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

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

Project Start Date: April 1, 2012
Project End Date: March 31, 2015

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_2 by mass, volumetric capacity of 40 g/L
  - "Ultimate full fleet" targets: 7.5% H_2 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_2 uptake greater than 2.5 wt% at room temperature
- Prepare a high-valent MOF with an initial H_2 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_2 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_2-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_2 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_2 adsorption measurements were completed on the M_2(dioxido-biphenyl-dicarboxylate, known as dobpdc) structure family. These materials and their expanded analogs are approaching the 2.5 wt% target.
- A new Zr^{4+}-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_2 binding enthalpy at open metal centers on these ligands as well as allowing for multiple H_2 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†	2013 Status†	2014 Status†
System Gravimetric Capacity*: Usable specific energy from H_2 (net useful energy/max system mass)**	kWh/kg (kg H_2/kg system)	1.8 (0.055)	2.5 (0.075)	(0.016 kg H_2/kg adsorbent)	(0.016 kg H_2/kg adsorbent)	(0.016 kg H_2/kg adsorbent)
System Volumetric Capacity*: Usable energy density from H_2 (net useful energy/max system volume)	kWh/L (kg H_2/L system)	1.3 (0.040)	2.3 (0.070)	(0.011 kg H_2/L adsorbent)	(0.011 kg H_2/L adsorbent)	(0.013 kg H_2/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.

† 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_2 uptake approaching the DOE targets.

- H_2 high-pressure adsorption was measured on Ni_2(4,6-dioxido benzene 1,3-dicarboxylate, known as *m*-dobdc) and Co_2(*m*-dobdc), with the former showing the highest known volumetric capacity for H_2 at room temperature and 100 bar.
- We have determined the structure of D_2 adsorbed in the 2-ring extended linker variant of MOF-74, M_2(dobpdc). These expanded variants of the M_2(2,5-dioxido benzene-1,4-dicarboxylate, known as dobdc) structure type show improvement of ~0.5 kJ/mol in H_2 binding enthalpy as compared to the M_2(dobdc) analogues.
- We have determined the rotational character of H_2 adsorbed to the metal center in Co_2(m-dobdc). This shows that we have a firm understanding of the ways in which H_2 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_2 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.

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INTRODUCTION

MOFs are promising solid sorbents for storage of H_2 at room temperature. They can be tailored to incorporate a large number of selected metal ions, thereby tuning the H_2 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_2 Interactions (Brown-NIST), Task 3) First-Principles Calculations of Hydrogen Binding Enthalpies (Head-Gordon-LBNL), and Task 4) High-Pressure H_2 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_2 molecules per metal center, giving a dramatic and groundbreaking boost in capacity as compared to currently known frameworks.

M_2(*m*-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*-dobdc) (M = Mg, Mn, Fe, Co, Ni) series of frameworks that our lab has discovered. This MOF is a structural isomer of the well-known M_2(dobdc) series, yet shows a significantly improved H_2 binding enthalpy as compared to the regular M_2(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*-dobdc) than in M_2(dobdc), leading to the experimentally determined higher isosteric heats of H_2 adsorption (~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 Co_2(m-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 Ni_2(*m*-dobdc) and Co_2(*m*-dobdc) frameworks as compared to their respective Ni_2(dobdc) and Co_2(dobdc) counterparts. This shift to a lower-energy 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*-dobdc) and M_2(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 Ni_2(*m*-dobdc), which is the highest reliably-obtained isosteric heat of adsorption in a MOF thus far.

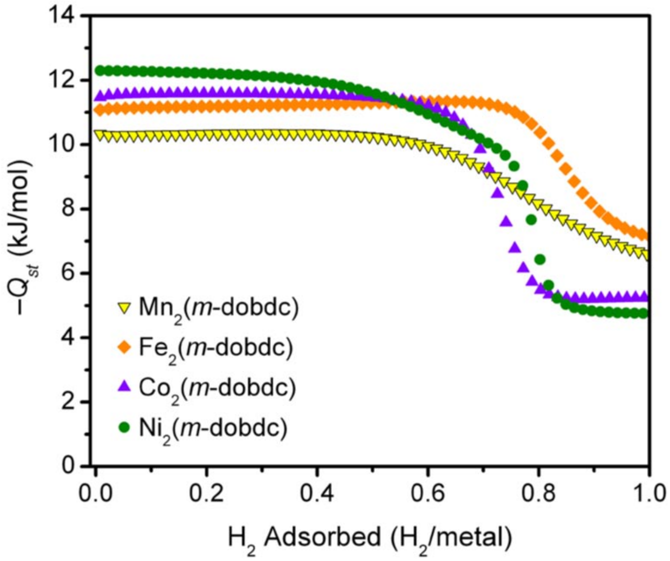

FIGURE 1. H_2 Isosteric Heat of Adsorption Curves for the M_2(*m*-dobdc) Series of Frameworks, as a Function of the Amount Adsorbed

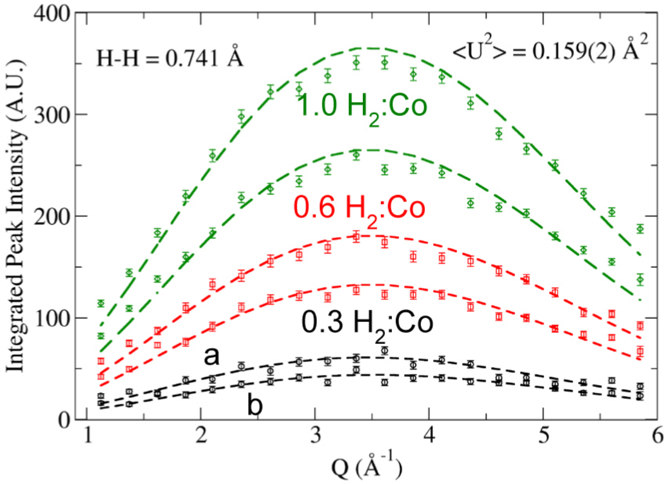

FIGURE 2. Extracted Rotational Level Areas for Different Loadings Fit to a Model Indicating the Classical Nature of the Adsorbed Molecule

