

IV.C.1 Hydrogen Storage in Metal-Organic Frameworks

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Subcontractors

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

Project Start Date: April 1, 2012

Project End Date: September 30, 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:
 - 2020 targets: 5.5% H₂ by mass, volumetric capacity of 40 g/L
 - “Ultimate full fleet” targets: 7.5% H₂ 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) 2015 Objectives

- Demonstration of a metal-organic framework with an initial H₂ adsorption enthalpy greater than the current record of 15.1 kJ/mol
- Synthesis of a metal-organic framework with reversible excess hydrogen uptake greater than 4.5 wt% at 298 K
- Demonstrate the use of quasielastic neutron scattering to help understand the roles of diffusion and entropy in H₂ binding to MOFs for the most interesting systems synthesized by Long
- Demonstrate the ability to determine H₂-metal interactions in realistic systems containing low-coordinate metal cations
- Pre-screen optimal metal-organic framework targets by identification of systems that produce an H₂ binding enthalpy greater than 20 kJ/mol

Technical Barriers

This project addresses the following technical barrier 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 2020 DOE targets for reversible uptake and, subsequently, the “ultimate full fleet” targets (see Table 1).

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

Storage Parameter	Units	2020 Target	Ultimate Target	2012 Status [†]	2013 Status [†]	2014 Status [†]	2015 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)	(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)	(0.013 kg H ₂ /L Adsorbent)

[†] 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.

FY 2015 Accomplishments

- The metal-organic framework $Zr_6O_4(OH)_4(\text{oxambpdc})_6$ (oxambpdc = 4,4'-oxalylbis(azanediyl)dibenzoic acid) was synthesized as an easily obtainable framework with a dianionic chelating ligand and subsequently metalated.
- An efficient synthetic route to the novel MOF cat-UIO-68 was developed, allowing for isolation of large quantities (multi-gram) of the material with a large measured Langmuir surface area of 4,025 m²/g.
- A comprehensive evaluation of the top-performing metal-organic frameworks for H₂ storage was carried out, including Ni₂(*m*-dobdc), Co₂(*m*-dobdc), Ni₂(dobdc), Co₂(dobdc), and MOF-5. High-pressure isotherms were measured at 100, 75, 50, 25, 0, -25, -40, -50, and -75°C in order to determine the optimal temperature process to maximize total volumetric H₂ usable capacity.
- We measured a high H₂ binding enthalpy of 12.1 kJ/mol in the metal-organic framework Cu[Ni(pdt)₂] (pdt = pyrazine-2,3-dithiolate), possibly suggesting the binding of two H₂ molecules to each metal center based on the optimal pore size.
- High-pressure neutron diffraction has been used to determine the binding profile of H₂ within MOF-5 at high pressures (up to 100 bar) and moderate temperature (77 K). This technique allows for the understanding of the density profile of H₂ in the pores of MOFs and is currently being expanded to use with other MOF materials.
- We synthesized a number of other ligands with chelating functionalities have been synthesized in order to attempt to bind extra-framework metal cations within the pores or MOFs and subsequently expose multiple sites per metal center for H₂ binding.
- First principles calculation was performed to determine optimal activation conditions for catecholate-based MOFs in order to maximize open-metal sites and enhance H₂ uptake.



INTRODUCTION

MOFs are promising solid adsorbents for storage of H₂ at room temperature. They can be tailored to incorporate a large number of selected metal ions, thereby tuning the H₂ binding energy. The overall aim of the project is to synthesize new MOFs capable of achieving the 20 kJ/mol adsorption enthalpy and 40 g/L volumetric storage density 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-H₂ interactions (Brown-NIST)
- Task 3 First-principles calculations of hydrogen binding enthalpies (Head-Gordon-LBNL)
- Task 4 High-pressure H₂ adsorption measurements (Dailly-GM)

RESULTS

This past year, efforts have continued to focus on the development of metal-organic frameworks with ligands containing chelating functionalities that can bind non-structural metal cations, in an effort to obtain a material that can bind multiple H₂ molecules per metal center. Additionally, full characterization of high-pressure adsorption of H₂ in M₂(dobdc) (M = Co, Ni) and M₂(*m*-dobdc) (M = Co, Ni) at multiple temperatures has been undertaken to determine the optimal conditions for H₂ adsorption to maximize the total volumetric usable H₂ capacity in industrially relevant temperature-swing adsorption processes. Neutron diffraction measurements and first-principles electronic structure calculations have worked alongside our synthetic efforts to further understand H₂ interactions with new adsorbate materials and inform synthetic efforts to synthesize a new generation of MOF materials with enhanced H₂ storage properties.

