

## IV.C.4 New Carbon-Based Porous Materials with Increased Heats of Adsorption for Hydrogen Storage

Randall Snurr (Primary Contact), Joseph Hupp,  
Mercuri Kanatzidis, SonBinh Nguyen  
Northwestern University (NU)  
2145 Sheridan Road  
Evanston, IL 60208  
Phone: (847) 467-2977  
E-mail: snurr@northwestern.edu

DOE Managers  
HQ: Carole Read  
Phone: (202) 586-3152  
E-mail: Carole.Read@hq.doe.gov  
GO: Katie Randolph  
Phone: (720) 356-1759  
E-mail: Katie.Randolph@go.doe.gov

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### Fiscal Year (FY) 2011 Objectives

Develop new materials to meet DOE gravimetric and volumetric targets for hydrogen storage:

- Develop and optimize strategies for introducing cations into metal-organic frameworks (MOFs).
- Synthesize new polymeric-organic frameworks (POFs) that contain cations.
- Use computational modeling to understand existing materials and design new materials for hydrogen storage.

### Technical Barriers

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

- (A) System Weight and Volume
- (E) Charging/Discharging Rates
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

### Technical Targets

TABLE 1. Progress towards Meeting Technical Targets for Hydrogen Storage

Characteristic	2015 Targets	NU 2011 Status
System Gravimetric Capacity	0.055 kg H <sub>2</sub> /kg system at ambient temperature and 100 bar	0.14 kg H <sub>2</sub> /(kg sorbent + H <sub>2</sub> ) at 77 K and 70 bar
System Volumetric Capacity	0.040 kg H <sub>2</sub> /L system at ambient temperature and 100 bar	0.045 kg H <sub>2</sub> /L sorbent at 77 K and 70 bar

### FY 2011 Accomplishments

- Computationally screened MOFs functionalized with Li, Mg, Mn, Ni, and Cu alkoxides for their deliverable hydrogen storage capacity and found that Mg-alkoxide is the most promising.
- Synthesized a MOF containing protected catechol groups and investigated methods for deprotection and introduction of Mg<sup>2+</sup> to form the alkoxide.
- Developed a new class of POFs based on click chemistry, with surface areas up to 1,440 m<sup>2</sup>/g.
- Developed POFs based on condensation of melamine and other building blocks and successfully incorporated up to 14 wt% Mg.



### Introduction

One option for storing hydrogen on vehicles is to use tanks filled with porous materials that act as “sponges” to take up large quantities of hydrogen without the need for extremely high pressures. The materials must meet many requirements to make this possible. This project is developing two related classes of porous materials to meet these requirements. All materials are synthesized from molecular constituents in a building-block approach. This allows us to create a wide variety of materials in a tailorable fashion. The materials have extremely high surface areas, to provide many locations for hydrogen to adsorb. In addition, they are designed to contain cations that create large electric fields to bind hydrogen strongly but not too strongly.

### Approach

The approach in this project is to introduce cations into MOFs and POFs to increase the hydrogen heats of adsorption, which will, in turn, increase the amount of