High-Pressure H_2 Isotherms

Further studies were completed on the expanded M_2(dobpdc) series of frameworks. These were shown to have a higher binding enthalpy than their M_2(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(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, Co_2(DiOxido-TerPhenyl-DiCarboxylate) (the Co_2(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 Ni_2(dobpdc) framework had a gravimetric uptake of 10.0 g/L at 298 K and 100 bar, which is approaching state of the art. The Ni_2(*m*-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-Astakohov model. This led to benchmark results that were consistent with expectations for these materials. Subsequently, the Ni_2(dobdc) and Ni_2(*m*-dobdc) frameworks were measured and shown to be very similar in their H_2 uptake. The Ni_2(*m*-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 $CuCl_2$ 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 σ bonding orbital onto a diffuse orbital on the cation.

Recently, a MOF containing a catechol ligand was prepared and metalated by Fe^{3+} and Cr^{3+}. This MOF was modeled using a catechol molecule metallated by Al^{3+} and one F^- counterion—this combination has a special interest, since AlF_3 was found to have a strong interaction with 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 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 H_2 to a sufficient extent such that

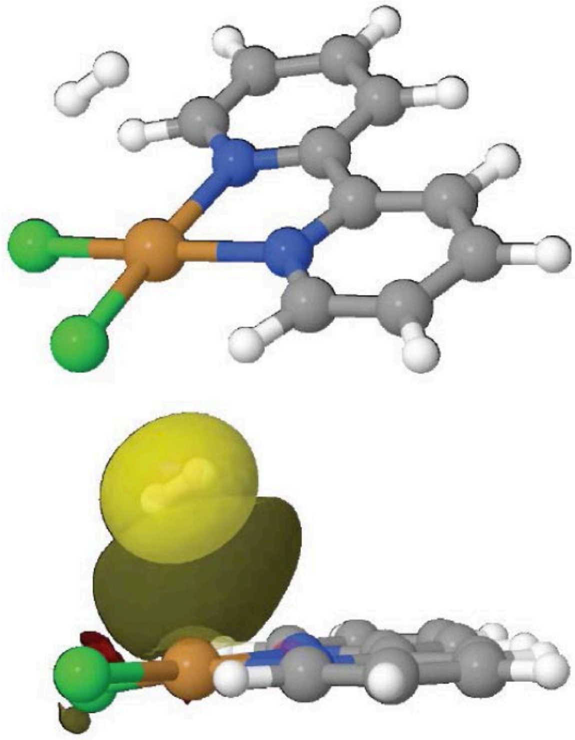

FIGURE 3. Optimized Structure of bpy-$CuCl_2$

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

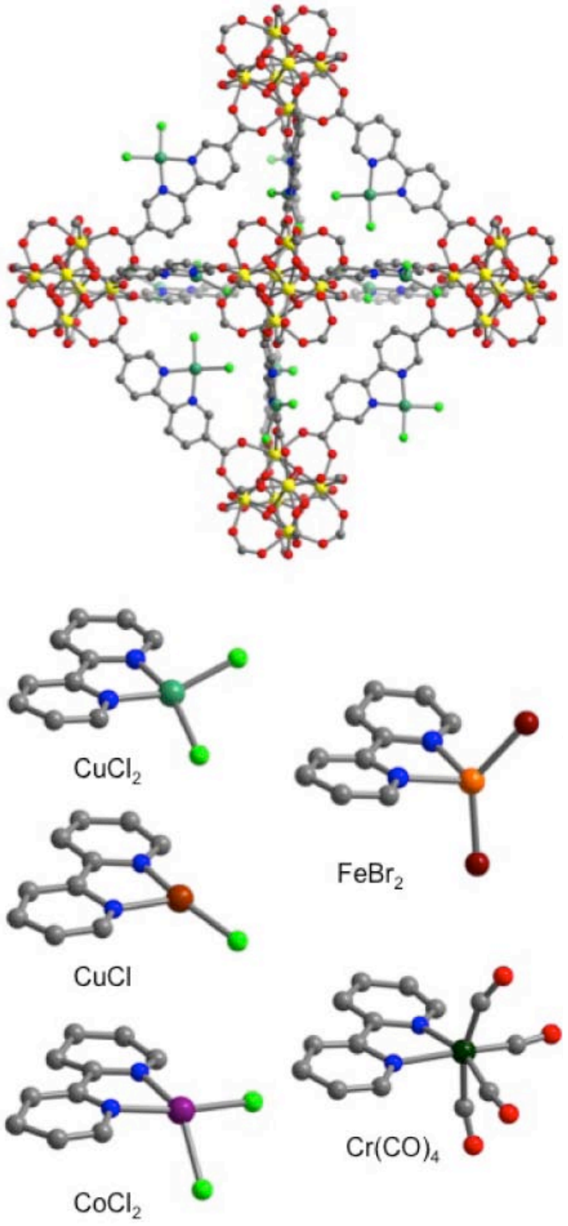

FIGURE 4. Structure of the Metalated UIO-67-bpydc, Showing the Partial Crystal Structures of Several of the Incorporated Metals

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*-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 13th International Conference on Clean Energy, June 2014, Istanbul, Turkey.

5. “M_2(*m*-dobdc) (M = 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 13th 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, 13th 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.