Binding Multiple H₂ Molecules per Metal

One of the main thrusts of this research is to improve the volumetric capacity of metal-organic frameworks in order to make them viable H₂ storage materials in automotive applications. In order to do this, focus in this research has been on increasing the binding enthalpy of H₂ to at least 15.1 kJ/mol and increasing the density of strong H₂ binding sites (primarily at open-metal coordination sites) within the material. To that end, multiple synthetic targets have been achieved that are working toward achieving our ultimate goals of a binding enthalpy exceeding 15.1 kJ/mol and obtaining a material with a volumetric capacity of 40 g/L.

The most effective method we see as being viable for obtaining these high capacities is to significantly increase the number of strong binding sites available to H₂ within the pores of the framework, which have thus far been shown to be primarily open-metal coordination sites. The

strategy being pursued for this is to synthesize metal-organic frameworks with ligands that contain free chelating functionalities, which can post-synthetically bind metals that are subsequently desolvated, exposing multiple coordination sites for H₂ binding.

Multiple ligands have been synthesized for this purpose with various chelating functionalities, including catechols, oxamides, and bipyridines, among others. The two ligands seen in Figure 1a are able to form the UIO-68 structure type and be subsequently metalated with a variety of metal sources. In particular, the boc-protected catechol ligand is highly promising. The catechol provides charge balance for a M²⁺ cation at that site, potentially allowing for the removal of other ligands from the metal center. The synthetic route for the subsequent MOF, cat-UIO-68, is shown in Figure 1b. The key is formation of the framework with benzoate-capped pre-formed Zr₆O₄(OH)₄ clusters, rather than simply starting with ZrCl₄.

Following synthesis of the framework and solvent-exchanges, the boc protecting groups can be thermalized off, leaving a free catechol in the pores of the framework. Deprotection of the boc groups has been confirmed by infrared spectroscopy and structure determination is underway from powder diffraction data collected at the Advanced Photon Source at Argonne National Laboratory. This cat-UIO-68 MOF has been shown to have a very high surface area of 4,025 m²/g. Metalation of this framework has been attempted with several metal sources, including Zn(C₂H₃)₂ and Ni(allyl)₂. Further studies are underway to optimize the metalation and desolvation of these materials

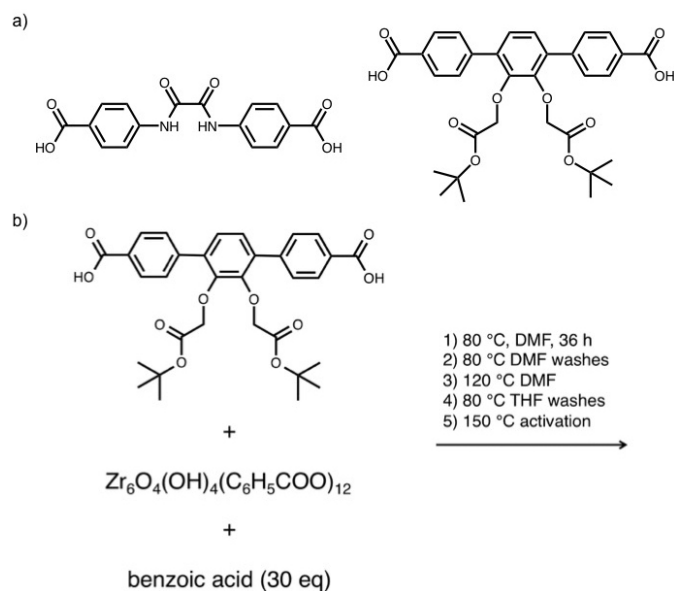


FIGURE 1. (a) The H₂(oxampbdc) (left) and boc-protected H₂(cat-bdc) (right) ligands. (b) The synthetic scheme for synthesizing the cat-UIO-68 MOF, including washes and thermalization of the boc protecting groups to expose free catechols in the pores of the framework.

to bind two H₂ molecules per metal center and ultimately produce a material that meets the volumetric storage targets set forth by DOE.

