## **Supplementary Material**

<sup>2</sup>H-solid state NMR and DSC study of isobutyric acid in mesoporous silica materials

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# 2. Samples and preparation

# 2.1. <sup>2</sup>H-NMR powder spectra

A detailed description of the theory of solid state <sup>2</sup>H-NMR is given in the textbooks<sup>1, 2</sup> which is briefly summarized here.

The leading interaction in <sup>2</sup>H solid state NMR is the quadrupolar interaction. In the usual high field approximation, the first order quadrupolar interaction is characterized by the Hamiltonian

$$\hat{H}_{\varrho} = 2\pi v_{\varrho}(\vartheta, \varphi) \left( \hat{I}_{z}^{2} - \frac{2}{3} \right), \tag{1}$$

where the orientation dependent resonance frequencies  $v_Q$  of the two transitions are given (see eqn.(2.78) in ref.<sup>2</sup>):

$$v_{\varrho}(\vartheta,\varphi) = \pm \frac{3}{4} \frac{eQeq}{\hbar} \frac{1}{2} (3\cos^2 \vartheta - 1 - \eta \sin^2 \vartheta \cos 2\varphi)$$
  
=  $Q_{zz} \frac{1}{2} (3\cos^2 \vartheta - 1 - \eta \sin^2 \vartheta \cos 2\varphi)$  (2)

Here  $\eta$  is the asymmetry parameter and  $Q_{zz}$  is the principal component of the quadrupolar interaction tensor, i.e. the strength of the quadrupolar interaction. While in single crystals only two lines at  $\pm v_Q$ are observable, the average over all possible orientations has to be calculated in a polycrystalline powder sample. Due to the axial symmetry of the magnetic field, it is sufficient to integrate over two angles ( $\vartheta$ ,  $\varphi$ ). Assuming for simplicity that the transversal relaxation time T<sub>2</sub> is independent on the orientation, the spectra can be calculated as a superposition of the lines with a line shape function  $f(v,\pm v_Q,T_2)$  of the individual crystallites:

$$I(\nu) = \int_{0}^{\pi} d\vartheta \sin(\vartheta) \int_{0}^{2\pi} d\varphi \left( f\left(\nu, -\nu_{\varrho}(\vartheta, \varphi), T_{2}\right) + f\left(\nu, +\nu_{\varrho}(\vartheta, \varphi), T_{2}\right) \right)$$
(3)

Thus for polycrystalline samples a powder average is observed giving rise to the Pake doublet or Pakepattern (see for example, the spectra in Fig. 1b - 1d).

For a deuterium atom bound to a carbon atom the most recent value of the quadrupolar coupling constant is found to be  $Q_{cc} \cong 170 \text{ kHz}$ ,<sup>3</sup> corresponding to a strength of the quadrupolar interaction  $Q_{zz} = \frac{3}{4}Q_{cc} = 128 \text{kHz}$  (Fig.1d). Owing to fast molecular motions and lattice vibrations in many solid state NMR experiments a reduced effective value of  $Q_{cc}$  is observed, even at low temperatures and thus, in most <sup>2</sup>H-NMR experiments  $Q_{cc}$  has to be considered as a fitting parameter. In the <sup>2</sup>H-NMR study of the iBA molecules, there is a succession of possible intramolecular and molecular rotations of the molecule which cause an averaging of the static quadrupolar interaction, denoted as  $Q_{zz}^{0}$ , to various reduced interactions, denoted as  $Q_{zz}^{n}$ , where n is an index used to distinguish these different averaged tensors.

#### 2.2. Data Evaluation

The echo spectra of d<sub>6</sub>-isobutyric acid in the fast and slow exchange regime were simulated employing a laboratory written Matlab program. Instead of numerically performing the powder integration, the faster analytical expression of the powder pattern in terms of elliptic integrals <sup>4</sup> was used to calculate the line shape for infinite T<sub>2</sub>. Effects of the finite pulse power were taken into account using the formula given in ref <sup>5</sup>. Since the width of the spectra is much larger than the natural line width of the individual crystallites a simple Lorentzian was chosen as line shape function  $f(v,\pm v_Q,T_2)$  in eqn.3. The resulting Pake-spectra were numerically convoluted with this Lorentzian by Fourier transformation into the time domain, multiplied with a decaying exponential function and transformed back into the frequency domain. In our case, where the spectrum is a superposition of different sub-spectra (see results), the relative intensities of different spectral contributions were calculated from the integrals over the lines of the corresponding sub-spectra.

The <sup>2</sup>H-NMR echo spectra of the acid in the intermediate exchange regime were simulated by a laboratory written Matlab program using a Liouville space formalism of the exchange process. For the powder integration over the polar angles (eq. (3)), optimized angle sets with 3554 angles were used.<sup>6-8</sup> Besides the common quadrupolar fit parameters  $Q_{zz}$  (strength of the quadrupolar interaction) and  $\eta$  (asymmetry parameter), the jump rate *k* for the methyl group rotation and for the isotropic rotation during the melting process is introduced.

