

## IV.F.2 New Carbon-Based Porous Materials with Increased Heats of Adsorption for Hydrogen Storage

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### 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 Hydrogen, Fuel Cells and Infrastructure 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

- This project is developing and testing new materials for hydrogen storage. These new materials can be applied in the future in the design of hydrogen storage systems that meet the following DOE 2010 hydrogen storage targets:
- System Gravimetric Capacity:  
1.5 kWh/kg = 0.045 kg H<sub>2</sub>/kg system
- System Volumetric Capacity:  
0.9 kWh/L = 0.028 kg H<sub>2</sub>/L system

### Accomplishments

- Synthesized a new MOF that exhibits an 11 kJ/mol heat of adsorption for hydrogen. As a comparison, note that unfunctionalized MOFs and carbon-based sorbents typically have hydrogen heats of adsorption around 4-5 kJ/mol. Modeling from several groups indicates that heats of 15-20 kJ/mol will be required to meet DOE hydrogen storage targets.
- Synthesized a variety of new POFs, some with surface areas over 1,500 m<sup>2</sup>/g. These materials have functional groups that can be tailored to increase the hydrogen heat of adsorption. One material synthesized has a hydrogen heat of adsorption of 8 kJ/mol before functionalization.
- Used molecular modeling to rule out catenation as a viable strategy for achieving room temperature hydrogen storage targets in unfunctionalized MOFs.
- Developed a model for MOFs containing alkoxide groups. Identified alkaline earth alkoxides as promising synthetic targets.
- Computationally constructed and subsequently experimentally synthesized a MOF material showing: a) record-high gravimetric uptake of H<sub>2</sub> under cryogenic (77 K) conditions (99.5 mg excess H<sub>2</sub> per g of MOF; 164 mg total H<sub>2</sub> per g of MOF at 70 bar) and b) record-high Brunauer-Emmett-Teller surface area (6,500 m<sup>2</sup>/g [modeled]; 6,200 m<sup>2</sup>/g [measured]).
- Showed that a recently published claim of 6 wt% uptake of H<sub>2</sub> by a comparatively low-area POF material is in error.



### 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.

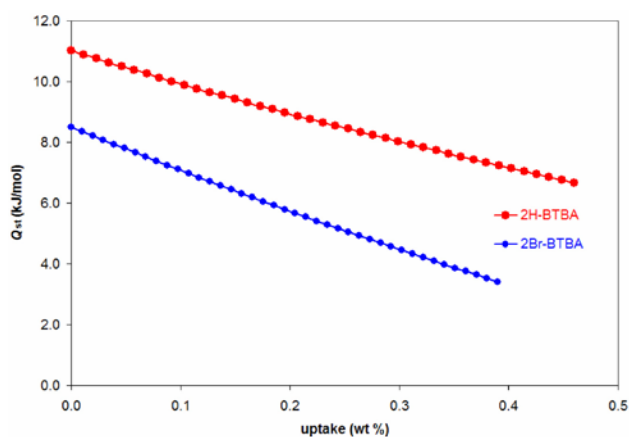
## Approach

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.

