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IR Micro-imaging of mesoporous silicon as a model system for the investigation of hysteresis phenomena

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Ensembles of molecules confined to mesopore spaces reveal features which may notably deviate from their behavior both in the bulk phase and under dominating host-guest interaction. A previous detailed investigation of molecular dynamics in Vycor porous glass with a pore diameter of 6 nm using pulsed field gradient nuclear magnetic resonance (PFG NMR) indicated that under identical external conditions (temperature, pressure), different "histories" of sample preparation may give rise to dramatic differences in their microdynamics [1–3]. One approach to rationalize the occurrence of history-dependent states in mesoporous host-guest systems is the occurrence of a geometric disorder-induced rugged landscape in the free energy. To get deeper insight into this phenomenon, novel options provided by the development of IR micro-imaging [4] have been used in the present work.

IR micro-imaging is a powerful tool for the investigation of sorption phenomena because it allows obtaining time- and space-resolved images of the concentration of guest molecules within the host material. The possibility of visualizing the variation of probe molecule arrangements at different pressures (see figure 1) is a promising experimental approach for a quantification of hysteresis phenomena and could also be the key for a more detailed insight in their correlation with underlying pore filling mechanisms.

Electrochemically etched mesoporous silicon with a spatially ordered pore system was chosen as host system for this study. The pore system has been designed in a way that 5 nm pores of 55 μm length are continued by channels of about 10 nm pore diameter with a length of 45 μm. The application of focused ion beam milling to a freshly etched porous silicon film enabled the preparation of a silicon sample with the channels open on both sides and aligned perpendicular to the incident IR beam. Before the measurements, the sample was oxidized under oxygen atmosphere to increase its optical transmissibility. Benzene was used as a guest molecule, the experiments were performed at room temperature.

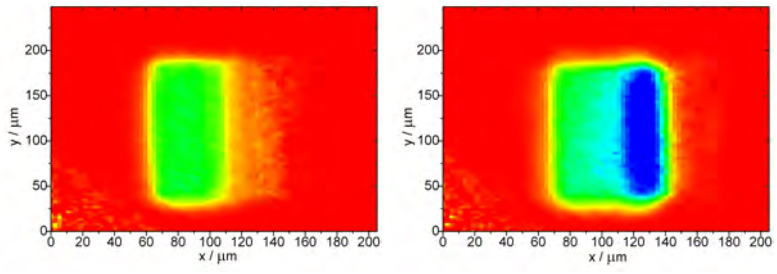

Figure 1: Selected FPA maps of benzene adsorption in a 175 μm × 100 μm × 52 μm piece of mesoporous silicon at a pressure of 75 mbar (left map) and 115 mbar (right map) with the 5 nm pores being arranged on the left half and the 10 nm pores on the right half of the sample. Light color represents low, dark color high benzene concentration.

From the maps recorded with the focal plane array (FPA) detector for pressures from 0 mbar up to saturated vapour pressure of benzene, concentration profiles were obtained (figure 2). Integration gave the

respective isotherm with a well-observable hysteresis loop. The kinetics of the concentration equilibration following each pressure step were studied separately using a single element detector (right graph of figure 2). In particular, at the onset of the hysteresis the uptake kinetics were found to be slowed down.

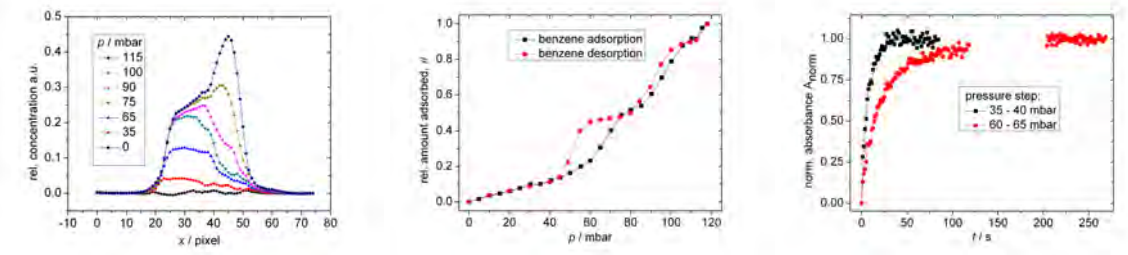

Figure 2: Concentration profiles for benzene adsorption (left graph). Sorption isotherms obtained upon integration of the concentration profiles (middle). Uptake curves showing the slowing down of the system kinetics within the hysteresis region (right graph).

By the development of suitable procedures of sample preparation and activation, we succeeded in using the full potential of IR micro-imaging for the application to mesoporous silicon. By this, the basis for further in-depth studies of a first, simply designed model system for both ad- and desorption of benzene, including FPA maps, concentration profiles, the corresponding isotherm and the uptake curves for each pressure step, was provided.

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