

## IV.C.2 Hydrogen Storage in Metal-Organic Frameworks

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- General Motors Corporation (GM), Warren, MI (Anne Dailly)

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### Overall Objectives

- Research and development of onboard systems that allow for a driving range greater than 300 miles
- Materials sought with the potential for meeting the DOE system targets of reversible uptake:
  - 2017 targets: 5.5% H<sub>2</sub> by mass, volumetric capacity of 40 g/L
  - “Ultimate full fleet” targets: 7.5% H<sub>2</sub> by mass, 70 g/L
- Synthesize new metal-organic frameworks (MOFs) capable of approaching the -20 kJ/mol adsorption enthalpy required for use as hydrogen storage materials operating under 100 bar at ambient temperatures

### Fiscal Year (FY) 2014 Objectives

- Synthesize MOFs exhibiting reversible excess H<sub>2</sub> uptake greater than 2.5 wt% at room temperature
- Prepare a high-valent MOF with an initial H<sub>2</sub> adsorption enthalpy greater than 12 kJ/mol
- Synthesize new MOFs with the multifunctional ligands prepared in year 1
- Demonstrate the post-synthetic insertion of metals into the open chelate sites of these new materials

- Prepare at least two MOFs with the optimal 7 Å between opposing pore surfaces as predicted with *in silico* screening techniques
- Demonstrate that improved understanding of MOF-H<sub>2</sub> interactions through inelastic neutron scattering experiments and that new approaches to calculate observed spectra provide new insight into the governing physics of adsorption in porous media
- Demonstrate the ability to determine H<sub>2</sub>-metal interactions in model systems containing low-coordinate metal cations
- Demonstrate a correlation between high-pressure measurements and theoretical and spectroscopic predictions
- Demonstrate the ability to measure H<sub>2</sub> adsorption in a test material up to 10 cycles at 298 K

### Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(A) System Weight and Volume

### Technical Targets

Specific efforts are focused on the research and development of onboard systems that allow for a driving range greater than 300 miles. Materials are sought with the potential for meeting the 2017 DOE targets for reversible uptake and, subsequently, the “ultimate full fleet” targets (see Table 1).

### FY 2014 Accomplishments

- High-pressure H<sub>2</sub> adsorption measurements were completed on the M<sub>2</sub>(dioxido-biphenyl-dicarboxylate, known as dobpdc) structure family. These materials and their expanded analogs are approaching the 2.5 wt% target.
- A new Zr<sup>4+</sup>-based framework featuring charge-balancing chelating ligands functionalized with a pyridine and a hydroxyl group and enhanced stability has been synthesized in gram-scale quantities. These MOFs have subsequently been metalated with high crystallinity. Charge balance is key to enhancing the H<sub>2</sub> binding enthalpy at open metal centers on these ligands as well as allowing for multiple H<sub>2</sub> molecules to bind to a single metal center, which will drastically increase both

**TABLE 1.** Progress towards Meeting Technical Targets for Onboard Hydrogen Storage for Light-Duty Vehicles

Storage Parameter	Units	2017 Target	Ultimate Target	2012 Status <sup>†</sup>	2013 Status <sup>†</sup>	2014 Status <sup>†</sup>
<b>System Gravimetric Capacity*:</b> Usable specific energy from H <sub>2</sub> (net useful energy/max system mass)**	kWh/kg (kg H <sub>2</sub> /kg system)	1.8 (0.055)	2.5 (0.075)	(0.016 kg H <sub>2</sub> /kg adsorbent)	(0.016 kg H <sub>2</sub> /kg adsorbent)	(0.016 kg H <sub>2</sub> /kg adsorbent)
<b>System Volumetric Capacity*:</b> Usable energy density from H <sub>2</sub> (net useful energy/max system volume)	kWh/L (kg H <sub>2</sub> /L system)	1.3 (0.040)	2.3 (0.070)	(0.011 kg H <sub>2</sub> /L adsorbent)	(0.011 kg H <sub>2</sub> /L adsorbent)	(0.013 kg H <sub>2</sub> /L adsorbent)

\* Room temperature, total adsorption capacity

\*\* Generally the full mass (including hydrogen) is used; for systems that gain weight, the highest mass during discharge is used. All capacities are net useable capacity able to be delivered to the power plant. Capacities must be met at end of service life.

