

IV.C.5 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, Qixiu Li, Yonggang Zhao, Qihan Gong, Zhijuan Zhang, Haohan Wu, Milton W. Cole

The Pennsylvania State University (PSU)
120 Hosler
University Park, PA 16802
Phone: (814) 863-6256
Email: adl11@psu.edu

DOE Managers

HQ: Ned Stetson
Phone: (202) 586-9995
Email: Ned.Stetson@ee.doe.gov

GO: Jesse Adams
Phone: (720) 356-1421
Email: Jesse.Adams@go.doe.gov

Contract Number: DE-FG36-08GO18139

Subcontractor:

Rutgers University, Piscataway, NJ

Project Start Date: January 1, 2009

Project End Date: June 30, 2013

Technical Targets

TABLE 1. System Gravimetric Capacity 2010/2017 Target (0.045/0.055) of Metal-Doped "Spillover" Materials

Sample	Pressure (bar)	Hydrogen in excess of He at 298 K (kg H ₂ /kg) ^a	Enhancement Relative to Physisorption (%) ^b
<u>Pt-Doped Carbon Samples</u>			
PtC(INER) ^{c,d}	1-20	0.012	780 (at 20 bar)
PtC/ACo ^d	1-20	0.014	
PtC (Maxsorb)	70-72	0.0079-0.0091 ^e	
PtAC (PtC)	1.01	0.00027	
Pt-oxCA (Pt ₂ oxCA)	1.02	0.00014	
<u>Direct Doped MMOF Samples</u>			
Pt/MMOF-NH ₂ -03	69.6	0.0047	430
Pt/MMOF-NH ₂ -04	70.1	0.0019	100
Pt-IRMOF8	1.02 (20)	0.00032 (0.00079)	1,200 (65)
<u>Preformed bridge samples</u>			
PtCA/IRMOF8	66-70	0.0063-0.0026	89 to (-27)
PtC/IRMOF8	71.1	0.00317	-15
PtC/CuTDPAT-air exposure	71.9	0.0026	-42
PtC/CuTDPAT	1.02	0.00044	600

^a Samples are referenced to He measurement at same pressure; Values do not include He adsorption.

^b (uptake - expected physisorption [same conditions])/expected physisorption

^c Provided by C. S. Tsao (Institute of Nuclear Energy Research, Taiwan).

^d Uptake is determined gravimetrically. Temperature-programmed desorption also done.

^e Range is for six separate sample preparations and measurements.

^f Value includes He adsorption for comparison with literature.

Fiscal Year (FY) 2012 Objectives

- Synthesize designer microporous metal-organic frameworks (MMOFs) mixed with catalysts to enable H-spillover for H₂ storage at 300 K-400 K and moderate pressures.
- Develop methods to reliably introduce catalyst into MMOFs.
- Demonstrate spectroscopic evidence for hydrogen spillover.

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
- (D) Durability: Min/max temperature/maximum pressure
- (E) Charging/Discharging rates
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (Q) Reproducibility of Performance

FY 2012 Accomplishments

- Developed and tested over 20 new MMOF structures (since project onset), with variations in surface chemistry, porosity, and metal incorporation.
- Tested four methods to introduce catalyst into MMOF samples, of which the 'pre-bridge' method provides best means to keep MMOF structure and surface area intact (see Table 2).
- Quantified advantages of differential volumetric system in measuring hydrogen uptake.
- Published spectroscopic evidence of spillover to CuBTC MMOF framework from hydrogen spillover catalyst, demonstrating unexpected hydrogenation site.
- Provided Pt-doped carbon samples to the National Renewable Energy Laboratory (NREL) for round-robin testing.
- Participated in "Weak Chemisorption" workshop.