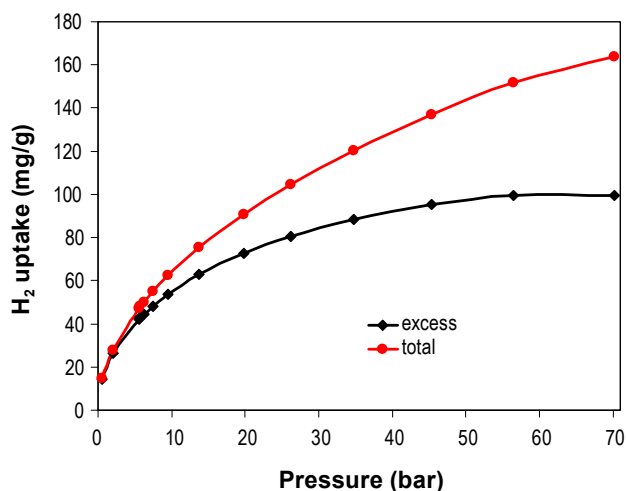
## Results

We designed and synthesized the first two examples of unique zwitterionic MOF materials (2H-BTBA and 2Br-BTBA). These materials are permanently microporous and feature fixed cationic sites on vertical struts and fixed anionic sites on horizontal struts. Together the struts (and associated metal nodes) define cavities having sizable electric fields. We reasoned that these cavities might stabilize polarizable molecules (dihydrogen has a small, but finite, polarizability), resulting in enhanced heats of adsorption. As shown in Figure 1, the limiting (low pressure) isosteric heat of adsorption is 11 kJ/mol for H<sub>2</sub> uptake by 2H-BTBA. To our knowledge, this is the first time the zwitterionic concept has been proposed or explored for enhancing framework/gas interactions.

Figure 2 shows the behavior of a new ultra-high-area MOF that was computationally characterized prior to experimental synthesis. Importantly, the computational studies promised record-high uptake of hydrogen by the new material (at 77 K). Using a supercritical activation methodology pioneered at Northwestern we were able to access essentially all of the MOF interior, i.e. little, if any, framework collapse or blockage occurred. The activated MOF exhibited,



**FIGURE 1.** Heats of adsorption in new zwitterionic MOFs. At low loadings of hydrogen, the heat of adsorption is 11 kJ/mol, which is considerably higher than in unfunctionalized MOFs. Notably, the heat of adsorption remains above 6 kJ/mol throughout the entire range of loadings.



**FIGURE 2.** Uptake of H<sub>2</sub> by a new ultra-high-area MOF as a function of pressure at 77 K. Black diamonds (lower curve) show the excess uptake. Red circles (upper curve) show the total uptake. For determining the amount of hydrogen that can be delivered by the material, the (red) curve showing total uptake is most relevant.

as predicted, exceptionally high hydrogen uptake. Ultimately, to reach desired ambient-temperature hydrogen storage goals, it will be important to combine the findings here with the advances we are making in the area of improvement of heats of adsorption.

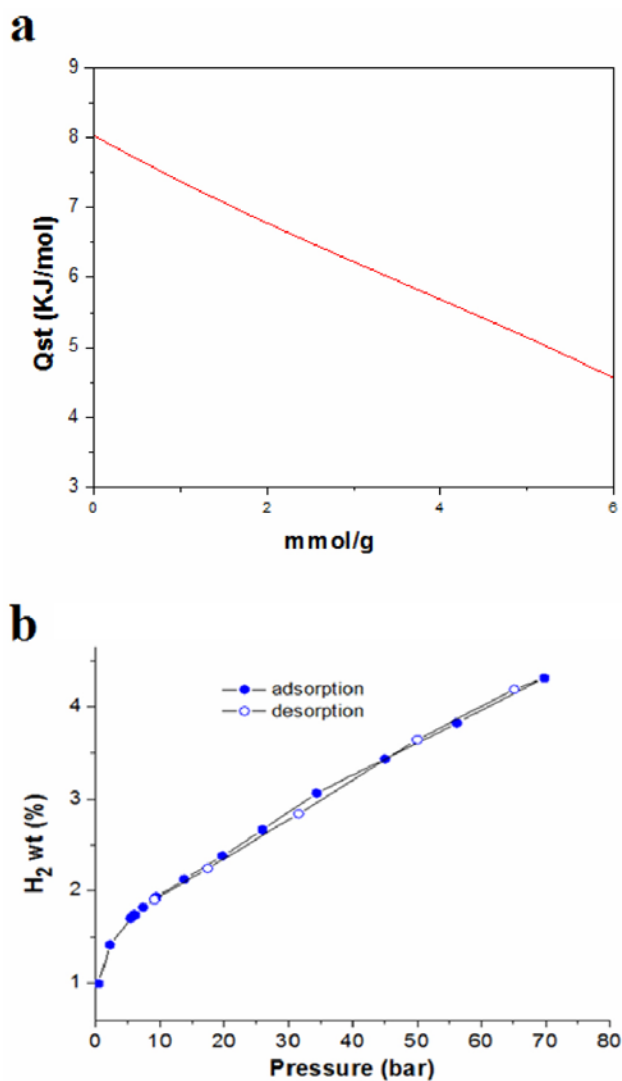
We have synthesized an important new variant of a well-known single-channel MOF. The variant features substituent alcohols that are amenable to conversion to metal alkoxides. We anticipate that this new MOF will enable us to test our computational predictions regarding enhanced interactions between H<sub>2</sub> and MOF components.