<sup>†</sup> Since the project deals with the development of storage materials, the performance status is given in terms of storage capacity for storage materials, not the whole storage system.

gravimetric and volumetric H<sub>2</sub> uptake approaching the DOE targets.

- H<sub>2</sub> high-pressure adsorption was measured on Ni<sub>2</sub>(4,6-dioxido benzene 1,3-dicarboxylate, known as *m*-dobdc) and Co<sub>2</sub>(*m*-dobdc), with the former showing the highest known volumetric capacity for H<sub>2</sub> at room temperature and 100 bar.
- We have determined the structure of D<sub>2</sub> adsorbed in the 2-ring extended linker variant of MOF-74, M<sub>2</sub>(dobpdc). These expanded variants of the M<sub>2</sub>(2,5-dioxido benzene-1,4-dicarboxylate, known as dobdc) structure type show improvement of ~0.5 kJ/mol in H<sub>2</sub> binding enthalpy as compared to the M<sub>2</sub>(dobdc) analogues.
- We have determined the rotational character of H<sub>2</sub> adsorbed to the metal center in Co<sub>2</sub>(*m*-dobdc). This shows that we have a firm understanding of the ways in which H<sub>2</sub> interacts with metal centers and can interpret the results from neutron diffraction.
- First principle calculations have shown that catechol-style ligands with divalent di-coordinated metals are promising candidates to achieve hydrogen binding energies in a suitable range as well as allow for more than one bound H<sub>2</sub> per metal, which would help approach the DOE capacity targets.
- Adsorption enthalpies were measured to 320 bar at ambient temperature on extended MOF-74 analogues. The adsorption enthalpy was observed to be 40% higher for the 2-ring extended MOF-74 compared to the standard MOF-74.
- We have shown that expanded versions of the cobalt and nickel MOF-74 have larger excess adsorption enthalpies at ambient temperature.



## INTRODUCTION

MOFs are promising solid sorbents for storage of H<sub>2</sub> at room temperature. They can be tailored to incorporate a large

number of selected metal ions, thereby tuning the H<sub>2</sub> binding energy. The overall aim of the project is to synthesize new MOFs capable of achieving the 20 kJ/mol adsorption enthalpy required for use as hydrogen storage materials operating under 100 bar at ambient temperatures.

## APPROACH

This research involves investigators with a range of capabilities—including synthesis and characterization of new materials, electronic structure calculations, neutron diffraction and scattering studies, and high-pressure gas sorption measurements. The team performs work in four areas: Task 1) Synthesis of Metal-Organic Frameworks (Long-LBNL), Task 2) Characterization of Framework-H<sub>2</sub> Interactions (Brown-NIST), Task 3) First-Principles Calculations of Hydrogen Binding Enthalpies (Head-Gordon-LBNL), and Task 4) High-Pressure H<sub>2</sub> Adsorption Measurements (Dailly-GM).

## RESULTS

### Introduction

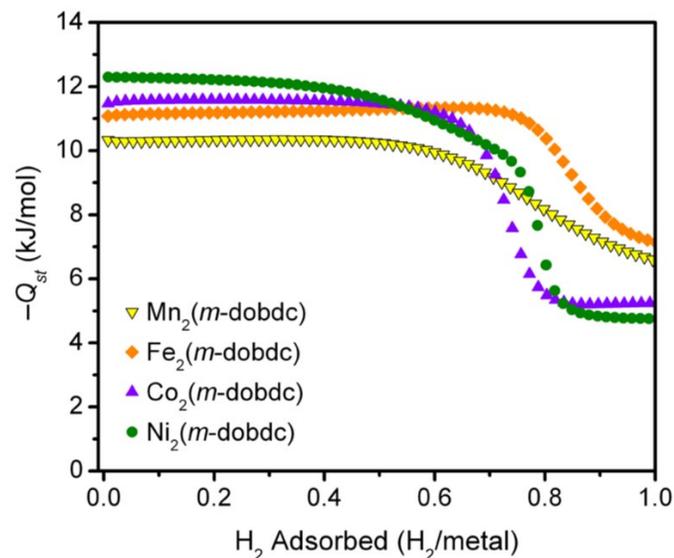
The approach taken in this past year is a multi-pronged approach. Conventional MOFs are still being targeted as materials that can adsorb large quantities of hydrogen. In addition to these more conventional strategies of improving binding enthalpy, gravimetric capacity, and volumetric capacity through framework modifications and the design of new materials, alternate strategies are being employed. The main focus of these strategies is to synthesize frameworks with a very high density of open metal coordination sites, either as part of the structure of the framework or as post-synthetically bound metal centers. The advantage of having non-structural metals bind in a MOF is that they could potentially be desolvated to expose multiple coordination sites and bind up to four H<sub>2</sub> molecules per metal center, giving a dramatic and groundbreaking boost in capacity as compared to currently known frameworks.

