

***In-situ* Small-Angle X-ray Scattering during Sorption in Silica Possessing an Ordered Hierarchical Mesopore Architecture**

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Recently, the fabrication of oxides with an ordered pore structure on the nanometre scale (“mesoporous materials”) has received substantial attention. Aside from potential applications in the field of separation, catalysis, etc., they can serve as model systems to study the condensation of gases in such confined geometries. Recently, we introduced a new class of mesoporous materials possessing a hierarchical arrangement of two types of pores of different size, i.e. 14 nm spherical mesopores being connected through worm-like mesopores of 3 nm in diameter (KLEC16 silica, see Figure 1). Such materials are favourable, because they combine a high surface area with large pore volume, and are particularly interesting to address the fundamental question how relatively large pores are filled and emptied through smaller pores. For instance, recently these materials were utilised as model systems to verify the existence of a special pore emptying mechanism (“cavitation”) [1].

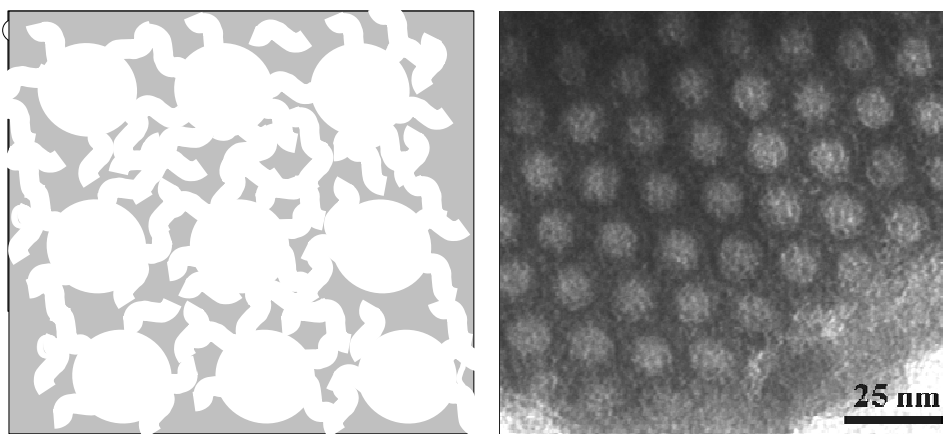


Figure 1: Schematic illustration (left) and transmission electron microscopy (TEM) image (right) of the SiO₂ material under study (KLEC16 silica). The sample contains highly ordered 3D arrays of spherical mesopores (14 nm in diameter), connected through worm-like mesopores of 3 nm in diameter, which are seen in the TEM images between the larger spherical mesopores.

In the present work, the KLEC16 silica material is used to study sorption of CH₂Br₂ *in situ*. Using this organic compound, the *in-situ* experiment takes advantage of the principle of “contrast matching” between condensed liquid and amorphous silica, which have almost identical scattering length densities. Hence, in the course of increasing the pressure p of CH₂Br₂, filled pores do no longer contribute to the scattering pattern, and thereby the filling process can be studied in detail. Due to the periodic arrangement of the spherical mesopores, it is possible to apply diffraction techniques to extract detailed information about the pore wall structure, the adsorbed films in the pores and also to clarify, if indeed the 3 nm pores are located between the larger 14 nm mesopores throughout the sample. The latter information could hardly be obtained by other techniques. For *in-situ* small-angle X-ray scattering (SAXS) in conjunction with sorption, a special cell was designed, which had already been successfully used in our previous study [2]. The specimen chamber was made of aluminium and the cell windows were equipped with Kapton foils, with the sample being positioned in between. The silica powder was poured in a brass ring with an inner diameter of 3 mm and pressed to a stable pellet. SAXS measurements were performed at the beamline A2 at

HASYLAB/DESY. The transmission of the sample at each sorption state was determined *in situ* by using an ionisation chamber before the adsorption cell to monitor the primary X-ray flux and a photodiode mounted in the beamstop to measure the transmitted photons. A typical exposure time of 60 – 80 s yields a scattering pattern with excellent measuring statistics. All scattering images were corrected for background scattering, electronic noise, transmission and polarisation by using the data reduction program FIT2D (A. P. Hammersley, ESRF, Grenoble, France). More experimental details are described in ref. [2].

