Neutron Powder Diffraction Studies of Metal-Organic Frameworks for Gas Storage and Separation

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The current need for basic research to identify and understand the fundamental principles governing gas adsorption and separation processes is as high as ever. The relevance has been highlighted in recent U.S. Department of Energy (DOE), Office of Basic Energy Science Roundtable Reports, including Foundational Science for Carbon Dioxide Removal Technologies and Foundational Science for Carbon-Neutral Hydrogen Technologies.

Thanks to its sensitivity to light elements and isotopes, neutron scattering experiments readily provide information on the position, occupancy, and short-range order about the guest-host interactions, providing unparalleled insight into long-range order, local steric hindrance, and dynamic local environments.

In this talk, I will present the most recent experimental results from the POWGEN diffractometer, SNS. In particular, two model systems will be discussed,

1. investigating the H2 adsorption behavior in MFM-170 and its derivatives. MFM-170 samples have demonstrated favorable H2 adsorption capabilities. Interestingly, introducing an amine group to the pyridine ring linked to the Cu metal in MFM-170 resulted in a different adsorption isotherm, despite the linker size and pore size remaining unchanged. In situ neutron scattering experiment identifying eight adsorbed sites after stoichiometric gas loading at 77 K. Total uptake ~ 0.055 g/g was achieved during the in situ experiment, comparable with the Ni2(m-dobdc) benchmark.1 I will discuss the effect of the side functional group on the adsorption behavior
2. optimizing pore size in M3(vtz)6 MOFs for H2/D2 separation . The pore size of MOFs plays a crucial role in determining their properties. Indeed, a linear correlation between volumetric absolute hydrogen uptake and volumetric surface area was observed,2 favoring small pores that could be better tuned chemically. One model system is M3(vtz)6, whose pore size could be tuned by substituting metal ions (M = Mg, Mn and Zn), and prompting drastically different H2/D2 adsorption selectivity, from ~30 to 15.3 Gas dosing experiment at POWGEN has identified two adsorption sites in the Zn3(vtz)6: one sitting in a “pocket” surrounded by 3 vtz linker, and the other located in an open position. Although both sites have similar H2 occupancy, they demonstrated varied selectivity: the H2 sitting in the "pocket" site is more likely to be replaced by D2 after exposing the H2-loaded sample under D2. The location of the adsorption and its implication for isotope separation will be discussed.

Refernces
{1} Kapelewski, M. T. et al. Chem. Mater. (2018) doi:10.1021/acs.chemmater.8b03276
{2} Balderas-Xicohténcatl, R. et al. Energy Technol. (2018) doi:10.1002/ente.201700636.
{3} He, C. T. et al. Chem. Sci. (2017) doi:10.1039/c7sc03067c

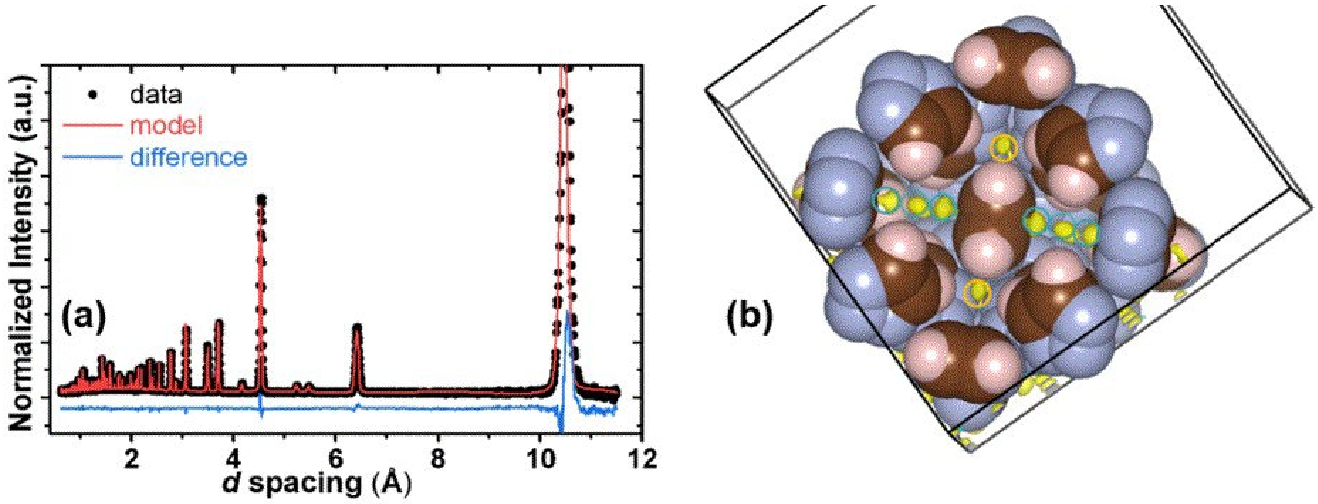

Fig 1. Diffraction data from POWGEN of $Mn_3(vtz)_6$ after H_2 loading at 40 K, identifying two distinctive adsorption sites.

Figure 1