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Neutron powder diffraction of metal-organic frameworks for hydrogen storage

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Abstract. We review recent structural studies that we have undertaken aimed at elucidating the fundamental properties of metal-organic framework materials and their interactions with hydrogen. We have shown that exposing coordinatively unsaturated metal centers can greatly enhance the hydrogen binding energy and that they result in a significant increase of the surface packing density of adsorbed hydrogen molecules on materials' surface. We will review some of the structural aspects of these materials, especially the adsorbed hydrogen molecule surface packing density in one type of metal-organic framework, MOF-74, which can be packed even denser than that in solid hydrogen.

Keywords. Neutron; diffraction; hydrogen; adsorption; structure.

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1. Introduction

Hydrogen gas is considered as a promising alternative fuel because it burns with high energy efficiency to produce only water. There are significant challenges remaining in making this ideal fuel into an on-board vehicular technology that is safe, cheap, and robust. The U.S. Department of Energy has set targets for on-board hydrogen storage with the gravimetric target of 6.0 wt% by 2010 and 9.0 wt% by 2015, and equally challenging volumetric density targets that approach the capacities of liquid hydrogen. Three main research classes that are being pursued have differing ranges of hydrogen adsorption enthalpies. The stronger of the hydrogen–material interactions are typically present in chemical and metal hydrides, while the weaker enthalpies are encountered in systems based upon physisorption mechanisms. Currently, there is no method that can achieve all the requirements. The physical method, for instance, is mainly limited by the gravimetric and volumetric requirements. For example, compression of hydrogen can only store 1 wt% of hydrogen at $\sim$200 bars. However, a potentially advantageous way of storing hydrogen may be possible using solid-state mechanisms.

Over recent years there have been reports of significant reversible hydrogen adsorption in a versatile class of crystalline adsorbents known as metal-organic frameworks [1–5]. These porous solids are comprised of metal ions/clusters linked together with organic ligands. Both of the structural components may be tuned in a logical fashion to alter the physical, chemical, and even catalytic properties of the host structure [6]. Typical synthesis routes to these materials results in a solvated product that requires an activation step or evacuation of the guest molecules to obtain the high-surface area materials that can adsorb hydrogen. However, there is only a weak interaction between the hydrogen molecules and the pore walls necessitating the use of cryogenic temperatures to obtain significant hydrogen uptake.

While there is significant evidence for the increase in saturation adsorption capacity of hydrogen (at 77 K) with increasing surface area within metal-organic frameworks (MOFs) [5], this is typically less than that obtained in carbon aerogels [7] and the case of activated carbons [8] where every 1 wt% H_2 uptake needs 500 m^2/g of surface area. A clearer understanding of frameworks exhibiting stronger binding interactions and the limitations of the hydrogen surface packing density are needed to facilitate H_2 adsorption at higher temperatures.

Here we will review the recent structural studies we have undertaken aimed at elucidating the fundamental properties of MOF materials that have coordinatively unsaturated metal centers. We have shown that exposing the coordinatively unsaturated metal centers can greatly enhance the hydrogen binding energy toward the theoretically desired binding energy range of 15–20 kJ/mol that has been predicted to maximize the amount of adsorbed H_2 accessible at 298 K within the pressure range 1.5–20 bar [9]. We also demonstrate that the coordinatively unsaturated metal centers can not only increase binding energy but also significantly increase the surface packing density of adsorbed hydrogen molecules on materials' surface. Especially, the adsorbed hydrogen molecule surface packing density in one type of metal-organic framework, MOF-74, can be even denser than that in solid hydrogen at 4 K.

2. Discussion

The neutron powder diffraction data for these measurements were taken using similar methodologies. All measurements were taken as a function of deuterium loading. During experiments, a known amount of deuterium gas is first loaded into the sample (of known mass) at 77 K. The sample is then cooled down to 4 K for about 1 h in order to perform measurements. The outgas pressure reading is zero well before reaching 25 K, except for the special cases where we wish to measure multilayer adsorption structures. This ensures that no bulk hydrogen is present in the MOFs.

