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

Angela D. Lueking (Primary Contact), Jing Li, Sarmishtha Sircar, Cheng-Yu Wang, Yonggang Zhao, Haohan Wu, Qihan Gong, Zhijuan Zhang
The Pennsylvania State University
120 Hosler
University Park, PA 16802
Phone: (814) 863-6256
Email: adl11@psu.edu

DOE Managers
Jesse Adams
Phone: (720) 356-1421
Email: Jesse.Adams@go.doe.gov
Channing Ahn
Phone: (202) 586-9490
Email: Channing.Ahn@ee.doe.gov

Contract Number: DE-FG36-08GO18139

Subcontractor:
Rutgers University, Piscataway, NJ

Project Start Date: January 1, 2009
Project End Date: June 30, 2014

Overall Objectives

- Synthesize designer microporous metal-organic frameworks (MMOFs) mixed with catalysts to enable H-spillover for H_2 storage at 300 K-400 K and moderate pressures
- Reproducibly introduce catalysts into MMOF without degrading MMOF structure
- Explore MMOF structural changes induced by pressure and hydrogen spillover
- Ensure spillover reproducibility with spectroscopic characterization and validation of measurement techniques

Fiscal Year (FY) 2013 Objectives

- Optimize synthesis procedure and hydrogen uptake of one catalyst-doped MMOF, using CuTDPAT (or $[Cu_3(TDPAT)(H_2O)_3]$•$10H_2O$•5DMA, H_6TDPAT = 2,4,6-tris(3,5-dicarboxylphenylamino)-1,3,5-triazine)
- After doping, compare uptake of CuTDPAT to CuBTC with similar paddle wheel structure and IRMOF8, which has the highest reported uptake for a catalytically-doped MMOF
- Determine and compare stability after various catalytic doping techniques and gas exposures
- Calculate theoretical capacity for hydrogenation of CuTDPAT using density functional theory
- Identify kinetic barriers to reach thermodynamic predicted capacity of doped CuTDPAT
- Spectroscopic verification of hydrogenation of CuTDPAT, before and after pre-bridging technique

Technical Barriers

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

(A) System Weight and Volume
(D) Durability/Operability: Min/max temperature/maximum pressure
(E) Charging/Discharging Rates
(O) Lack of Understanding of Hydrogen Physisorption and Chemisorption
(P) Reproducibility of Performance

Technical Targets

Technical targets for this project are listed in Table 1.

FY 2013 Accomplishments

- CuTDPAT MMOF (Figure 1) was selected for detailed studies due to favorable pore structure; high surface area; stability with time, temperature, and moisture exposure; and surface chemistry that facilitates multiple catalytic doping methods.
- Preliminary density-functional calculations suggest reversible hydrogenation of CuTDPAT is possible up to 3.25 wt%, with a binding energy that is favorable for reversible room temperature hydrogenation (ΔE_{avg}= -0.55 eV; target is -0.6 < dE < -0.2 eV, as calculated by Yakobson et al. [1]).
- In addition to CuTDPAT, Cu-BTC and IRMOF8 were selected for comparison. The former has a similar Cu paddlewheel structure, whereas IRMOF8 has the highest reported uptake via spillover, to date.

TABLE 1. System Gravimetric Capacity 2017/Ultimate Target (5.5/7.5 wt%) of Metal-Doped "Spillover" Materials

Sample	Hydrogen in excess of He at 298 K (wt%)	
	1 bar	70 bar [or 20 bar]
Activated carbon (AC) used for catalyst support	0.0185	0.646
Catalyst used in pre-bridging technique: Pt/AC	0.0362	0.791
Pt/AC (prior FY 2012 results; six + samples tested)	0.01-0.03	0.79-0.91
a: IRMOF8 (as-received)	0.0118	0.357 0.337
b: PB-IRMOF8 (pre-bridge doping with Pt/AC catalyst)	0.0247	0.317
c: CuTDPAT (as-received)	0.00568	0.351
d: PB-CuTDPAT (pre-bridge doping with Pt/AC catalyst); three batches, multiple replicates	0.0441	0.30-0.56 (24 hours) ~1.0 (80 hours) kinetic limitations observed
e: CuBTC (as-received)	0.0179	[0.17, at 20 bar]
f: PB-CuBTC (pre-bridge doping with Pt/AC catalyst)	0.0186	[0.61, at 20 bar]