The radially averaged SAXS curves obtained between the situation of the evacuated sample and the condensed liquid (ca. 56 mbar) showed various interesting features regarding the porosity and the filling process (Fig. 2). First, the pressure-dependent experiments proved that the SAXS data themselves could be attributed to a superposition of two different types of pores: at $p = 0$, the part of the curve $s < 0.25 \text{ nm}^{-1}$ was attributable to the spherical 14 nm mesopores. ($s = (2/\lambda) \sin \theta$, with 2θ being the scattering angle and λ the wavelength.) The broad maximum at $s = 0.25 \text{ nm}^{-1}$ is generated by the worm-like 3 nm mesopores. Interestingly, at $p > 13 \text{ mbar}$ further oscillations became visible belonging to the form factor of the 14 nm spherical mesopores. This occurrence of higher order form factor oscillations indicated a high degree of perfection of the 3D cubic arrangement of the spherical mesopores. Fitting the data with a model of polydisperse spheres placed on a fcc lattice provides a pore diameter of 14 nm, in excellent agreement with the TEM analysis. Second, and more importantly, the relative overall intensity of the SAXS curves showed interesting changes as a function of pressure. Starting from $p = 0$, the SAXS curve (below $s = 0.1 \text{ nm}^{-1}$) underwent a significant, continuous increase, which coincides with the filling of the small 3 nm mesopores. These findings provide direct evidence of the hierarchical nature according to the following considerations based on “contrast matching”. In essence, the filling of the 3 nm mesopores corresponds to an increase of the density of the matrix between the 14 nm mesopores, which in turn results in an increase of the overall intensity due to $I(s) \sim (\rho_{\text{matrix}} - \rho_{\text{pore}})^2$. The experimentally observed increase proves indeed the presence of a hierarchical pore architecture, and a first semi quantitative analysis proved that the entire sample consists of this hierarchical mesostructure of pores. Hence, our results indicate that the combination of SAXS with *in-situ* sorption provides an excellent conceptual methodology to study hierarchy and connectivity of pores on the nanometre scale. Suitable model functions will be used to fit the SAXS data to get further information about the pore filling mechanisms.

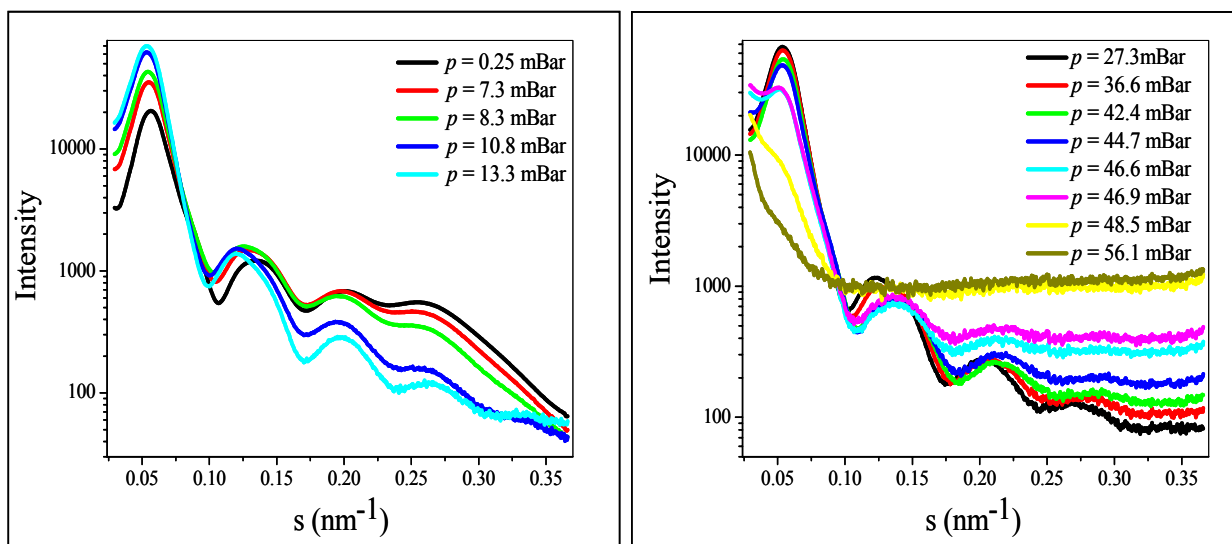


Figure 2: *In-situ* SAXS data recorded in KLEC16 silica during sorption of CH_2Br_2 at various pressures.

References

- [1] M. Thommes, B. Smarsly, M. Groenewolt, P. I. Ravikovitch, and A. V. Neimark, *Langmuir* 22, 756 (2006)
- [2] G. A. Zickler, S. Jähnert, W. Wagermaier, S. S. Funari, G. H. Findenegg, and O. Paris, *Phys. Rev. B* 73, 18410 (2006)