It is obvious that in such cases the validity of the interpretation of the \(^{129}\)Xe NMR spectra would be substantially supported if the diffusivities could be measured directly.

As yet, owing to their large gyromagnetic ratios, pulsed field gradient NMR (PFG NMR) self-diffusion measurements of adsorbed molecules have been exclusively carried out with \(^1\)H and \(^{19}\)F nuclei. However, experimental progress in the PFG NMR technique (ref. 34) recently enabled the application of \(^{129}\)Xe NMR to a direct measurement of xenon self-diffusion in zeolites (ref. 35).
Fig. 7 provides an example of the measurement of the mean square displacements \( \langle r^2(\Delta) \rangle \) of the xenon atoms in the three different zeolite types NaX, NaCaA and ZSM-5 in dependence on the observation time \( \Delta \). For comparison, the data for methane in ZSM-5 are included. According to Einstein's relation

\[
\langle r^2(\Delta) \rangle = 6 D \Delta
\]

each of the observed linear relations yields a value for the self-diffusion coefficient \( D \). Fig. 8a shows the results of \(^{129}\text{Xe} \) measurements in a representation of the thus determined self-diffusion coefficients in dependence on the sorbate concentrations. The sorbate concentrations are given in atoms per 24 Si(Al)-atoms, corresponding to one channel intersection in the case of ZSM-5 and to one large cavity in the case of the X and A type zeolites. The error bars indicate the uncertainty in the self-diffusion coefficients resulting from the scattering of the experimental data of the mean square displacements. A comparison of the diffusivities of xenon and of methane presented in Figs. 8a and 8b, respectively, shows similar tendencies: For both adsorbates, the mobility in zeolite NaX is found to be higher
than in the other adsorbents. This corresponds to the fact that
the diameters of the windows between the large cavities in the X-
type structure (0.75 nm) are considerably larger than the
corresponding diameters in zeolite NaCaA (0.4...0.5 nm) or the
channel diameters in zeolite ZSM-5 (0.55 nm).

In zeolite A, the degree of calcium exchange determines the
relative number of "open" windows, i.e. the number of windows
unblocked by cations, which thus are easily penetrable for the
adsorbate molecules (refs. 36, 37). A numeric calculation given
in ref. 36 yields that a reduction of the calcium content from
63% to 45% should reduce the diffusivity by a factor of about 2.
The experimental results collected in Table 1 (3rd and 6th column) are in satisfactory agreement with this prediction.

Considering the concentration dependence of the diffusivities, for xenon and methane again identical tendencies are observed: While in zeolites NaX and ZSM-5 the diffusivities are found to decrease monotonously with increasing concentration, for zeolite NaCaA the diffusivities either remain constant or increase slightly with increasing concentration. It has been demonstrated in ref. 38 that concentration dependences of the first type are due to a reduction of the jump length (in NaX) or of the jump rate (in ZSM-5), while the latter behaviour results if mass transfer is controlled by the passage through an "activated" state as represented by the windows in the A type structure. Obviously, the similar size and shape of xenon and methane lead to coinciding dependences.

Probing Surface Barriers by $^{129}$Xe PFG NMR

Besides the possibility of a direct comparison with the "conventional" $^{129}$Xe NMR line shift analysis of the same system, the application of xenon in NMR diffusion studies may offer promising prospects in providing a more sensitive tool for probing the existence of surface barriers. These prospects are based on the expectation that (i) due to their larger kinetic diameter (ca. 0.49 nm, ref. 39) in comparison to methane (ca. 0.41 nm, ref. 39) the xenon atoms should be more affected by any narrowing in the zeolite pore systems, and that (ii) the reduced magnetic interaction of $^{129}$Xe with the environment should allow a significant enhancement of the observation time.

