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Characterization of Worm-Like Micro- and Mesoporous Silicas by Small-Angle Scattering and High-Resolution Adsorption Porosimetry

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Abstract. Mesoporous silica with worm-like pores of 9–10 nm in size were studied by small-angle neutron scattering (SANS) and high-resolution porosimetry, using nitrogen at 77 K and argon at 87 K. The pore sizes determined from SANS are in excellent agreement with those obtained from a recently developed non-local density functional theory (NLDFT) approach. Furthermore, the additional micropores in the mesopore walls could be quantified by SANS and physisorption, and again good agreement between both methods was observed. Our results clearly demonstrate that the NLDFT approach allows an accurate determination of the pore size distribution of materials which contain both narrow micropores and mesopores larger than 10 nm.

Keywords: SANS, nitrogen sorption, mesoporous silica

1. Introduction

In the past years, significant progress has been made in the pore size characterization of micro- and mesoporous materials by physisorption methods. In particular, non-local density functional theory approaches provide consistent pore size determinations for mesoporous materials with highly ordered pore arrangements, such as M41S materials. However, the exact determination of porosity parameters of materials with pore sizes larger than 9–10 nm and, in addition, showing a pronounced inhomogeneity in the pore shape and size, has not reached a comparable accuracy. The influence of pore geometry and the effect of "disorder" on the shape of isotherms are still under investigation, which is partly due to the lack of appropriate independent characterization techniques. In particular, the origin of the hysteresis in such materials is not completely understood. In this work, we performed detailed nitrogen and argon sorption studies and small-angle neutron scattering (SANS) on recently reported mesoporous silicas in order to test recently developed NLDFT approaches. These silicas were reported to consist of elongated "worm-like" pores of ca. 9 nm in diameter and additional micropores in the walls separating the mesopores. Also, a broad hysteresis was observed in nitrogen sorption. For the SANS measurements, a unique setup is used (located at Hahn-Meitner-Institut, Berlin, Germany), which allows the simultaneous study of SANS during nitrogen sorption, thereby providing invaluable information on the pore filling process.

Hence, our study was focused on the following detailed aspects:

(i) A comparison of the SANS pore size results with mesopore size distributions as determined from nitrogen and argon sorption by using a suitable NLDFT approach.
(ii) A thorough determination of the additional microporosity, both regarding the size and micropore volume.
(iii) A comparison between nitrogen and argon sorption isotherms, which provides further insight into the hysteresis phenomenon in this kind of materials (see Thommes et al., 2005).

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2. Experimental Section

The combined N_2-sorption/SANS experiments are described in detail in Smarsly et al. (2001). As mesoporous silica, we used the so-called "SE3030" which consists of wormlike mesopore channels of pore sizes 9–10 nm according ot SAXS and TEM studies (see Smarsly et al., 2001). The nitrogen and argon adsorption/desorption isotherm measurements were performed over the relative pressure range from $p/p_0 = 10^{-6} - 1$ with an Autosorb- I-MP sorption instrument (Quantachrome).

3. Results

Figure 1 shows the nitrogen sorption isotherm (measured at 77.35 K) of "SE3030" silica, revealing a pronounced hysteresis.

The adsorption data were analyzed using a novel NLDFT approach, which allows the quantification of both micro- and mesopores. The NLDFT model that has been previously shown to describe adequately adsorption/desorption hysteresis in cylindrical silica mesopores (Ravikovitch and Neimark, 2001, 2002) has been extended to micropores. The pore size distribution obtained by applying the novel NLDFT kernel of metastable adsorption isotherms to the adsorption data is shown in Fig. 2 (this NLDFT kernel describes correctly that pore condensation is delayed due to the occurrence of a metastable pore fluid; see Ravikovitch and Neimark, 2001). From both nitrogen and argon adsorption we obtain an average mesopore diameter of 9.5 nm. In addition, a significant degree of microporosity is observed with an average pore size of ca. 1 nm.

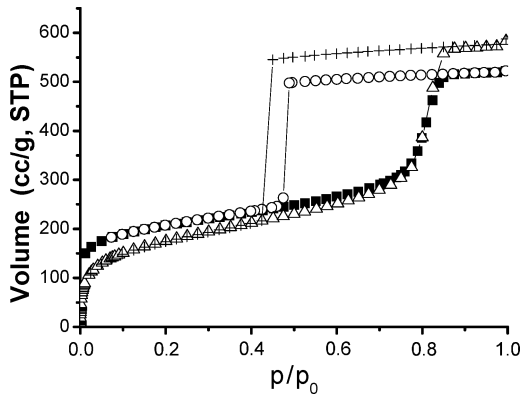

Figure 1. Nitrogen (77.35 K, open circles and filled squares) and argon sorption isotherms (87.27 K, crosses and open triangles) of the "SE3030" silica.

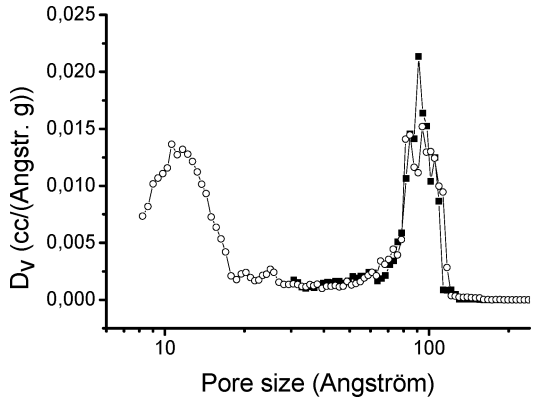

Figure 2. Pore size distributions obtained from nitrogen (open circles) and argon sorption (filled squares) (see Fig. 1).

