

## IV.F.3 Hydrogen Trapping through Designer Hydrogen Spillover Molecules with Reversible Temperature and Pressure-Induced Switching

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(D) Durability/Operability

(E) Charging/Discharging Rates

### Technical Targets

**TABLE 1.** Summary of Excess Hydrogen Uptake via Spillover at 298 K. MMOFs mixed 9:1 with Pt/AC via ball milling are denoted with a '+'.

Sample	Pressure (bar)	wt% of Hydrogen
IRMOF-8 <sup>1</sup>	20, 70, & 100	0.09, 0.37, 0.52
+ 5%Pt/AC <sup>1</sup>	20, 80, & 100	0.38, 1.4, 1.80
+ Bridge <sup>1</sup>	20, 70, & 100	0.74, 2.68, 3.94
<b>+ IRMOF-8<sup>a</sup></b>	<b>80</b>	<b>1.5</b>
+ IRMOF-8 <sup>b</sup>	75-85	0.306 ± 0.026
+ IRMOF-8 <sup>c</sup>	75	0.78
+ Zn(NDC)(TED)	82	1.12
+ Zn <sub>3</sub> (bpdC) <sub>3</sub> (bpy)	20 80	0.09 0.63
+ Ni(HCOO) <sub>6</sub> [Ni-FA]	20 80	0.17 0.93
CuBTC (HKUST-1)	20	0.1
+ 5% Pt/AC <sup>2</sup>	20	0.165
+ 5% Pt/AC	20, 80	0.61, 1.32
<b>+ MMOF=0<sup>a</sup></b>	<b>80</b>	<b>2.4</b>

<sup>a</sup> Meets or Exceeds Benchmark for PtC/IRMOF8 in Ref. 1.

<sup>b</sup> Reproducibility Measurements, four measurements

<sup>c</sup> Increased mixing intensity relative to b

### Objectives

- Synthesize designer microporous metal-organic frameworks (MMOFs) mixed with catalysts to enable H-spillover for H<sub>2</sub> storage at 300 K to 400 K and moderate pressures.
- Adapted volumetric measurements to enable rapid screening tests (RSTs) at high-pressure, towards Go/No-Go decision point. Validate RSTs against published activated carbon and spillover materials at P≤80 bar and 298 K.
- Use RST to down-select MMOFs and determine effect of structure and surface chemistry.
- Explore methods for pressure-induced hydrogen/gas trapping.

### Technical Barriers

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

(A) System Weight and Volume

### Accomplishments

- A total number of eight MMOFs synthesized, with variations in surface chemistry and porosity.
- RST was developed and validated against published data for GX-21 activated carbon. Propagation of error and reproducibility measurements insured precision of method and demonstrated effect of preparation conditions when mixing with standard catalyst.
- IRMOF-8 with Pt/C confirms literature data; multiple tests indicate reproducibility of volumetric RST method and track how subtle variations in synthesis leading to increased/decreased uptake.
- PtC/CuBTC and PtC/IRMOF8 showed importance of preparation conditions: pretreatment, handling, mixing, and gas exposure are key parameters to ensure reproducibility.
- Oxygenated ligand exceeds uptake of IRMOF-8 benchmark with rapid initial uptake.
- On-going development of models to understand P-switching behavior and validate experiment with theory.



## Introduction

The term *hydrogen spillover* has been used to describe a synergistic effect between high-surface area adsorbents and associated catalysts. The associated catalyst 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 to a much higher uptake than expected for the metal catalyst alone. To date, hydrogen storage reports for spillover systems suggest moderate temperature adsorption (i.e. 300 K) can be achieved, with uptake approaching DOE goals at 298 K and 100 bar. The highest uptake reported for spillover materials has utilized MMOFs as the receptor for spilled over hydrogen: bridged ('br') PtC/IRMOF8 achieved 4 wt% excess adsorption at 100 bar and 298 K [1]. Independent groups have demonstrated up to 4.2 wt% at 6.9 MPa after extended equilibration for brPtC/IRMOF8 [2]. As the process is highly dependent upon synthesis, measurement, and catalytic particle size, [3,4] the process remains poorly understood. It is anticipated that optimization of the MMOF structure, surface chemistry, and porosity will further increase uptake via spillover. Meeting DOE hydrogen storage targets at moderate temperature will have significant engineering advantages for mobile applications, as temperature of operation has implications for system weight.