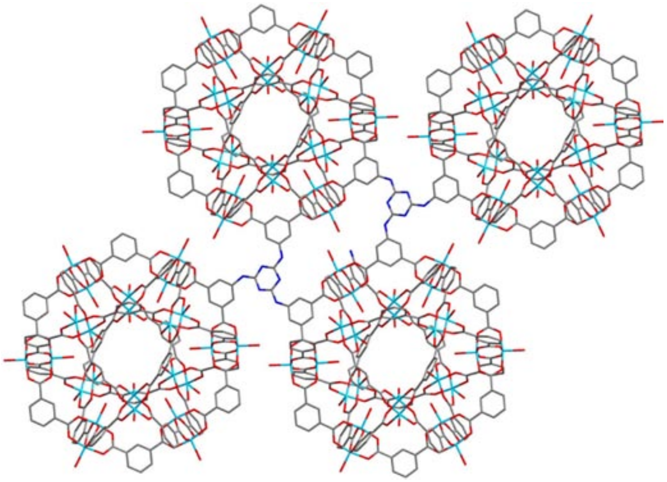

FIGURE 1. CuTDPAT structure, in which copper paddlewheel metal cluster is connected via the TDPAT organic ligand to form the long-range crystalline order. TDPAT contains N in the center rings as well as three branches stretching from the center ring, similar to melamine. (Gray: C, Blue: N, Red: O, Cyan: Cu)

- Extending the FY 2012 doping studies, the pre-bridge catalytic doping technique retains surface area (97-107%) and structure (X-ray diffraction [XRD] remains intact) for CuTDPAT, CuBTC, and IRMOF8, comparing 'as received MMOFs' to samples after this doping technique. In contrast, direct-doping reduced the surface area to 30-49% relative to the precursor.

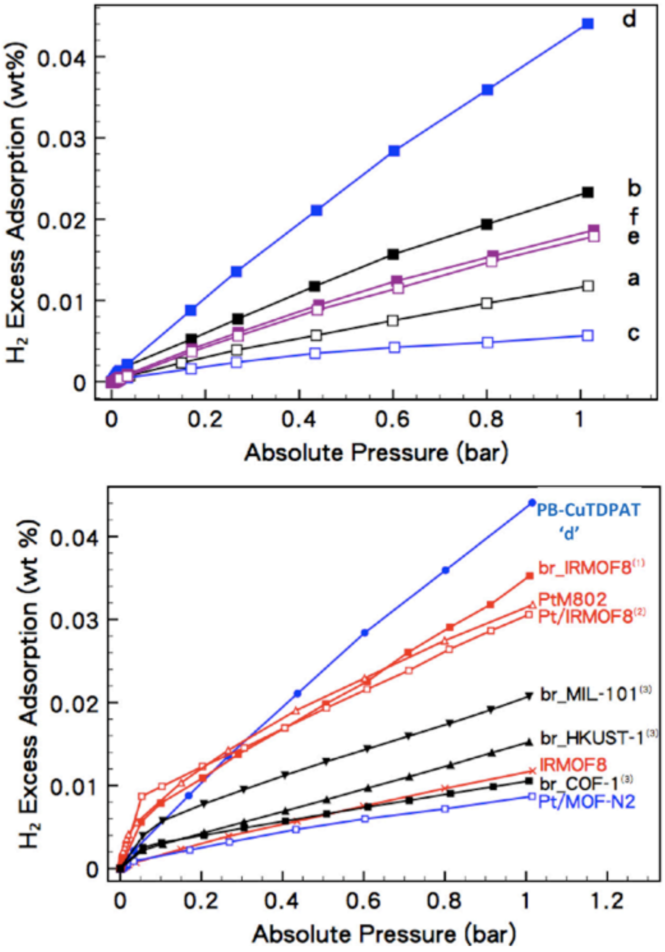

FIGURE 2. Top: low-pressure H_2 isotherms at 298 K for the three MMOF samples doped via the pre-bridge doping technique to introduce ~10% Pt/AC catalyst. Labels correspond to samples in Table 1. Bottom: comparison of data for 'd' (PB-CuTDPAT) relative to other published literature for catalyst-doped MMOFs. Data taken from: (1) *J. Am. Chem. Soc.* 2006, 128, 8136-8137; (2) *J. Phys. Chem. C.* 2011, 115, 4793-4799; (3) *AIChE Journal.* 2008, 54, 269-279.

