

## IV.C.7 Hydrogen Trapping through Designer Hydrogen Spillover Molecules with Reversible Temperature and Pressure-Induced Switching

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(A) System Weight and Volume

(D) Durability/Operability

(E) Charging/Discharging Rates

### Technical Targets

**TABLE 1A.** PSU/RU Progress toward Meeting DOE Targets for Hydrogen Storage (Room temperature H<sub>2</sub> adsorption data collected)

Characteristics	Units	2010/2015 Targets	PSU/RU Status
Gravimetric Capacity (Material)	kg H <sub>2</sub> /kg System	0.045/0.055	Cu(hfipbb)H <sub>2</sub> (hfipbb) <sub>0.5</sub> (Figure 1) 0.0011 (20 bar; with 5%Pt/C in 9:1; Figure 1)  Zn(bdc)(ted) <sub>0.5</sub> (See Figure 1) 0.0027 (20 bar; with 5%Pt/C in 9:1; Figure 1)  Cu <sub>3</sub> (btc) <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> (Figure 3) 0.0027 (20 bar; Figure 3; PSU) 0.004 (20 bar, RU; Figure 3v) 0.012 (60 bar; RU) ~0.02 (100 bar extrapolation, Figure 3, RU)
Operating Temperature	°C	-30 to 50/-40 to 60	25
Pressure	atm	100/100	20[PSU]/60[RU]/100[extrapolated]

### Objectives

Synthesize designer microporous metal-organic frameworks (MMOFs) mixed with catalysts to enable H-spillover for H<sub>2</sub> storage at 300 K - 400 K and moderate pressures.

For year 1 (Jan-Dec. 2009) of the project:

- Explore the effect of surface chemistry, porosity, and structure on hydrogen spillover (RU, synthesis) *-50% complete*; (PSU, hydrogen measurements) *-10% complete*
- Method development for catalyst studies and MMOF compatibility with catalysts (PSU) *-10% complete*
- Explore the incorporation of active hydrogen dissociation centers directly into the MMOF framework – (RU synthesis) *-50% complete*; (PSU method development, measurements) *-5% complete*

### Technical Barriers

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

Additional samples synthesized and characterized for porosity/surface chemistry studies but not yet tested for hydrogen adsorption:

- Cu(ipa)(bpy)<sub>3</sub>H<sub>2</sub>O
- MMOF-2-Cu and MMOF-2-Ni ([M<sub>2</sub>(bpdca)<sub>2</sub>(ted)]·nDMF, where M = Cu or Ni)
- MMOF-3-Zn ([Zn<sub>2</sub>(oba)<sub>2</sub>(bpy)]·DMF)

Additional technical issues being addressed: pressure savings over empty tank; temperature and pressure switching.

This project is conducting fundamental studies regarding hydrogen spillover, MMOF structural changes, and incorporating temperature and pressure switches into material design. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the DOE 2010 hydrogen storage targets outlined previously.

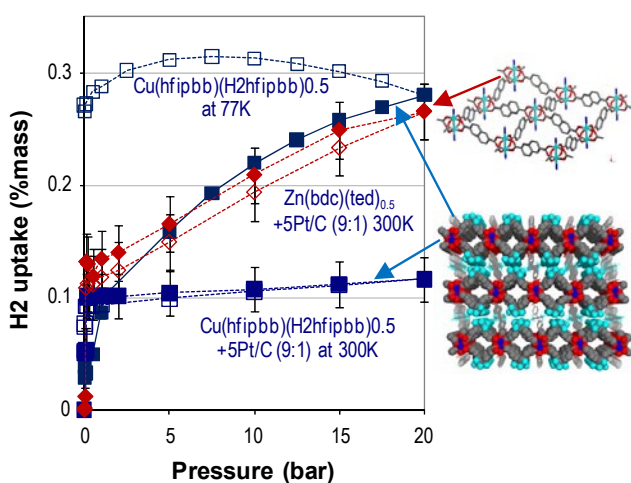
**TABLE 1B.** PSU/RU Progress toward Meeting DOE Targets for Hydrogen Storage (Low temperature H<sub>2</sub> physisorption data collected)

