Electronic Supplementary Information: Static Field Gradient NMR Studies of Water Diffusion in Mesoporous Silica

M. Weigler,¹ E. Winter,¹ B. Kresse,¹ M. Brodrecht,² G. Buntkowsky,² and M. Vogel¹ ¹⁾Institut für Festkörperphysik, Technische Universität Darmstadt, Hochschulstr. 6, 64289 Darmstadt, Germany ²⁾Eduard-Zintl-Institut für Anorganische und Physikalische Chemie, Technische Universität Darmstadt, Alarich-Weiss-Str. 8, 64287 Darmstadt, Germany

I. EVALUATION OF THE PORE STRUCTURE

In the main article, we study water diffusion in prepared MCM-41 and purchased SBA-15 silica. The former materials comprise samples denoted as C10, C12, C14, and C16, depending on the number of carbon atoms in the alkyl chains of the used template molecules. Moreover, the nomenclature C14 and C14^{*} is used to distinguish two samples obtained from slightly different routes of preparation. To evaluate the pore parameters of these materials, we performed nitrogen adsorption/desorption experiments at 77 K. The obtained isotherms were presented in previous work.¹ A variety of methods can be used to analyze the adsorption/desorption isotherms relating to specific surface area, pore volume, and pore diameter. In our previous study,¹ the specific surface area was determined by applying the Brunauer-Emmett-Teller (BET) method² and analyzing the curves in the P/P₀ range between 0.03 and 0.3. The pore volume was obtained by the Gurvich method and the P/P₀ value at 95% of the step height. The evaluation of pore size distributions leaves, however, more room for interpretation. Therefore, we compare the results of different methods in the following.

Several different methods allow the analysis of the adsorption/desorption isotherms, each developed for specific materials, surfaces and shapes of pores.³ For the analysis of the pore systems of our MCM-41 and SBA-15 materials with pore diameters in the range between ca. 2 and 6 nm, there is no exclusive method. Rather, the obtained pore diameters depend on the applied method and on whether the adsorption or desorption isotherm is used for the evaluation. The widely employed Barrett-Joyner-Halenda (BJH) method⁴ for mesoporous materials tends to underestimate pore sizes for SBA-15 materials^{5,6} and even fails to deliver any value for MCM-41 materials with small pore sizes. The median pore diameters obtained for the studied mesoporous silica materials from the BJH method are given in Tab. I. The corresponding pore size distributions are shown in Fig. 1. A more recent approach to pore size determination uses density functional theory. The nonlocal density functional theory (NLDFT) method enables analyses over large pore size ranges and for different surface structures, but reportedly tends to overestimate pore sizes.⁶ The median pore sizes of our materials resulting from the NLDFT method are also given in Tab. I. The corresponding pore size distributions are presented in Fig. 2.



FIG. 1. Pore diameter distributions of the studied MCM-41 and SBA-15 materials as obtained by BJH analysis from nitrogen adsorption/desorption isotherms at 77 K. For clarity, results for different samples are vertically shifted.



FIG. 2. Pore diameter distributions of the studied MCM-41 and SBA-15 materials as obtained by NLDFT analysis from nitrogen adsorption/desorption isotherms at 77 K. For clarity, results for different samples are vertically shifted.

TABLE I. Median pore diameters resulting from the BJH and NLDFT methods for the prepared MCM-41 and purchased SBA-15 materials. Due to discernible discrepancies, we assign intermediate values to C14(*), C16, and SBA-15. The assigned values for C10 and C12 use additional knowledge from HK and SF analyses.

sample	pore diameter (nm)	pore diameter (nm)	pore diameter (nm)
	by BJH	by NLDFT	assigned
MCM-41 C10	/	2.5	2.1
MCM-41 C12	/	2.9	2.4
MCM-41 C14	2.3	3.4	2.8
MCM-41 C14*	2.4	3.5	2.8
MCM-41 C16	2.5	3.5	3.0
SBA-15	4.7	6.0	5.4

This comparison of results from BJH and NLDFT analyses shows that it is not straightforward to pinpoint the pore diameters of the studied mesoporous silica. Due to the observed discernible discrepancies, it is reasonable to use intermediate diameters for C14, C14^{*}, C16, and SBA-15, see Tab. I. We note that the thus obtained values for C16 and SBA-15 differ somewhat from the previous ones,¹ which were extracted from less elaborate analysis (C16, 3.3 nm) or provided by the supplier (SBA-15, 6.0 nm). For MCM-41 C10 and C12, the NLDFT results can be regarded as an upper limit for the pore diameter, while the BJH method fails and, hence, does not yield a lower limit. This failure is caused by the fact that MCM-41 C10 and C12 feature narrow pores, which can be regarded neither as classical nanopores nor as mesopores. To overcome this problem, we use the Horvath-Kawazoe (HK) and the Saito-Foley (SF) methods^{7,8} to obtain a lower limit. The HK method is optimized for materials with slit pores.⁷ The SF method uses the HK method as a basis and is adapted to analyze argon adsorption of zeolites.⁸ Thus, none of the methods is fully applicable to the synthesized MCM-41 materials, but a combination of the HK, SF and NLDFT methods proved useful to determine the pore diameters of 2.1 nm and 2.4 nm for the C10 and C12 samples, respectively,¹ see Tab. I. In summary, the characteristic pore diameters of the samples C14, C14^{*}, C16 and SBA-15 are based on the values obtained from the BJH and