TABLE 2. Development of MMOF Catalyst Doping Methods

Doping Technique Sample Name from PSU *Literature Report	Comparison of X-Ray Diffraction Quality (Before vs. After Doping)	Brunauer-Emmett-Teller (BET) Specific Surface Area (m ² /g) Before/After doping (%)
<u>Physical Mixing/Ball Milling</u> PtC/IRMOF8-iv	New Peak	1384/380 (28%)
<u>Bridging Technique</u> PtC/IRMOF8-x *PtC/IRMOF1—Ref 1 *PtC/IRMOF8—Ref 1 *PtC/COF1—Ref 2 *PtC/CuBTC—Ref 2 *PtC/MIL101—Ref 2	Different ND† ND ND ND ND	1384/310-760 (22-55%) 1021/890 (87%) 548/466 (85%) 628/582 (93 %) 1,296/1,116 (86%) 3,023/2,580 (85%)
<u>Direct Doping</u> Pt/IRMOF8 Pt/MMOFNH2 *Pt/IRMOF8-Ref 3 *Pd/MIL101(Al)—Ref 4	Missing Peak Different Intact Intact	1,384/674 (49%) 1,250/350-370 (30%) 1,430/1,175 (82%) 1,200/380 (31%)
<u>Prebridging Technique</u> PtC/IRMOF8 PtCA/IRMOF8 PtC/CuTDPAT *PtC/IRMOF1—Ref 5 *PtMWNT/IRMOF1—Ref 6	Intact Intact Intact Intact Intact	1,384/1,471 (106%) 1,384/1,421 (103%) 1,938/1,748 (90%) 1,820/730 (40%) 1,758/1,692 (96%)

† Not Determined



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 H₂ into atomic H species, which may then 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. 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 [1]. Independent groups have demonstrated up to 4.2 wt% at 6.9 MPa after extended equilibration for brPtC/IRMOF-8 [7]. 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 [8,9], 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, cost, and wells-to-wheels efficiency.

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 mixed with catalyst to test hydrogen storage and the effect of functional groups. We are investigating novel methods to incorporate a hydrogen dissociation catalyst into MMOFs, such that the hydrogen spillover mechanism can be applied to well-defined MMOF structures. For carbon-based catalysts, acid, base, and high temperature after-treatments were used to have various surface functional groups and to test hydrogen uptake. We are utilizing both gravimetric and differential volumetric adsorption methods to quantify hydrogen uptake, the former allows for precise catalyst activation whereas the latter allows for high-pressure measurements and is more accurate than conventional volumetric techniques. In addition, we are complementing hydrogen adsorption measurements with spectroscopy to identify the active sites that bind with spilled over hydrogen.

Results

In Phase 1 of the project, we have developed and tested some 20 new MOF structures, investigated the roles of pretreatment and reactor configuration on the PtC catalyst (Section I, below), verified spillover to MOFs with spectroscopic evidence (Section II), conducted extensive reproducibility tests on standard samples including the effect

of measurement, synthesis, and pretreatment conditions, and as of January 2012, tested four methods to incorporate the catalyst into the MOF (Section III), using methods that do not degrade the structure of the MOF yet maintain high catalytic activity. Highlights of results I-III are discussed below.

I. Optimization of PtC Catalysts.

We have found surface oxidation (using KOH activation) to be essential to observe high uptake in PtC catalyst via spillover [10]. Interestingly, high uptake was observed only when trace water was present in the system during catalyst reduction, which we attribute to a modification of Pt-C interfacial surface chemistry, as evidenced by X-ray photoemission spectroscopy (XPS) and Fourier transform infrared (FTIR) data. At 300 K, the hydrogen uptake of multiple preparations of activated PtC_{KOH} was 1.4 wt% at 20 bar (Figure 1), exceeding the above benchmarks. As the sample was reduced in H₂ in situ and the uptake significantly exceeded the stoichiometric amount attributable to the catalyst, the uptake is attributed to spillover. Temperature-programmed desorption with mass spectroscopy showed no evidence of water desorption as the sample was heated; the rate of hydrogen desorption was slow at ambient temperatures but could be increased with mild heating to

~100°C. The isotherm showed a significant portion of the uptake was at low-pressure (1.1 wt% at 100 mbar), providing a material with high catalytic activity for subsequent introduction of this PtC into MOF materials (see, e.g. PtC@CuTDPAT in Section III). In addition, our group provided gravimetric measurements of an oxidized Pt-doped activated carbon material (PtC_{INER}, Table 1) in support of inelastic neutron scattering studies conducted by Tsao et al. [11]. Uptake of this PtC_{INER} exceeded 1.0 wt% at 20 bar and 298 K (also exceeding benchmarks), with the majority of the uptake occurring at low pressure (Figure 2). The similar isotherm shape of PtC_{KOH} and PtC_{INER} are surprising given the extreme differences in catalyst content, structure, and introduction method, and will be explored in the upcoming year. These Pt-doped activated carbons only show dependence on the method by which they are measured (reactor size, gas flow, and history), which will be verified in the upcoming year.