- Good reproducibility of hydrogen uptake was demonstrated for four batches of PB-CuTDPAT sample on three different measurement techniques (gravimetric, low-pressure, and high-pressure volumetric).
- PB-CuTDPAT has 7.8-fold enhancement relative to CuTDPAT, which is the highest of the three selected MMOFs and highest of published low-pressure H_2 uptake data for catalytically-doped MMOFs (Figure 2).
- Kinetic limitations were identified as the main hurdle to achieve theoretically predicted hydrogen uptake at high pressure for PB-CuTDPAT. (Experimentally, the 70 bar H_2 uptake was not complete after 24+ hours, Figure 3.) Preliminary (as well as on-going) stability studies of the 'as-received' CuTDPAT with high-pressure H_2 exposure show loss of surface area despite retention of the XRD pattern.

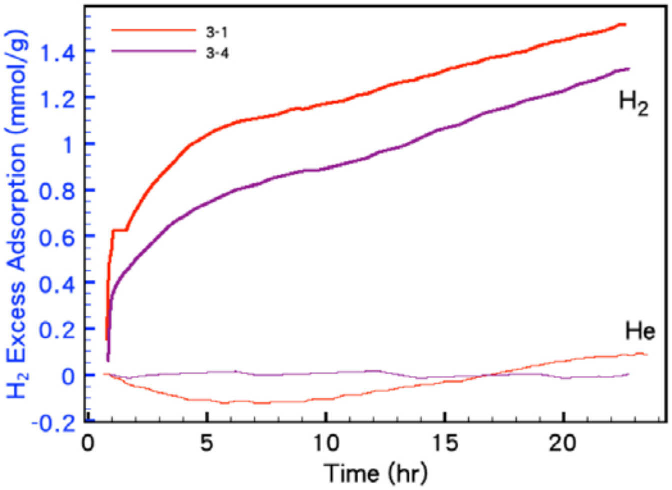

FIGURE 3. Select high-pressure (70 bar, 298 K) hydrogen uptake for PB-CuTDPAT for two replicates. Kinetic limitations are observed at high pressure that were not evident for the 1-bar data shown in Figure 1.

- Spectroscopic evidence for hydrogenation of the nitrogen sites was identified for PB-CuTDPAT (and not found for as-received CuTDPAT) via X-ray photoelectron spectroscopy (XPS) (Figure 4). Combined with density-functional calculations, N-hydrogenation should help to further elucidate the mechanism of hydrogen spillover.
- A paper was published on the accuracy of improved differential volumetric methods.

✧ ✧ ✧ ✧ ✧

INTRODUCTION

The term *hydrogen spillover* has been used to describe a synergistic effect between high-surface area adsorbents and associated catalysts. The associated catalyst dissociates molecular H_2 into atomic H species, which may then diffuse to and chemisorb to the support. This process occurs at moderate temperature (i.e., 300 K) and generally leads to a much higher uptake than expected for the metal catalyst or high-surface area adsorbent alone under comparable conditions. Spillover materials using MMOFs have been reported to have high uptake at ambient temperature: bridged ('br') PtC/IRMOF8 achieved 4 wt% excess adsorption at 100 bar and 298 K [2]. Independent groups have demonstrated up to 4.2 wt% at 6.9 MPa after extended equilibration for brPtC/IRMOF8 [3]. Subsequent reports on spillover materials at room temperature have varied from less than physisorption to almost 9 wt%, demonstrating difficulties in reproducibility and invoking controversy. These uptakes approach DOE goals; however, as the process is highly dependent upon synthesis, measurement, and catalytic particle size [4,5], 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

