In-situ Neutron Powder Diffraction Measurement of the Hydrogen Storage Properties of Novel Metal-Organic Frameworks

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The hydrogen storage properties of a series of metal-organic frameworks (MOFs) were probed through the use of neutron powder diffraction (NPD), which allowed the determination of site-specific adsorption properties as a function of *in-situ* deuterium (D_2) loading. The present experiment was performed at base temperature (4 K) using a closed-cycle refrigerator (CCR) with a sample stick equipped with a stainless-steel gas dosing line. NPD patterns were collected for various materials dosed with known quantities of gas as has been demonstrated previously [1,2].

NPD data was collected for the desolvated frameworks and then for *in-situ,* sequential D_2 loadings of 0.5, 1.0, 2.0, and 3.0 D_2 molecules per metal atom site. Some of the diffraction patterns are shown in Figure 1. Through Rietveld analysis of the diffraction data for the host framework and subsequent Fourier difference mapping of the excess scattering density for each gas dosing, the positions, occupancies, and relative binding energies can be determined for each gas loading. In Fe-MOF-74, the initial D_2 adsorption is at the unsaturated (desolvated) Fe-atom, the secondary adsorption occurs at the oxygen atoms that bridge the iron and organic linkers, and the weakest, tertiary adsorption occurs at the benzene linkers. The diffraction results are ideal for correlation with the complimentary inelastic neutron scattering and gas uptake measurements as was recently demonstrated in Fe-MOF-74 [2].

References

[1] K. Sumida, S. Horike, S. S. Kaye, Z. R. Herm, W. L. Queen, C. M. Brown, F. Grandjean, G. J. Long, A. Dailly, and J. R. Long. Chem. Sci., 2010, 1, 184–191.

[2] W. L. Queen, E. D. Bloch, C. M. Brown, M. R. Hudson, J. A. Mason, L. J. Murray, A.J. Ramirez, V. K. Peterson, and J. R. Long, Dalton Transactions, 2012, Advance Article, doi: 10.1039/c2dt12138g

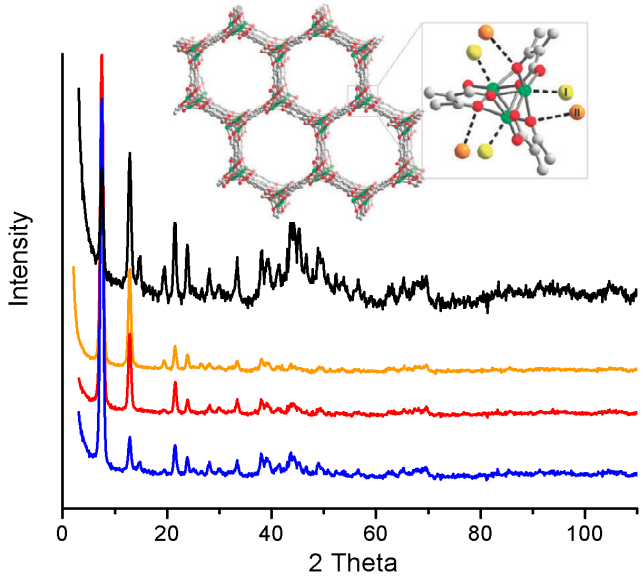

Fig. 1 NPD patterns collected on the C2 diffractometer for deuterium (D_2) dosed Mg/Fe-MOF-74 as a function of gas pressure per metal atom binding site. The black trace shows a zoomed view of the fine details that give the positions of the D_2 versus loading. A representation of site-binding information that is gained is given (top) as previously determined in Fe-MOF-74 [2].