New options for measuring molecular diffusion in zeolites by MAS PFG NMR

André Pampel *, Moisés Fernandez, Dieter Freude, Jörg Kärger

Fakultät für Physik und Geowissenschaften, Universität Leipzig, Linnéstraße 5, 04103 Leipzig, Germany

Received 25 February 2005; in final form 10 March 2005
Available online 7 April 2005

Dedicated to Professor Dieter Michel on the occasion of his 65th birthday

Abstract

Combination of pulsed field gradient (PFG) NMR with magic-angle spinning (MAS) NMR is demonstrated to have remarkable advantages in comparison with conventional PFG NMR, if applied to diffusion measurements in beds of nanoporous particles, notably zeolites. These advantages are based on the effect of line narrowing and concern: (i) a prolongation of the intervals during which the magnetic field gradients may be applied and a corresponding enhancement in the sensitivity towards small molecular displacements, and (ii) an enhanced resolution in the chemical shift scale. Both options are illustrated by measuring the diffusion coefficient of n-butane adsorbed in silicalite-1.

© 2005 Elsevier B.V. All rights reserved.

1. Introduction

NMR diffusion measurements are based on recording the differences,

$$\Delta \varphi = \gamma g \frac{z_2 - z_1}{2},$$

in the precessional phases $\gamma g z_i$ of any individual spin of the nuclei under study, accumulated during the application of the first and second gradient pulses, i.e., during the (total) time interval $\delta$ during which an additional, inhomogeneous field $B_{add} = gz$ is superimposed upon the constant magnetic field $B_0$. The quantities $z_i$ and $\gamma$ denote the $z$ coordinate (pointing into the direction of the magnetic field gradient) at the time of the first ($i = 1$) and second ($i = 2$) pulses, and the gyromagnetic ratio of the spin under study, respectively [1–3]. The application of this measuring principle to guest molecules in nanoporous solids [4], notably zeolites [5], has revolutionized our understanding of the transport properties of this type of materials with extreme relevance for both fundamental research and application [6].

Because the amplitude $g$ of the magnetic field gradient pulses is limited by the specification of the given amplifier for the gradient pulses, sensitivity enhancement towards smaller displacements ($z_2 - z_1$) has to be based on an enhancement of the total time $\delta$ of gradient application. Long magnetic field gradient pulses, in turn, imply correspondingly long periods of time within the PFG NMR pulse sequences, during which nuclear magnetization is oriented in the plane perpendicular to the direction of the magnetic field. The application of magnetic field gradient pulses of long duration $\delta$ is limited, therefore, by the rate of the decay of transverse magnetization. Even if applying very strong field gradients and thus reducing $\delta$, the induction of eddy currents necessitates a delay between applications of gradient pulses and detection or subsequent radio frequency (r.f.) pulses.

In heterogeneous systems, there are essentially two major mechanisms giving rise to a decay of the transverse proton magnetization, viz. (i) a sustainable dipolar interaction between the spins under consideration and
(ii) differences in the internal magnetic fields, brought about by sample heterogeneities and the consequent heterogeneities in the susceptibility. Those disturbing influences, which will also result in reduced spectral resolution, can be drastically reduced by magic-angle spinning (MAS). Modern MAS probes are also equipped with PFG capabilities [7] enabling the use of MAS in combination with PFG NMR for investigations of systems that are hardly accessible by standard techniques without sample spinning [8–13].

The present letter describes investigations that mainly profit from the elimination of the disturbing influence of the inhomogeneity of the sample susceptibility playing a decisive role for PFG NMR diffusion measurements of molecules in beds of zeolites.

2. Susceptibility effects on NMR signals of adsorbed molecules

The large line broadening observed in particular in the $^1$H NMR spectra of molecules adsorbed in zeolites [14] is not only caused by the restricted molecular mobility but originates also from the presence of random local magnetic fields within the polycrystalline materials. This is particularly true in the case of those zeolites, whose crystallloid shape notably deviates from cubic symmetry. Zeolites of type MFI (viz. ZSM-5 and its all-silica analog silicalite-1) are most prominent examples [5,15] with great relevance in heterogeneous catalysis. It is this effect of line broadening which so far has most decisively limited the range of applicability of PFG NMR diffusion measurement, prohibiting in particular the extension of the range of measurement towards long-chained guest molecules [16]. A significant enhancement in resolution of the spectra of molecules sorbed in zeolites may be achieved when the induced static local magnetic fields are averaged out by the application of MAS. This type of exploiting the benefit of MAS was introduced in previous publications [17,18]. Here, we summarize the details that are necessary to understand the ideas outlined in this Letter.

In general, NMR spectra of polycrystalline materials are broadened by anisotropic interactions such as dipolar coupling, chemical shift anisotropy, quadrupolar coupling, and susceptibility effects. Depending on their strength and the achievable rotation frequency, MAS can reduce or even completely suppress these effects during the time course of an NMR experiment. If, in addition to the motion of the spins by the sample rotation, thermal motions are stochastically modulating the NMR interactions, both effects will compete in their influence on the time evolution of the spin system.

