MS26-04 Get more for your porous system: heats of adsorption from powder diffraction data

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In this talk I shall present problems that can be tackled by diffraction experiments under gas pressures. The nature of the porous phase and the strength of solid-gas interaction define what information is assessable:

- For large-pore systems, macroscopic information can be obtained, such as on occurrence of phase transitions, variation of cell parameters, size of hysteresis loops. These data are very useful in combination with other techniques, phenomenological models and theoretical calculations.
- For the small-pore systems, in-situ diffraction data allow to access microscopic information, such as location of guest molecules, nature of host-guest interactions and sometimes even energy differences for adsorption sites.
- When a strong chemical interaction occurs between the crystalline material and the gas, complex sequences of chemical reactions can be disentangled from diffraction data alone. De- and re-hydrogenation reactions of complex (chemical) hydrides are the examples.

Experimental setups and pressure cells will be presented, as well as our new methodological developments aiming for extracting isosteric heats of adsorption *vs*. loading from diffraction data alone [1]. The latter is possible for small-pore systems, where a guest can be reliably located and its occupancy refined as a function of gas pressure and temperature. Experimental data can be collected in a form of isotherms or isobars, and the interpolation or an analytical description should be used in order to get values for the equal loadings. The enthalpies are obtained using the Clausius-Clapeyron equation. Systematic errors related to correlations with atomic displacements will be addressed.

[1] Y. Filinchuk, B. Richter, T.R. Jensen, V. Dmitriev, D. Chenryshov, H. Hagemann (2011) *Angew. Chem. Int. Ed.* **50**, 11162-11166.

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MS26-05 GPa pressure modification of a scandium microporous metal organic framework (MOF).

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High-pressure crystallographic techniques have recently arisen as a useful means of probing the guest inclusion behavior of metal organic frameworks. Previously, in a high-pressure study on the zeolitic imidazolate framework ZIF-8 [(Zn(2-methylimidazolate)$_2$] we surrounded a crystal with a liquid hydrostatic medium inside a merrill bassett diamond anvil cell (DAC).[1] The liquid medium here is used to apply pressure evenly to the sample. On increasing pressure we discovered that not only could we force the medium into the pores causing the sample to expand, but at 1.47 GPa (≈ 15000 atm.) the sample underwent a phase transition which resulted in a significant increase in porous volume and content.

Here we present results on a microporous scandium (benzene-1,4-dicarboxylate), Sc_2BDC_3 framework and its –NO_2 derivative to 3 GPa.[2] On applying pressure using methanol as the hydrostatic medium, we have been able to force methanol molecules inside the hydrophobic pores of Sc_2BDC_3, initially causing the sample to expand, something which is impossible to acheive under ambient pressure conditions. On increasing pressure above 1.0 GPa, the small channels in Sc_2BDC_3 are then hyperfilled with methanol molecules, resulting in very high density methanol containing pores, containing ordered methanol molecules with a density greater than that of solid methanol at 4.0 GPa.

On applying pressure to Sc_2BDC_3 using a non-penetrating medium, we discovered that quite different behavior occurs, with the sample becoming amorphous at very low pressures (0.2 GPa). The amorphisation is also accompanied by a change in colour, with the crystal changing from colourless to black. This unusual result is fully reversible within a single crystal, with the full crystallinity of the original crystalline phase retained on decompression.

The results here have clear implications for the use of GPa pressures in seperation technologies, and we aim to develop these in the future.

[1] Moggach, S. A., Bennett, T. D. & Cheetham, A. K. (2009). *Angew. Chem., Int. Ed.* **48**, 7087-7089.
[2] Ashbrook, S. E., Thompson, S. P., Fairen-Jimenez, D., Banu, A.-M., Düren, T. & Wright, P. A. (2011). *Inorganic Chemistry* **50**, 10844-10858.