## Approach

The project relates to materials development and optimization of surface chemistry, crystal and pore structure, catalyst, and system parameters for the hydrogen spillover phenomenon. In this stage of the project, we are screening materials against benchmark spillover data for brPtC/IRMOF8 mentioned above. Our current gravimetric goals are relative to this benchmark in the literature, with the assumption that bridging will further improve excess adsorption to bring total uptake to DOE goals. Prior to bridging, the PtC/IRMOF8 material had 1.4 wt% and 1.8 wt% of hydrogen uptake at 298 K and 80 and 100 bar, respectively [1]. Other relevant literature data listed in Table 1 include variation of MMOF structures in Ref 5. The project is currently exploring materials without bridging, as bridging has unknown effects on the surface chemistry and structural parameters we hope to optimize. The project is currently using secondary spillover studies such that the catalyst, or H species 'supply', remains constant in order to independently determine the effect of MMOF

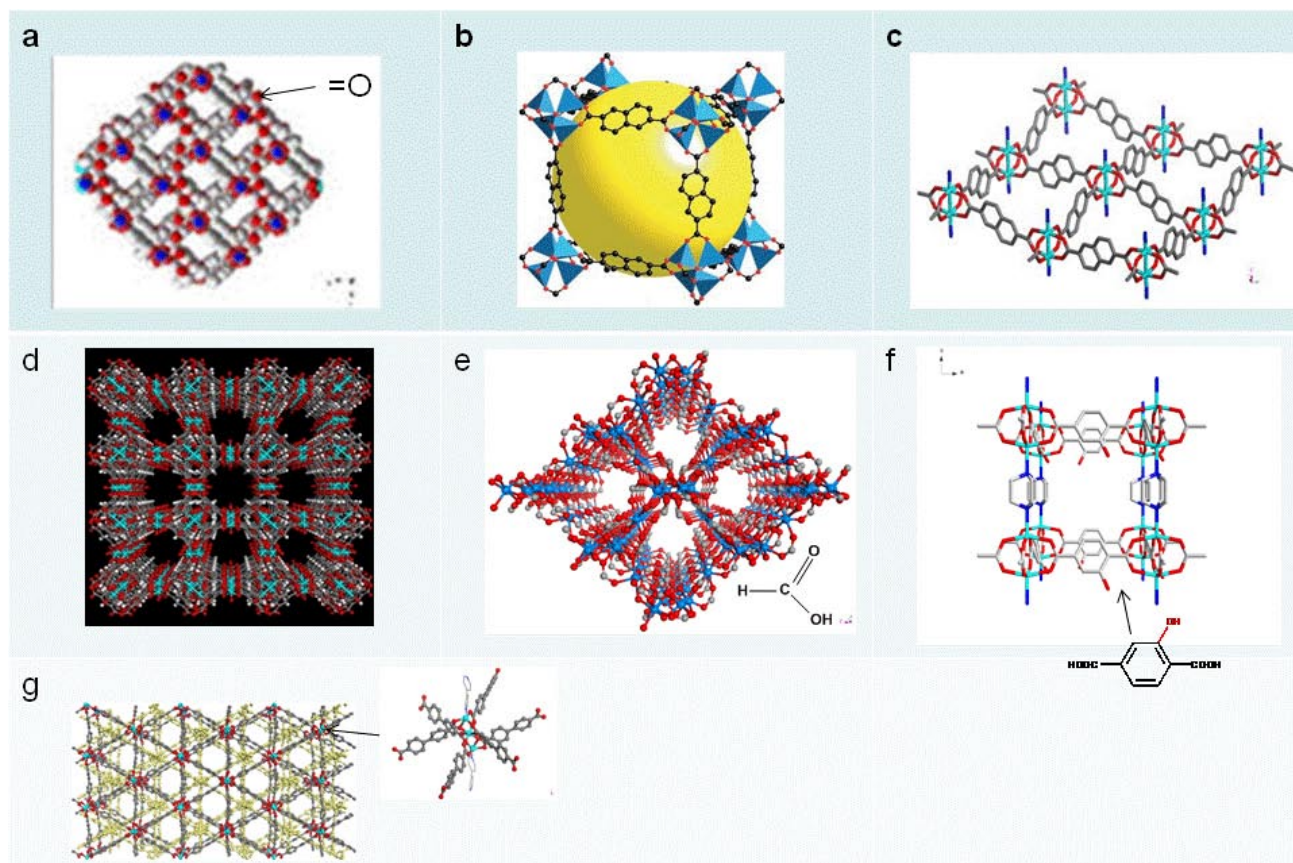
structure. A later phase will explore direct incorporation of catalytic sites into the MMOF structure for further optimization of the hydrogen spillover process. As spillover equilibration times may be significant, a RST (i.e., one-point isotherm at 80 bar) has been developed and validated against published data [6] for GX-31 superactivated carbon. Materials that exceed benchmark uptake, or are deemed interesting from a mechanistic standpoint, are moved from the volumetric RST to a gravimetric unit equipped with mass spectrometry for more detailed mechanistic and temperature studies. The latter, along with rate determinations, are relevant to the temperature-switching for decoupled adsorption-desorption optimization, outlined above.

