

# ***In-situ* SAXS study of the Adsorption Behaviour of Periodic Mesoporous Organosilicas (PMOs)**

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Mesostructured silica-based materials with structural units on the nanometre scale are attracting a great deal of attention, both because of potential technical applications and the fundamental interest in their special properties. Since the introduction of these materials about one and a half decade ago, much progress has been made in design and synthesis of novel porous materials. Nevertheless, conventional silica-based mesoporous materials are limited in their range of functional surface properties. Silica-based organic-inorganic hybrid materials, so-called modified periodically ordered mesoporous organosilicas (PMOs) containing both organic moieties and Si-OR groups are representing the next step in development. Recently, a novel group of PMOs was reported, which offers the possibility of pore surface modifications by nearly any desirable functional groups [1,2]. In particular, the attraction towards separation is enhanced by the chance of having a material possessing a chemically selective surface, being able to allocate a special chemical compound. Small-angle X-ray scattering (SAXS) is a powerful experimental technique for obtaining data for the characterization of shape, size, arrangement, and volume fraction of PMOs. The combination of *in-situ* gas adsorption with SAXS is an elegant tool for understanding pore architectures and adsorption mechanisms in mesoporous materials [3].

For the present study, PMOs were synthesised according to the prescription given in references [1,2]. The pore surfaces obtained various chemical modifications: (a) PMO-COOH, (b) PMO-COOH-NH<sub>2</sub> contains half-and-half COOH and NH<sub>2</sub> groups, (c) PMO-COO<sup>-</sup> containing a COO<sup>-</sup> group, and (d) PMO-V=O<sup>2+</sup>-COOH-NH<sub>2</sub> with additional V=O<sup>2+</sup> ions.

SAXS experiments were performed at 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 gas dosing apparatus to the liquid adsorbent dibromomethane (CH<sub>2</sub>Br<sub>2</sub>) in an external reservoir. For physisorption experiments, the sample cell was thermostated to be the coldest point in the system, and the reservoir stayed at ambient temperature. CH<sub>2</sub>Br<sub>2</sub> vapour was supplied to the sample in the adsorption cell, where the vapour pressure was measured continuously. The X-ray beam was monochromatised to a nominal wavelength of 0.1381 nm and focused horizontally and vertically using a fixed cylindrical mirror and a plane mirror with a mirror bender, respectively. 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 μm<sup>2</sup>). SAXS patterns covered a total range in length of scattering vector of 0.03 nm<sup>-1</sup> < *s* < 0.58 nm<sup>-1</sup>. The length of the scattering vector *s* is given by  $|s| = s = 2\lambda^{-1} \sin \theta$ , with  $\lambda$  being the X-ray wavelength and  $2\theta$  the scattering angle. The transmission of the samples 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 taken continuously during adsorption scans of CH<sub>2</sub>Br<sub>2</sub>. The scattering 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 1 shows a series of SAXS patterns for physisorption of CH<sub>2</sub>Br<sub>2</sub> in PMO-COOH. In the evacuated state, the sample shows a characteristic peak of intensity at  $s \approx 0.12 \text{ nm}^{-1}$ , which significantly changes during adsorption and desorption of CH<sub>2</sub>Br<sub>2</sub>. In the early stages of adsorption up to relative pressures of about 0.20, the peak rises in intensity and its position continuously shifts towards smaller values of *s* (Figure 1a). In the case of contrast matching, only void pores contribute

to the SAXS signal. Therefore, the shift apparently corresponds to an increase of the average pore-to-pore distance between empty mesopores, assuming that the pore size does not correlate with the pore position in the material. Besides the changes of the characteristic peak, an increase in SAXS intensity at small scattering vectors is observed, which might be due to the rather broad size distribution of the mesopores. In pressure range starting from  $p/p_0 \approx 0.20$ , the height of the peak decreases, the peak position still shifts towards smaller  $s$  values, however, the intensity at small  $s$  increases continuously (Figure 1b). These variations of the SAXS patterns can be qualitatively interpreted as continuous filling of the remaining mesopores. After exceeding the pore condensation point, a strong decrease of scattering intensity is observed (Figure 1c). The SAXS signal almost vanishes and only a small hump can be recognised at  $s \approx 0.12 \text{ nm}^{-1}$ . This effect might be interpreted as an imperfect contrast matching condition between the average electron density of the PMO material and  $\text{CH}_2\text{Br}_2$ .

