Accessing micro- and macroscopic pictures of gas adsorption by in situ powder diffraction

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Two methods are traditionally used to characterize gas adsorption properties in porous solids: volumetric and gravimetric. They have a number of limitations, but most importantly, they yield a macroscopic picture of interactions (*properties*), without access to a microscopic picture (mechanisms on an atomic level). Diffraction is commonly used as a complementary technique to explain these properties, giving insight into structure and thus revealing the underlying guest-host and guest-guest interactions. Various anomalies (deviations from a typical behaviour) detected by the macroscopic methods require an in situ diffraction experiment, aiming to identify the responsible phenomena like a guest rearrangement / repacking, framework deformation etc. Thus, a separate diffraction experiment is usually providing a microscopic picture for the properties found by other physico-chemical methods.

In this presentation we will show examples of using in situ powder diffraction to simultaneously access the structure and adsorption properties of a small pore crystalline solid. (Quasi)-equilibrium isotherms and isobars can be built directly from sequential Rietveld refinements, both on adsorption and desorption, thus addressing the hysteresis and kinetics of gas adsorption/desorption. Detailed picture of guest reorganization with an increasing uptake can be obtained. Note that the reorganization of the individual guest sites is not accessible to volumetric and gravimetric methods, as they give only total amounts of gas uptake.

Interestingly, the adsorption isobars and isotherms obtained directly from diffraction data can be fitted by known equations, such as a logistic function (isobars) or a Langmuir equation (isotherms). Thermodynamic properties, such as enthalpy and entropy of gas adsorption can be extracted from these curves. The limitations of this technique are very different from traditional methods, thus making it highly complementary.

Lastly, the adsorption kinetics can be followed by in situ powder diffraction at given P,T conditions versus time. The guest uptake extracted by a sequential Rietveld refinement can be fitted and analysed in terms of Arrhenius theory giving access to the activation energies for gas diffusion. Thanks to the microscopic picture these barriers can be tentatively attributed to various diffusion paths inside the solid.

This talk will be illustrated by examples of noble gas adsorption in a porous hydride, γ-$Mg(BH_4)_2$ [1], featuring 1D channels suitable to distinguish and likely separate some of these gases. Besides published results [2,3], a lot of unpublished data will be shown.

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Keywords: thermodynamics; kinetics; in situ powder diffraction