Determining the Optimal Conditions for H₂ Adsorption

Other efforts over the past year have focused on determining the optimal conditions for storing H₂ at relevant temperatures and pressures in known MOF materials. The previously reported M₂(*m*-dobdc) framework is particularly suitable for this study, as the Ni₂(*m*-dobdc) analog has among the highest known H₂ binding enthalpies of any MOF [1], leading to the expectation that this material will be particularly well-suited to storing large amounts of H₂.

In order to determine the best conditions and materials for storing H₂, top-quality samples (meaning those with Langmuir surfaces areas comparable to or exceeding those published in the literature) of several MOFs (Co₂(*m*-dobdc), Ni₂(*m*-dobdc), Co₂(dobdc), Ni₂(dobdc), and MOF-5) have been synthesized and tested for their high-pressure H₂ capacities at nine different temperatures: 100, 75, 50, 25, 0, -25, -40, -50, and -75°C. With such a wide sampling of temperatures, conclusions can be drawn about not only the ability of each material to store H₂ at a given temperature, but also how to optimize a temperature-swing process to maximize the usable H₂ stored in the system. Adsorption at 100 bar and desorption to a pressure of 5 bar are the DOE criteria for determining usable capacity, so all usable capacities were calculated between these two pressures in terms of the total volumetric capacity of the material.

The results for several of these materials can be seen in the isotherms in Figure 2. Ni₂(*m*-dobdc) is the top performing material as evaluated by multiple characteristics. It has a total usable capacity (the amount adsorbed between 100 bar and 5 bar) of 11.0 g/L at 25°C with no temperature swing process, which is superior to any other known MOF. Additionally, the usable capacity with a temperature swing from -40°C to 25°C is 18.2 g/L and from -75°C to 25°C is 23.0 g/L. These are each significantly higher than the usable capacities for all other measured materials. Table 2 presents a comparison of the total volumetric usable capacities for each material studied at relevant temperature swings.

TABLE 2. Total volumetric H₂ usable capacities for four MOF materials for various temperature swings (assuming single crystal density). All units are in g/L.

Swing	Ni ₂ (<i>m</i> -dobdc)	Co ₂ (<i>m</i> -dobdc)	Ni ₂ (dobdc)	Co ₂ (dobdc)
25°C, no swing	11.0	10.5	10.0	8.8
-75°C, no swing	19.0	18.2	18.4	16.5
-40 to 25°C	18.2	17.3	16.6	14.0
-75 to 25°C	23.0	21.9	21.4	18.3