We have developed two new families of microporous POFs. The first family of POFs (imine-linked) were synthesized *via* Schiff base condensation between 1,3,5-triformylbenzene and several readily available diamine monomers. Our facile, one-pot approach results in quantitative yields (~90%) of POFs with the flexibility to incorporate several functional groups in their pores for tuning the interaction of their surface with different guest molecules.

We initially prepared POFs using *para* diaminobenzene and *meta* diaminobenzene. Because the specific surface area of the POF prepared using *meta* diaminobenzene (POF-2) was higher than the POF prepared using *para* diaminobenzene (POF-1), we focused on *meta* diamines as the amine building blocks most likely to give rise to materials with high surface areas. We also optimized the reaction conditions to maximize surface area and micropore volume. A surface area of  $1,063 \text{ m}^2 \text{ g}^{-1}$  (POF-2) was initially obtained by combining monomers at the beginning of the reaction. Notably, slowly adding amine monomer to a solution of aldehyde monomer significantly increased this surface area by ~50%, to  $1,521 \text{ m}^2 \text{ g}^{-1}$  (POF-3), which is the highest specific surface area obtained among our synthesized POFs. POF-3 was found to possess  $\text{H}_2$  adsorption capacity of 1.5 wt%, at 1 bar and 77 K and a good isosteric heat of  $\text{H}_2$  adsorption of  $8.2 \text{ kJ mol}^{-1}$  at low coverage (Figure 3a). In addition, the  $\text{H}_2$  adsorption measurement performed for this POF, at high pressures and 77 K, shows an increase in  $\text{H}_2$  uptake with the increase in pressure giving maximum  $\text{H}_2$  uptake of 4.3 wt% at 70 bar (Figure 3b). Pore size distribution analysis for POF-3, performed using non-local density functional theory, confirms a primary pore width of 6 Å. Interestingly, even though the synthesized POFs are amorphous, their pore size distributions are not wide.

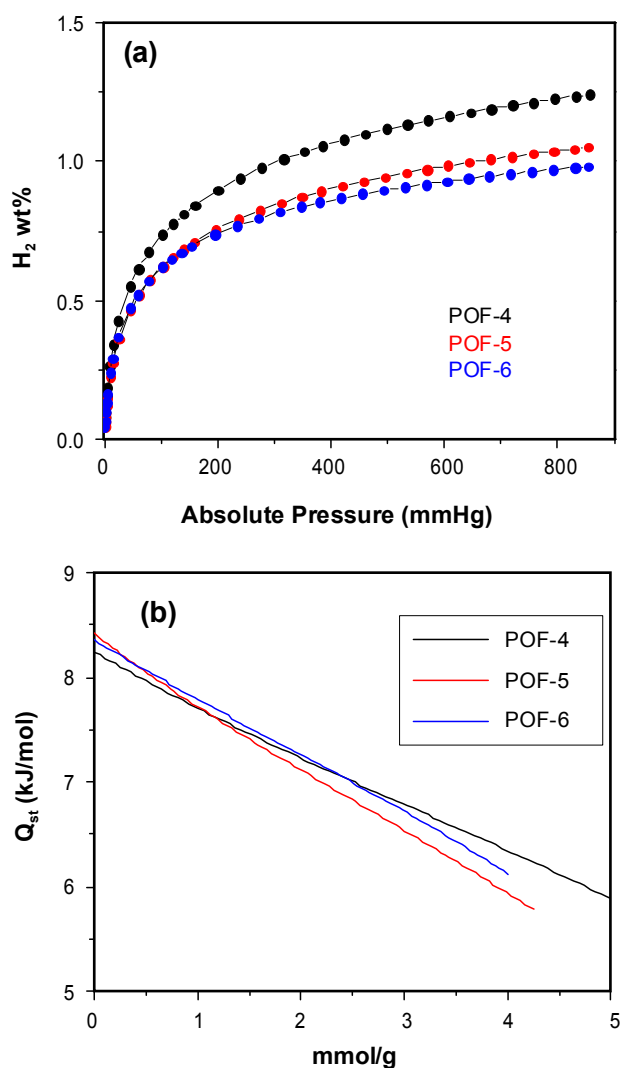
The second POF family is based on reaction between phloroglucinol and aldehydes. This is a straightforward reaction that produces highly cross-linked polymers. The polymerization took place under solvothermal conditions using dioxane as solvent at  $220^\circ\text{C}$  producing solid materials in high yield (~90%). These synthesized POFs contain large numbers of hydroxyl groups which are available for functionalization. All these POFs are microporous materials, and they exhibit specific surface areas from 600 to  $900 \text{ m}^2 \text{ g}^{-1}$  and a main pore width of 6 Å. Scanning electron microscope images of POF-4 show spherical particles with smooth surfaces in the range of 1–3  $\mu\text{m}$ . Phloroglucinol POF samples were tested for  $\text{H}_2$  adsorption at 77 and 87 K up to atmospheric pressure (Figure 4a). POF-4 shows  $\text{H}_2$  uptake of 1.25 wt%; POF-5 and POF-6 show uptake of 1 wt%. Heat of  $\text{H}_2$  adsorption is estimated to  $\sim 8.3 \text{ kJ mol}^{-1}$  at low coverage for all samples (Figure 4b).