### $M_2(m\text{-dobdc})$ with Increased $H_2$ Binding Enthalpy

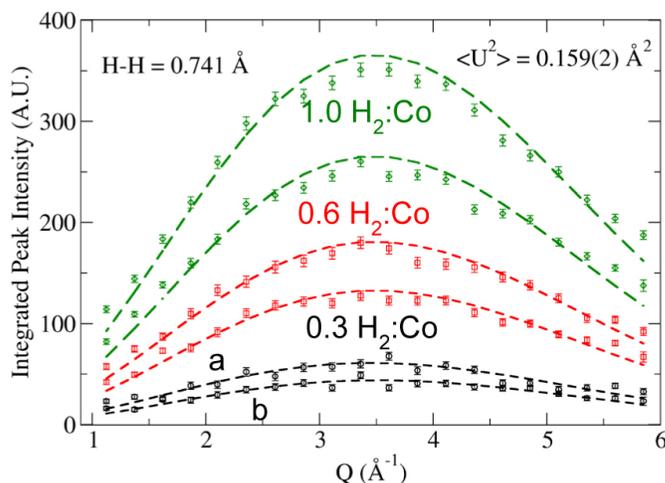
The first strategy is that of modifying conventional frameworks. In the last year, we have gained a complete understanding of the  $M_2(m\text{-dobdc})$  ( $M = \text{Mg}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$ ) series of frameworks that our lab has discovered. This MOF is a structural isomer of the well-known  $M_2(\text{dobdc})$  series, yet shows a significantly improved  $H_2$  binding enthalpy as compared to the regular  $M_2(\text{dobdc})$  for the Mn, Fe, Co, and Ni analogues. The open metal coordination sites are shown to have a greater positive charge in  $M_2(m\text{-dobdc})$  than in  $M_2(\text{dobdc})$ , leading to the experimentally determined higher isosteric heats of  $H_2$  adsorption ( $\sim 1.0$  kJ/mol higher on average, as seen in Figure 1) [1]. This is quite a significant increase by simply changing to a structural isomer of the linker, so this was investigated further.

Quasi-elastic and inelastic neutron scattering measurements were used to locate  $H_2$  molecules in  $\text{Co}_2(m\text{-dobdc})$  (Figure 2). Two-dimensional inelastic neutron scattering was further used to demonstrate improved understanding of MOF- $H_2$  interactions. The extracted intensities for different loadings of  $H_2$  distinguish between the spatial dependence of the rotations/phonons and here were used to determine that all of the observed transitions are rotational in nature, as expected based on the neutron diffraction data [2].

Further experiments involving infrared spectroscopy with bound  $H_2$  were completed. It can be seen from looking at the  $H_2$  stretch in these experiments that the  $H_2$  is bound more strongly in the  $\text{Ni}_2(m\text{-dobdc})$  and  $\text{Co}_2(m\text{-dobdc})$  frameworks as compared to their respective  $\text{Ni}_2(\text{dobdc})$  and  $\text{Co}_2(\text{dobdc})$  counterparts. This shift to a lower-energy



**FIGURE 1.**  $H_2$  Isosteric Heat of Adsorption Curves for the  $M_2(m\text{-dobdc})$  Series of Frameworks, as a Function of the Amount Adsorbed



**FIGURE 2.** Extracted Rotational Level Areas for Different Loadings Fit to a Model Indicating the Classical Nature of the Adsorbed Molecule

stretching frequency is expected based on the higher isosteric heats of adsorption from the obtained isotherms. It is worth noting that the secondary binding sites saw no change in  $H_2$  stretching frequency between the  $M_2(m\text{-dobdc})$  and  $M_2(\text{dobdc})$  series, indicating that the change in binding enthalpy is solely due to a change in the electronic structure at the open metal coordination site. Variable-temperature infrared spectroscopy experiments were used to probe the site-specific binding enthalpies at the open metal center, which were calculated to be as high as 13.7 kJ/mol for  $\text{Ni}_2(m\text{-dobdc})$ , which is the highest reliably-obtained isosteric heat of adsorption in a MOF thus far.