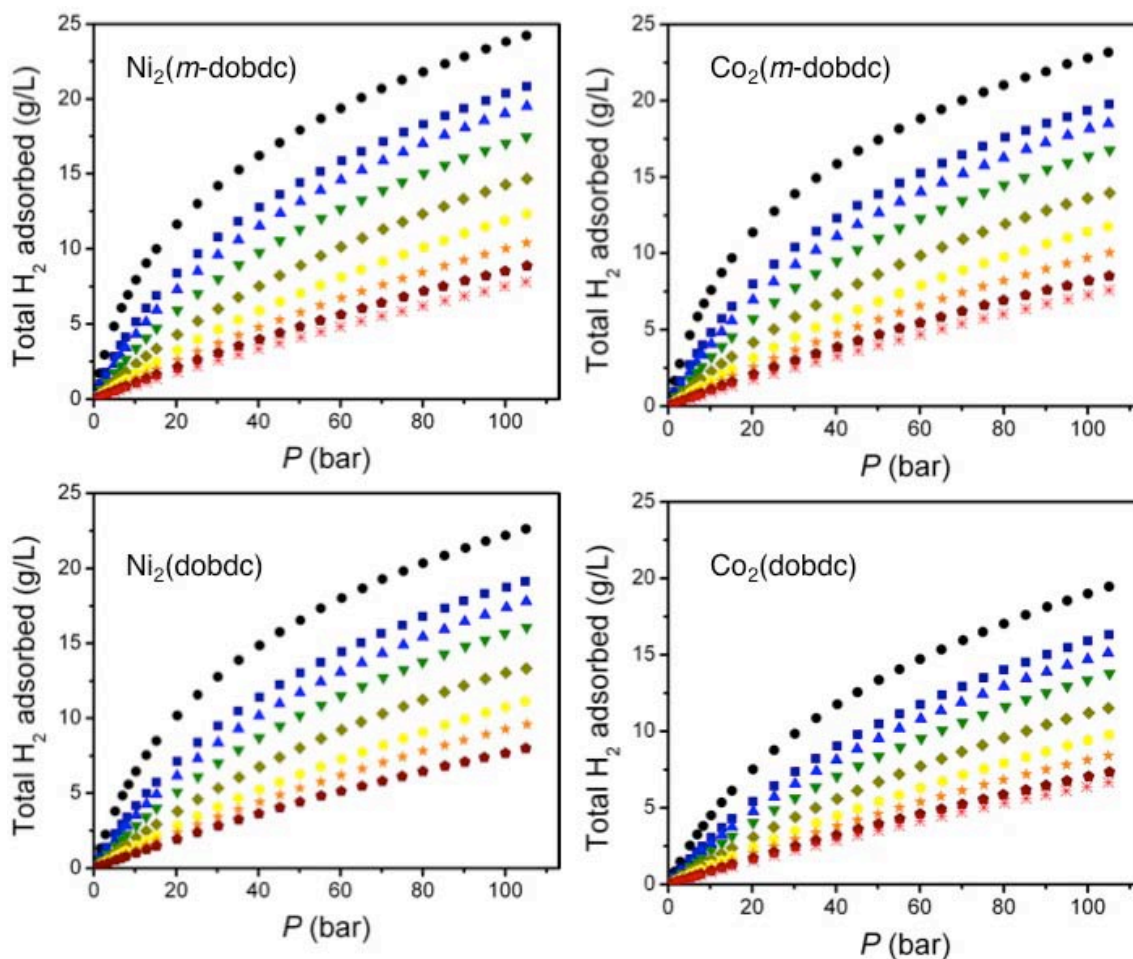


FIGURE 2. High-pressure H_2 isotherms for $Ni_2(m-dobdc)$, $Co_2(m-dobdc)$, $Ni_2(dobdc)$, and $Co_2(dobdc)$. The temperatures reported are $-75^\circ C$ (black circles), $-50^\circ C$ (navy squares), $-40^\circ C$ (blue triangles), $-25^\circ C$ (green downward-pointing triangles), $0^\circ C$ (gold diamonds), $25^\circ C$ (yellow circles), $50^\circ C$ (orange stars), $75^\circ C$ (dark red pentagons), and $100^\circ C$ (red crosses). The capacity of each MOF at 100 bar decreases as temperature increases (assuming single crystal density).

First Principles Calculations

First principles electronic structure calculations were used in conjunction with experimental results to both explain the results seen from experimental studies and to inform future experimental targets. In order to devise successful hydrogen storage strategies, there is a need for a fundamental understanding of the weak and elusive physisorption interaction. We reported a range of calculations of the weak intermolecular interactions of adsorbed hydrogen molecules on MOF linkers by using cluster models.

Since physical interactions such as dispersion and polarization have a major contribution to attraction energy, we analyzed the adsorption interaction using energy decomposition analysis that distinguishes the contribution of the physical interactions from the charge-transfer “chemical” interaction [2]. Surprisingly, it is found that charge transfer from the adsorbent to the $\sigma^*(H_2)$ orbital is present in all studied complexes and can contribute up to approximately

-2 kJ/mol to the interaction. When metal ions are present, donation from the $\sigma(H_2)$ to metal Rydberg-like orbital, along with the adsorbent to $\sigma^*(H_2)$ contribution, can contribute between -2 kJ/mol and -10 kJ/mol, depending on the coordination mode. To reach a sufficient adsorption enthalpy for practical usage, we find that the hydrogen molecule must be substantially polarized. Ultimately, the ability of the metalated linker to polarize the hydrogen molecule is highly dependent on the geometry of the metal ion coordination site, where a strong electrostatic dipole or quadrupole moment is required. MOFs containing metals bound to catechol functionalities were found to be superior to those containing metals bound in square planar and tetrahedral coordination modes. For example, an Al^{3+} bound to a catechol with a single F^- counterion was found to bind H_2 with a strength of about 20 kJ/mol, which is higher than any experimentally found binding enthalpy thus far. Thus, maximizing the number of available coordination sites on the metal cation is an important goal in order to allow for a maximum dipole moment and thus the strongest possible interaction with H_2 .