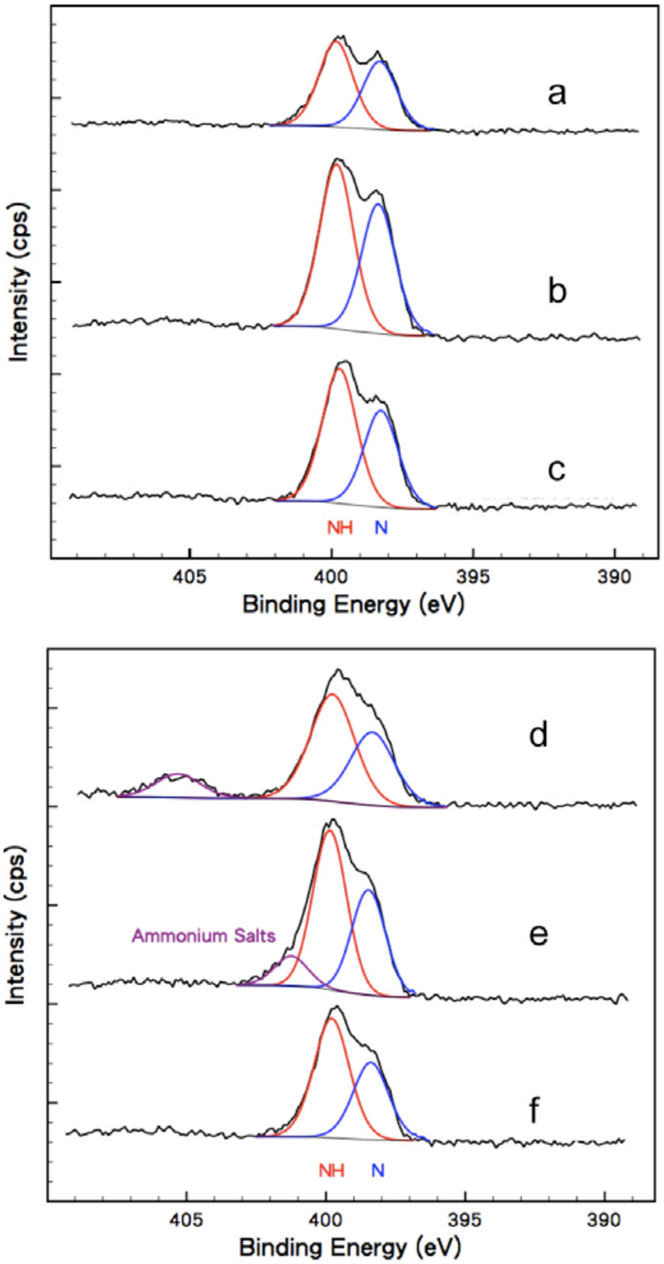

FIGURE 4. The XPS N 1s spectra of (a) as-received CuTDPAT, (b) CuTDPAT after H_2 exposure at 300 K and 70 bar, (c) sample 'b' after subsequent desorption at 120°C in flowing Ar; (d) PB-CuTDPAT after H_2 exposure at 300 K and 70 bar, (e) PB-CuTDPAT after H_2 exposure at 150°C and 1 bar, and (f) sample 'd' after a subsequent treatment at 120°C in flowing Ar. The two N peaks in CuTDPAT are attributed to the two types of N groups (aromatic and NH in the melamine-like branches) in the TDPAT ligand. The undoped CuTDPAT has negligible changes in the N 1s spectra after the various treatments, whereas PB-CuTDPAT shows evidence for nitrogen hydrogenation (matching 'ammonium salt' reference spectra), which is reversible after the 150°C Ar desorption treatment.