### High-Pressure $H_2$ Isotherms

Further studies were completed on the expanded  $M_2(\text{dobdc})$  series of frameworks. These were shown to have a higher binding enthalpy than their  $M_2(\text{dobdc})$  analogues; the larger pores have a positive effect on the binding enthalpy, despite having similar open metal coordination site geometries. Additionally, powder neutron diffraction showed five unique binding sites in the pores of the framework, which is significantly more than the three unique sites seen in the  $M_2(\text{dobdc})$  series. The high-pressure volumetric uptake of these frameworks was shown to be greater than that of pure  $H_2$  compressed in a tank, which is also advantageous and is working toward the volumetric hydrogen storage goals set forth by the DOE. By further expanding the pores of this same series of frameworks, it is believed that even higher capacities can be reached at 298 K and room temperature, approaching the DOE target of 1.3 kg  $H_2$ /L system. While we did not demonstrate an increase in the excess uptake as compared to the literature standard,  $\text{Co}_2(\text{DiOxido-TerPhenyl-DiCarboxylate})$  (the  $\text{Co}_2(\text{dobdc})$  analogue with three aromatic rings in the linker) has a total uptake of 2.5 wt% at 298 K and 140 bar as well as at 273 K and 100 bar. The  $\text{Ni}_2(\text{dobdc})$

framework had a gravimetric uptake of 10.0 g/L at 298 K and 100 bar, which is approaching state of the art. The  $\text{Ni}_2(m\text{-dobdc})$  framework mentioned before surpassed this and set a record for volumetric hydrogen storage with a capacity of 12.5 g/L at 298 K and 100 bar. This is higher than the previous state-of-the-art framework, Mn-1,3,5-BenzeneTrisTetrazole.

High-pressure adsorption isotherms were also measured at GM up to 320 bar. A method for determining the adsorption enthalpy from a single isotherm was developed by applying the van't Hoff formula directly to the Dubinin-Astakhov model. This led to benchmark results that were consistent with expectations for these materials. Subsequently, the  $\text{Ni}_2(\text{dobdc})$  and  $\text{Ni}_2(m\text{-dobdc})$  frameworks were measured and shown to be very similar in their  $\text{H}_2$  uptake. The  $\text{Ni}_2(m\text{-dobdc})$  framework was then cycled between 50 bar and 320 bar 10 times at 298 K; the variability in each isotherm was shown to have no correlation with the cycle, meaning that the results are reproducible.

### Computational Work

To gain a fundamental view into the adsorption of hydrogen in MOFs, we study and analyze the adsorption of hydrogen into “standard,” i.e., undecorated, linkers. Although the binding enthalpies are not expected to be significant for storage purposes, they exist in any MOF and contribute to the overall adsorption. We study the adsorption of hydrogen with several molecules that are commonly used as a building block for MOF linkers. For each one, we optimize the structure, calculate binding enthalpy, and analyze the fundamental linker-hydrogen interaction. It is found that hydrogen adsorption enthalpies could be as high as 3 to 5 kJ/mol, which could contribute significantly to the adsorption enthalpy. Most of the enthalpy stems from the “frozen interaction,” which indicates both van der Waals interactions and non-induced electrostatic interactions. Surprisingly, and contrary to conventional wisdom, it was found that charge transfer interaction (i.e., the formation of a dative chemical interaction) makes a significant contribution to the adsorption of hydrogen on these conjugated organics—with hydrogen accepting charge to its anti-bonding vacant orbital. This charge transfer interaction corresponds to about 30% of the total hydrogen-linker interaction.

