

## Strategies to Improve Hydrogen Adsorption in Metal-Organic Frameworks (MOFs)

Dennis Butcher

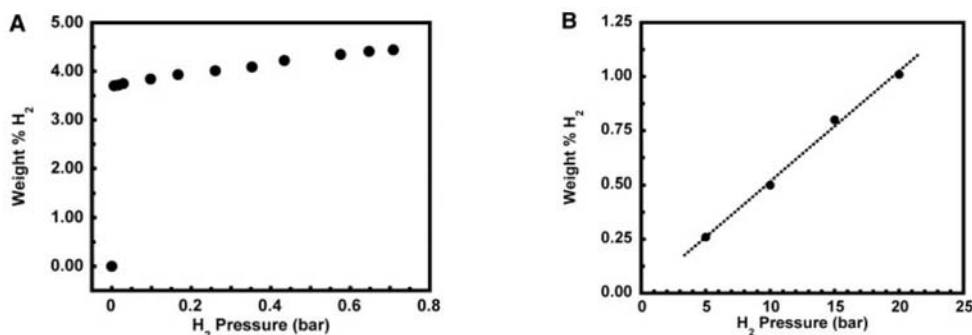
Literature Seminar

October 28, 2008

Hydrogen ( $H_2$ ) has several properties which make it a potentially ideal energy carrier for transportation, military hardware, and auxiliary power generation. The primary ecological benefits of  $H_2$  as a fuel are that its combustion results in the release of water instead of greenhouse gasses or other pollutants, and that it can be generated from renewable sources. As a fuel,  $H_2$  (120 MJ/kg) contains more energy per kilogram than either gasoline (44.5 MJ/kg) or natural gas (50 MJ/kg), but has not seen widespread use because of its low density and difficulty of storage.<sup>1</sup> Liquid  $H_2$  has a density of about 71 g/L at 20 K compared to about 700 g/L for gasoline at ambient temperatures; as a result,  $H_2$  requires a much greater storage volume to achieve the same amount of energy.<sup>1</sup>

The US Department of Energy has set forth targets for  $H_2$  storage systems, which must operate at ambient temperatures (-20 to 50 °C), at pressures below 100 bar, and allow a vehicle range of about 300 miles. To achieve these goals, systems must be robust, lightweight, cost effective, and achieve capacity of 9 wt%  $H_2$  and 81 g/L  $H_2$  by 2015.<sup>2</sup> Various approaches including chemical hydrides, liquid  $H_2$ , compressed  $H_2$ , and physisorption onto metal-organic frameworks have been investigated, but none is economically viable at present.<sup>3,4</sup> Metal-organic frameworks (MOFs) are particularly interesting because they bind  $H_2$  reversibly and have highly tunable structures. MOFs consist of metal containing building units linked together by organic struts to give a highly porous, repeating network.

Currently, the benchmark for  $H_2$  adsorption in a metal-organic framework is 7.5 wt% and 32 g/L (77 K, 70 bar) for MOF-177 prepared by Yaghi and coworkers.<sup>5</sup> The primary determinant of overall  $H_2$  uptake is the surface area and pore volume of the MOF; however, for most MOFs, effective adsorption takes place under cryogenic conditions.

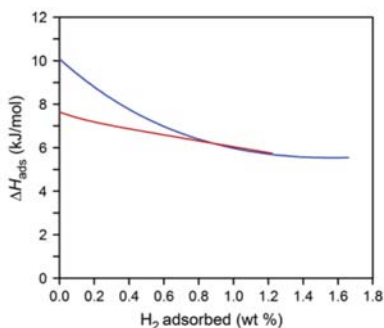


**Figure 1.** A: Hydrogen gas sorption isotherm for MOF-5 at 78 K B: 298 K<sup>6</sup>

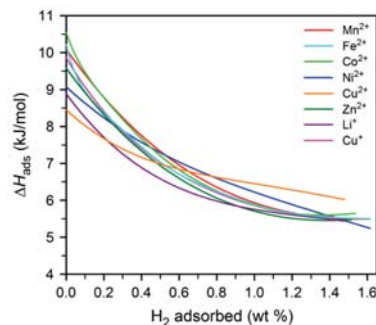
$H_2$  uptake is low at ambient temperature because the MOF- $H_2$  interactions are weak; specifically, the heat of adsorption of  $H_2$  to MOFs ( $\Delta H_{ads}$ ) is too low. Bhatia and Myers have calculated that a heat of adsorption of 15.1 kJ/mol is required for reversible physisorption of  $H_2$