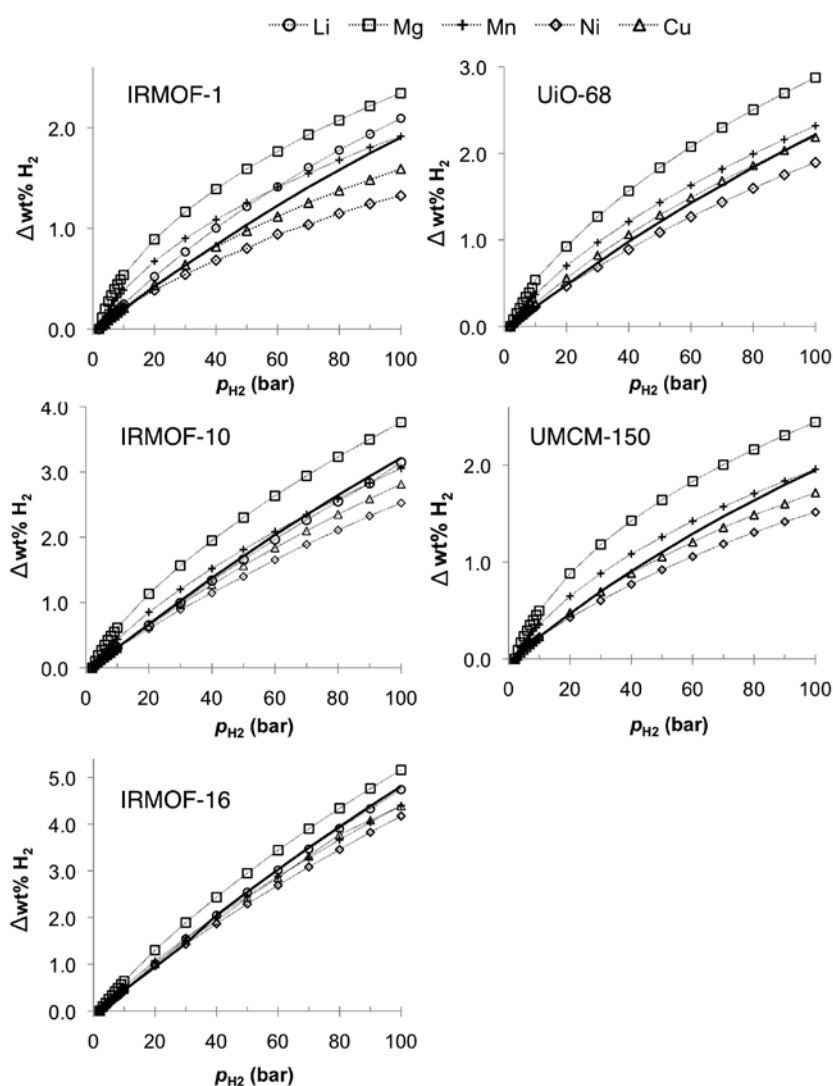
hydrogen that can be stored near room temperature. Many MOFs have enough surface area to meet the DOE hydrogen storage targets if the entire surface were covered with a monolayer of hydrogen. However, at room temperature, the energetic interactions between hydrogen and the surfaces are too weak to bind hydrogen. Thus, we are focused on increasing these energetic interactions. A variety of synthetic chemistries are being explored to increase the chances of success. In addition, molecular modeling is used to help explain experimental observations and provide guidance to the synthetic efforts.

## Results

In FY 2010, we had developed a model for simulating hydrogen uptake in MOFs containing alkoxide groups. Briefly, second-order Moller-Plesset perturbation theory calculations with a large basis set (6-311+G\*\*) were performed for a hydrogen molecule in ~200 different geometries near the alkoxide group, and these energies were fit with a combined Morse + Coulomb + Lennard-Jones potential. In FY 2011, we used this model in grand canonical Monte Carlo (GCMC) simulations to explore metal alkoxide functionalization for improving H<sub>2</sub> storage in isoreticular metal organic framework (IRMOF)-1, IRMOF-10, IRMOF-16, UiO-68, and UCMC-150, as some representative MOF structures [1]. We examined functionalization with lithium, magnesium, manganese, nickel, and copper alkoxides. We showed that lithium and magnesium alkoxides physically bind H<sub>2</sub> and manganese, nickel, and copper alkoxides chemically bind H<sub>2</sub>. Hydrogen binding energies calculated with quantum mechanics are -10, -22, -20, -78, and -84 kJ mol<sup>-1</sup>, respectively, for the first hydrogen molecule. Of these, lithium and manganese alkoxides bind H<sub>2</sub> too weakly to enhance adsorption at ambient temperature, even at 100 bar. Owing to the strong binding energies, Ni and Cu exhibit high uptake at low pressure, but metal alkoxide sites saturate at pressures as low as 1 bar. They thus exhibit poor deliverable capacities (calculated here as the wt% H<sub>2</sub> at 100 bar minus the wt% H<sub>2</sub> at 2 bar). The deliverable capacities from the simulations are shown in Figure 1 for MOFs with one functional group per linker. Magnesium alkoxide exhibits low uptake at low pressure and high uptake at high pressure and is a promising functional group for enhanced ambient-temperature hydrogen storage in all MOFs studied.

Additionally, we explored the effect of the number of alkoxide groups per MOF linker on hydrogen adsorption and the enthalpy of adsorption. We found that increasing the density of functional groups leads to an increase in hydrogen adsorption for a Mg-alkoxide-functionalized MOF but not for a Mn-alkoxide-functionalized MOF. The behavior can be explained by examining the enthalpies of adsorption in the different materials. These results show that increasing the number of alkoxide groups per linker significantly enhances the H<sub>2</sub> uptake and is thus a promising strategy for improving H<sub>2</sub> storage, but the strategy must be focused on the right metals.

