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Tracing pore connectivity and architecture in nanostructured silica SBA-15

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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.

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 H_3PO_4 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.

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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 (^{1}H). Dependent on gradient duration δ, gradient strength g and observation time t, the spin echo amplitude $M(\delta g, t)$ 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

$$\Psi(\delta g, t) = \frac{M(\delta g, t)}{M(\delta g = 0, t)} = \int P(z, t) e^{-i(\gamma \delta g) z} dz \quad (1)$$

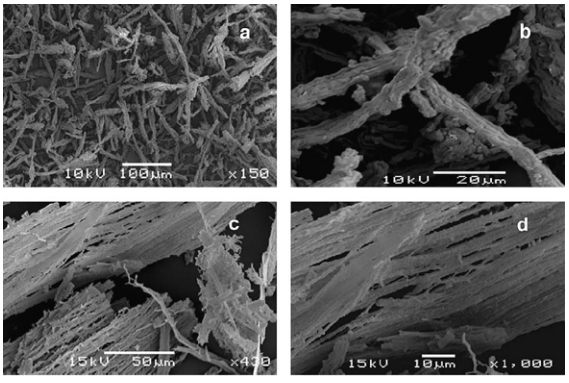

Fig. 1. SEM images of SBA-15 fibers (a and b) and bundles (c and d) [5].

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 $\gamma = 2.67 \times 10^8$ (T s)$^{-1}$ for the probed ^{1}H 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:

$$\Psi(\delta g, t) = e^{-(\gamma \delta g)^2 D_z t} = e^{-D_z q^2 t} \quad (2)$$

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]:

$$\Psi(\delta g, t) = \frac{1}{4\pi} \int_0^{2\pi} \int_0^{\pi} \exp\{-(\gamma \delta g)^2 t (D_{xx} \cos^2\theta + D_{yy} \sin^2\theta \cos^2\phi + D_{zz} \sin^2\theta \sin^2\phi)\} \sin\theta \, d\theta \, d\phi \quad (3)$$

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

Table 1
Textural properties of SBA-15

Morphology	S_{BET} (m^2/g)	V_t (cm^3/g)	d_{BJH} (nm)	V_μ (cm^3/g)	V_{meso} (cm^3/g)	a (nm)	t (nm)
Fibers	968	1.26	8.8	0.15	629	10.6	1.8
Bundles	626	0.83	8.0	0.092	421	10.6	2.6

S_{BET} – BET surface area, V_t – total pore volume, d_{BJH} – BJH pore diameter obtained by applying the BJH model to the adsorption branch of the isotherm, V_μ – micropore volume, V_{meso} – mesopore surface area, a – cell parameter, t – pore wall thickness ($t = a - d_{BJH}$).