II. Spectroscopic Evidence of Spillover to MMOFs

Spectroscopic evidence for spillover was a primary recommendation of the 2010 NREL-led spillover commission. In early studies conducted as a part of this work, a CuBTC (BTC=benzene tricarboxylate) MOF exhibited a 3.5-fold increase at 298 K and 20 bar after addition of a

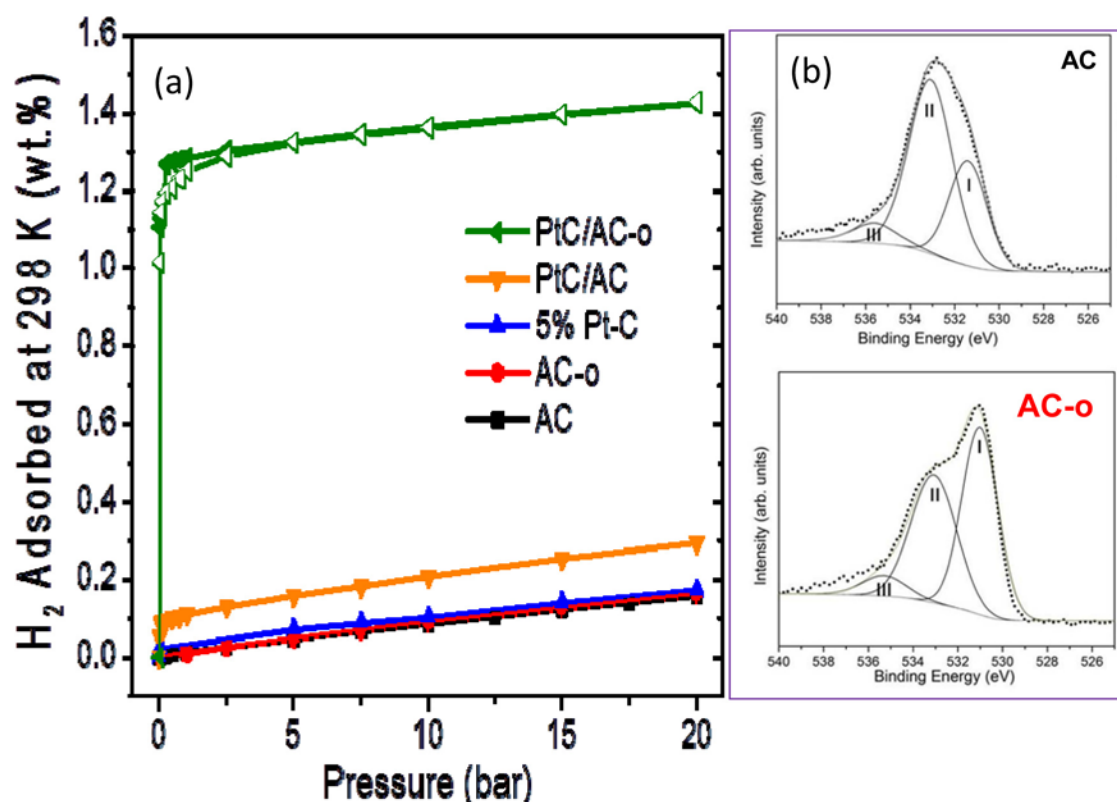


FIGURE 1. Oxidation of an activated carbon significantly increases low-pressure hydrogen spillover, as measured by gravimetric adsorption (a) in hydrogen at 298 K. XPS demonstrates changes in oxygen-carbon binding after oxidation and after introduction of trace water during the pretreatment step (b).

