Tracing pore connectivity and architecture in nanostructured silica SBA-15

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Received 12 June 2007; received in revised form 7 August 2007; accepted 10 August 2007
Available online 22 August 2007

Abstract

We record the probability distribution of molecular displacements (i.e., the distribution of the lengths of the diffusion paths) of guest molecules in nanostructured SBA-15 silica by means of pulsed field gradient (PFG) NMR. Two different morphologies of SBA-15 were studied, namely isolated fibers and bundles. The guest molecules (nitrobenzene) are applied in excess so that, by measurement below the bulk freezing point but above the freezing point in the nanopores, the space between the host particles becomes inaccessible for notable mass transfer, and the range of molecular displacements, as observed in the experiments, is determined by the nanopores and the shape of the individual particles. The measurements clearly reflect the 1-D channel architecture of SBA-15. Over the displacements traced in the experiment (5 μm) there is a distinct difference in the time dependence of the coefficients characterizing diffusion anisotropy. Diffusion measurements with the isolated fibers (embedded in the frozen guest phase surrounding the host particles) reveal increasing transport resistance with increasing observation time, acting both parallel and perpendicular to the channel direction. By contrast, in the bundles diffusivity in the channel direction remains constant while the rate of displacements perpendicular to this direction increases. These dependencies may be rationalized by the different sample morphologies.

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Keywords: SBA-15; PFG NMR; Self-diffusion; Pore connectivity

1. Introduction

Novel synthesis routes have led to an impressively large spectrum of nanoporous materials of different composition, pore architecture, and shape. In many cases, appropriate fluid transport properties are essential for their technical application [1,2]. Hence, in addition to the well-established methods of textural characterization [3], diffusion measurements are often indispensable to completely characterize these materials. In many cases, the mechanisms and structural properties thus identified as rate limiting for overall mass transfer deviate dramatically from those expected on the basis of the “text-book” structure of these materials.

The present paper deals with the application of the pulsed field gradient technique of nuclear magnetic resonance (PFG NMR) to diffusion studies in nanoporous silica SBA-15 [4]. The materials under study were synthesized following the original procedure described in [5], which includes the weak acid H3PO4 instead of HCl. By simply controlling the stirring rate of one and the same starting mixture, a simple route was found to generate particle shapes of a broad variety. It shall be demonstrated that the structural differences associated with two different morphologies of the SBA-15 specimens under study, namely isolated fibers and bundles, are nicely reflected by the transport properties of guest molecules.
2. Experimental

Fig. 1 shows SEM images of the two SBA-15 specimens studied here. Details of their synthesis may be found in [5] and their textural properties are given in Table 1. Nitrobenzene was used as an NMR probe molecule. Prior to introduction into the NMR sample tubes (7.5 mm OD, 10 mm filling length), the SBA-15 material was activated by heating (24 h at 323 K) under evacuation. After activation, the bulk nitrobenzene was added in excess to the evacuated probe material at a temperature of 297 K.

All diffusion measurements were performed at 253 K, i.e., considerably below the melting-point of bulk nitrobenzene (T_melt = 278 K). In this way, the space outside of the mesopores is essentially blocked by the phase of frozen nitrobenzene, while the pore space – owing to the melting-point depression [6, 7] – is still accommodated by liquid nitrobenzene. The diffusion behavior of the molecules within this liquid phase was studied in our experiments.

The PFG NMR diffusion measurements have been performed on an NMR spectrometer at 400 MHz with a home-built gradient unit [8]. The measurement, based on the sequence of radio frequency and gradient pulses, generates an NMR signal, the so-called spin echo of resonant nuclei (1H). Dependent on gradient duration δ, gradient strength g and observation time t, the spin echo amplitude M(δg, t) becomes sensitive to the translational motion of molecules in the probe (diffusion). Assuming that the pulsed field gradients are applied along the z-axis in the laboratory frame of reference, the echo attenuation factor [9, 10] is given by

\[ \Psi(\delta g, t) = \frac{M(\delta g, t)}{M(\delta g = 0, t)} = \int P(z, t)e^{-i(\delta g)z}dz \]  

(1)

The diffusion propagator P(z, t) denotes the probability that during the observation time t the molecules are displaced over a distance z in the field gradient direction. The gyromagnetic ratio is γ = 2.67 × 10^4 (T s)^{-1} for the probed ^1H nuclei. According to 1, the spin echo attenuation \( \Psi(\delta g, t) \) can be used to monitor the self-diffusion process. In the case of normal unrestricted self-diffusion, the averaged propagator is a Gaussian and the spin echo attenuation is described by a mono-exponential decay:

\[ \Psi(\delta g, t) = e^{-(\delta g)^2D_zt} = e^{-D_gq^2t} \]  

(2)

with \( q = \gamma \delta g \). In complex systems, the averaged propagator may deviate from a Gaussian. In PFG NMR, these deviations allow us to determine additional characteristic parameters which influence self-diffusion under the given constraints.