We also completed work on larger systems and investigated hydrogen adsorption on several MOF ligands that were reported in the scientific literature (or prepared by the Long group) to be metalated. For each of the ligands, we optimize the structure, calculate interaction energy, and analyze the result in order to provide a rational explanation of the hydrogen adsorption capacity. We modeled a MOF consisting of bpy ligands that was prepared and metalated with  $\text{CuCl}_2$  by the Long group. The optimized structure is shown in Figure 3. The calculated adsorption energy is 9.1 kJ/mol, and the charge transfer interaction is again found

to dominate. This could also be inferred (or confirmed) by observing that the hydrogen molecule is placed “side-on” to the transition-metal cation, in order to maximize donation from the  $\sigma$  bonding orbital onto a diffuse orbital on the cation.

Recently, a MOF containing a catechol ligand was prepared and metalated by  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$ . This MOF was modeled using a catechol molecule metalated by  $\text{Al}^{3+}$  and one  $\text{F}^-$  counterion—this combination has a special interest, since  $\text{AlF}_3$  was found to have a strong interaction with  $\text{H}_2$  of about 20 kJ/mol. It is therefore interesting to estimate the same interaction in a realistic system. Interaction energy is 8.7 kJ/mol, which is considerably smaller than -21.7 predicted for  $\text{AlF}_3$ , mostly due to a reduced polarization component of the interaction. Since metals in planar and tetrahedral coordination were found to have insufficient hydrogen adsorption, we began to study systems that are expected to develop a strong dipole moment. The systems based on the catechol ligand (or its sulfur-based analog) have been prepared in experiments and are expected to have strong dipole moments. The calculated binding energies are close to 20 kJ/mol, and adsorption of a second hydrogen molecule is also feasible, with only a small decrease in interaction energy with respect to the first hydrogen molecule.

To conclude, we find that planar and tetrahedral coordination of the metallic ion have an intrinsic limitation of not being able to polarize  $\text{H}_2$  to a sufficient extent such that