The SANS data as a function of p/p_0 are shown in Fig. 3. Significant changes are observed as a function of the nitrogen sorption. The data were fitted using an approach already discussed in Smarsly et al. (2001), based on a system of polydisperse cylinders to model the mesoporosity, while their distorted mutual arrangement is described by a hard-disc model by Rosenfeld (Smarsly et al., 2001). As a main advantage of the analysis presented here, the only parameters in this model are the volume fraction of the mesopores, their

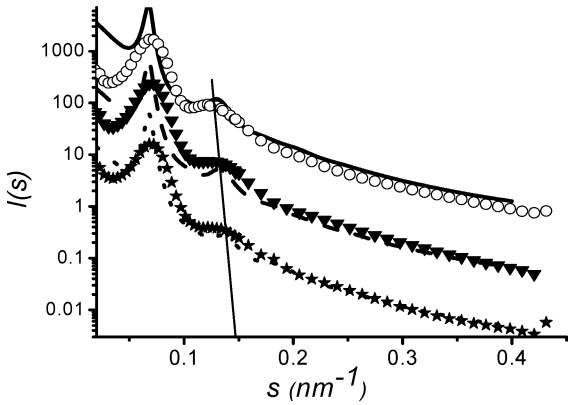

Figure 3. In situ-SANS/nitrogen sorption (at 77 K) for SE3030 silica as a function of p/p_0 (open circles: $p/p_0 = 0$, filled triangles: $p/p_0 = 0.63$, stars: $p/p_0 = 0.81$). The fits were performed on the basis of the approach suggested in Smarsly et al. (2001) to model the SANS of the mesopores. The shift in the position of the second maximum is indicated by a solid line. $s = 2/\lambda\sin(\theta)$, λ wavelength (0.607 nm).

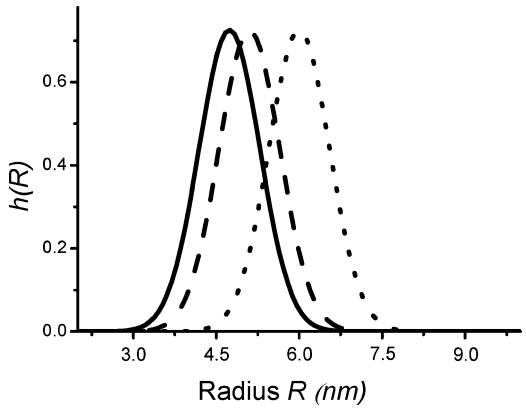

Figure 4. Pore-size distribution for the SE3030 silica as a function of the nitrogen sorption p/p_0 as obtained from Fig. 4. Solid line: $p/p_0 = 0$, dashed line: $p/p_0 = 0.63$, dotted line: $p/p_0 = 0.81$.

average distance (within the Rosenfeld model), the average pore size and its variance. It is seen that the SANS data are reasonably fitted by this basic approach for the mesopores, in particular at larger scattering vectors. Interestingly, at larger s the fit for $p/p_0 = 0$ is not as nice as for the two other SANS curves obtained at higher relative pressures, which is attributable to the unfilled micropores, which were determined to be of ca. 1 nm in size based on the concept of the "chord-length distribution" function (Göltner et al., 2001; Smarsly et al., 2001).

It is seen (Fig. 4) that the pore size apparently increases as a function of p/p_0, which has to be interpreted as the increase in the pore size of the remaining open mesopores. The shape of the curves in Fig. 4 was set constant, while evidently it should become asymmetric during the condensation, because it turned out to be impossible to extract both the pore size and the shape of the pore size distributions from the data (Smarsly et al., 2001). More importantly, the pore diameter for the evacuated sample ($p/p_0 = 0$) is about 9.5 nm, which is in excellent agreement with the sorption analysis. A suitable approach to derive the microporosity from SANS data was presented in Göltner et al. (2001).

4. Conclusions

Detailed SANS and sorption experiments and analyses were carried out to study the porosity in worm-like mesoporous silicas. As a main result, the mespore size obtained from high-resolution nitrogen and argon sorption, and SANS are in excellent agreement, using a novel NLDFT approach introduced by Ravikovitch and Neimark. In particular, our results indicate that this NLDFT approach is applicable to mesoporous silicas consisting of a network of worm-like mesopores which exhibit pore sizes significantly larger than those of the M41S class and SBA-class. In addition, also for the microporosity an excellent agreement is achieved between the NLDFT approach and small-angle scattering techniques. These mesoporous silicas possess additional micropores of ca. 1–1.3 nm, which are located in the walls separating the mesopores.

Furthermore, our sorption studies also shed some light on the origin of the pronounced hysteresis observed in these types of silicas. Since the isotherms differ significantly as a function of the adsorptive used (nitrogen, argon), especially the closure points of the desorption branch, our data reveal clearly that, contrary to our original conclusion (Smarsly et al., 2001) the hysteresis is not attributable to pore blocking, but rather a cavitation phenomenon (for details see Thommes et al., 2005). In addition, further experiments are planned to elucidate more details about the hysteresis in novel adsorbents containing both micro- and ordered mesoporosity.

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