Our approach for optimization of system parameters for spillover considers decoupling of adsorption and desorption, such that optimization of temperature and pressure for each may be considered separately. Towards this end, we are exploring MMOF structural changes that are pressure-induced in order to incorporate this phenomenon into hydrogen trapping, via both physisorption and hydrogen spillover. We are validating theoretical models with extensive adsorption isotherms for a MMOF with demonstrated pressure-induced structural changes (Zn<sub>2</sub>(bpdC)<sub>2</sub>(bpee)), and exploring the effect of adsorption time, adsorbate, pressure, and temperature. Once validated, it is anticipated the theoretical model will be able to predict the feasibility of using various MMOFs for hydrogen trapping at pressures and temperatures of interest.

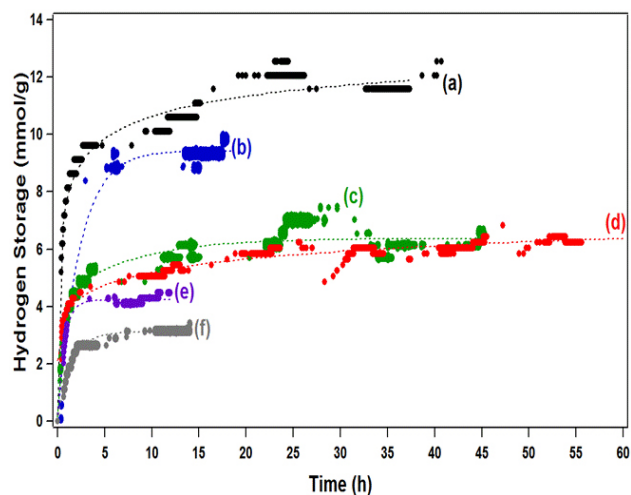
## Results

A total of eight MMOFs were synthesized in 2009-10 (Figure 1), with variations in ligands and secondary building units (i.e. corners) leading to expected differences in structure, surface area, pore dimension, and surface chemistry. RST adsorption results (Figure 2) show no real trend with surface area or pore dimension, contradicting previous claims, [5] and suggesting coverage from spillover is not related to surface area in a simple fashion. Two PtC/MMOFs had uptake exceeding that of literature benchmarks (IRMOF8 and MMOF=O, Figures 1-2 a-b). The latter significantly exceeded benchmark data, with 2.4% at 80 bar and 298 K, suggesting that surface chemistry will play a predominant role in surface coverage via spillover. These findings (correlation with surface chemistry not area) are consistent with a chemical kinetic consideration of spillover, in which the relative rates of adsorption, desorption, and surface diffusion must be considered [7].