Fig. 9 represents typical plots of the signal intensity (spin echo amplitude) versus the width of the gradient pulses as observed in $^{129}$Xe NMR pulsed field gradient experiments (ref. 40). Obviously, for zeolites NaX and ZSM-5 the obtained NMR data may be satisfactorily represented by the relation (ref. 34)

$$\gamma (\delta, g, \Delta) = \exp \left\{-\frac{\gamma^2 \delta^2 g^2 <r^2(\Delta)>}{6}\right\}$$

with $\gamma$ denoting the attenuation of the NMR signal (spin echo attenuation) under the influence of the field gradient pulses of intensity $g$, width $\delta$ and separation $\Delta$. 
\[ \langle r^2(\Delta) \rangle \] stands for the mean square displacement of the molecules during \( \Delta \), and \( \gamma \) is the gyromagnetic ratio of the considered nuclei. Thus, for the self-diffusion measurements of xenon in zeolites NaX and ZSM-5, the complete information turned out to be contained in the mean square displacements. In Figs. 10a and 10b, these mean square displacements are represented in dependence on the observation time \( \Delta \).

For the A-type zeolites, the observed echo attenuations (cf. Fig. 9c) turned out to be represented by a superposition of two exponentials. One has to conclude, therefore, that the xenon atoms contributing to the NMR signal may be subdivided into two groups having different transport properties.

\[ \Psi(d, \Delta) \] stands for the mean square displacement of the molecules during \( \Delta \), and \( \gamma \) is the gyromagnetic ratio of the considered nuclei. Thus, for the self-diffusion measurements of xenon in zeolites NaX and ZSM-5, the complete information turned out to be contained in the mean square displacements. In Figs. 10a and 10b, these mean square displacements are represented in dependence on the observation time \( \Delta \).

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Following the conception of the NMR tracer desorption technique (ref. 34), these two subgroups result very easily by distinguishing between those diffusants which remain in the interior of the individual crystallites over the whole observation time \((i = \text{intracrystalline diffusion})\) and those which may leave their crystallites and which are able, therefore, to cover large diffusion paths through the intercrystalline space \((1.r. = \text{long range diffusion})\). The echo attenuation is given therefore by

\[
\psi(\delta, g, \Delta) = (1 - \Gamma(\Delta)) \exp\left\{-\frac{\gamma^2 \delta^2 g^2 \langle r^2(\Delta) \rangle_i}{6}\right\} \\
+ \Gamma(\Delta) \exp\left\{-\frac{\gamma^2 \delta^2 g^2 \langle r^2(\Delta) \rangle_{1.r.}}{6}\right\}
\]  

(10)
with $<r^2(\Delta)>_i$ and $<r^2(\Delta)>_{l.r.}$ representing the mean square displacements of the two subgroups, respectively, and with $\Gamma(\Delta)$ denoting the relative amount of the latter subgroup, i.e. the relative amount of atoms leaving the individual crystallites during the observation time $\Delta$. For a discussion of the transport properties of the zeolite crystallites, an echo attenuation of the form of eq. (10) contains two types of information: the mean square displacement $<r^2(\Delta)>_i$ of the atoms in the intracrystalline space as obtained from the slope of the second, slower decaying part of the $\ln \gamma$-vs.-$\delta^2$ plot, and the quantity $\Gamma(\Delta)$, resulting from the relative contributions of the two constituents. Both quantities are represented in Figs.10c and 11, respectively, in dependence on the observation time. It is obvious, that the function $\Gamma(\Delta)$ contains the same information as a conventional tracer desorption curve (ref. 34). In previous NMR self-diffusion studies with methane, in general echo attenuations of the type of Fig. 9c have been observed (ref. 34). Such a behaviour has again been found on investigating the methane diffusivities in the zeolite specimens applied in this study.

For a comparison of the NMR tracer desorption curves with each other as well as with other transport related properties it is useful to introduce a mean intracrystalline life time

$$\tau_i = \int_0^\infty (1 - \Gamma(\Delta)) d\Delta$$

(11)

This definition coincides with that of the first statistical moment of an uptake curve (ref. 41). If the tracer exchange is controlled by intracrystalline diffusion it can be shown that
for crystallites of spherical shape $\tau_i$ is equal to

$$\tau_i^D = \frac{<R^2>}{15 D_i} \quad (12)$$

with $<R^2>$ and $D_i$ denoting the mean square radius of the crystallites and the intracrystalline self-diffusion coefficient, respectively (refs. 34, 41). Numerical values of the relation between $D_i$ and $\tau_i^D$ for crystallites with the shape of parallelepipeds are given in ref. 53.