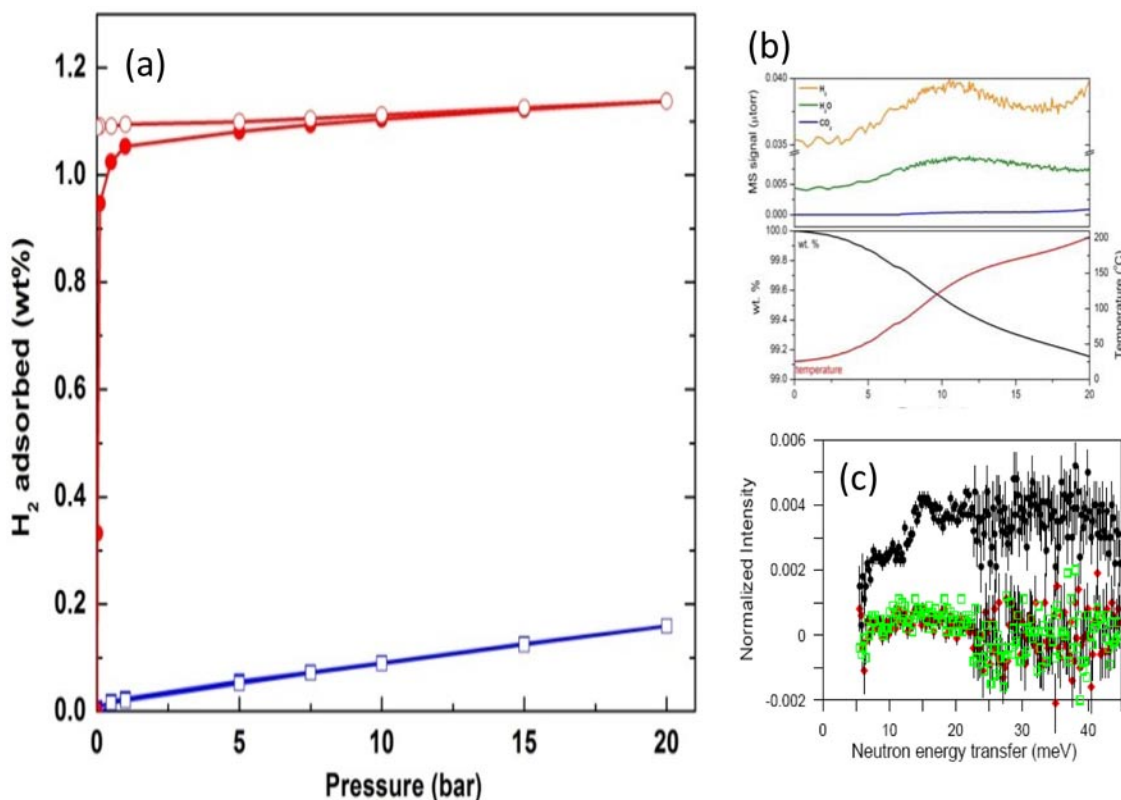


FIGURE 2. (a) A Pt-doped oxidized activated carbon provided by the Institute of Nuclear Energy Research, Taiwan had high gravimetric hydrogen uptake at 298 K (red) versus the activated carbon precursor (blue). (b) Only trace water is detected during temperature-programmed desorption. These results were used to support (c) inelastic neutron scattering measurements, which demonstrated this sample had a reduction in the H₂ modes after spillover occurred at 298 K.

carbon-spillover catalyst (PtC), from 0.17 to 0.61 wt% [12], exceeding the above benchmarks. Maintaining the structural integrity of the MOF upon mixing with the catalyst was important to achieve demonstrable chemisorption to the CuBTC. The rates of adsorption and temperature dependence were suggestive of irreversible chemisorption, making this material not viable for practical applications but an ideal candidate for early ex situ spectroscopic studies. FTIR of the hydrogenated PtC/CuBTC conclusively demonstrated hydrogenation of the carboxylate group of the BTC supported Pt ligand [12], providing the first published spectroscopic evidence for spillover to a MOF (Figure 3).