Previous published spillover data has suffered from reproducibility issues. Recent data for brPtC/IRMOF8 varies from 1.5-4.0 wt% at 298 K and 100 bar; [4] with little concrete explanation provided to explain the discrepancy. Therefore, PtC/IRMOF8 was chosen to



**FIGURE 1.** Structures of MMOFs synthesized and tested in 2009-10: (a)  $\text{MMOF}=\text{O}$ ; (b)  $\text{Zn}_4\text{O}(\text{NDC})_3$  or IRMOF-8; (c)  $\text{Zn}(\text{NDC})(\text{TED})_{0.5}$ ; (d)  $\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3$  or Cu-BTC; (e)  $\text{Ni}(\text{HCOO})_6$  or Ni-FA; (f)  $\text{Zn}(\text{BDC-OH})(\text{TED})_{0.5}$ ; (g)  $\text{Zn}_3(\text{BPDC})_3(\text{BPY})$ .



**FIGURE 2.** Rate data for one-step adsorption isotherm, i.e. 'rapid-screening test'. Data is labeled as in Figure 1.

study the effect of various synthesis and measurement parameters on instrument precision and material reproducibility. The accuracy of the RST measurement

is calculated at  $\pm 0.026$  mmol ( $\pm 0.05$  wt% for 100 mg sample) via propagation of error when a He blank measurement is done to determine the differential pressure due to volume differences. Validation of the equipment with GX31 shows agreement within 20% relative to published data [6] at 80 bar, a difference which can be attributed (in part) to slight variations in pretreatment and sample. When equipment, sample, and pretreatment are the same, the RST reproduces a multiple point isotherm within 8% at 80 bar. For PtC/IRMOF8, multiple experimental RST replicates with identical procedural and temporal conditions show a standard deviation of less than 10% (i.e.  $0.31 \pm 0.03$  wt%, Table 1), even with a 10 bar variation in the equilibrium adsorption pressure (i.e. 75-85 bar). With this level of precision in uptake, we were able to confirm that increased mixing intensity leads to increased uptake via spillover for PtC/IRMOF8: from 0.31 wt% to 0.78 wt%. The increase cannot be directly attributed to differences in catalyst size, as the catalyst source is identical in the secondary spillover studies, unlike previous reports [4,8]. Despite the increased uptake, no significant changes in MMOF structure were detected by power X-ray diffraction, suggesting