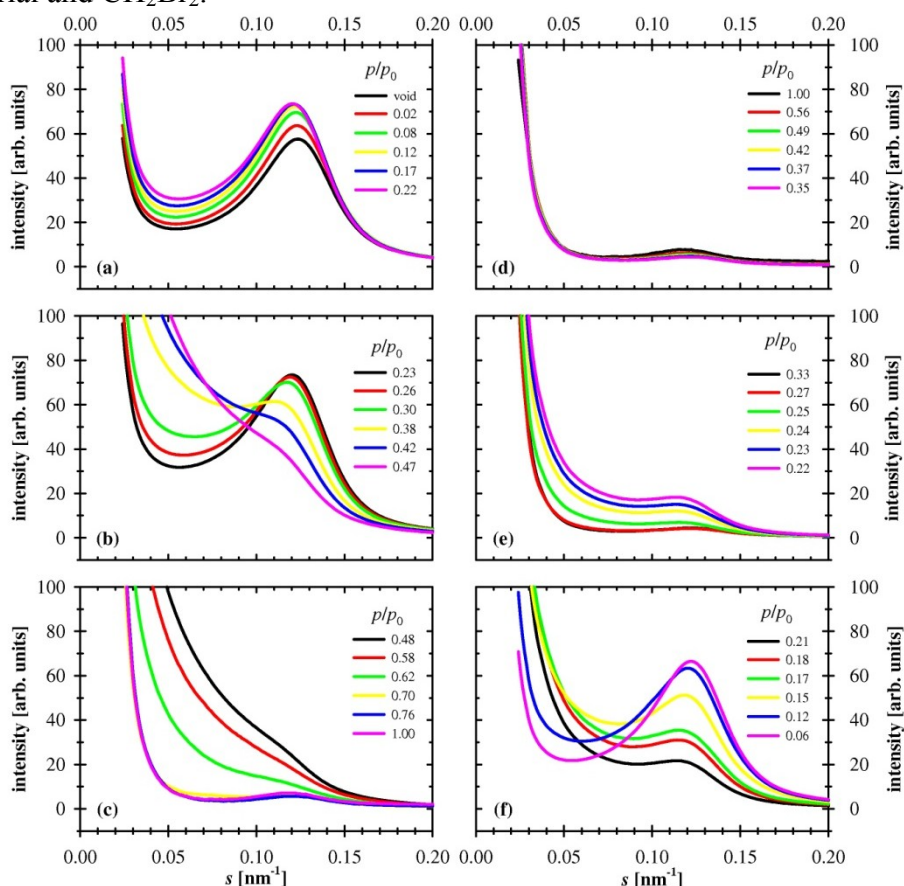


Figure 1: *In-situ* SAXS patterns for adsorption (a-c) and desorption (d-f) of  $\text{CH}_2\text{Br}_2$  in PMO-COOH. The values given in the figure legends refer to relative gas pressures  $p/p_0$ .

The scattering curves for desorption are shown in Figures 1d-f, where it can be seen that the effects are completely reversible, i.e. after desorption the initial state is reached again. Minor changes in the SAXS patterns are observed down to relative pressures of about 0.30, where only the scattering intensity increases at small values of  $s$  (Figure 1d). At  $p/p_0 < 0.30$ , which corresponds to the region of pore emptying, the scattering intensity of the characteristic increases (Figure 1e). Figure 1f shows desorption at low pressures ( $p/p_0 < 0.21$ ), where the scattering peak further increases in intensity and shifts towards bigger scattering vectors. At very low pressures, the intensity at the small-angle minimum decrease, which can be interpreted in the reverse way as for adsorption. A more detailed method of interpretation is currently in progress.

## References

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