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 catalyst, surface chemistry, crystal and pore structure, and system parameters for the hydrogen spillover phenomenon. For surface chemistry, different MMOFs were doped with catalyst to test hydrogen storage and the effect of functional groups. Novel methods to incorporate a hydrogen dissociation catalyst into MMOFs were evaluated by focusing on methods that lead to well-dispersed catalytic entities without compromising the original pore structure and surface area of the MMOF. The current ‘pre-bridge’ technique is adapted from methods published previously [6,7], with adaptation to use an optimized hydrogenation catalyst and MMOFs with various structures and surface chemistry. Hydrogen uptake is quantified utilizing both gravimetric and differential volumetric adsorption methods; the former allows for precise catalyst activation whereas the latter allows for high-pressure measurements and is more accurate than conventional volumetric techniques. Complementary spectroscopic techniques are being used to identify the active sites that bind with spilled-over hydrogen.

RESULTS

In prior years of this project, we have developed and tested some 20 new metal-organic framework (MOF) structures; worked to reproducibly optimize the uptake of carbon-based PtAC catalysts; developed techniques to verify spillover to specific surface sites on MMOFs with spectroscopy; conducted extensive reproducibility tests on standard samples, including the effect of measurement, synthesis, and pretreatment conditions; and quantitatively validated our differential adsorption measurement. After testing four techniques to incorporate catalysts into the MMOF (in FY 2012), the ‘pre-bridge’ technique was selected due to its high retention of surface area and MOF structure, combined with the resulting high dispersion of the introduced Pt/AC catalyst. For three MMOFs, the ‘pre-bridge’ technique maintained 90-110% of the surface area of the original MOF while retaining structure (as measured by XRD). In contrast, common catalyst doping techniques, when applied to MOFs, may degrade surface area by as much as 20-70% and may lead to complete amorphitization of structure.

In FY 2013, CuTDPAT (Figure 1) was selected for more extensive studies due to its structure and stability. CuTDPAT is the smallest member of (3,24)-connect nets of *rht* topology made of a three-armed hexacarboxylate ligand and 24 $M_2(COO)_4$ paddle wheel based supramolecular building blocks. The CuTDPAT framework is highly porous and contains three different types of cages; cuboctahedron, truncated tetrahedron, and truncated octahedron. The pore volume, Brunauer-Emmett-Teller and Langmuir surface areas are estimated to be 0.93 cc/g, 1,938 and 2,608 m^2/g, respectively, calculated from N_2 adsorption isotherms (77 K). CuTDPAT is featured with a high density of both open metal sites (1.76/nm^3) and Lewis basic sites (3.52/nm^3), as well as high thermal and water stability. At 77 K and 67 bar, CuTDPAT takes up 4.83 (excess) and 6.77 (total) wt% of H_2, respectively. At 298 K and 60.9 bar, the uptake of the as-received CuTDPAT is 0.61 (excess) and 1.04 (total) wt%, respectively, as measured by Rutgers University.

A hydrogen dissociation catalyst, PtAC, was successfully incorporated into the CuTDPAT structure via the pre-bridge technique, with almost complete surface area retention for four preparations. At low pressure and 298 K, the hydrogen uptake of PB-CuTDPAT was enhanced 7.8-fold relative to the ‘as-received’ CuTDPAT (Figure 2). The enhancement of CuTDPAT is greater than that for either IRMOF8 or CuBTC using the same doping technique (Figure 2, top), and shows the highest uptake to date of any published data for catalyst-doped MMOFs (Figure 2, bottom). The slope of the low-pressure isotherm is high, suggesting that increasing the pressure should further enhance the capacity. However, high-pressure measurements demonstrate severe kinetic limitations at 80 bar (Figure 3), and analysis of the PB-CuTDPAT after this high-pressure H_2 exposure demonstrates almost complete degradation of N_2 surface area, despite the XRD pattern remaining intact. Alternate methods to introduce H_2 into PB-CuTDPAT are being tested, and tests to confirm the stability of as-received CuTDPAT in high-pressure He and H_2 are underway. X-ray photoelectron spectroscopy demonstrates reversible hydrogenation/dehydrogenation of N surface sites after the pre-bridge doping technique, and similar results are not found for the as-received CuTDPAT (Figure 4). Infrared spectroscopy was used to confirm the XPS results and further elucidate the mechanism of hydrogen spillover in this structure.