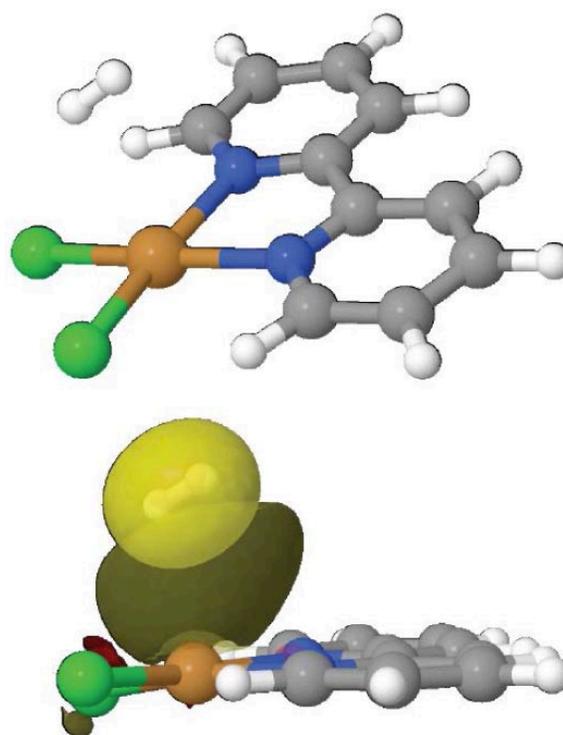


FIGURE 3. Optimized Structure of bpy- $\text{CuCl}_2$

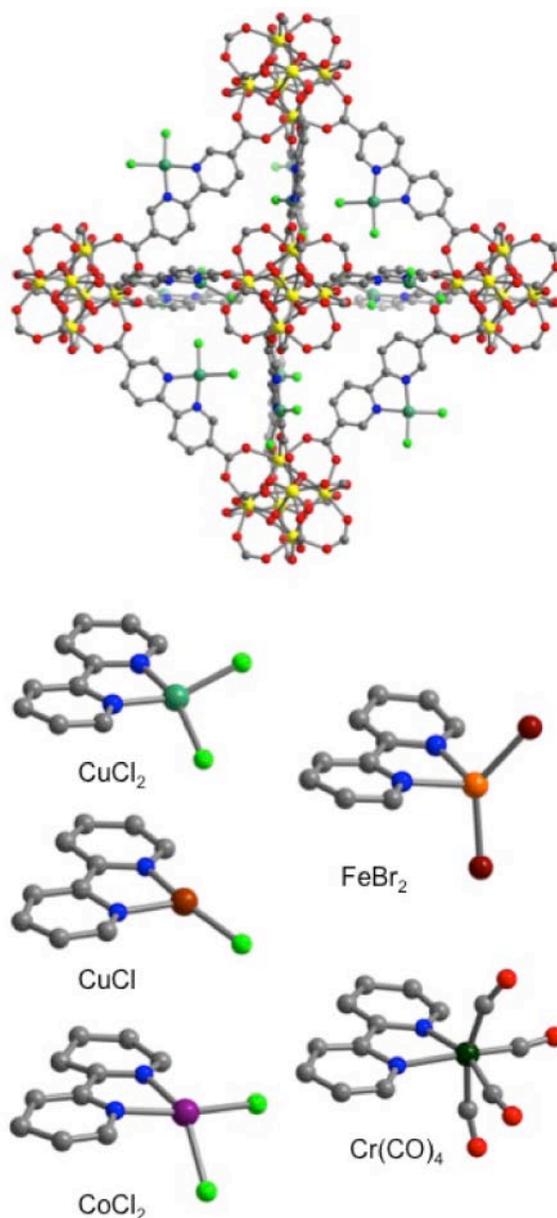
an adequate adsorption energy for hydrogen can be attained. By contrast, a metal attached to a linker with a coordination number of two, or another arrangement of the coordination environment of the metal that results in a strong local dipole moment, appears to give hydrogen binding energies in a suitable range. As examples, the catechol-style ligands with divalent di-coordinated metals such as those we investigated above are promising candidates. Overall, this work demonstrates our understanding of  $H_2$ -metal interactions in a variety of model systems containing low-coordinate metal cations.

### Multiple $H_2$ per Metal Center

As previously mentioned, our approach includes both studying conventional MOFs as well as attempting to synthesize MOFs with the ability to bind additional metal centers and subsequently bind  $H_2$  both more strongly and with a higher density than currently known MOFs. This is quite a challenging task, as there are many challenges to synthesizing these materials. However, a potential breakthrough could be reached if multiple  $H_2$  molecules could be bound per metal center, with uptakes as high as 6.6 wt% excess uptake possible at room temperature if four  $H_2$  molecules were bound to a metal center bound to a catechol within a framework. This would also result in a significant improvement in volumetric capacity.

One framework we have synthesized that can bind additional metal centers is the UIO-67-Bipyridine dicarboxylate (bpydc) framework, which has a bipyridine in the linker (Figure 4). This framework bpydc has been metalated with a variety of metal salts and investigated for its  $H_2$  storage properties. It was anticipated that metalation with metals that form square planar complexes with the ligand would leave available hydrogen binding sites in the axial positions on the metal center. It was found from single-crystal X-ray diffraction that the metal center distorts from square planar for several of these complexes, however, and that the anticipated binding sites may not be available (Figure 4). Nonetheless, several samples show higher uptake than the bare framework at selected pressures, most notably the  $PdCl_2$ - and  $CuCl_2$ -metalated samples. It is estimated that, based on the excess  $H_2$  adsorption at 1 bar and 77 K, there are 2.6 and 1.5  $H_2$  molecules per metal center for the  $PdCl_2$  and  $CuCl_2$  samples, respectively.

Another framework that has been synthesized is the UIO-67-pyOHdc framework, which has a single pyridine and a hydroxyl group in the linker rather than a bipyridine. This functional group affords charge balance to the metal center to which it binds, which will allow for the easier desolvation of this framework. This framework has been prepared in gram-scale quantities with high crystallinity and surface area. After synthesis of the bare framework, these frameworks have been metalated with a variety of metal species, but the  $H_2$  uptake was not improved over the bare framework.



**FIGURE 4.** Structure of the Metalated UIO-67-bpydc, Showing the Partial Crystal Structures of Several of the Incorporated Metals

Further metalation is underway with other metal salts with more labile ligands.

Overall, we have laid a basis with this work for understanding the best methods for synthesizing frameworks that can post-synthetically bind metal centers. With this understanding, we are poised for a breakthrough in room-temperature hydrogen storage by binding multiple  $H_2$  molecules per metal center and quite significantly improving the volumetric and gravimetric  $H_2$  densities that are possible in MOFs.