Characteristics	Units	2010/2015 Targets	PSU/RU Status
Gravimetric Capacity (Material)	kg H <sub>2</sub> /kg System	0.045/0.055	Cu(hfipbb)H <sub>2</sub> (hfipbb) <sub>0.5</sub> 0.0028 (20 bar; Figure 1) 0.0027 (0 bar; desorption hysteresis; Figure 1)  Zn <sub>2</sub> (bpdC) <sub>2</sub> (bpee): 0.014 (20 bar; Figure 2) 0.0182 (70 bar, RU, not shown)  Cu <sub>3</sub> (btc) <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> (Figure 3) 0.021 (1 atm; RU)  Zn(bdc)(ted) <sub>0.5</sub> 0.021 (1 atm; RU)
Operating Temperature	°C	-30 to 50/ 40 to 60	-196 (-186)
Operating pressure	Atm	100/100	20/60/100

## Results

To date, MOF materials showing H<sub>2</sub> trapping include:

- Cu(hfipbb)H<sub>2</sub>(hfipbb)<sub>0.5</sub> at 77 K exhibits 90% trapping as pressure (P) is reduced from 20 bar to 0 bar (Figure 1).



**FIGURE 1.** Low temperature H<sub>2</sub> adsorption data for Cu(hfipbb)(H<sub>2</sub>hfipbb)<sub>0.5</sub> (top, squares) shows significant hysteresis at 77 K, relevant to the trapping aspect of the project (gravimetric; PSU); Mixing MOFs with 5% Pt/C induces hydrogen spillover at 300 K. Increased spillover uptake for Zn(bdc)(ted)<sub>0.5</sub> relative to Cu(hfipbb)(H<sub>2</sub>hfipbb)<sub>0.5</sub> is attributed to increased porosity of the former. Structures shown at right: Cu (blue), Zn (teal in top), O (red), C (grey), and F (teal in bottom).

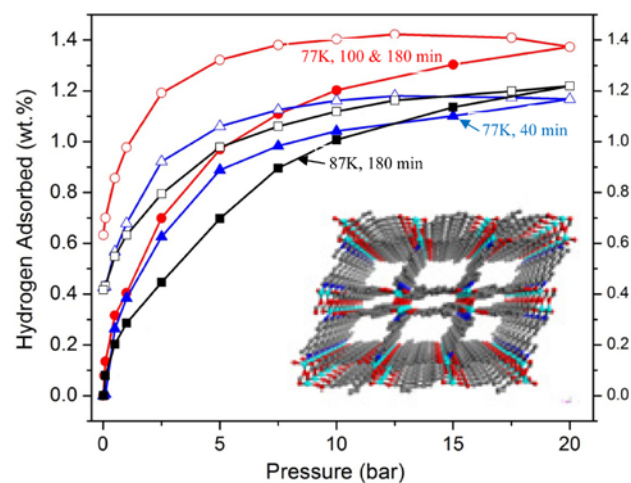
- Zn<sub>2</sub>(bpdC)<sub>2</sub>(bpee) at 87 K exhibits 35% trapping as P is reduced from 20 bar to 0 bar (Figure 2). This is dependent on equilibration time (data not shown).
- Zn<sub>2</sub>(bpdC)<sub>2</sub>(bpee) at 77 K exhibits 45% trapping as P is reduced from 20 bar to 0 bar (Figure 2). This is dependent on equilibration time (see Figure 2).
- Note: Zn<sub>2</sub>(bpdC)<sub>2</sub>(bpee) also shows very large hysteresis at 77 K and  $P < P_{sat}$  for Ar and N<sub>2</sub>, which is typical of 'gate-opening' as observed by Li & Kaneko, [1].

Additional MMOFs synthesized for fundamental hysteresis studies (for both H<sub>2</sub> and other gases) include:

- Cu(dhbc)<sub>2</sub>(bpy) –from Kitagawa, [2].
- Cu(bpy)(BF<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>·bpy –from Li & Kaneko, [1].