III. Development of New MMOFs and Catalyst-Doping

The best candidate MOF for future studies is Cu-TDPAT [a.k.a. Cu₃(TDPAT)(H₂O)₃, where H₆TDPAT = 2,4,6-tris(3,5-dicarboxylphenylamino)-1,3,5-triazine]. Cu-TDPAT is the smallest member of (3,24)-connect nets of *rht* topology made of a three-armed hexacarboxylate ligand and 24 M₂(COO)₄ paddle-wheel based supramolecular building blocks, as shown in Figure 4 (inset). The Cu-TDPAT framework is highly porous and contains three different types of cages, cuboctahedron (cub-*O_h*), truncated tetrahedron (T-*T_d*),

and truncated octahedron (T-*O_h*). The pore volume, BET and Langmuir surface areas are estimated to be 0.93 cc/g, 1,938 and 2,608 m²/g, respectively, calculated from N₂ adsorption isotherms (77 K). Cu-TDPAT is featured with a high density of both open metal sites (1.76/nm³) and Lewis basic sites (3.52/nm³), as well as high thermal and water stability. At 77 K and 67 bar, Cu-TDPAT takes up 4.83 (excess) and 6.77 (total) wt% of H₂, respectively. At 298 K and 60.9 bar, these numbers are 0.61 (excess) and 1.04 (total) wt%, respectively. The hydrogen adsorption is further enhanced upon a pre-bridging method we have recently developed to incorporate the PtC catalyst into the material during synthesis, with catalyzed uptake exceeding other common doping methods by a factor of 5 at 1 bar and ambient temperature (e.g. compare Pt/AC@CuTDPAT to Pt/CuTDPAT in Figure 4). Compared to other low-pressure measurements of doped MOF systems from the literature (see Figure 4), uptake of pre-bridged Pt/AC@CuTDPAT shows the highest uptake to date, and the slope of the low-pressure isotherm is high, suggesting high-pressure measurements (which are in progress) will also exceed the other materials. The high uptake of Pt/AC@CuTDPAT can be attributed to the doping technique, which typically maintains 90-110% of the surface area of the original MOF. In contrast, common