According to Einstein's relation (eq. (8)) which is valid for self-diffusion in homogeneous systems, the intracrystalline self-diffusion coefficient $D_i$ may be easily determined from the slope of the representation of the mean square displacement versus the observation time $\Delta$, provided that the mean square displacements $<r^2(\Delta)>$ are still smaller than the mean square radii of the crystallites.

**TABLE 1**

Values for the intracrystalline self-diffusion coefficients $D_i$ and the intracrystalline mean life time $\tau_i$ of xenon and methane in various specimens of zeolites NaCaA, NaX and ZSM-5 at 293 K and a sorbate concentration of about 3 methane molecules or xenon atoms per 24 Si(Al) atoms.

<table>
<thead>
<tr>
<th>Adsorbents and the mean crystallite diameters in μm</th>
<th>D_i (m^2·s⁻¹)</th>
<th>τ_i (ms)</th>
<th>r_i (μm)</th>
<th>Methane D_i (m^2·s⁻¹)</th>
<th>τ_i (ms)</th>
<th>r_i (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCaA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca-cont.</td>
<td>45%</td>
<td>13</td>
<td>1.0±0.3</td>
<td>3.0±1.0</td>
<td>80±20</td>
<td>1.0±0.3</td>
</tr>
<tr>
<td></td>
<td>63%</td>
<td>20</td>
<td>1.5±0.4</td>
<td>4.0±1.0</td>
<td>45±10</td>
<td>1.5±0.4</td>
</tr>
<tr>
<td></td>
<td>80%</td>
<td>5</td>
<td>1.5±0.4</td>
<td>0.4±0.2</td>
<td>25±8</td>
<td>1.5±0.4</td>
</tr>
<tr>
<td>NaX</td>
<td>50</td>
<td>5.0±1.5</td>
<td>8.0±2.0</td>
<td>15±10</td>
<td>20±5</td>
<td>2±1</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>5.0±1.5</td>
<td>1.5±0.5</td>
<td>5±3</td>
<td>20±5</td>
<td>0.4±0.2</td>
</tr>
<tr>
<td>ZSM-5(a)</td>
<td>25</td>
<td>0.9±0.3</td>
<td>11±3</td>
<td>&gt;40</td>
<td>4±1</td>
<td>3±1</td>
</tr>
<tr>
<td>ZSM-5(b)</td>
<td>100x30x30</td>
<td>0.9±0.3</td>
<td>160±40</td>
<td>&gt;70</td>
<td>4±1</td>
<td>45±10</td>
</tr>
</tbody>
</table>

Table 1 gives a summary of the self-diffusion coefficients thus determined for sufficiently short observation times from the
presentations of Fig. 10 and from corresponding results for methane. Furthermore included are values for the intracrystalline mean life time $\tau_i$ and the quantity $\tau_i^D$ calculated from $D_i$ and $<R^2>$ via eq. (12).

For those adsorbents (ZSM-5 and NaX) which did not reveal a two-phase behaviour in the $\ln \gamma$-vs-$\delta^2$ plots, the values for the intracrystalline mean life time were estimated by realizing that the rms displacements can only exceed the mean crystallite radii by a noticeable value if during the observation time $\Delta$ a substantial part of the adsorbate molecules or atoms have left their crystallites, i.e. if the observation time $\Delta$ is at least of the order of the magnitude of the intracrystalline mean life time $\tau_i$. Thus, for NaX the intracrystalline mean life times have been put equal to those observation times, for which the mean square displacements coincided with the mean square radii. For both ZSM-5 specimens even for the largest observation times the mean square displacements remained smaller than the crystallite dimensions, so that $\tau_i$ must be assumed to be larger than the maximum observation time $\Delta$.