## 2.3. Synthesis of 2-methyl-d<sub>3</sub>-propionic-3,3,3-d<sub>3</sub> acid (d<sub>6</sub>-isobutyric acid)

To a suspension of sodium hydride 3.51 g (146.3 mmol, 60 % in oil) in di-isopropylamine 9.15 g (90.4 mmol) solved in absolute tetrahydrofuran 100 ml (99.9 %), d<sub>3</sub>-propionic acid 5 g (64.9 mmol, 99.8 % deuterated) was added dropwise under argon atmosphere. Firstly the mixture was heated in an oil bath to reflux, then cooled in an ice bath, and n-butyl-lithium 45.3 ml (1.6 M solution in hexane) was added under argon atmosphere. The mixture was warmed to  $30^{\circ}$ C in the oil bath and cooled in the ice bath again. The d<sub>3</sub>-methyl iodide 4.3 ml (69.1 mmol) was added slowly and the mixture stirred at  $20^{\circ}$ C for 4.5 hour, poured into 800 ml of dist. water and the organic phase was separated. The aqueous phase was acidified with 37 %-aqueous solution of hydrochloric acid and extracted eight times with 200 ml diethyl ether. The combined organic phases were washed with 20 %-aqueous sodium bisulphate, dist. water, saturated aqueous sodium chloride and dried with magnesium sulphate. After the solvent was removed, the raw product (3.78 g) was distilled in a bulb tube at  $50^{\circ}$ C -  $60^{\circ}$ C and 27-29 mbar and then purified by HPLC to give 2.3 g (24.4 mmol, 37.6 % yield) of 2-methyl-d<sub>3</sub>-propionic acid as a liquid. The final product was characterized by liquid state <sup>1</sup>H NMR spectroscopy, giving a deuteration fraction of 97.4 % as determined by peak integration.

# 2.5 NMR Samples

For the bulk sample,  $d_6$ -iBA was placed into a standard 5 mm o.d. NMR-tube to a height of ca. 1 cm, put on a vacuum line for de-gassing, frozen in liquid nitrogen and sealed off. The samples of  $d_6$ -iBA imbibed in mesoporous silica were prepared as follows. The silica powder was loaded into the standard 5 mm NMR tubes to a height of ca. 2 cm. The sample was heated to ca. 130°C under vacuum for 24 hours to remove any moisture and then weighed on an analytical balance (METTLER), to determine the total pore volume of each sample. The samples were flushed with argon and a well-defined amount of  $d_6$ -iBA, corresponding to a nominal degree of filling of 85 % of the pore space, was added by means of a syringe. The samples were then kept at ambient temperature for several hours to ensure that all liquid enters into the pore space. Finally the samples were frozen in liquid nitrogen and sealed off.

	$V_{IBA}$ (ml)	V <sub>IBA</sub> (mmol)	m <sub>silica</sub> (g)	Loading level IBA/silica
				(mmol/g)
CPG 10-75	0.0906	0.963	0.193	5.00
SBA-15	0.0273	0.290	0.0283	10.27
MCM-41	0.0299	0.319	0.0411	7.76

The following table gives the exact amounts of iBA inside the three NMR samples:

# **References for supplementary materials**

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**Figure 1:** Simulated <sup>2</sup>H spectra of CD<sub>3</sub> molecular groups corresponding to the different values of the quadrupolar coupling constant  $Q_{zz}$  stemming from the motionally reduced tensors  $Q_{zz}^{n}$ . These spectra illustrate the effect of the conceivable motions (see Fig.2) on the <sup>2</sup>H-NMR spectra of the methyl group of the iBA molecule. The methyl group rotation around the three-fold axis reduces the static spectrum (Fig.1d) with quadrupolar interaction  $Q_{zz}^{0}=128$ kHz to a reduced spectrum (Fig.1c) with quadrupolar interaction  $Q_{zz}^{1}=42$  kHz. If the molecule undergoes a second rotation around the C-COOH axis then  $Q_{zz}^{1}$  is further reduced to  $Q_{zz}^{2}=14$  kHz (Fig. 1b). Finally, if the isotropic motion is fast on the NMR time scale, as for example in the liquid iBA, a complete averaging of the quadrupolar tensor ( $Q_{zz}^{iso} = 0$ ) is expected (Fig. 1a).



Figure 2: TEM micrographs of MCM-41 (a), SBA-15 (b) and CPG-10-75 (c).



Fig. 3a



Fig. 3b



Fig. 3c

**Figure 3:** DSC heating scans for isobutyric acid (iBA) and  $d_6$ -isobutyric acid ( $d_6$ -iBA) imbibed in CPG-10-75, MCM-41 and SBA-15 silica:

(a) DSC scans for iBA in the three silica materials, exhibiting the melting peak of excess material (onset temperature 226.8 ± 0.7 K) and the melting peaks of iBA in the pores; (b) enlarged section of Fig. 3a for the temperature region of the melting peaks of iBA in the pores. The pore melting temperature  $T_{m(pore)}$  is defined as the peak maximum temperature, the peak half width  $\delta T_m$  is expressed by the difference between the peak maximum and peak onset temperatures (see Table 1 of the paper); (c) similar graph as in Fig. 3b for the pore melting peaks of d<sub>6</sub>-iBA in the three materials. Results of the DSC measurements are summarized in Table 1 of the paper.