A rigorous treatment for the influence of thermal motion upon line shape of MAS spectra broadened by dipolar coupling or chemical shift anisotropy, was suggested by Fenzke et al. [19]. It was shown by Roland and Michel [18] that this treatment is also valid for the description of susceptibility-broadened $^1$H NMR spectra of organic molecules adsorbed in zeolites.

The observed NMR signal, the free induction decay (FID), is generally described by the relation,

$$S(t) = \Phi(t) \exp(i\omega_0 t),$$

where $\omega_0$ is the Larmor frequency.

The phase sensitive detected FID is given by

$$\Phi(t) = \exp\left\{ -\frac{2M_2}{3} \left[ J(\omega_c t) + \frac{1}{2} J(2\omega_c t) \right] \right\}. \tag{4}$$

$M_2$ denotes the second moment of the considered NMR interaction.

In this notation, $J(\omega_c t)$ is the spectral density function describing the combined effect of thermal motion and sample rotation at $\omega_c$.

$$J(\omega_c t) = \frac{t\tau_c}{(1 + (\omega_c t)^2)^2} \times \left[ 1 - \exp\left(-t/\tau_c\right) \cos(\omega_c t) \right] \frac{2\omega_c \tau_c^3}{(1 + (\omega_c t)^2)^3} \times \exp\left(-t/\tau_c\right) \sin(w_c t). \tag{5}$$

In order to evaluate whether the described assumptions are valid for the investigation of the system under study, we have measured additional MAS NMR spectra of ethane sorbed in silicalite-1 at very low rotation frequency. At slow sample spinning, this signal resolves into one centerband and sidebands whose intensities follow the envelope formed by the non-spinning spectra. An NMR signal was calculated using Eq. (5) and the resulting spectrum is compared with the experimental spectrum. Ethane was used here because its spectrum contains only a single line, which simplifies the analysis in comparison with $n$-butane whose diffusion properties are studied below. The results are shown in Fig. 1. The simulations meet the major properties of the experimentally observed spectrum, although some differences are observable. The width of the signal envelope is fairly well predicted. Furthermore, as it is always the case if thermal motion is present, the line shape observed is varying with sideband order and can be approximated by a superposition of Gaussian and Lorentzian line shape [18].

A second moment $M_2 = 50 \times 10^6 \text{ s}^{-2}$ was calculated that is 2–3 time larger compared to the value of $M_2$ found for 1-butene sorbed in NaX zeolite [18]. This might tentatively be attributed to the fact that deviations
from cubic symmetry in the MFI-type zeolites under study are much more pronounced. The correlation time \( \tau_c = 28 \times 10^{-3} \) s characterizing the thermal motion is almost an order of magnitude larger than observed for 1-butene in NaX. However, the values given here must not be overemphasized. A more quantitative analysis requires a detailed knowledge of the correlation function describing the motion of the sorbed molecules, whose simplest form has been used here. Also, the model does not predict the inequality of the intensities of the first-order sidebands. Obviously, the magnetic susceptibility tensor is not axially symmetric, which is understandable considering the shape of the silicalite-1 crystallites used in this study [17]. Furthermore, it cannot be excluded that residual, i.e., partially averaged dipolar coupling between the protons is present that also would have been considered in the spectral density function. Nevertheless, the broadness of the spectra without MAS and thus, the fast decay of the transverse magnetization can be explained now.

Using the parameters obtained from the sideband analysis, it is possible to estimate the decay of transverse proton magnetization of ethane sorbed in silicalite-1 for observation in PFG experiments without MAS by means of Eq. (5) with \( \omega_c = 0 \). During a time delay of 300 \( \mu \)s, a value that is easily met by PFG investigations using the 13-interval pulse sequence by Cotts et al. [20], the transverse magnetization is already decaying to just 10% of its equilibrium value, which makes experiments rather difficult and time-consuming. The stochastic modulation of the broadening mechanism explains why a 180° pulse cannot refocus it, which would be possible for investigations of real solids.

3. PFG MAS experiments for observing \( n \)-butane diffusion in silicalite-1

Depending on the relation between the observed root mean square displacements \( \langle r^2(t) \rangle^{1/2} \) and the mean crystallite diameter \( d \), PFG NMR is able to measure the coefficients of both intracrystalline diffusion \( \langle r^2(t) \rangle^{1/2} \ll d \) and long-range diffusion \( \langle r^2(t) \rangle^{1/2} \gg d \) [4]. While long-range (i.e., the rate of bed-) diffusion is easily accessible by conventional techniques like uptake or release measurements, the ability to measure intracrystalline diffusion turned out to be a particular virtue of PFG NMR. It is this mode of diffusion, which is determined by the architecture of the intracrystalline pore system. In the present study, with \( n \)-butane, we have therefore selected a guest molecule suitable for this purpose. Ethane, e.g., turned out to be so mobile that under the given experimental conditions only the observation of long-range diffusion would have been possible, while for the longer alkanes the mobility soon drops below those values, for which the displacements during the observation time turned out to be below the limit of measurability [16].