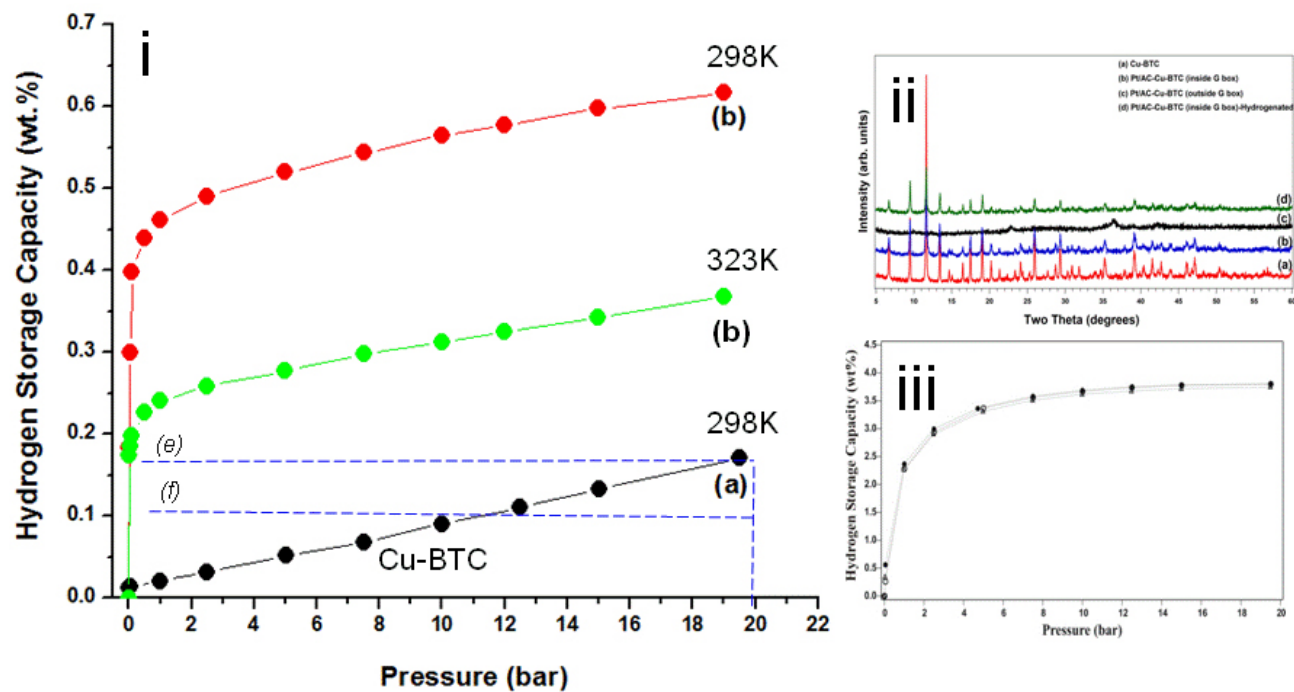
mixing intensity may affect particle size and/or interface. Currently, additional mixing parameters are being tested with alternate characterization of the physical properties after mixing. Sample handling for PtC/CuBTC is also shown to drastically affect overall uptake and material integrity. When mixed in an inert environment, PtC/CuBTC has 0.61 wt% at 20 bar, exceeding published reports by a factor of three. The uptake due to spillover at low-pressure is found to be pronounced using gravimetric methods (Figure 3).

In an attempt to develop a means for hydrogen trapping and to facilitate decoupled optimization of adsorption vs. desorption, work to validate and understand pressure-induced MMOF structural changes is ongoing. Although adsorption-induced gate opening (GO) in MMOFs is well documented, it is poorly understood. Experimental data collected for  $Zn_2(bpd)_2(bpee)$  suggest the process is highly sensitive to adsorbate, time, temperature, and pressure. The process behaves consistently, but in a unique and often unpredictable way. Parallel theoretical studies are seeking to understand experimental data and validate models, and further, to use the concepts towards predictive understanding of the phenomenon. Current studies have used well-defined and analogous systems to demonstrate that GO is favored when the relative gas-solid interaction energy exceeds the energetic cost of structural rearrangement. Parametric studies with

mean-field theory are also on-going. We anticipate the modeling will provide a means to expedite experimental studies such that the behavior of a MMOF can be correlated to its adsorption potential. Such modeling is intended to provide a road map to utilize this process for hydrogen trapping.