CONCLUSIONS AND FUTURE DIRECTIONS

- The pre-bridge doping technique successfully introduces well-dispersed hydrogenation catalysts into three MMOFs, while retaining surface area (97-107%) and structure (as determined with XRD).
- Although the low-pressure hydrogen uptake (1 bar, 298 K) for PB-CuTDPAT was extremely promising (7.8-fold enhancement relative to CuTDPAT; highest reported uptake at 1 bar and 298 K relative to other literature reports), high-pressure measurements are plagued by kinetic limitations.
- Stability of as-received CuTDPAT after high-pressure H_2 exposure is being investigated.
- Hydrogen spillover is verified with spectroscopic measurements. Specifically, XPS of PB-CuTDPAT shows

evidence of nitrogen hydrogenation, whereas as-received CuTDPAT does not.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. A. Lueking completed an Incoming Marie Curie Fellowship for her work related to spillover.

FY 2013 PUBLICATIONS/PRESENTATIONS

1. Liu, X.M.; Tang, Y.; Xu, E.S.; Fitzgibbons, T.C.; Gutierrez, H.R.; Tseng, H.H.; Yu, M.S.; Tsao, C.S.; Badding, J.V.; Crespi, V.H.; Lueking, A.D. Evidence for Ambient-Temperature Reversible Catalytic Hydrogenation in Pt-doped Carbons, *Nano Letters,* 13, 137-141, 2013.

2. Gong, Q.H.; Zhang, R.; Emge, T.J.; Li, J. “Systematic Design and Synthesis of New Metal Organic Framework Structures”, *Chimia*, 67, 393-396, 2013.

3. Sircar, S.; Wang, C.Y.; Lueking, A.D. “Design of High Pressure Differential Volumetric Adsorption Measurements with Increased Accuracy”, *Adsorption*, In Press, Available On-Line (http://link.springer.com/article/10.1007/s10450-013-9558-8), July 2013.

4. **Li, J. (Invited speaker)**, “MOFs: Structures, Functions, and Applications”, Wuhan University, Wuhan, China, October 11, 2012.

5. **Li, J. (Invited speaker)**, “Metal Organic Frameworks: Microporosity, Multifunctionality, and Adsorption Based Applications”, ExxonMobil Research and Engineering Company, Annandale, NJ, November 28, 2012.

6. **Li, J. (Invited speaker)**, “Microporous Metal Organic Frameworks: Solvothermal Synthesis, Structure-Pore Functionalization, and Potential Applications”, The 3rd International Solvothermal and Hydrothermal Association Conference, Austin, Texas, January 13–17, 2013.

7. **Lueking, A.D. (Invited speaker**), “Hydrogen Storage via Spillover through a Combined Experimental and Modeling Approach”, Marie Curie Fellow Seminar, University of Crete, Heraklion, April 4, 2013.

8. **Li, J. (Invited Speaker)**, “Engineering Structure and Porosity of Microporous MOFs for Enhanced Functionality and Performance”, 3rd International Conference on Multifunctional, Hybrid and Nanomaterials, Sorrento, Italy, March 3–7, 2013.

REFERENCES

1. Singh, A.K.; Ribas, M.A.; Yakobson, B.I. *Acs Nano* **2009**, *3*, 1657.

2. Li, Y. and Yang, R.T. *J. Am. Chem. Soc.* 2006, 128, 8136-8137.

3. Tsao, C.S.; Yu, M.S.; Wang, C.Y.; Liao, P.Y.; Chen, H.L.; Jeng, U.S.; Tzeng, Y.R.; Chung, T.Y.; and Wu, H.C. *J. Am. Chem. Soc.* 2009, 131, 1404-1406.

4. Stadie, N.P.; Purewal, J.J.; Ahn, C.C.; and Fultz, B. *Langmuir.* 2010, 26, 15481-15485.

5. Stuckert, N.R.; Wang, L.; and Yang, R.T. *Langmuir.* 2010, *26*, 11963-11971.

6. Yang, S.J.; Cho, J.H.; Nahm, K.S.; and Park, C.R. *Int J Hydrogen Energ.* 2010, 35, 13062-13067.

7. Lee, S.Y. and Park, S.J. *Int J Hydrogen Energ.* 2011, 36, 8381-8387.