## CONCLUSIONS AND FUTURE DIRECTIONS

Overall, much work was completed during FY 2014 toward the DOE hydrogen storage targets. The  $M_2(m\text{-dobdc})$  series of frameworks was completely studied, and its higher  $H_2$  binding enthalpy was determined to be from a higher positive charge at the open metal centers. Powder neutron diffraction and inelastic neutron scattering were used to study a variety of systems and learn more about MOF- $H_2$  interactions as well as methods for doing high-pressure, high-temperature powder neutron diffraction of  $D_2$ -dosed samples. Several samples were measured on the high-pressure system at GM, which is now operating at full potential and is fully calibrated. Many systems were studied for understanding metal- $H_2$  interactions in order to guide synthetic efforts for binding multiple  $H_2$  molecules per metal center. Finally, many synthetic efforts were completed in order to attempt to bind two  $H_2$  molecules per metal center.

Moving forward, we believe that the most probable method for achieving the DOE hydrogen storage targets is post-synthetic incorporation of metal centers into ligands and use of these centers to interact with multiple  $H_2$  molecules. All future synthetic efforts will be concentrated on this target, which will provide a huge breakthrough in the capacities for hydrogen storage. The following goals will be targeted in FY 2015:

- Further study metalated UIO-67-bpydc samples and determine if any of the samples are binding multiple  $H_2$  molecules per metal center.
- Develop the UIO-67-pyOHdc framework and metalate this framework with metal sources that contain significantly more labile ligands than those we have previously used.
- Synthesize more ligands with charge-balancing functionalities for optimal metal binding properties.
- Explore other possible functional groups for protecting and deprotecting these charge-balancing functionalities.

## FY 2014 PUBLICATIONS/PRESENTATIONS

### Publications

1. “Structure and spectroscopy of hydrogen adsorbed in a nickel metal-organic framework”, C.M. Brown, A.J. Ramirez-Cuesta, J.-H. Her, P.S. Wheatley, R.E. Morris, *Chem Phys.* 2013, 427, 3.
2. “Adsorption Enthalpy Calculations of Hydrogen Adsorption at Ambient Temperature and Pressures Exceeding 300 bar”, M. Beckner, A. Dailly, *Am. J. Anal. Chem.* 2013, 10C, 8-16.
3. “Kinetic trapping of  $D_2$  in MIL-53(Al) observed using neutron scattering”, R.A. Pollock, J.-H. Her, C.M. Brown, Y. Liu, A. Dailly, *J. Phys. Chem. C* [DOI: 10.1021/jp504870n].
4. “Hydrogen and Natural Gas Storage in Adsorbent Materials for Automotive Applications”, M. Beckner, A. Dailly, Proceedings of the 13<sup>th</sup> International Conference on Clean Energy, June 2014, Istanbul, Turkey.
5. “ $M_2(m\text{-dobdc})$  ( $M = \text{Mg, Mn, Fe, Co, Ni}$ ) Metal-Organic Frameworks Exhibiting Increased Charge Density and Enhanced  $H_2$  Binding at the Open Metal Sites”, M.T. Kapelewski, S.J. Geier, M.R. Hudson, D. Stuck, J.A. Mason, J.N. Nelson, D.J. Xiao, Z. Hulvey, E. Gilmour, S.A. FitzGerald, M. Head-Gordon, C.M. Brown, J.R. Long. *J. Am. Chem. Soc. Article ASAP.*

### Presentations

1. “Hydrogen and Natural Gas Storage in Adsorbent Materials for Automotive Applications”, M. Beckner, A. Dailly, Proceedings of the 13<sup>th</sup> International Conference on Clean Energy, June 2014, Istanbul, Turkey.
2. “Neutron Powder Diffraction:  $D_2$  vs  $H_2$ ”, Z. Hulvey, C.M. Brown, IAEA experts meeting, Key Largo, Florida, Dec. 2013.
3. “High-pressure, ambient temperature hydrogen storage in metal-organic frameworks and porous carbon”, M. Beckner, A. Dailly, APS March Meeting 2014, Denver, Colorado, March 2014.
4. “Hydrogen and Natural Gas Storage in Adsorbent Materials for Automotive Applications”, M. Beckner, A. Dailly, 13<sup>th</sup> International Conference on Clean Energy, June 2014, Istanbul, Turkey.

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2. Liu, Y.; Kabbour, H.; Brown, C.M.; Neumann, D.A.; Ahn, C.C. *Langmuir* **2008**, *24*, 4772.