For systems with an anisotropic pore structure, as in the case of both SBA-15 silica samples, we expect the propagation to be dependent on the direction of propagation within the system. The self-diffusivity parallel to the direction of the 1-D channel (\( D_{par} \)) should be much larger than the self-diffusion coefficient perpendicular to it (\( D_{perp} \)). Thus, displacements along the channels are much less inhibited by transport resistances than displacements perpendicular to the channel axis. The latter may result from defects in the channel walls or the channel ends.

3. Results and discussion

Fig. 2 provides a typical representation of the signal attenuation in the PFG NMR experiments. It notably deviates from the simple Eq. (1), which predicts an exponential decay, and, therefore, a straight line in a logarithmic plot. However, in view of the sample anisotropy, such a deviation is to be expected, since 1 holds for isotropic diffusion only.

PFG NMR signal attenuation in the case of anisotropic diffusion in a powder sample (i.e., with crystals oriented in all directions with equal probability) satisfies the following equation in a spherical coordinate system [11, 12]:

\[ \Psi(\delta g, t) = \frac{1}{4\pi} \int_0^{2\pi} \int_0^\pi \exp\left\{-(\gamma \delta g)^2t(D_{xx} \cos^2 \theta + D_{yy} \sin^2 \theta \cos^2 \phi + D_{zz} \sin^2 \theta \sin^2 \phi)\right\} \sin \theta d\theta d\phi \]  

(3)

where the quantities \( D_{xx}, D_{yy} \) and \( D_{zz} \) indicate the principal elements of the diffusion tensor. Due to rotational symme-

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Table 1

<table>
<thead>
<tr>
<th>Morphology</th>
<th>( S_{BET} ) (m²/g)</th>
<th>( V_t ) (cm³/g)</th>
<th>( d_{BET} ) (nm)</th>
<th>( V_m ) (cm³/g)</th>
<th>( V_{meso} ) (cm³/g)</th>
<th>( a ) (nm)</th>
<th>( t ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fibers</td>
<td>968</td>
<td>1.26</td>
<td>8.8</td>
<td>0.15</td>
<td>629</td>
<td>10.6</td>
<td>1.8</td>
</tr>
<tr>
<td>Bundles</td>
<td>626</td>
<td>0.83</td>
<td>8.0</td>
<td>0.092</td>
<td>421</td>
<td>10.6</td>
<td>2.6</td>
</tr>
</tbody>
</table>

\( S_{BET} \) – BET surface area, \( V_t \) – total pore volume, \( d_{BET} \) – BJH pore diameter obtained by applying the BJH model to the adsorption branch of the isotherm, \( V_m \) – micropore volume, \( V_{meso} \) – mesopore surface area, \( a \) – cell parameter, \( t \) – pore wall thickness (\( t = a - d_{BET} \)).
try of the system under study, in our case Eq. (3) simplifies to (again with $q = \frac{4\pi n}{\lambda}$)

$$W(q; t) = \frac{1}{2} \int_0^\pi \exp \left\{ -q^2 t \left( D_{\text{par}} \cos^2 \theta + D_{\text{perp}} \sin^2 \theta \right) \right\} \sin \theta \, d\theta$$

(4)

where $D_{\text{par}}$ and $D_{\text{perp}}$ are the self-diffusivities as introduced above. Since the host particles within our sample tube may assume all directions with equal probability, Eq. (4) may be finally transformed into

$$W(q; t) = \frac{\sqrt{\pi}}{2} e^{-q^2 t D_{\text{perp}}} \times \text{erf} \left( \sqrt{q^2 t (D_{\text{par}} - D_{\text{perp}})} \right)$$

(5)

Fig. 2 displays those representations of Eq. (5) which provide the best fit to the experimental data. The values for $D_{\text{par}}$ and $D_{\text{perp}}$ used in the fit are shown in the inset.