Direct information about the existence of surface barriers is provided by a comparison between the values for the intracrystalline mean life time $\tau_i$ and the quantity $\tau_i^D$ which represents the minimum possible life time calculated via eq. (12) from the intracrystalline diffusivities. Table 1 shows that for methane these two quantities are in reasonable agreement. One has to conclude therefore that molecular exchange is mainly controlled by intracrystalline diffusion and that, consequently, possible surface barriers can only be of minor importance. This result is in agreement with the finding of previous studies (ref. 33) that on applying methane as a probe molecule, in zeolite NaCaA surface barriers do only occur after coking or hydrothermal pretreatment. It appears from Table 1, that xenon reveals a completely different situation: In all NaCaA specimens as well as in the considered ZSM-5 specimen with the smaller crystallites, xenon desorption is significantly retarded by influences different from intracrystalline diffusion, i.e. by an additional transport resistance on the external surfaces or in a surface layer of the crystallites. This result may be related to the larger kinetic diameter of the xenon atoms, making them suitable for probing the surface permeability of adsorbents with limiting
free diameters of this order of magnitude (0.4...0.5 nm for NaCaA, ca. 0.55 nm for ZSM-5). It is not unexpected that for zeolite NaX, also with xenon no surface resistances are observed, since the increase of the diameter of the probe particle in comparison to methane is still insignificant compared with the limiting free diameters of NaX (ca. 0.75 nm). The experimental finding that the existence of a surface barrier may depend on the sort of the diffusing particles reflects an essential feature of the surface barrier: Though being determined by structural or energetic peculiarities at the crystallite surface (cf. ref. 43), the surface barrier can only be defined in connection with a certain probe molecule. This statement becomes self-evident on considering the reciprocal of the surface barrier, the surface permeability which - as the diffusity - must be a function of the diffusant. It is possible that the low literature data for intracrystalline diffusion of xenon in zeolite NaCaA deduced from uptake measurements (1x10^-14 m^2/s (ref. 44), 1.2x10^-11 m^2/s (ref. 45) or 8x10^-11 m^2/s (ref. 46), determined for a loading of about 1 atom per cavity and at temperatures of about 300 K) are caused by the significant surface barriers for this system.

**Diffusion Anisotropy**

Among the problems connected with new zeolite structures, a possible anisotropy of self-diffusion deserves special consideration. Since the PFG NMR method allows the observation of molecular migration with respect to the direction of the applied field gradient (ref. 34) which may be easily changed by applying suitable gradient coil arrangements, favourable conditions exist for the investigation of diffusion anisotropy. Literature provides various examples of such diffusion studies with liquid crystals and membranes where molecular diffusion proceeds in a well oriented sample of macroscopic dimensions.

A completely different situation exists if one considers molecular diffusion in crystalline catalysts and adsorbents. Being of the order of a few micrometers, the diameters of the individual crystallites are too small to allow the conventional method of studying diffusion anisotropy. However, also in this case PFG NMR may provide information about the extent of diffusion anisotropy. This information is contained in the shape of the NMR spin echo attenuation versus the gradient intensity, which in the case of isotropic diffusion yields a simple
exponential dependence (cf. eq. (9)), but which in the case of anisotropic diffusion may be shown to obey the relation (refs. 34, 47)

\[ \gamma(C, \theta, \phi) = \exp \left\{ -C \left[D_{xx} \cos^2\theta \sin^2\phi + D_{yy} \sin^2\theta \sin^2\phi + D_{zz} \cos^2\theta \right] \right\} \]

(13)

where the quantities \( D_{xx}, D_{yy} \) and \( D_{zz} \) denote the principal values of the diffusion tensor. The orientation of the field gradient with respect to the principal axes system is represented by the angles \( \theta \) and \( \phi \). The quantity

\[ C = \gamma^2 g^2 \delta^2 (\Delta - \delta/3) \]

(14)

is determined by the parameters of the pulse sequence, explained in connection with eq. (9).

In the case of powder samples, i.e. of randomly oriented crystals, averaging over all possible directions leads to the expression

\[ \langle \gamma(C) \rangle = \frac{1}{4\pi} \int_{-1}^{1} \exp\left\{ -C \left(D_{zz} \cos^2\theta + D_{yy} \sin^2\theta \right) \right\} I(\theta) d(\cos\theta) \]

(15)

with

\[ I(\theta) = \int_{0}^{2\pi} \exp\left\{ -C \sin^2\phi (D_{xx} - D_{yy}) \cos^2\phi \right\} d\phi . \]

As an example, Fig. 12 shows the result of a numerical calculation of eq. (15) for an axial symmetric diffusion tensor (ref. 47). It is obvious, that for \( D_{zz} > D_{yy} \), the sensitivity of the PFG NMR method with respect to deviations from isotropic diffusion is higher than in the reverse case.