A rather astonishing experimental and computational report of very substantially enhanced



**FIGURE 3.** (a) Isosteric heat of  $\text{H}_2$  adsorption of POF-3. (b)  $\text{H}_2$  adsorption isotherm of POF-3 at 77 K, up to 70 bar.

uptake of  $\text{H}_2$  by a permanently microporous, organic framework material appeared earlier this year in the literature (*Angew. Chem., Int. Ed.* 2010, 49, 3330-3333). The report was remarkable on three counts. First, doping with a very small amount of lithium led to a quadrupling of hydrogen uptake. Secondly, the material features only a modest internal surface area – raising the question of how the material could imbibe such large amounts of  $\text{H}_2$ . Thirdly, we had previously examined a related material (unpublished) but not encountered the spectacular enhancements reported in the new article. While we have previously described large lithium-based enhancement effects upon sorption of hydrogen by three MOF materials, the mechanism invoked to account for the MOF results is inapplicable to the new POF material. Follow-up work in our labs has now clearly established that the stunning new results described in



**FIGURE 4.** (a)  $H_2$  adsorption isotherms of phloroglucinol POFs at 77 K. (b) Heat of adsorption for all POFs.

*Angewandte Chemie* are in error, with the new material behaving instead in a more-or-less conventional way.

Using classical grand canonical Monte Carlo (GCMC) simulations, hydrogen storage and delivery in eight representative MOFs was investigated. The simulations demonstrate that the optimal isosteric heat of adsorption ( $Q_{st}$ ) for maximum hydrogen delivery using MOFs is approximately 20 kJ/mol. We considered the delivered hydrogen as the amount adsorbed at 120 bar minus the amount adsorbed at 1.5 bar. The results also suggest that increasing  $Q_{st}$  for MOFs with large surface areas is required to attain current hydrogen storage targets in terms of deliverable capacity. Using the same model, hydrogen adsorption isotherms in 20 MOFs were obtained from GCMC simulations and used to develop quantitative correlations to quickly estimate the  $H_2$  uptake of MOFs at 120 bar from the free volume of the adsorbent. These correlations were

subsequently validated with a diverse set of 22 MOFs that were not used in developing the correlations.

We also used classical GCMC simulations to assess whether catenation is a viable strategy for meeting DOE hydrogen storage targets. We simulated hydrogen uptake in a series of catenated MOFs along with their non-catenated counterparts. The MOFs were chosen to cover a wide range of pore sizes and free volumes. The results indicate that catenation does increase the heats of adsorption, as expected. However, the effect is not enough, at room temperature, to compensate the loss of free volume that also arises from catenation. These results indicate that catenation is not a viable strategy for meeting room temperature hydrogen storage targets in unfunctionalized MOFs. Strong binding sites that increase the heats of adsorption will be required. These calculations support the main premise of this project.