Quantum mechanical results have also provided information on the nature of the hydrogen interactions



**FIGURE 1.** Deliverable hydrogen storage capacity [ $\Delta\text{wt}\% = \text{wt}\%(p_{\text{H}_2}) - \text{wt}\%(2 \text{ bar})$ ] as predicted by GCMC simulations for metal alkoxide functionalized MOFs at 243 K. The MOFs are functionalized with one alkoxide site per linker. Deliverable capacities for unfunctionalized MOFs are depicted by thick solid lines without symbols.

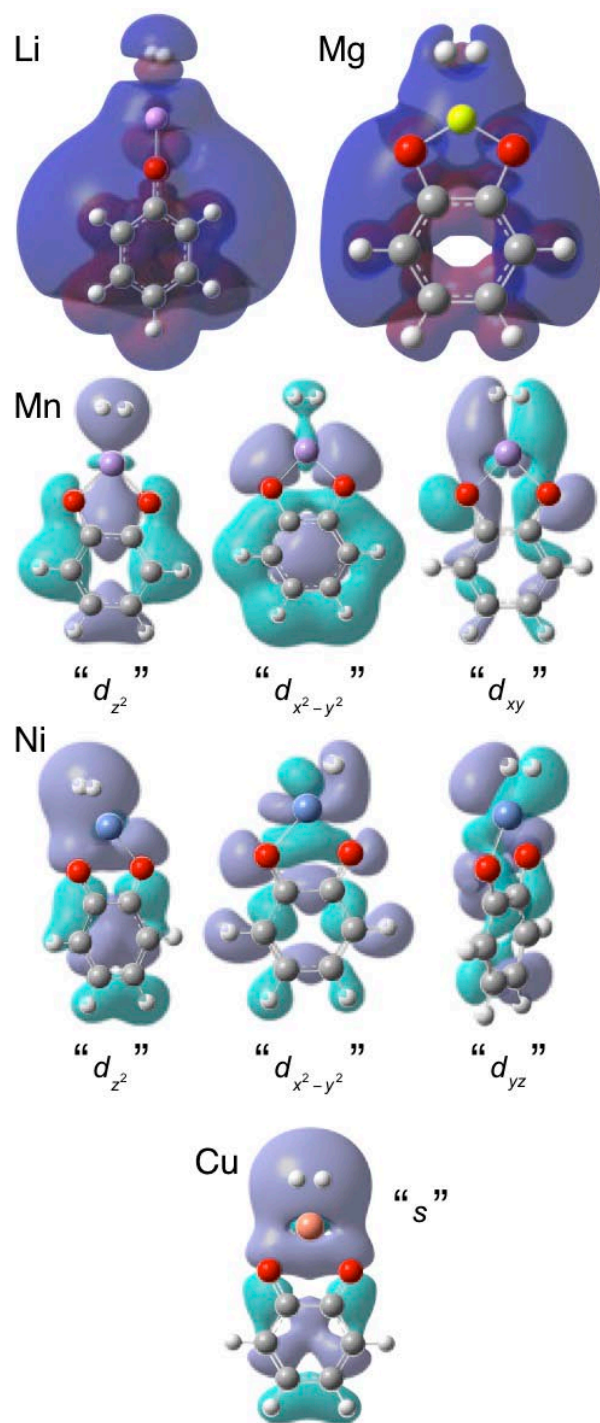
with the exposed metal sites. (See Figure 2.) The average and differential hydrogen binding energies were also calculated for up to five  $H_2$  molecules per metal atom. Results are shown in Figure 3. The binding energy on Li remains relatively constant for up to 3  $H_2$  molecules and then starts to weaken, whereas the binding energy on Mg weakens between  $n = 1$  and  $n = 2$  and then levels off before weakening again at  $n = 4$ . The binding energy to Mn alkoxide decreases between  $n = 1$  and  $n = 2$  and then remains relatively constant up to  $n = 5$ . (These trends are more easily seen in the differential binding energies of Figure 3.) In contrast, Ni and Cu bind  $H_2$  very strongly initially, but the binding energies weaken dramatically as additional  $H_2$  molecules adsorb.

Motivated by the modeling work, the experimental effort on MOFs this year has focused on synthesizing MOFs with divalent cations, especially  $Mg^{2+}$ , bound through a catecholate functionality. We synthesized a candidate MOF strut featuring a protected catechol group and successfully synthesized a MOF containing the strut in protected form. Suitable crystals for X-ray examination are in hand and awaiting analysis in our centralized X-ray characterization facility. Deprotecting the catechols once they are built into MOFs has proven challenging. We have tested several techniques. Preliminary studies (mainly with organic polymer analogues) indicate that high yields for deprotection are achievable with at least one of the techniques.