## Approach

The term *hydrogen spillover* has been used to describe a synergistic effect between high-surface area adsorbents and associated metals. The associated metal may act to dissociate molecular H<sub>2</sub> into atomic H species. The atomic H is then free to migrate to surface sites on the high-surface area support; the net surface H concentration is a function of the relative rates of surface migration versus desorption from the surface. This process increases the active adsorption temperature of the high-surface area adsorbent and generally leads

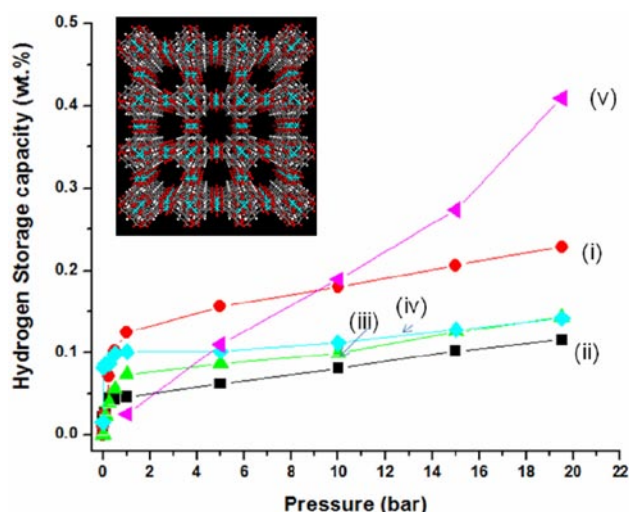


**FIGURE 2.** H<sub>2</sub> isotherms for MOF sample Zn<sub>2</sub>(bpdC)<sub>2</sub>(bpee), with temperature and equilibration time as labeled. All displayed data collected at PSU with a gravimetric apparatus; data were in excellent agreement with RU data collected on a volumetric system. Solid signs represent adsorption, hollow signs represent desorption. Lines are used to lead the eyes. Data suggests 40 minute equilibrium time is insufficient at 77 K for this sample. Isotherm measured for 100 min (not shown in the figure) matches 180 minute equilibration time. Hysteric adsorption is suggestive of diffusion limitations of H<sub>2</sub> uptake and release, or possible contamination in the H<sub>2</sub> stream. Inset: Structure of Zn<sub>2</sub>(bpdC)<sub>2</sub>(bpee) along axis showing 1-dimensional pores.

to a much higher uptake than expected for the metal alone. To date, hydrogen storage reports for spillover systems suggest moderate temperature adsorption (i.e. 300 K) and hydrogen uptake approaching DOE goals at 298 K and 100 bar. The highest uptake reported for spillover materials has utilized microporous MMOFs as the receptor for spilled over hydrogen. It is anticipated that optimization of the MMOF structure, surface chemistry, and porosity will further increase this uptake. It is further expected that direct incorporation of metals into the MOF structure will increase surface coverage associated with hydrogen spillover. Our project thus synthesizes new MMOF structures with systematic variation in surface chemistry and porosity to fundamentally explore these factors on the hydrogen spillover process, in order to ultimately optimize the MMOF structure for hydrogen spillover. Further, we will explore direct incorporation of catalytic sites into the MMOF structure to optimize the hydrogen spillover process. We will also fundamentally explore pressure-induced MMOF structural changes in order to incorporate this phenomenon into hydrogen trapping, via both physisorption and hydrogen spillover.