Fig. 3 presents a complete survey of the self-diffusivities $D_{\text{par}}$ and $D_{\text{perp}}$ and their dependence on the observation time as resulting from the PFG NMR signal attenuation curves for the different observation times considered. In addition to the observation times $t$, in the abscissa we have also indicated the mean square displacements $\langle s^2_{\text{par}} \rangle$ and $\langle s^2_{\text{perp}} \rangle$, resulting from an average value of the diffusivities in the respective directions by application of Eq. (6).

$$\langle s^2 \rangle = 2Dt$$

(6)

The following summarizes our main findings:

(a) Irrespective of a pronounced diffusion anisotropy over the considered temporal and spatial scales (as indicated in the abscissa), diffusion is by far not ideally one-dimensional. This suggests (as in the case of water in the MCM-41 sample studied in [14]) the following:

(i) Displacements in the channel direction within the bundles are described with a constant diffusivity. This means that over the observed displacements of $4 \mu m$, molecular transport in the longitudinal direction is not affected by additional transport resistances that might confine the propagation.

(ii) However, the channel walls are, to some extent, permeable. Indeed it is known that the walls of SBA-15 are microporous [15, 16].

(iii) The length of individual channel segments is small in comparison with displacements in the channel direction (up to $5 \mu m$ for the abscissa...
in Fig. 3) so that, at the end of each channel segment, the molecules may move into a direction perpendicular to the channel direction or through the segment ends.

(b) Additionally, in the bundles there is a tendency that displacements perpendicular to the mean channel direction proceed at a rate increasing with increasing observation time. This finding suggests the absence of a perfect channel structure over distances of the order of these displacements (1 μm), which facilitate propagation perpendicular to the mean channel direction.

(c) In the fibers, both diffusivities are found to (slightly) decrease with increasing observation time. This points to some confinement and, hence, to a retarded propagation over longer distances, in contrast to what is observed with the bundles. The lateral extension of the fibers is far below that of the bundles, therefore it could be expected that in the case of the fibers the external frozen phase will lead to spatial confinement within much narrower dimensions than in the bundles. This agrees with the experimental findings.

4. Conclusions

Differences in SBA-15 silica morphology lead to specific differences in the propagation pattern of guest molecules, as revealed by PFG NMR, using nitrobenzene as the probe molecule. Nitrobenzene was used in excess, so that inside the NMR sample tubes, the host particles were surrounded by a bulk phase of the guest molecules. Thus, by selecting a temperature below the melting-point of the bulk (253 K) and above that of the guest in the host mesopores, molecular propagation, as traced by PFG NMR, is essentially confined to the individual host particles. In both types of particles (fibers and bundles), the Brownian motion of molecules in the pores was found to be anisotropic, and characterized by a rotationally symmetrical diffusion tensor. The diffusion coefficient in the direction of the axis of symmetry (\(D_{\text{par}}\)) is one to two orders of magnitude larger than that in a direction perpendicular to it (\(D_{\text{perp}}\)). The quantity \(D_{\text{par}}\) is therefore referred to as the diffusion coefficient in channel direction, while \(D_{\text{perp}}\) describes the rate of propagation perpendicular to the channel axis, due to either a finite permeability of the channel walls or to deviations from an ideal structure with infinitely extended straight channels. PFG NMR is unable to discriminate between these options, but it is known that the mesopore walls of SBA-15 are microporous.

With increasing observation time, \(D_{\text{par}}\) in bundles of SBA-15 “threads” is found to be constant. This indicates that, over the covered displacement range (up to 4 μm), there are no particularly pronounced transport resistances slowing down the rate of molecular propagation along the SBA-15 nanopores.

The rate of propagation in the perpendicular direction, which is one and a half orders of magnitude slower, is found to increase with increasing propagation time. This suggests the existence of defects, which facilitate the escape of guest molecules out of the threads constituting a bundle. In contrast to this behavior, in the fiber-like particles the diffusivity in directions perpendicular to the nanopores is found to decrease with increasing observation times, and, hence, with increasing displacements. This behavior may be related to the smaller size of the silica particles constituting a fiber, which result in stronger confinement of the fluid phase inside the silica pores. Variation in size of the guest molecules as well as of the amount of the excess guest phase between the particles would enable to trace the exchange rates between the different parts of the hierarchical pore space of a nanostructured material.

This novel option of pore space exploration, namely “porometry by diffusion”, should enhance our understanding of structured nanoporous materials.

Acknowledgments

Financial support by the European Community (NoE INSIDE PORES) as well as by DFG and NWO (International Research Training Group Diffusion in Porous Materials) is gratefully acknowledged. We also gratefully acknowledge Albemarle Catalysts B.V. for sponsoring the SBA-15 synthesis work.

References