Samples were pre-treated by heating 8 mm deep layers of zeolite silicalite-1 in glass tubes 3 mm outer diameter at a rate of 10 K h\(^{-1}\) under vacuum. After maintaining the samples at 673 K and less than 10\(^{-2}\) Pa for 24 h, they were loaded under vacuum at room temperature with six molecules per unit cell and then sealed to enable stable magic angle sample spinning. All NMR experiments were performed at room temperature on a Bruker AVANCE 750 spectrometer operating at 749.98 MHz for \( ^1 \)H. A Bruker 4 mm HR-MAS probe, equipped with \( ^1 \)H, X and \( ^2 \)H lock channels and pulsed field gradient capabilities, was used. The typical 90° pulse length was about 10.5 \( \mu \)s. The maximum gradient strength achievable at this system is 0.54 T m\(^{-1}\). The gradient was calibrated by measuring the water diffusion coefficient. Diffusion measurements were performed using the stimulated echo sequence with bipolar gradient pulses and eddy current delay before detection [21]. A delay of about 500 \( \mu \)s between gradient pulse and subsequent r.f. pulse was set. The delay was adjusted to ensure that the duration of the dephasing and rephasing period is a multiple of the rotor period. Gradients were applied in sine-shaped manner with duration \( \delta \) of 2 ms each and consecutively increasing.
the strength up to 80% of the maximum value. The repetition time was set to 2 s. (Fig. 2).

Fig. 3 shows the $^1$H NMR spectra of $n$-butane adsorbed on silicalite-1 at a loading of six molecules per unit cell. The spectrum recorded without applying magic angle spinning is broad and featureless, i.e., it is impossible neither to see any characteristic $n$-butane signals nor to check the sample for undesired impurities. At low rotation frequency, the sideband pattern observed is in qualitative agreement with those shown in Fig. 1. At a rotation frequency of 10 kHz, the spectrum of $n$-butane is observed with a residual line width of 44 and 73 Hz of the signals of the CH$_3$- and CH$_2$-groups, respectively. The performance of the PFG NMR diffusion experiment is straightforward under these conditions. The results obtained are shown in Fig. 3. The

![Fig. 2. $^1$H MAS NMR (observation frequency 749.98 MHz) spectra of $n$-butane adsorbed in silicalite-1 observed at room temperature. (a) Spectrum observed without sample spinning. (b) Spectrum observed using MAS at 1 kHz rotation frequency. (c) Spectrum observed using MAS at 10 kHz rotation frequency.](image)

![Fig. 3. (a) Spin-echo attenuation versus gradient intensity of the CH$_3$ line of the $n$-butane signal. (b) Semi-logarithmic plot of the spin–echo attenuation versus squared gradient intensity of the CH$_3$ line of the $n$-butane signal. The lines represent the best fit. Observation time $\Delta = 30$ ms. Duration $\delta = 2$ ms for each gradient, respectively.](image)
total duration of this experiment was 1.5 h. The diffusion coefficient calculated from the decay of integrals of the signal of the CH₃ peak is $3.17 \times 10^{10}$ m² s⁻¹ and is within the range of the values obtained by previous diffusions studies of this system by both PFG NMR [16] and quasi-elastic neutron scattering [22].

4. Conclusions and outlook

For the first time, PFG NMR and MAS NMR have been combined to measure intracrystalline zeolitic diffusion. It has been illustrated by model calculation and demonstrated experimentally that in this way line broadening due to the susceptibility heterogeneities inevitable in such systems may be dramatically reduced. Thus, one of the most decisive limitations of the application of PFG NMR to zeolitic host–guest systems, viz. the heterogeneity-induced line broadening and the associated rolling back of the total time over which the magnetic field gradient may be applied, may be overcome.

The attainable spectral resolution clearly depends on the conditions of the system under study. Sometimes, line widths in the range of as little as 1–2 Hz were observed. Under such fortunate circumstances even DOSY [23] experiments for characterizing complex mixtures adsorbed to zeolites seem to be possible. For technical reasons, the gradient strength available at standard HR-MAS probes is limited, thus enforcing the use of rather long gradient pulses and, for the same reasons, long eddy current delays are necessary. Recently, it was shown, how the strength of the gradients and the general performance of PFG MAS experiments could be improved by using a micro-imaging device in combination with a MAS probe [24]. The gradient strength of 2.6 T m⁻¹ achieved there will enable recording of much slower diffusion processes over shorter observation times, facilitating in this way the exploration of intracrystalline diffusion phenomena.

Acknowledgements

We are obliged to Professor Dieter Michel for countless stimulating discussions and manifold advice. Support by the German Science Foundation (DFG), the Max–Buchner–Stiftung, and the Fonds Chemischer Industrie is gratefully acknowledged. We thank Dr. Wolfgang Schmidt (Max-Planck-Institut für Kohlenforschung) for supplying us with the zeolite material used in this study.

References