Direct observation of the xenon physisorption process in mesopores by combining in situ Anomalous Small-Angle X-ray Scattering and X-ray Absorption Spectroscopy

A. Hoell[1], E. Gericke[1,2], D. Wallacher[1], R. Wendt[1], G. Greco[1], M. Krumrey[3], S. Raoux[1,4], S. Mascotto[5]

[1]Helmholtz-Zentrum Berlin, 14109 Berlin, Germany, [2]Institut für Chemie, Humboldt-Universität zu Berlin, Germany, [3]Physikalisch-Technische Bundesanstalt (PTB), 10587 Berlin, Germany, [4]Institut für Physik, Humboldt-Universität zu Berlin, Germany, [5]Institut für Anorganische und Angewandte Chemie, Universität Hamburg, Germany.

hoell@helmholtz-berlin.de

Mesoporous materials are excellent materials to be used in energy and environmental related applications. Methods to characterize the pore structures and the filling and emptying processes are physisorption and small-angle scattering. Gas physisorption in mesoporous materials and the associated capillary hysteresis intrigue the scientific community since decades. These phenomena are largely exploited for the characterization of porous solids, which justify the strong need for their complete understanding. To date, the major hurdle lies in a reliable description of the state of the confined fluid, which is usually given by measuring macroscopic observable, i.e. the amount of adsorbed gas.

Despite computational methods, *in situ* techniques combining gas physisorption with X-ray scattering methods showed in the last years to be valuable tools to get deeper insights into gas adsorption phenomena [1, 2]. Combining the different contrasts of SAXS and SANS and applying contrast matching [1], a more detailed, locally resolved description of the process could be given by the analysis of the scattering signals of the material pore structure. However, clear and comprehensive assessment of the adsorption process is still missing since the adsorbate evolution in the mesoporous host could be only indirectly investigated.

This presentation deals with the development of a novel *in situ* method based on the combination of anomalous small-angle X-ray scattering (ASAXS) and X-ray absorption near edge structure (XANES) spectroscopy to directly probe the evolution of the xenon adsorbate phase in mesoporous silicon during gas adsorption at its boiling point of 165 K [3]. The interface area and size evolution of the confined xenon phase alone were determined from ASAXS demonstrating that filling and emptying the pores follows two distinct mechanisms. The mass density of the confined xenon was found to decrease prior pore emptying. XANES analyses showed that Xe exists in two different species when confined in mesopores. This combination of methods provides a smart new tool for the study of nanoconfined matter for catalysis, battery electrodes, and for gas and energy storage applications.

The instrumental setup used allowed us to reach the Xenon L_3 X-ray absorption edge at 4.781 keV. The combination of that three experiments, ASAXS, XANES and physisorption were done *in situ* on different points of the adsorption and desorption branch of the isotherm. Thus, from the resonant scattering curves of xenon the mesoscopic evolution of the adsorbate (multilayer formation, capillary condensation and desorption) could be directly investigated.

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