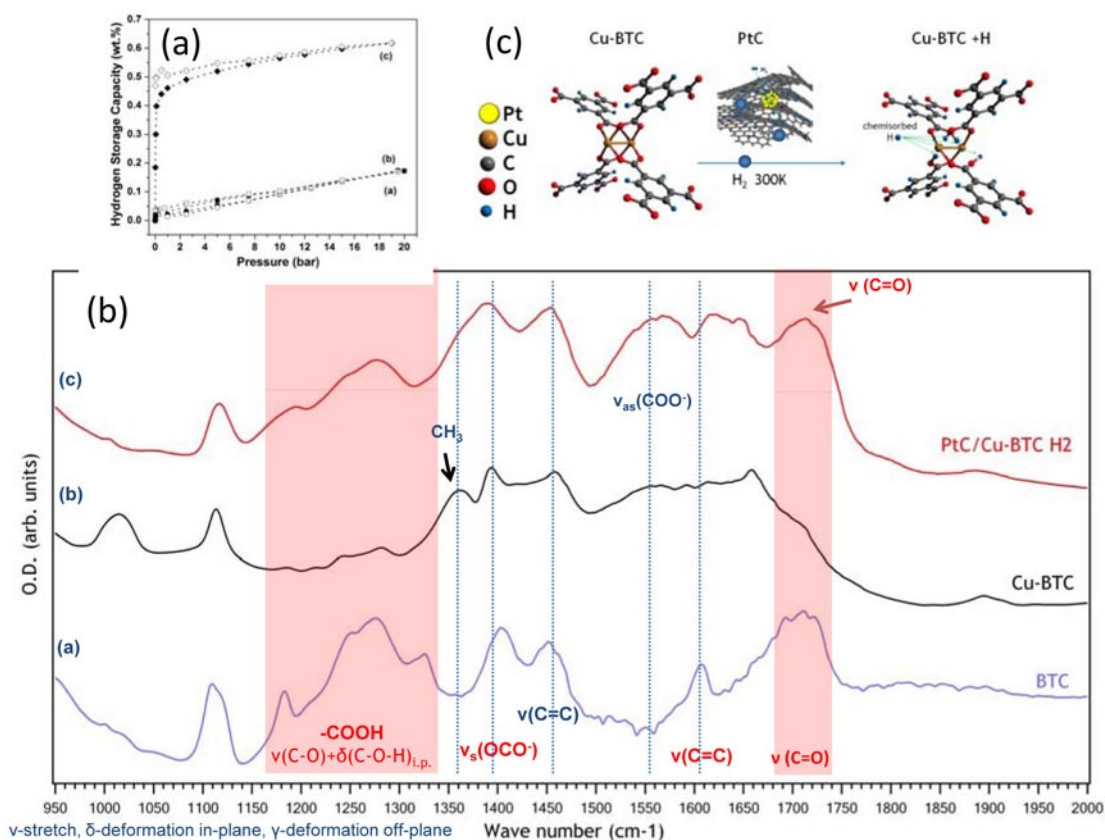


FIGURE 3. Introduction of a PtC spillover catalyst via mixing with CuBTC significantly increases low-pressure gravimetric hydrogen uptake at 298 K, achieving 0.61 wt% at 20-bar (a). FTIR spectra (b) demonstrate that this induces chemisorption to the Cu corners of the MOF by hydrogenating the carboxylate group, as demonstrated in the schematic (c).

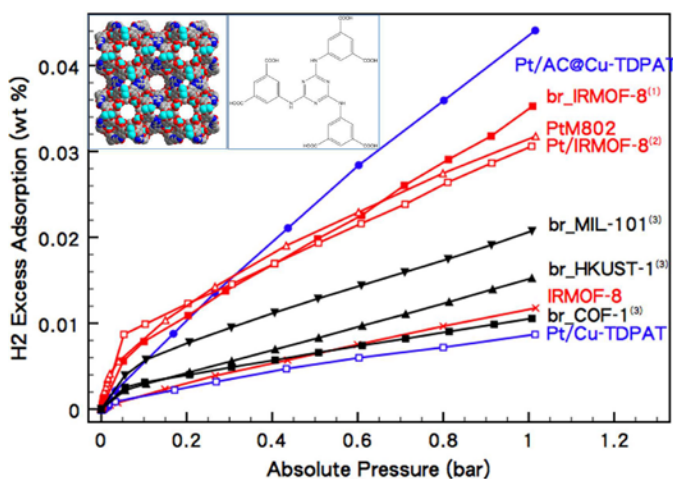


FIGURE 4. Room temperature H₂ uptake of "prebridged" Pt/CuTDPAT (blue circles) relative to direct-doped Pt/CuTDPAT (blue squares). The latter doping technique degrades structure and significantly decreases N₂ BET surface area. The inset shows the CuTDPAT crystal structure and the H₂TDPAT ligand. Other doped MOFs from the literature are included for comparison (1) Li, Y.; Yang, F.H.; and Yang, R.T. J. Phys. Chem. C. 2007, 111, 3405-3411; (2) Wang, L.F.; Stuckert, N.R.; Chen, H.; and Yang, R.T. J. Phys. Chem. C. 2011, 115, 4793-4799; (3) Li, Y. and Yang, R.T. AIChE Journal. 2008, 54, 269-279.

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. Clearly, the developed doping procedure yields the best room temperature uptake among all samples investigated. This method to incorporate the catalyst will be used to explore other MOF structures, with varying surface chemistry.

Conclusions and Future Directions

- Hydrogen spillover is verified with spectroscopic measurements. However, results with Pt-doped activated carbons suggest co-catalysts, trace water, and/or reactor configuration may play a role in systematically achieving high uptake via spillover. Future work will deduce role of energy propagation and co-catalysts in optimizing hydrogen spillover.
- Type and form of oxygen groups on carbon substrate affects Pt particle size and ultimate spillover on carbon materials (Figures 1 and 2). Future work will explore role of oxygen group and catalyst activators in optimizing spillover.