Other work completed focused on the determination of an optimal method for desolvating metal cations bound post synthetically to the ligands in metal organic frameworks. This is the primary hurdle to obtaining low-coordinate metal cations in MOFs; the ability to desolvate the metal cation is of the utmost importance in exposing coordination sites that will serve as H₂ binding sites. To overcome this barrier, a series of stepwise solvent exchanges is proposed as a suitable route to exposing coordination sites. One potential route for this has been calculated and determined based on the ability of each solvent to penetrate the coordination sphere around the metal and displace the previously bound solvent molecule. Solvent substitution reactions are dynamic processes, involving the detachment of the previous solvent and its solvation in the new solvent and the attachment of the new solvent to the metal site. Thus, temperature is expected to play a significant role in the dynamics of the system and these dynamics must be appropriately modeled. Molecular dynamics simulations on large number of atoms/molecules are beyond the reach of accurate density functional theory, due to the heavy computational requirements for systems of these sizes. In light of this, we evaluated another method, the effective fragment potential (EFP) method, as a tool for carrying out calculations of solvent exchange. The EFP approach enables more direct construction of force fields without the need for extensive calibrations. Indeed, we were able to successfully use this approach to model the molecular dynamics of solvent exchange, for example in Figure 3 where we demonstrate that a single water molecule, marked by a red circle, is effectively replaced at the metal site by an acetone molecule, and propagated to the surface of the solvent droplet.

We further expanded the solvent-exchange methodology to examine experimentally relevant solvents that would be used in the metalation process of the MOF, and therefore eventually require removal to activate metal sites for H₂ uptake. Commonly used solvents, with an electron lone pair attached to the metal-coordinated atom, have an expected interaction energy (per solvent molecule) of about 100 kJ/mol

with a catechol-Mg open-metal site and about 90 kJ/mol with a catechol-Ca open metal site. Given these large interaction energies, direct removal of these solvents from the open-metal site is not practical. Instead, these solvents may be substituted by other solvent molecules, such that each substitution step reduces the interaction of the solvent with the open-metal site. Computations enabled us to determine that an optimal sequence of solvent substitutions would be to use acetonitrile as a synthetic solvent, and to do successive exchanges with dichloroethane, ethylene, ethane, and methane, a sequence that would to successively minimize interaction energies at the metal site by approximately -15 kJ/mol. Ultimately, then, we have been able to use first principles calculations to support experimental efforts by determining optimal material activation conditions, which is essential in maximizing hydrogen uptake and meeting desired targets.

Neutron Diffraction Studies

The square-pore MOF Cu[Ni(pdt)₂]₃ (pdt²⁻ = pyrazine-2,3-dithiolate) shows potential for demonstrating the ability to bind two H₂ molecules to a single metal center (Figure 4). Data from H₂ isotherms indicated a strong H₂ binding enthalpy; thus, D₂-dosed samples were studied with neutron diffraction in order to determine the binding location of D₂ in the pores. Our efforts enabled the identification of the primary binding site being between the aromatic rings in the ligand, which is not what was expected. However, the diffraction data contained several peaks at low angles that could not be identified; we are working on determining the source of these peaks, but they are most likely due to an impurity in the bare material. Improved synthetic conditions have since produced a more pure material, which will again be studied using D₂-dosed neutron diffraction.