(298 K, 1.5-30 bar).<sup>7</sup> Several strategies have been suggested to improve the H<sub>2</sub> heat of adsorption to MOFs. Reducing the pore size and dimensions has the effect of introducing weak H<sub>2</sub>-framework interactions from both the adsorbing surface as well as the opposite surface, thus increasing the overall  $\Delta H_{\text{ads}}$ .<sup>8</sup> Catenation achieves a similar effect by interweaving two frameworks within one another to reduce pore volume.<sup>9</sup> Incorporating unsaturated metal sites into MOFs is the most promising strategy for improving H<sub>2</sub>  $\Delta H_{\text{ads}}$ ; metal cations induce a dipole in H<sub>2</sub>, resulting in a stronger interaction than the dispersion forces observed in standard MOFs.<sup>4</sup>

One method of introducing metal cations involves removal of coordinated solvent molecules to create coordinatively unsaturated metal centers. Research on dehydrated Prussian blue analogues by Kaye and Long revealed that unsaturated metal ions within a framework can alter the observed  $\Delta H_{\text{ads}}$  because of the differing strengths of M<sup>2+</sup>-H<sub>2</sub> interaction.<sup>10</sup> Dinca and Long extended this work to metal-organic frameworks by using neutron diffraction to study Mn<sup>2+</sup> sites within methanol exchanged, partially desolvated Mn<sub>3</sub>[(Mn<sub>4</sub>Cl)<sub>3</sub>(BTT)<sub>3</sub>(CH<sub>3</sub>OH)<sub>10</sub>]<sub>2</sub>, which showed a higher initial H<sub>2</sub>  $\Delta H_{\text{ads}}$  than the initial DMF solvated framework, [Mn-(DMF)<sub>6</sub>]<sub>3</sub>[(Mn<sub>4</sub>Cl)<sub>3</sub>(BTT)<sub>8</sub>(DMF)<sub>12</sub>]<sub>2</sub> (Figure 2).<sup>11</sup> Cation exchange reactions were performed on this framework to study cation effects and revealed a dependence of H<sub>2</sub> adsorption on the metal cation identity (Figure 3).<sup>12</sup> Zecchina and coworkers verified the effect of varying cations within frameworks by probing the metal-H<sub>2</sub> interaction with variable temperature IR spectroscopy.<sup>13</sup>



**Figure 2:** Initial  $\Delta H_{\text{ads}}$  for solvated (red) and desolvated (blue) Mn<sup>2+</sup> sites



**Figure 3:** Metal cation dependence of  $\Delta H_{\text{ads}}$

Another method to incorporate unsaturated metal sites into MOFs is metal doping of existing MOFs through framework reduction. Han and Goddard have shown through theoretical calculations that alkali metal doping can increase H<sub>2</sub>  $\Delta H_{\text{ads}}$  and H<sub>2</sub> uptake at ambient temperatures over non-doped MOFs.<sup>14</sup> Mulfort and Hupp explored the correlation of  $\Delta H_{\text{ads}}$  and alkali doping ions and found experimentally that cation doping can increase heat of adsorption.<sup>15</sup>

Incorporation of unsaturated metal cations into metal-organic frameworks is a promising strategy to increase H<sub>2</sub> adsorption capacity at ambient conditions. Future research coupling these stronger interactions with large surface area will allow greater H<sub>2</sub> storage capacity in practical operating ranges.