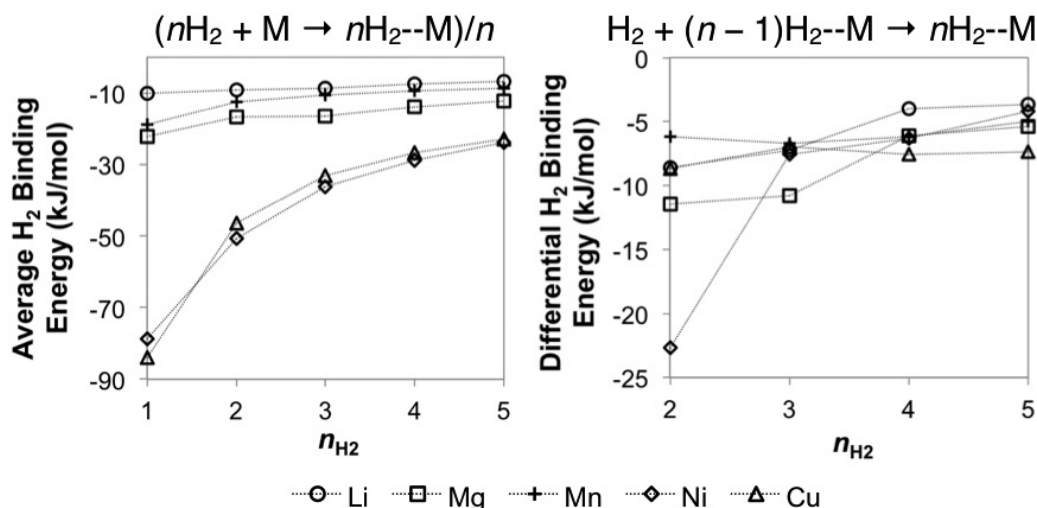
We have synthesized additional quantities of MOF NU-100, which will be sent to the National Renewable Energy Laboratory (NREL) for corroboration of our findings of high hydrogen uptake that were reported last year [2]. We also worked with NREL on validation and calibration of our own high-pressure sorption instrument.

In previous years of the project, we had developed microporous POFs using Schiff base and Bakelite chemistries. During FY 2011, we also reported a third class of highly stable, microporous POFs using “click chemistry.” They are synthesized via copper-catalyzed alkyne-azide coupling between two rigid tetrahedral building blocks. We investigated the effect of the amount of the reducing agent (sodium azide) used on the pore properties of these “click-based” POFs. The highest surface area achieved for this type of POF was  $1,440 \text{ m}^2\text{g}^{-1}$  and the hydrogen uptake was also promising at low pressure (up to 1.6 wt% at 1 bar). Some effort this year was devoted to further optimizing the reaction conditions for the POF syntheses to enhance the microporosity and hydrogen uptake in these materials.

We have also attempted to attach metal cations in the phloroglucinol and “click-based” POFs to increase the hydrogen adsorption enthalpy. For example, phloroglucinol POFs have large numbers of OH groups that can react with alkyl metal compounds to produce metal functionalized POFs. We employed a variety of metal compounds and synthetic strategies to accomplish the metal introduction. In one case, we used POFs based on condensation reaction between melamine and different aromatic aldehyde



**FIGURE 2.** Binding properties for  $H_2$  to metal alkoxide benzenes from quantum chemical calculations. (Top row) Charge density differences indicate Li and Mg polarize  $H_2$ , resulting in charge density accumulation between the metal cations and  $H_2$ . Regions of charge density accumulation and depletion are red and blue, respectively. (Second row) Molecular orbitals for  $H_2$  adsorption to Mn alkoxide benzene indicate a variety of interactions between  $H_2$   $1\sigma^*$  and Mn d orbitals.  $H_2$  is strongly polarized and can interact with both spherical ( $d_{z^2}$ ) and nonspherical ( $d_{xy}$ ) orbitals. (Third row) Nickel alkoxide benzene has a variety of d orbitals for interaction with  $H_2$   $1\sigma^*$ , and a representative subset is shown here. (Bottom row) Copper alkoxide benzene forms a strong  $\sigma$  bond with  $H_2$ .