Another focus has been on the development of methods to understand H₂ adsorption at high pressures. Previously, we had conducted experiments on MOF-5 at high D₂ pressures to determine the binding profile of H₂ at high pressures in this material. Since then, this experiment has been conducted

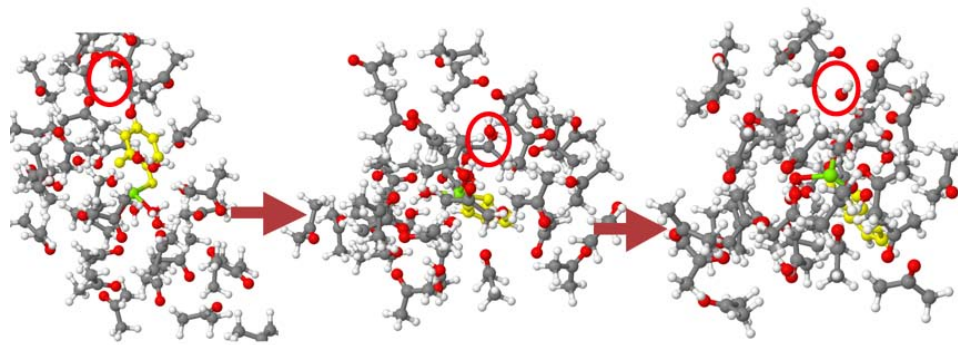


FIGURE 3. Evaluation of removal of water coordinating the metal site in catechol-Mg by acetone. The catechol molecule is in yellow and the metal ion is in green.

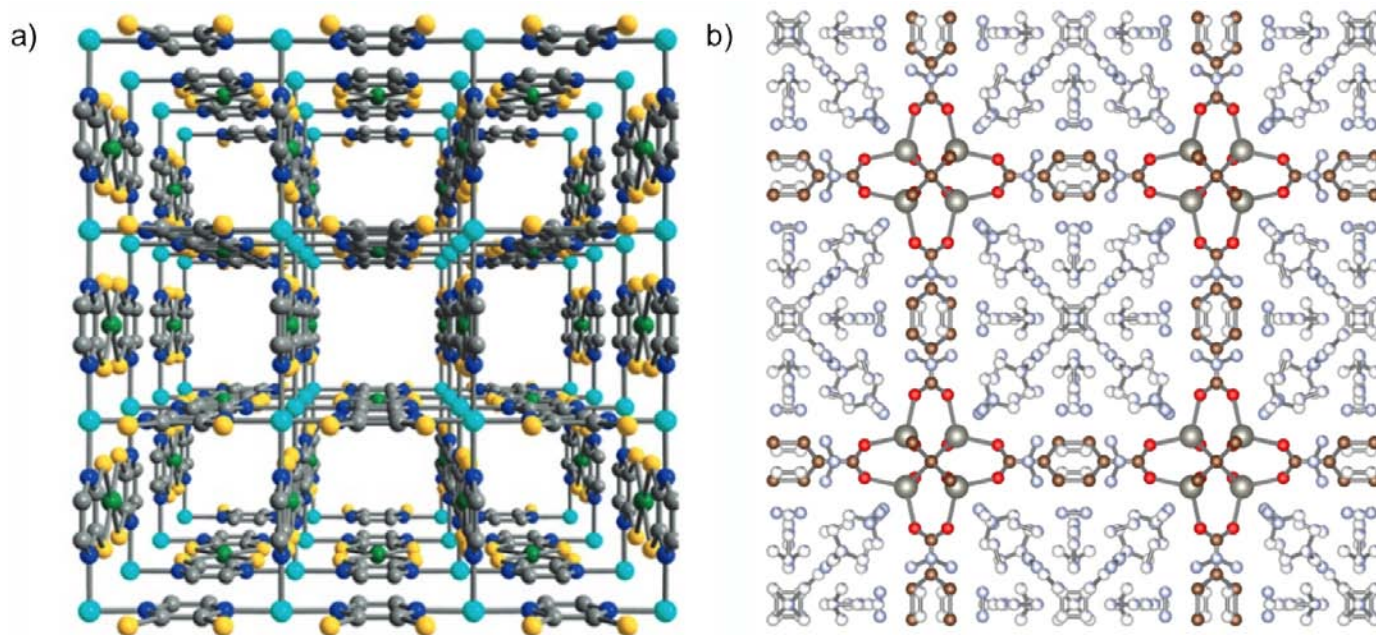


FIGURE 4. (a) The structure of Cu[Ni(pdt)₂] showing the square channels and close Ni²⁺ to Ni²⁺ distances. (b) The structure of MOF-5 loaded with 100 torr N₂ at 77 K, showing the binding profile of N₂ within the pores.

with N₂ at similar conditions as the experiments done with D₂. We observed the N₂ molecules to be localized in specific locations in the pore, similar to what was observed for D₂, even when a nominal pressure of gas is present at the time of the data collection. The conditions used in this experiment mimic those in a standard surface area measurement and thus revealed that the simplified model of covering pores with a layer of N₂ molecules does not adequately describe adsorption of H₂ at the atomic level. These data confirm the validity of our method of solving high-pressure structures with D₂ and will aid in a rigorous understanding of gas interactions with open-metal sites in the framework, further informing the optimization of H₂ uptake in new materials.