- A method to introduce a hydrogen dissociation catalyst into MMOF materials has been developed and tested. The new method provides substantial improvements over other common methods in terms of maintaining MMOF surface chemistry, structure, and surface area (Table 2). The doping method will be optimized in the upcoming year.
- PtC@CuTDPAT, produced via this new doping method, has the highest uptake via spillover at 1 bar (Figure 4), relative to all previously studied catalyst-doped MMOFs. The uptake is reversible and recoverable for three adsorption-desorption cycles, and XRD after adsorption shows the MMOF structure matches the as-synthesized CuTDPAT. Future studies will measure the uptake of PtC@CuTDPAT at high pressure and explore reproducibility of synthesis and measurement.
- Time permitting, this new catalyst doping method will be used to revisit effect of surface chemistry/structure on a variety of MMOFs that were previously tested after physical mixing with a hydrogen dissociation catalyst.
- Finalize papers on: (1) methods validation and reproducibility in differential volumetric analyzer; (2) development of direct-doping studies and instability of MMOFs; and (3) cross-comparison of catalyst doping techniques for MMOF materials.

Special Recognitions & Awards/Patents Issued

1. A. Lueking was selected as an Incoming Marie Curie Fellow for her work related to spillover.

FY 2012 Publications

1. Sircar, S.; Wu, H.; Li, J.; Lueking, A.D., Effect of Time, Temperature, and Kinetics on Hysteretic Adsorption-Desorption of H₂, Ar, and N₂ in the Metal-Organic Framework Zn₂(bpdC)₂(bpee), *Langmuir* 27 (23), 14169-14179, 2011.
2. Tsao, C.S.; Liu, Y.; Chuang, H.Y.; Tseng, H.H., Chen, T.Y.; Chen, C.H., Yu, M.S.; Li, Q., Lueking, A.D, Chen, S.H.. Hydrogen Spillover effect of Pt-doped Activated Carbon Studied by Inelastic Neutron Scattering. *J. Phys. Chem. Lett.* 2, 2322-2325, 2011.
3. Li, Q.; Lueking, A.D. Effect of Surface Oxygen Groups and Water on Hydrogen Spillover in Pt-Doped Activated Carbon. *J. Phys. Chem. C.* 115, 4273-4282, 2011.
4. Noa, K.E.; Lueking, A.D.; Cole, M.W., Imbibition transition: gas intercalation between graphene and silica. *J Low Temp Phys* 163, 26-33, 2011.
5. Lee, J.Y.; Pan, L.; Huang, X.Y.; Emge, T.J.; Li, J. A Systematic Approach to Build Highly Porous, Non-interpenetrating Metal Organic Frameworks with Large Capacity in Adsorbing H₂ and CH₄. *Adv. Func. Mater.*, 21, 993-998, 2011.

6. Liu, X.M.; Rather, S.; Li, Q.; Lueking, A.D., Zhao, Y.; Li, J. Hydrogenation of CuBTC framework with the introduction of a PtC hydrogen spillover catalyst. *J Phys. Chem. C*, 116 (5), 3477-3485, 2012.
7. Cole, M.W.; Gatica, S.M.; Kim, H.Y.; Lueking, A.D.; Sircar, S. Gas Adsorption in Novel Environments, Including Effects of Pore Relaxation. *J. Low Temp. Phys.* 166 (5-6), 231-241, 2012.