## Conclusions

Hydrogen spillover continues to show promise for considerable excess adsorption at moderate temperatures and pressures (i.e. 300 K, <100 bar). On-going studies aim to provide a mechanistic understanding of the spillover process. Current data suggest that surface chemistry, rather than surface area or structure, is the controlling factor in maximizing surface coverage via spillover. Further tests are on-going to validate this finding and increase mechanistic understanding. First, however, tests with PtC/IRMOF suggest laboratory environment and mixing conditions—rather than (or in addition to) catalyst particle size—may lead to significant differences in uptake via catalytic spillover and the effect is now being studied in a systematic way. Similarly, uptake for PtC/CuBTC is increased 3-fold (at 20 bar; 298 K) relative to published literature data when mixed in an inert environment. With the validated RST, introduction of a carbonyl group to the ligand led to 2.4 wt% (80 bar, 298 K), and significantly exceeded



**FIGURE 3.** (i) Hydrogen uptake for (a) Cu-BTC, and (b) Cu-BTC+PtAC, mixed 9:1 in an inert atmosphere, with adsorption temperature as noted. (ii) X-ray diffraction of (a) and (b) shows crystalline structure, whereas (c) mixing in atmosphere destroys crystallinity; (d) crystal structure in sample 'b' is retained after  $H_2$  measurement shown in (i). Mixing in inert environment contributes to the three-fold increase in  $H_2$  uptake for 'b' relative to published literature, shown as dotted lines in (i) at 20 bar and 298 K for (e) Cu-BTC, and (f) PtC+Cu-BTC. (iii) Adsorption isotherms for (a) at 77 K.

benchmark data (1.4 wt%, 80 bar, 298 K), prior to bridging. We anticipate uptake can be further increased with additional modifications of structure, bridging, and careful consideration of synthesis conditions. Methods to incorporate pressure-induced hydrogen trapping into the materials is on-going, and will provide a further means to increase pressure savings for the storage *system* relative to *system* targets.

### Future Directions

- Finalize systematic studies of mixing environment on uptake.
- Detailed study of ligands with modified surface chemistry.
- Introduce pore modification in synthesis of like compounds.
- With validated measurements and optimized mixing conditions, develop correlations between porosity, surface area, and surface chemistry of PtC/MMOFs with overall H<sub>2</sub> uptake, kinetics, and hysteretic adsorption-desorption.
- Write and submit papers on: (1) methods validation and reproducibility with a focus on PtC/IRMOF8 and brPtC/IRMOF8; (2) sample preparation on PtC/CuBTC; and (3) variation of MMOF structure/chemistry with secondary spillover studies.
- Validate theoretical imbibition study with experiment; evaluate pressure-trapping of MMOF structures at ambient conditions; assess opening via spilled over H.
- Evaluate potential for temperature trapping with PtC/MMOFs that exceed benchmarks using combined multiple temperature adsorption isotherms and temperature-programmed desorption studies.
- Develop MMOFs containing built-in catalytic functionality using metalloligands.
- Independent measurement of Tsao et al. sample.

### 2010 Publications/Presentations

1. Zhao, Y.G.; Li, K.H.; Li, J. "Solvothermal Synthesis of Multifunctional Coordination Polymers", *Z. Naturforsch.* **2010**, *65b*, in press.
2. A. Lueking, J. Li, M.W. Cole, Four Quarterly Reports, FY2010; Annual Report, FY2010.
3. A. Lueking, Presentation at 2010 Hydrogen Program Annual Merit Review Meeting, June 9, 2010.
4. A. Lueking, Invited Research Seminar, National Institute of Standards and Technology, Gaithersburg, MD, July 14, 2009.

5. A. Lueking, Invited Department Seminar at Chemical Engineering Penn State University, February 11, 2010.
6. J. Li, Invited Department Seminar at Rutgers University, Newark, NJ, October 16, 2009.
7. J. Li, Presentation at 238<sup>th</sup> ACS National Meeting, Washington DC, August 16, 2009.
8. J. Li, Invited Talk, The 179<sup>th</sup> Lecture of Zhong-Guan-Cun Forum on Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing, P.R. China, January 19, 2010.
9. Li, J., Presentation at the 1<sup>st</sup> Crystal Engineering Gordon Research Conference, Waterville Valley, NH, June 6–11, 2010.

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