In-situ SAXS Study of the Deformation of the SBA-15 Pore Lattice during Argon and Xenon Adsorption

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Mesoporous silica-based materials with structural units on the nanometre scale are attracting a great deal of attention, because of both potential technical applications and the fundamental interest in their special properties. The capillary adsorption and desorption of solids and liquids in nanometre sized pores shows a considerable effect on the pore lattice itself. Due to the presence of solid/liquid condensate inside the pores, the pore lattice can be expanded or contracted, respectively. In previous studies several combinations of condensate and substrate were examined, however, contradictory results were obtained [1-5]. As the experimental results vary, there are also different theoretical approaches on this topic. In some studies, the effects are explained by the Laplace pressure [1,3,5] or by some kind of dispersion force [2].

In the present study, the adsorption of rare gases argon and xenon in SBA-15 was studied in-situ by small-angle X-ray scattering (SAXS). SAXS experiments were performed at the beamline BW4 (HASYLAB/DESY). A custom-made gas adsorption apparatus was applied for in-situ studying physisorption by SAXS. The sample cell was temperature-controlled and connected via a capillary and a dosing apparatus to an external gas reservoir. The X-ray beam was monochromatised to a nominal wavelength of 0.1381 nm and focused horizontally and vertically. The quadratic cross-section of the beam was defined by pairs of aperture slits to 0.5 mm × 0.5 mm at the sample position. A vacuum flight tube was inserted between the sample and the detector in order to avoid air scattering. The scattered photons were detected by a CCD detector with a resolution of 2048 × 2048 pixels (pixel size: 79.1 × 79.1 μm²). SAXS patterns covered a total range of scattering vector of 0.12 nm⁻¹ < q < 2.12 nm⁻¹. The length of the scattering vector q is given by |q| = q = 4πλ⁻¹ sinθ, with λ being the X-ray wavelength and 2θ the scattering angle. The transmission of the sample at each physisorption state was determined in-situ by using an ionisation chamber to monitor the primary flux and a photodiode positioned at the beamstop to detect the transmitted intensity. SAXS patterns were corrected for parasitic background scattering, detector efficiency, solid angle, primary flux, and sample transmission. All samples showed isotropic scattering patterns, which were azimuthally averaged for equal radial distances from the central beam.

Figure 1a shows the isotherm of argon in SBA-15 at a temperature of 80 K, showing a pronounced hysteresis between the adsorption and desorption branch. The physisorption of argon in SBA-15 was studied at a temperature of 80 K (liquid argon) and 70 K (solid argon), respectively. The SAXS patterns showed a shift of the Bragg peaks towards smaller q-values for capillary condensation (adsorption) as well as for pore evaporation (desorption) for both temperatures which is equivalent to an expansion of the pore lattice (relative strain: ε = Δd/d ≈ −Δq/q). Figure 1b and 1c show the relative lattice strain ε, derived from the shift of the (10)-Bragg-peak (Fig. 2a), as a function of relative pressure p/p₀ and filling fraction n/n₀ for adsorption and desorption of argon, respectively. At a temperature of 70 K (solid argon) the effects are similar. The observed effect of lattice strain can be explained by the Laplace pressure. Using the Laplace pressure Δε = 2γ/R the relative strain ε is calculated by

ε = Δp(1−2ν) / E(1−P)³.

The following numerical values are used for physisorption of argon: Surface tension γ = 15 mN/m, radius of the meniscus r = 2.75 nm, Poisson’s ratio ν = 0.17, Young’s modulus E = 71.7 GPa, and porosity P = 0.74, which results in a strain of about 0.5%. This value is in reasonable agreement
with the observed strain. However, the direction of deformation, i.e. expansion, seems questionable regarding the fact that the Laplace pressure is directed towards the pore centre, which should result in a contraction of the lattice. For the calculation of the xenon isotherms the surface tension $\gamma = 19.2$ mN/m was used, which results a relative strain of 0.65%. This value does not fit as well to the data as it does for argon.

The shifting of the Bragg peaks can also be explained by the electron density contrast. It is known that the pores in SBA-15 show a finite size distribution, where the smaller pores are filled first at lower pressure $p/p_0$. As the electron density of argon and especially xenon matches the one of SBA-15, filled pores are less visible to X-ray diffraction, thus, mainly pores with larger diameter are detected, which would have a similar effect as an increasing lattice parameter. In order to check this hypothesis we have analyzed the shape of the Bragg-peaks (Fig. 2). Assuming that only half of the FWHM is due to a lattice constant distribution, while the rest is due to the experimental setup, one can see that the peak for the partial filling shifts out of the peak for the empty sample (Fig. 2b). This is a contradiction to the assumption of a contrast-matching-effect as there are lattice constants in the partially filled pores that are not in the empty one and thus there are two possible interpretations: either the observed expansion (Fig. 1) is not an artefact caused by contrast matching or the filling of the smaller pores has to be modelled in a more sophisticated way (e.g. with an altered form factor).

![Figure 1: Physisorption of argon in SBA-15 at 80 K (liquid argon): (a) Sorption isotherm. (b) Strain of the pore lattice vs. relative pressure $p/p_0$. (c) Strain of the pore lattice vs. filling fraction $n/n_0$.](image1)

![Figure 2: (a) (10)-Bragg-peak of SBA-15 for various pressures of argon at 70 K: Evacuated sample (black line), completely filled sample (green), and partially filled sample (red). (b) Lattice constant distribution derived from the (10)-Bragg-peak ($d = 2\pi (q \sin(60^\circ))^{-1}$) considering half of the FWHM is due to the experimental setup.](image2)

References