## References

1. van den Berg, A. W. C.; Arean, C. O. "Materials for Hydrogen Storage: Current Research Trends and Perspectives," *Chem. Commun.* **2008**, 6, 668.

2. DOE Office of Energy Efficiency and Renewable Energy Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development, and Demonstration Plan. <http://www.eere.energy.gov/hydrogenandfuelcells/mypp>.
3. Zhao, D.; Yuan, D.; Zhou, H. C. "The Current Status of Hydrogen Storage in Metal-Organic Frameworks," *Energy Environ. Sci.* **2008**, 1, 222.
4. Dinca, M.; Long, J. R. "Hydrogen Storage in Microporous Metal-Organic Frameworks with Exposed Metal Sites," *Angew. Chem. Int. Ed.* **2008**, 47, 6766.
5. Furukawa, H.; Miller, M. A.; Yaghi, O. M. "Independent Verification of the Saturation Hydrogen Uptake in MOF-177 and Establishment of a Benchmark for Hydrogen Adsorption in Metal-Organic Frameworks," *J. Mater. Chem.* **2007**, 17, 3197.
6. Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. "Hydrogen Storage in Microporous Metal-Organic Frameworks," *Science* **2003**, 300, 1127.
7. Bhatia, S. K.; Myers, A. L. "Optimum Conditions for Adsorptive Storage," *Langmuir* **2006**, 22, 1688.
8. Latroche, M.; Surble, S.; Serre, C.; Mellot-Draznieks, C.; Llewellyn, P. L.; Lee, J. H.; Chang, J. S.; Jung, S. H.; Férey, G. "Hydrogen Storage in the Giant-Pore Metal-Organic Frameworks MIL-100 and MIL-101," *Angew. Chem. Int. Ed.* **2006**, 45, 8227.
9. Ma, S. Q.; Sun, D. F.; Ambrogio, M.; Fillinger, J. A.; Parkin, S.; Zhou, H.-C. "Framework-Catenation Isomerism in Metal-Organic Frameworks and its Impact on Hydrogen Uptake," *J. Am. Chem. Soc.* **2007**, 129, 1858.
10. Kaye, S. S.; Long, J. R. "Hydrogen Storage in the Dehydrated Prussian Blue Analogues  $M_3[Co(CN)_6]_2$  ( $M = Mn, Fe, Co, Ni, Cu, Zn$ )," *J. Am. Chem. Soc.* **2005**, 127, 6506.
11. Dinca, M.; Dailly, A.; Liu, Y.; Brown, C. M.; Neumann, D. A.; Long, J. R. "Hydrogen Storage in a Microporous Metal-Organic Framework with Exposed  $Mn^{2+}$  Coordination Sites," *J. Am. Chem. Soc.* **2006**, 128, 16876.
12. Dinca, M.; Long, J. R. "High-Enthalpy Hydrogen Adsorption in Cation-Exchanged Variants of the Microporous Metal-Organic Framework  $Mn_3[(Mn_4Cl)_3(BTT)_8(CH_3OH)_{10}]_2$ ," *J. Am. Chem. Soc.* **2007**, 129, 11172.
13. Vitillo, J. G.; Regli, L.; Chavan, S.; Ricchiardi, G.; Spoto, G.; Dietzel, P. D. C.; Bordiga, S.; Zecchina, A. "Role of Exposed Metal Sites in Hydrogen Storage in MOFs," *J. Am. Chem. Soc.* **2008**, 130, 8386.
14. Han, S. S.; Goddard, W. A. "High  $H_2$  Storage of Hexagonal Metal-Organic Frameworks from First-Principles-Based Grand Canonical Monte Carlo Simulations," *J. Phys. Chem. C* **2008**, 112, 13431.
15. Mulfort, K. L.; Hupp, J. T. "Alkali Metal Cation Effects on Hydrogen Uptake and Binding in Metal-Organic Frameworks," *Inorg. Chem.* **2008**, 47, 7936.