## Accomplishments

- Synthesis of four series of new MMOFs using linker and pillar molecules of various length, shape and hydrogen affinity in order to vary pore size, topology, and internal surface. Identification of MMOF structure by these MMOFs was described in the first quarterly report for 2009, and included powder X-ray diffraction patterns, selected pore characteristics, and preliminary low temperature  $H_2$  adsorption data to determine isosteric heats of adsorption. Incorporation of  $Li^+$  metal centers into the  $(hfpbb)(H_2hfpbb)_{0.5}$  structure. Measurement of isosteric heats of hydrogen (currently ranging from 5-13 kJ/mol) will be useful for comparison of spillover samples based on these MMOFs.
- Validation of RU (1.25 wt%) and PSU (1.25 wt%) hydrogen storage measurements for  $Zn_2(bpdC)_2(bpee)$  at 77 K and pressures up to 20 bar on gravimetric equipment (Figure 2).
- Comparison of RU (0.4 wt%) and PSU (0.27 wt%) hydrogen storage measurements at 298 K for the  $Cu_3(btc)_2(H_2O)_3$  sample at 300 K and 20 bar (See Figure 3).
- Upgrade of laboratory to include high-purity  $H_2$  delivery system and mass spectrometer for validation of  $H_2$  purity and  $H_2$  desorption. Development of  $H_2$  temperature programmed desorption methods.
- Prediction of gate-opening pressure for Cu-dhbc-bpy of 86 atm [2] based on treatment with statistical mechanics. Analysis of width of hysteresis loop



**FIGURE 3.** Room temperature (298 K)  $H_2$  adsorption data for  $Cu_3(btc)_2(H_2O)_3$ : (i) Cycle 1 data obtained gravimetrically at PSU; (ii) Cycle 2 (Repeat Cycle 2 with same sample, equipment, and intermittent pretreatment without air exposure); (iii) mixed 9:1 with 5% PtAC; (iv) sputtered with Pt; and (v) Cycle 1 obtained volumetrically at RU. (inset): View of  $Cu_3(btc)_2(H_2O)_3$  structure along the axis of 1-dimensional open channels.

against general predicted behavior for adsorption with substrate relaxation [3].

## Future Directions

- The MMOFs to be synthesized during this remainder of 2009 will be designed to vary porosity and surface chemistry.
- Evaluate possible reasons for discrepancies in uptake for  $Cu_3(BTC)_2(H_2O)_3$ , including differences in pretreatment and sample transfer.
- The hydrogen capacity of these materials will be measured at 77 and 300 K in order to develop a quantitative relation between these structural variables and hydrogen spillover. Once the correlation is developed, we will look to optimize MMOF uptake in order to meet gravimetric and volumetric targets outlined in Tables 1A and 1B.
- Catalyst Tests: We will finalize methods to dope the various MMOF structures with catalyst for efficient transfer of spilled over hydrogen while minimizing the activation temperature of the catalyst in order to maintain MMOF structural integrity. We will develop methods to assess the hydrogen spillover from catalytic centers directly incorporated into the MMOF structure.
- Once catalyst doping methods are finalized, all MMOFs will be doped with Pt catalyst to determine 300 K uptake and enhancement due to spillover effect.

- Hysteresis Effect and Modeling: Validation of theoretical predictions against our own experimental measurements for both Cu-dhbc-bpy and Zn-bpdc-bpee.

### FY 2009 Publications/Presentations

1. A. Lueking, Presentation at 2009 Hydrogen Program Annual Merit Review Meeting, May 20, 2009.
2. “MMOFs for Gas Separation and Hydrogen Storage”, Guangxi Normal University, Guilin, P.R. China, April 13, 2009.
3. Jing Li, “Microporous Metal Organic Frameworks: New Sorbent Materials for Hydrogen Storage”, 4<sup>th</sup> Conference on Hydrogen Storage Materials, Guangzhou, P.R. China, April 10–12, 2009.
4. A. Lueking, “Novel Nanomaterials for Hydrogen Storage via Hydrogen Spillover and Hydrogen Trapping,” Invited Seminar, Texas A&M University, February 27, 2009.
5. Jing Li, “Porosity and Functionality: Development of MMOFs for Gas Storage and Separation”, University of Leipzig, Leipzig, Germany, October 30, 2008.
6. A. Lueking “Hydrogen Trapping through Designer Hydrogen Spillover Molecules”, DOE Kick-Off Meeting, September 29, 2008.

### References

1. Li, D.; Kaneko, K., *Chem. Phys. Lett.* **2001**, 335, 50-56.
2. Kitaura, R.; Seki, K.; Akiyama, G.; Kitagawa, S., *Angew. Chem. Int. Ed.* **2003**, 42, 428.