We typically analyze the neutron diffraction patterns using the Rietveld refinement method [10,11]. The atomic model of the bare material is usually refined first and used as the starting point for subsequent refinements of the D_2-loaded samples. Using Fourier difference maps for each successive D_2 loading, the positions of the D_2 adsorption sites can often be clearly observed. Accurate values for the D_2 locations and occupancy numbers are subsequently obtained using further Rietveld refinements. Deuterium molecules are treated as point scatterers with double

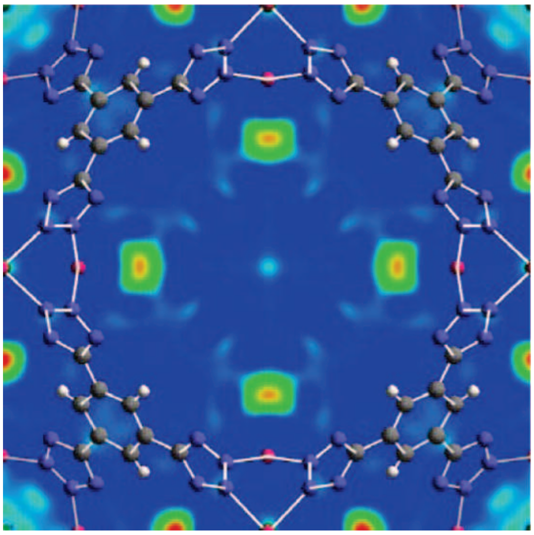

Figure 1. Positive real space Fourier difference scattering length intensity superimposed with the crystal structure of Mn-BTT that indicates the first two D_2 adsorption sites (red-yellow-green regions) for the case of 12 D_2/f.u. (from supplementary material of ref. [14]).

occupancy since they are good quantum rotors that are expected to rotate around its center of mass.

It had been proposed that the occurrence of desolvated metals in MOF systems could increase hydrogen adsorption enthalpies through the interaction of hydrogen with the coordinatively unsaturated metal centers (CUMC) [4,12,13]. Crystallographic data on a partially desolvated Mn-BTT ($Mn_3[(Mn_4Cl)_3(BTT)_8(CH_3OH)_x]_2$, $x \approx 8$, BTT = 1,3,5-benzenetristetrazolate, space group Pm–$3m$) material was the first to show this. We successfully correlated the record maximum isosteric heat of adsorption of 10.1 kJ/mol, the highest observed for a metal-organic framework at the time, to H_2 binding at coordinatively unsaturated Mn^{2+} centers within the framework [14]. Topographically similar to a sodalite cage, chloride-centered square-planar $[Mn_4Cl]^{7+}$ units are linked via BTT^{3-} ligands to form an anionic, three-dimensional framework. The Fourier difference map of the nuclear density between the desolvated framework and the lowest loading of D_2 clearly indicates the positions of D_2 adsorption sites (figure 1). Accurate values for the D_2 locations and occupancy numbers are then obtained by Rietveld refinement with the process being repeated for higher loading of D_2. Significantly, the first adsorption site is located ≈2.3 Å from the Mn^{2+} ions in the framework skeleton, providing the first neutron diffraction evidence for a metal–H_2 interaction within a metal-organic framework. The subsequent loading sites are more associated with the tetrazole ligands possessing interaction distances on the order of 3.5 Å which are typical of van der Waals interactions. There is premature saturation at the first site due to the residual solvent content, however loading to saturation occurs at the following two sites.

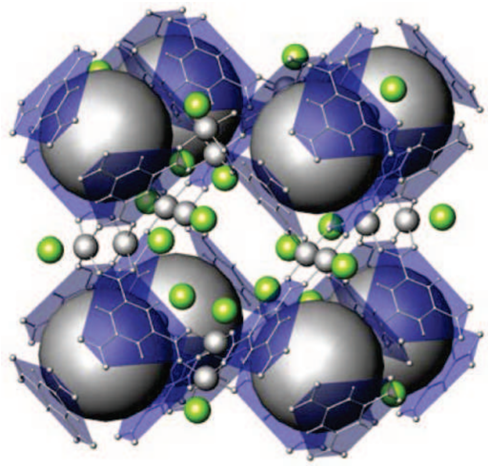

Figure 2. Crystal structure of Cu-BTC with the plane of the ligand moiety shaded (blue). Large gray spheres (radius = 4 Å) indicate the void in the small cage. Cu atoms are drawn as medium sized gray spheres (not to scale). The strongest binding site (green sphere) is along the Cu–Cu axis with a D_2–Cu distance of 2.4 Å [16].