**FIGURE 3.** Average (left) and differential (right) binding energies for H<sub>2</sub> to metal alkoxide benzenes for 1–5 H<sub>2</sub> molecules, from quantum chemical calculations. Note that the average and differential energies are equal when  $n = 1$ .

building blocks with sites for metal binding. In our initial experiments we have successfully incorporated high amounts of metals like manganese (Mn) and magnesium (Mg) in our POFs (Table 2). Our next step is to study the effect of metal incorporation on the hydrogen uptake and the heats of adsorption in these POFs.

**TABLE 2.** Metal Loadings in POFs 2a and 2b

POF	Metal Source	wt% metal
POF 2a	Mn(CH <sub>3</sub> COO) <sub>2</sub>	30 wt% Mn
POF 2a	Mg(CH <sub>3</sub> ) <sub>2</sub>	14 wt% Mg
POF 2b	Mn(CH <sub>3</sub> COO) <sub>2</sub>	23 wt% Mn

## Conclusions and Future Directions

### Conclusions

- We computationally screened Li, Mg, Mn, Ni, and Cu alkoxide-functionalized MOFs for their deliverable hydrogen storage capacity and found that Mg-alkoxide is the most promising of these metals.
- We synthesized a MOF containing protected catechol groups and found that the deprotection and introduction of Mg<sup>2+</sup> is challenging. Preliminary studies with organic polymer analogs indicate that high yields for deprotection are achievable with at least one of the techniques investigated.
- We have developed a new class of POFs based on click chemistry, with surface areas up to 1,440 m<sup>2</sup>/g.
- We have developed POFs based on condensation of melamine and other building blocks. Levels of Mg incorporation up to 14 wt% can be achieved.

### Future Directions

- Finish validation (with NREL) of very high cryogenic hydrogen uptake in MOF NU-100.
- Finish optimization of deprotection strategies for introducing alkaline earth alkoxide functional groups into MOFs.
- Explore other chemistries for introducing alkaline earth alkoxide functional groups into MOFs and POFs.
- Test hydrogen uptake in recently synthesized POFs with high metal loading.
- Combine strategies for introducing cations into MOFs and POFs with strategies for producing MOFs and POFs with very large surface areas.
- Model new functionalities for introducing cations into MOFs and POFs.

### FY 2011 Publications/Presentations

- P. Pandey, A.P. Katsoulidis, I. Eryazici, Y. Wu, M.G. Kanatzidis, S.T. Nguyen, "Imine-linked microporous polymer organic frameworks," *Chem. Mater.* **22**, 4974-4979 (2010).
- Y.-S. Bae, R.Q. Snurr, "Molecular simulations of very high pressure hydrogen storage using metal-organic frameworks," *Microporous and Mesoporous Materials* **135**, 178-186 (2010).
- O.K. Farha, A.Ö. Yazaydin, I. Eryazici, C.D. Malliakas, B.G. Hauser, M.G. Kanatzidis, S.T. Nguyen, R.Q. Snurr, J.T. Hupp, "*De novo* synthesis of a metal-organic framework material featuring ultra-high surface area and gas storage capacities," *Nature Chem.* **2**, 944-948 (2010).
- R.B. Getman, J.H. Miller, K. Wang, R.Q. Snurr, "Metal alkoxide functionalization in metal-organic frameworks for enhanced ambient temperature hydrogen storage," *J. Phys. Chem. C* **115**, 2066-2075 (2011).



5. P. Pandey, O.K. Farha, A.M. Spokoyny, C.A. Mirkin, M.G. Kanatzidis, J.T. Hupp, S.T. Nguyen, "A 'click-based' porous organic polymer from tetrahedral building blocks," *J. Mater. Chem.* **21**, 1700-1703 (2011).
6. A.P. Katsoulidis, M.G. Kanatzidis, "Phloroglucinol microporous polymeric organic frameworks with -OH functional groups and high CO<sub>2</sub> capture capacity," *Chem. Mater.*, in press.

## References

1. R.B. Getman, J.H. Miller, K. Wang, R.Q. Snurr, "Metal alkoxide functionalization in metal-organic frameworks for enhanced ambient temperature hydrogen storage," *J. Phys. Chem. C* **115**, 2066-2075 (2011).
2. O.K. Farha, A.Ö. Yazaydin, I. Eryazici, C.D. Malliakas, B.G. Hauser, M.G. Kanatzidis, S.T. Nguyen, R.Q. Snurr, J.T. Hupp, "De novo synthesis of a metal-organic framework material featuring ultra-high surface area and gas storage capacities," *Nature Chem.* **2**, 944-948 (2010).