Fig. 13 compares the echo attenuation obtained in PFG NMR measurements of methane diffusion in ZSM-5 (ref. 47) with the theoretical dependence calculated from eq. (15) with the tensor elements \( D_{xx} (= 1.22 \times 10^{-9} \text{ m}^2\text{s}^{-1}) \), \( D_{yy} (= 14.9 \times 10^{-9} \text{ m}^2\text{s}^{-1}) \) and \( D_{zz} (= 1.22 \times 10^{-9} \text{ m}^2\text{s}^{-1}) \) as determined in recent Molecular Dynamics calculations (ref. 48). It turns out that the calculated pattern is already beyond the range compatible with the experimental behaviour, so that one has to conclude that the influence of anisotropy is overestimated in the Molecular Dynamics calculations.
Fig. 12. Spin echo attenuation due to anisotropic diffusion in randomly oriented crystallites with axial symmetry for $D_{||} > D_\perp$ and $D_{||} < D_\perp$ as a function of the product of the field gradient intensity parameter $C$ defined by eq. (14) and the quantity $\langle D \rangle = (D_{xx} + D_{yy} + D_{zz})/3$.

Fig. 13. Spin echo attenuation of the proton NMR signal of methane adsorbed in an assembly of ZSM-5 crystallites at 23 °C (○), and comparison with the theoretical curve obtained from eq. (15) with the tensor elements $D_{xx} = 3.59 \times 10^{-9}$ m$^2$ s$^{-1}$, $D_{yy} = 14.9 \times 10^{-9}$ m$^2$ s$^{-1}$ and $D_{zz} = 1.22 \times 10^{-9}$ m$^2$ s$^{-1}$ (ref. 48) (---), respectively.

**Limits of Application**

The versatility of the PFG NMR method to study diffusion processes in zeolites and its successful application to numerous problems in zeolite science and technology (cf. ref. 42) implies the temptation to apply it also under such conditions where
extreme caution is recommended. This is in particular true for heterogeneous or, in general, multi-phase systems, where the contribution of the various phases to the spin echo is controlled by their nuclear magnetic relaxation properties (ref. 52) or, with other words, where with increasing observation time $\Delta$ the contribution of the phases with the largest relaxation times will become more and more dominant. So it may happen that by formally applying the PFG NMR method one determines the diffusivity of a trifling amount of very mobile molecules (occurring e.g. in tracks within the zeolite crystallites or on their outer surfaces) rather than that of the phase represented by most of the adsorbed molecules. It is most likely that the surprisingly high values for the diffusivity of benzene in silicalite which were recently determined using PFG NMR (ref. 49) are due to this effect.

In order to exclude the possibility of such artifacts in NMR self-diffusion measurements, a modification of the traditional rf pulse sequence has been proposed (ref. 50). It allows an unambiguous check whether the obtained diffusivities are in fact unaffected by the influence of a trifling amount of very mobile molecules.

**NMR Tracer Exchange**

The lowest diffusivities accessible by PFG NMR in zeolites are of the order of $10^{-11} \ldots 10^{-12} \text{ m}^2\text{s}^{-1}$ (refs. 34, 42). However, for systems with diffusivities below this limit an alternative NMR method for studying mass transfer may be applied (ref. 52). Under such conditions and for crystallite diameters $\gtrsim 10 \mu\text{m}$, the rates of molecular adsorption or desorption become small enough so that it is possible to study these processes by an analysis of the intensity of the NMR signal. As an example, Fig. 14 shows the arrangement of such an experiment for the investigation of the rate of molecular exchange for benzene in H-ZSM-5 with the surrounding atmosphere (refs. 52, 53). The exchange experiment is started by crushing the glass vial using the glass cylinder as a striker: The hydrogen form of benzene initially adsorbed on the zeolite will then be exchanged by the deuterated compound stemming from the gas phase.
Fig. 14. Experimental arrangement for the NMR tracer exchange measurements.