FY 2012 Presentations and Reports

1. Lueking, A.D. (invited) "Hydrogen storage in metal-organic frameworks via spillover and gate-opening mechanism". International Workshop: Adsorption at the nanoscale, a new frontier in fundamental science and applications Sep 21–24, 2011 at the University of Missouri, Columbia, MO.
2. Wang, C.Y. (speaker); Li, Q. Sircar, S. Liu, X. Lueking, A.D., Li, J. Cole, M. "Hydrogen Trapping through Designer Hydrogen Spillover Molecules with Reversible Temperature and Pressure-induced Switching" (Invited/Report) Hydrogen Storage Tech Team Meeting, Detroit, MI, September 15, 2011.
3. Lueking, A.D. (speaker), "Hydrogen Trapping through Designer Hydrogen Spillover Molecules with Reversible Temperature and Pressure-Induced Switching," (Report), Annual Merit Review Meeting, Washington, DC, May 12, 2011.
4. Lueking, A.D. (speaker), "Effect of Equilibration Time and Reduced Conditions on Adsorption to "Gate-Opening Metal-Organic Frameworks", AIChE Annual Meeting, Minneapolis, MN, October 19, 2012.
5. Lueking, A.D. (Invited speaker), "Nanomaterials for Gas Storage and Separations via a Trapping Mechanism," James and Catherine Patten Seminar, University of Colorado at Boulder, November 1, 2012.
6. Lueking, A.D. (Invited speaker), "Spectroscopic Evidence for Hydrogen Spillover," NREL working group on Weak Chemisorption, National Renewable Energy Laboratory, Golden, CO, February 2, 2012.
7. Li, J. (Invited speaker), "Microporous Metal Organic Frameworks: Porosity, Functionality and Potential Applications," Institute of Chemistry, Chinese Academy of Sciences, Beijing, China, April 30, 2012.
8. Li, J. (Invited speaker), "Functional Porous Materials: Design, Synthesis, Characterization and Applications", University of Texas at Dallas, Dallas, TX, April 5, 2012.
9. Li, J. (Invited speaker), "Designing and Functionalizing MMOFs for Energy Related Applications", Institute of Chemistry, Chinese Academy of Sciences, Beijing, China, April 30, 2012.
10. Li, J. (Invited speaker), "Microporous Metal Organic Frameworks: Porosity, Functionality and Gas Adsorption Properties", Jilin University, Changchun, China, May 3, 2012.
11. Li, J. (Invited speaker), "Porosity and Functionality in Metal Organic Framework Structures", Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, China, May 4, 2012.

References

1. Li, Y. and Yang, R.T. *J. Am. Chem. Soc.* 2006, 128, 8136-8137.
2. Li, Y. and Yang, R.T. *AIChE Journal*. 2008, 54, 269-279.
3. Wang, L.F.; Stuckert, N.R.; Chen, H.; and Yang, R.T. *J. Phys. Chem. C*. 2011, 115, 4793-4799.
4. Zlotea, C.; Campesi, R.; Cuevas, F.; Leroy, E.; Dibandjo, P.; Volkringer, C.; Loiseau, T.; Férey, G.; and Latroche, M. *J. Am. Chem. Soc.* 2010, 132, 2991-2997.
5. Lee, S.Y. and Park, S.J. *International Journal of Hydrogen Energy*. 2011, 36, 8381-8387.
6. Yang, S.J.; Cho, J.H.; Nahm, K.S.; and Park, C. R. *International Journal of Hydrogen Energy*. 2010, 35, 13062-13067.
7. 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.
8. Stadie, N.P.; Purewal, J.J.; Ahn, C.C.; and Fultz, B. *Langmuir*. 2010, 26, 15481-15485.
9. Stuckert, N.R.; Wang, L.; and Yang, R.T. *Langmuir*. 2010, 26, 11963-11971.
10. Li, Q.; Lueking, A.D. Effect of Surface Oxygen Groups and Water on Hydrogen Spillover in Pt-Doped Activated Carbon. *J. Phys. Chem. C*. 2011, 115, 4273-4282.
11. Tsao, C.S.; Liu, Y.; Chuang, H.Y.; Tseng, H.H., Chen, T.Y.; Chen, C.H., Yu, M.S.; Li, Q., Lueking, A.D, Chen, S.H.. Hydrogen Spillover effect of Pt-doped Activated Carbon Studied by Inelastic Neutron Scattering. *J. Phys. Chem. Lett.* 2011, 2, 2322-2325.
12. Liu, X.M.; Rather, S.; Li, Q.; Lueking, A.D., Zhao, Y.; Li, J. Hydrogenation of CuBTC framework with the introduction of a PtC hydrogen spillover catalyst. *J Phys. Chem. C*, 2012, 116 (5), 3477-3485.