Finally, we have developed a model for simulating hydrogen uptake in MOFs containing alkoxide groups. MP2 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. Models were developed for a range of metal alkoxides, including Na, Li, Mg, and some transition metals. GCMC simulations have been performed using these models to predict the hydrogen adsorption isotherms. In addition, the Second-order Moller-Plesset perturbation theory calculations provide useful details of the orbitals involved in the hydrogen-metal interactions. There has been much attention in the literature on Li-functionalized MOFs, but our calculations indicate that Mg provides a larger enhancement in hydrogen uptake. Based on these calculations, synthetic efforts in the group are now focused on Mg alkoxides in addition to Li.

## Conclusions and Future Directions

### Conclusions

- Multiple strategies have now been demonstrated in our labs for introducing sites into MOFs that increase hydrogen heats of adsorption, including framework reduction, alkoxide formation, and zwitterionic cavities. These provide a powerful platform for tailoring MOFs to increase the heats of adsorption toward meeting DOE hydrogen storage targets.
- One MOF synthesized in our labs exhibits an 11 kJ/mol heat of adsorption for hydrogen.
- A variety of new POFs, some with surface areas over 1,500  $m^2/g$ , have been synthesized in this project. These materials have functional groups that can be tailored to increase the hydrogen heat of adsorption. One material synthesized has a hydrogen heat of



adsorption of 8.3 kJ/mol at low coverage before functionalization.

- We showed that a remarkable new claim in the literature of 6 wt% uptake of hydrogen by a comparatively low-area POF material is, in fact, in error.
- Catenation is not a viable strategy for achieving room temperature hydrogen storage targets in unfunctionalized MOFs.
- A new MOF displaying record-high internal surface area and record-high (cryogenic) uptake of H<sub>2</sub> (total H<sub>2</sub> of 14.4 wt%) has been synthesized.
- Modeling indicates that alkaline earth cations may be more promising than alkalis for increasing hydrogen heats of adsorption in alkoxide-containing MOFs.

#### Future Directions

- Synthesis of Mg and other alkaline earth alkoxide MOFs.
- Characterization of a new “framework reducible” MOF designed to localize added dications (i.e. alkaline earth and transition-metal species) on the reduced strut, rather than at comparatively inaccessible metal-carboxylate node sites.
- Functionalization of POFs, especially with alkaline and alkaline earth alkoxides.
- Initiation of POF synthesis using “click” chemistry.
- Combination of strategies for introducing cations into MOFs and POFs and strategies for producing MOFs and POFs with very large surface areas.
- Modeling of additional metal-substituted MOFs.
- Modeling of POFs.

#### Special Recognitions & Awards/Patents Issued

1. Profile of Randy Snurr and his group’s work on hydrogen storage in the May/June 2010 issue of *The Pennsylvania Gazette*, the alumni magazine of the University of Pennsylvania.
2. Joseph Hupp, Distinguished Alumni Lectureship, Department of Chemistry, Michigan State University, April, 2010.

#### FY 2010 Publications/Presentations

1. Y.-S. Bae, R.Q. Snurr, “Optimal isosteric heat of adsorption for hydrogen storage and delivery using metal-organic frameworks,” *Micropor. Mesopor. Materials* **132**, 300-303 (2010).
2. P. Pandey, A.P. Katsoulidis, I. Eryazici, Y. Wu, M.G. Kanatzidis, S.T. Nguyen, “Imine-linked microporous polymer organic frameworks,” *Chem. Mater.*, in press.
3. 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 extraordinary gas storage capacities,” *Nature Chem.*, submitted.
4. A.P. Katsoulidis, M.G. Kanatzidis, “Microporous polymeric organic frameworks with –OH functional groups based on phloroglucinol,” *Chem. Commun.*, submitted.
5. Y.-S. Bae, R.Q. Snurr, “Molecular simulations of very high pressure hydrogen storage using metal-organic frameworks,” *Micropor. Mesopor. Materials*, submitted.
6. Multiple Presentations at universities and conferences