1H NMR Signal Broadening in Spectra of MFI Type Zeolites

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1. Introduction

Isotropic mobility of molecules adsorbed in zeolites should completely average out spin interactions which cause line broadening in nuclear magnetic resonance (NMR) spectroscopy. But it is well-known that additional application of magic-angle spinning (MAS), Hahn-Echo (HE) or Carr-Purcell (CPMG) pulse sequences reduces the effective line broadening in such systems. This is essential for pulsed field gradient (PFG) NMR experiments, since the cutback of line broadening corresponds to a prolongation of the effective transverse relaxation time $T_2$, which increases the sensitivity of NMR diffusometry. Short relaxation times limit the duration of the gradient pulses in PFG NMR.

2. Results of $^1$H NMR

For zeolite types like faujasite, which belong to a cubic symmetry group, MAS, CPMG or HE effect a drastic prolongation of $T_2$, whereas under the influence of a non-cubic symmetry like MFI significantly shorter relaxation times are obtained, see Tab. 1.

<table>
<thead>
<tr>
<th>Zeolite Type</th>
<th>$T_2^{\text{FID}}$/ms</th>
<th>$T_2^{\text{CPMG}}$/ms</th>
<th>$T_2^{\text{HE}}$/ms</th>
<th>$T_2^{\text{MAS}}$/ms</th>
</tr>
</thead>
<tbody>
<tr>
<td>silicalite-1/methane</td>
<td>0.242</td>
<td>12.5</td>
<td>1.02</td>
<td>8.8</td>
</tr>
<tr>
<td>silicalite-1/n-butane</td>
<td>0.137</td>
<td>8.0</td>
<td>0.91</td>
<td>6.5</td>
</tr>
<tr>
<td>silicalite-1/n-hexane</td>
<td>0.142</td>
<td>10.4</td>
<td>1.24</td>
<td>5.5</td>
</tr>
<tr>
<td>Na-X/n-butane</td>
<td>0.518</td>
<td>62.0</td>
<td>1.65</td>
<td>14.4</td>
</tr>
</tbody>
</table>

Table 1: Relaxation times $T_2$ of adsorbed molecules. CPMG measurements were performed with a $\pi$-pulse-distance of $2\tau = 200$ $\mu$s. The MAS frequency was 10 kHz. Samples of silicalite-1 were loaded with one molecule per channel intersection, the faujasite sample with two molecules per supercage.

Fig. 1: Plot of the echo decay of the $^1$H NMR signal of n-butane applying CPMG pulse sequences with different $\pi$-pulse distances of $2\tau$ from 20 $\mu$s to 1000 $\mu$s. Silicalite-1 was loaded with one n-butane molecule per channel intersection. Observation time intervals range from 0 to 10 ms. Extrapolating the curves to 0 ms, we obtain relative intensities of 99% for $\tau = 10$ $\mu$s, 90% for 50 $\mu$s, 59% for 100 $\mu$s, 36% for 250 $\mu$s, and 17% for $\tau = 500$ $\mu$s.

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3. Results of static $^2$H NMR

Concluding the line spacing 17.25 kHz in the 2H NMR spectrum of CD$_2$ groups, we got an order parameter of $17.25 / 60 = 0.29$ or $-0.29$.

4. Snapshots of molecular simulation

The order parameter can be obtained by molecular simulation. For n-butane in the zeolite faujasite which has a cubic symmetry, we obtain the expected order parameter zero. But for a loading of 4 butane molecules per unit cell in zeolite silicalite-1, an order parameter of $-0.40$ is obtained at a temperature of 300 K. This is not far from the value $-0.29$ obtained by $^2$H NMR.

5. Conclusions

The present studies allow the conclusion that the observed slower decaying weak component is part of the signal of molecules with a uniform mobility and can be explained by NMR relaxation effects. For linear molecules like n-alkanes the mobility in a confined environment can be anisotropic. For example, very fast rotation of linear n-alkanes around one rigid axis reduces the NMR linewidth compared to the immobile molecule by a factor of only two, whereas the linewidth should be reduced to zero in the case of fast isotropic rotation. Anisotropy of the mobility should not be expected for methane in any zeolite and also not for linear n-alkanes in zeolites of a cubic symmetry. For the latter, the molecule jumps between different adsorption sites in such a way that the molecular axis takes all orientations with respect to the external magnetic field with the same probability. This averages out all intramolecular dipolar interactions. However, for n-alkanes in zeolite silicalite-1 an adsorption in the channels is expected, and the channel system does not provide a cubic symmetry. With other words, in one crystallite the molecular orientation is not isotropically distributed. The static linewidth of alkane is some 10 kHz, and also a slight deviation from the cubic symmetry of orientation possibilities can cause a residual dipolar linewidth of about 1 kHz. Now we are only left with the explanation, why methane, with tetrahedral symmetry, also shows an anisotropic behavior in silicalite-1. This can be explained by the additional intermolecular dipolar interaction between the adsorbed molecules. It depends on the symmetry of adsorption sites, which is subjected to a cubic and non-cubic symmetry in zeolites faujasite and silicalite-1, respectively.

Fig. 2: Static 2H NMR spectra of selectively observed CD$_2$ and CD$_3$ groups of fully deuterated n-butane adsorbed in MFI type zeolites. Line fits yield quadrupole coupling constants of 11 kHz and 23 kHz and asymmetry parameters $\eta = 0.4$ and $\eta = 0.24$ for CD$_2$ and CD$_3$ groups, respectively.