The limitation of having only a few CUMCs being accessible to hydrogen was overcome using copper ions in place of the manganese ions [15]. This approach leads to a compound that can be fully desolvated to expose a greater number of open metal coordination sites, while being isostructural to the Mn complex. A reduction in unit cell parameters on moving from the Mn^{2+} (19.116(1) Å) to Cu^{2+} (18.595(7) Å) materials explains the concomitant decrease in surface areas and saturated hydrogen adsorption capacities of 6.9 wt% and 5.7 wt% at 90 bar and 77 K, for Mn-BTT and Cu-BTT, respectively. The deuterium binding sites in Cu-BTT follow the same order as that in Mn-BTT, but there are some differences in the characteristics of the sites. In particular, the Cu^{2+} ions have a weaker binding affinity for hydrogen than Mn^{2+} ions, as evidenced by the smaller isosteric heat of adsorption of 9.5 kJ mol^{-1} and a longer M–H_2 distance of ≈2.5 Å.

The hydrogen affinity is not determined only by the transition metal; other influences could be the topology, accessibility or the chemical nature of the associated ligands. For instance, Cu-BTC ($Cu_3(BTC)_2$, where BTC = 1,3,5 benzenetricarboxylate) [16] has a moderate hydrogen capacity (≈3 wt% at 77 K and 90 bar) and a relatively low initial enthalpy of adsorption of hydrogen (6.6 kJ mol^{-1}) [5]. Powder diffraction analysis indicates that the Cu^{2+} ion is again the initial adsorption site and that the Cu–H_2 distance is ≈2.4 Å (figure 2) [17]. However, the isosteric heat of adsorption is sufficiently low that there is a competitive filling of the sites [18] and a complex deuterium rearrangement upon increased loading [19]. The activation procedures used in preparing MOFs can have a significant impact on the final surface areas and adsorption capacities. In particular, the Cu-BTC material used here was recently shown to have a low pressure hydrogen adsorption capacity

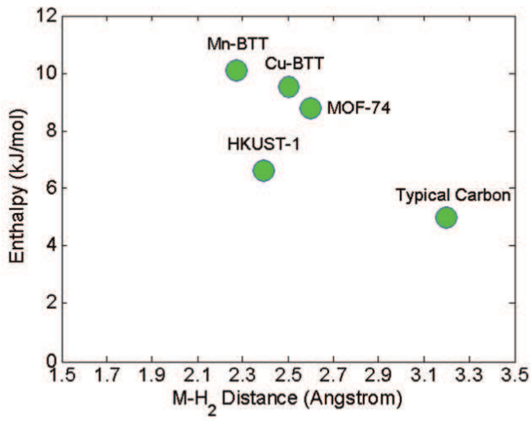

Figure 3. Graph showing the experimental metal–hydrogen distance extracted from neutron diffraction data with the initial isosteric heats measured at 77 K. For comparison, a typical van der Waals interaction of hydrogen on a carbon surface and the nominal value for the isosteric heat is shown.

and high pressure saturation value resembling most other Cu-BTC materials in the literature, but somewhat lower than has been claimed by others [20].

We have just completed a further thermodynamic and neutron diffraction study on a fourth MOF with Zn^{2+} CUMCs and an initial isosteric heat of adsorption of 8.8 kJ mol^{-1} [21]. Known as MOF-74 [22], this is a 1D-pore system with exposed Zn^{2+} ions lining the pore channels. Not only do we find that the initial deuterium binding site is located just 2.6 Å away from the CUMC, but the nearest-neighbor D_2–D_2 distances are surprisingly shorter than in bulk D_2 resulting in an overall surface packing density larger than that of the bulk solid at 4 K.

Having reviewed some of the characteristics of hydrogen adsorption in MOFs, we can plot the relationship between the measured isosteric heat of adsorption against the metal–hydrogen distance of the dominant adsorption site (that should be responsible for the larger than typical enthalpies). While there is no strong correlation and there are other significant factors at play, as mentioned previously, there is perhaps a trend of increasing enthalpy with shorter M–D_2 distances. Further work needs to be performed on a wider variety of materials to enable a stronger inference of the factors affecting the isosteric heats in MOFs.

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