Fig. 15. Comparison of the self-diffusion coefficients obtained from NMR tracer exchange measurements (● 293 K; △ 386 K) with values calculated from sorption uptake experiments (○ 303 K; □ 363 K; △ 393 K) using eq. (17). Both experimental series have been carried out with the same silicalite specimens.

This exchange process may be directly recorded via the intensity of the $^1$H NMR signal. It is shown in Fig. 15 that the self-diffusivities determined from these experiments are in satisfactory agreement with the results of uptake experiments, when the relation between the coefficient of diffusion ($D_d$) which
follows from the uptake experiment and the coefficient of self-diffusion \( (D) \) is assumed to be (ref. 54)

\[
D = D_0 \frac{\ln c(p)}{\ln p}
\]

(17)

with \( c(p) \) denoting the sorbate concentration in equilibrium with the sorbate pressure \( p \). Clearly, the experimental arrangement as shown in Fig. 14 may be easily modified to allow both adsorption or desorption experiments (in this case, the sorbate pressure in the surrounding atmosphere must be much greater or much less than over the adsorbent within the glass vial) and counter diffusion experiments. Taking advantage of high resolution NMR spectroscopy (ref. 55), such experiments (e.g. the observation of the exchange between aliphatic and aromatic compounds) may even be carried out without the necessity of applying deuterated compounds.

**TABLE 2**

Comparison of PFG NMR diffusivities with the results of quasi-elastic neutron scattering and Molecular Dynamics simulations as well as with the results of macroscopic non-equilibrium measurements (uptake, zero length column, permeation). Data refer to the limit of small sorbate concentrations, the unit is \( \text{m}^2\text{s}^{-1} \).

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>NaCaA</th>
<th>NaX</th>
<th>Na-ZSM-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorbate</td>
<td>methane ethane</td>
<td>ethylene benzene</td>
<td>methane xenon</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>300 250</td>
<td>300 458</td>
<td>250 293</td>
</tr>
<tr>
<td>PFG NMR</td>
<td>(10^{-9}) (6\times10^{-11}) ref. 37 ref. 37</td>
<td>(1.5\times10^{-9}) (8\times10^{-10}) ref. 61 ref. 63</td>
<td>(7\times10^{-9}) (4\times10^{-9}) ref. 67 ref. 35</td>
</tr>
<tr>
<td>Neutron Scattering</td>
<td>(6\times10^{-10}) ref. 59</td>
<td>(3\times10^{-10}) (7\times10^{-10}) ref. 62 ref. 64</td>
<td>(5\times10^{-9}) ref. 68</td>
</tr>
<tr>
<td>Molecular Dynamics</td>
<td></td>
<td></td>
<td>(=5\times10^{-9}) (2\times10^{-9}) ref. 48 ref. 70 ref. 71</td>
</tr>
<tr>
<td>Uptake</td>
<td></td>
<td>(3\times10^{-10}) ref. 65</td>
<td>(8\times10^{-11}) ref. 46</td>
</tr>
<tr>
<td>Zero length column</td>
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<td></td>
</tr>
<tr>
<td>Permeation</td>
<td></td>
<td>(8\times10^{-12}) ref. 66</td>
<td></td>
</tr>
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</table>
Comparison of PFG NMR Diffusivities with the Results of other Techniques

The comparison of the diffusivities determined in PFG NMR measurements with the results of other techniques has concerned zeolite workers over more than a decade (refs. 56, 57). While there is still some controversy whether in general the results of uptake (i.e. of non-equilibrium) measurements after applying eq. (17) should or should not agree with the NMR self-diffusivities (cf. ref. 52), in the last few years by other microscopic techniques (neutron scattering, $^2$H NMR) as well as by Molecular Dynamics calculations a large amount of diffusivity data has been provided which are in remarkable agreement with the results of PFG NMR measurements. Some of these results are compared in Table 2.

REFERENCES

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