CONCLUSIONS AND FUTURE DIRECTIONS

Overall, the work this year has been quite successful in working toward MOF materials that can store large amounts of H₂. The development of synthetic methods both for the boc-protected catechol ligand and the cat-UIO-68 MOF are crucial toward synthesizing MOFs with a high density of open-metal coordination sites, which is the most promising method moving forward for having a significant breakthrough in the total volumetric H₂ storage capacity of MOFs. Relatedly, a full evaluation of the current top H₂-storage MOF materials was undertaken to determine the conditions in a temperature-swing process that maximize the volumetric H₂ usable capacity. First principles electronic structure calculations and neutron diffraction experiments helped to direct synthetic efforts, as well as help determine where and how H₂ is binding within these frameworks.

Future work will primarily focus on obtaining materials that can bind non-structural metal cations that can subsequently be desolvated to expose multiple coordination sites for H₂ binding. This will be imperative in order to increase the volumetric capacity of these materials and reach the DOE targets. The following goals will be targeted in FY 2016.

- Further study the metalation of cat-UIO-68 in order to determine optimal metalation and desolvation conditions
- Test the metalated cat-UIO-68 for its H₂ storage properties
- Develop other ligands and MOFs for use in post-synthetic metalation
- Extend the high-pressure neutron diffraction experiments to other materials in order to understand the binding profile of H₂ in the pores of those MOFs
- Continue to optimize the solvent exchange cascade to fully desolvate metals bound to catechols in MOFs

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Kapelewski, M.T.; Geier, S.J.; Long, J.R. "Metal-Organic Frameworks with a High Density of Highly Charged Exposed Metal Cation Sites." Submitted, patent pending.

FY 2015 PUBLICATIONS/PRESENTATIONS

Publications

1. Kapelewski, M.T.; Geier, S.J.; Hudson, M.R.; Stuck, D.; Mason, J.A.; Nelson, J.N.; Xiao, D.J.; Hulvey, Z.; Gilmour, E.; FitzGerald, S.A.; Head-Gordon, M.; Brown, C.M.; Long, J.R. “ $M_2(m\text{-dobdc})$ ($M = \text{Mg, Mn, Fe, Co, Ni}$) Metal-Organic Frameworks Exhibiting Increased Charge Density and Enhanced H_2 Binding at the Open Metal Sites,” *J. Am. Chem. Soc.* **2014**, *136*, 12119–12129.
2. Tsivion, E.; Long, J.R.; Head-Gordon, M. “Hydrogen Physisorption of Metal-Organic Framework Linkers and Metalated Linkers: A Computational Study of the Factors that Control Binding Strength,” *J. Am. Chem. Soc.* **2014**, *136*, 17827–17835.

Presentations

1. Brown, C.M. Invited talk, Metal-Hydrides 2014, July 20, 2014, Manchester, U.K.
2. Brown, C.M. Invited talk, Chemistry Dept. Seminar, May 8, 2014, Drexel, PA, U.S.A.
3. Kapelewski, M.T.; Geier, S.J.; Hudson, M.R.; Stuck, D.; Mason, J.A.; Nelson, J.N.; Xiao, D.J.; Hulvey, Z.; Gilmour, E.; FitzGerald, S.A.; Head-Gordon, M.; Brown, C.M.; Long, J.R. “Structural Isomer of $M_2(\text{dobdc})$ with Increased Charge Density and Stronger H_2 Binding at the Open Metal Sites.” 248th American Chemical Society National Meeting, San Francisco, CA: August 2014.
4. Jarad Mason. U.S. Car Hydrogen Storage Tech Team Presentation, Detroit, MI: September 2014.

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2. Tsivion, E.; Long, J.R.; Head-Gordon, M. *J. Am. Chem. Soc.* **2014**, *136*, 17827–17835.