FIG. 3. SEM images of the prepared MCM-41 samples: (a) C10, (b) C12, (c) C14, and (d) C16. The magnification is 35000 (a,b) and 50000 (c,d) respectively. The scale bar corresponds to 1 μ m for all images.

NLDFT methods, while that of the C10 and C12 samples are based on the NLDFT method with additional information gained from HK and SF analyses.

II. SCANNING ELECTRON MICROSCOPY

The morphology and microscopic structure of the synthesized MCM-41 C10, C12, C14 and C16 samples were studied by scanning electron microscopy (SEM). The SEM samples were coated with gold for 100 s at 30 mA using a Quorum Q300T D sputter coater and the SEM images were taken using a FEI/Philips XL30 FEG with accelerating voltages between 15 and 25 kV. Figure 3 shows the results. We see that the silica particles have nearly spherical shapes and sizes between ~300 nm and ~1 μ m, where particles with narrower pores (C10) tend to be larger than that with wider pores (C16).



FIG. 4. Self-diffusion coefficients D_{\parallel} of H₂O in MCM-41 C14 (d = 2.8 nm) from ¹H SFG NMR at T = 269 K as a function of the inverse generalized scattering vector $q^{-1} = (g\gamma t_e)^{-1}$. Results for samples with open and capped pore exits are compared. The values of the applied static field gradient (SFG) g are indicated. Moreover, γ is the gyromagnetic ratio of the proton and t_e is the adjustable evolution time of the applied stimulated-echo pulse sequence.

III. Q-DEPENDENT SFG NMR DIFFUSION STUDIES

NMR diffusion studies, which use the stimulated-echo pulse sequence, probe displacements on a length scale set by the inverse generalized scattering vector $q^{-1} = (g\gamma t_e)^{-1}$.⁹⁻¹¹ Here, g is the strength of the applied magnetic field gradient, γ denotes the gyromagnetic ratio of the probe nucleus, and t_e specifies the evolution time in the pulse sequence. To study the relevance of the experimental length scale in approaches to water diffusion in mesoporous silica, we determine the dependence of the obtained diffusion coefficients on the used value of q^{-1} . Figure 4 shows results from ¹H SFG NMR on H₂O in MCM-41 C14 with open and capped pore exits at T = 269 K. For a systematic variation of the experimental length scale in this study, we use different static field gradients g and we perform stimulated-echo (STE) experiments for various evolution times t_e . To determine the diffusion coefficients, we fit the STE decays for various experimental parameters individually. In doing so, we consider the anisotropy of water diffusion in silica pores and interpolate the data for the samples with open and capped pore exits to Eq. (2) and Eq. (3) of the main article, respectively. The resulting diffusion coefficients D_{\parallel} characterize water displacements parallel to the pore axes. In Fig. 4, we observe that the dependence of D_{\parallel} on q^{-1} is different for open and capped pore exits. For open exits, D_{\parallel} continuously grows when q^{-1} is increased between 0.2 and $4\,\mu$ m, i.e., when the covered range of experimental length scales encloses the typical silica particle sizes. Consistent with our findings in the main text, this observation confirms that water motion through voids between silica particles will significantly affect the outcome of NMR diffusion studies if no specific measures are taken. For capped exits, by contrast, D_{\parallel} does not systematically depend on the value of q^{-1} . Minor changes can be caused by experimental uncertainties, deviations from Gaussian displacements statistics when water molecules are reflected at the blocked exits, and NMR artifacts such as cross relaxation or dipolar correlation effects. Due to the absence of a systematic q^{-1} dependence, it is possible to overcome such experimental imperfections and gain reliable information about water diffusion inside silica pores when we perform global fits of STE decays measured for capped samples using various g and/or t_e values, as is exploited in the main article.

Comparing D_{\parallel} for open and capped exits in more detail, we find a difference by a factor of about five for $q^{-1} > 1 \,\mu$ m typical of PFG approaches, i.e., when the length scale of the experiment is larger than the size of the silica particles, while the values for the open pores approach the nearly constant value for the capped ones when we exploit the high field gradients of our SFG setup to reach low inverse generalized scattering vectors of $q^{-1} \approx 0.2 \,\mu$ m and, hence, high spatial resolution. These findings once more demonstrate the superior performance of SFG approaches as compared to PFG counterparts for studies on diffusion processes in mesoporous silica particles.

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