



2008 DOE Hydrogen Program Review

Hydrogen Storage by Spillover

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University of Michigan
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Project ID: ST17

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Overview

Timeline

- Project start date: FY05
- Project end date: FY10
- Percent complete: 65%

Budget

- Total project funding
 - DOE share: \$939,356
 - Contractor share: \$280,000
- Funding received in FY07: \$225,000
- Funding for FY08: \$225,000

Barriers

- General
 - Weight & Volume
 - Rates (Refueling and discharge)
- Reversible Solid-State Material
 - Hydrogen Capacity & Reversibility
 - Lack of Understanding of H₂ Spillover

Partners

- Sample/adsorbed H Verification, Characterization & Mechanism **NREL, NIST, Rice U, MU/TAMU, APCI**
- Plan industrial collaboration after the initial phase of study and sorbent optimization

Project Objectives

- To develop hydrogen storage materials with capacities in excess of 6 wt% (and 45 g/L) at ***ambient temperature*** by using the spillover mechanism
 - To develop and optimize our new Bridge-Building techniques for spillover to enhance hydrogen storage in MOFs
 - To develop direct doping techniques for spillover on carbons with ultra-high surface areas (higher than all MOFs) (because of the enormous potential of carbon for H₂ storage by spillover as to be explained)
 - To obtain a mechanistic understanding for hydrogen spillover in nanostructured materials for the purpose of hydrogen storage

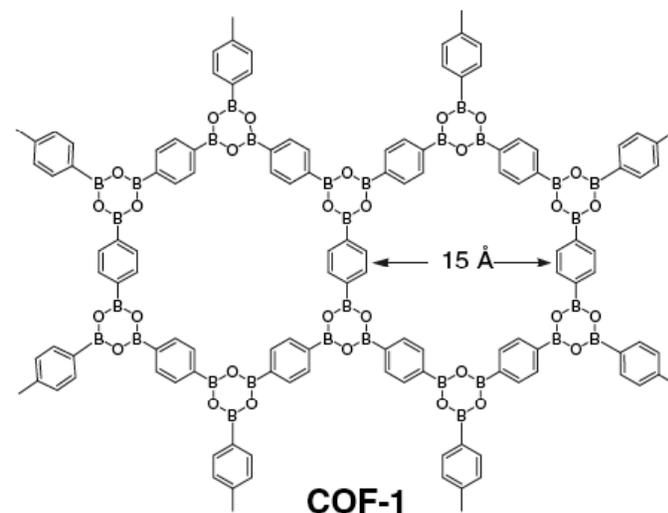
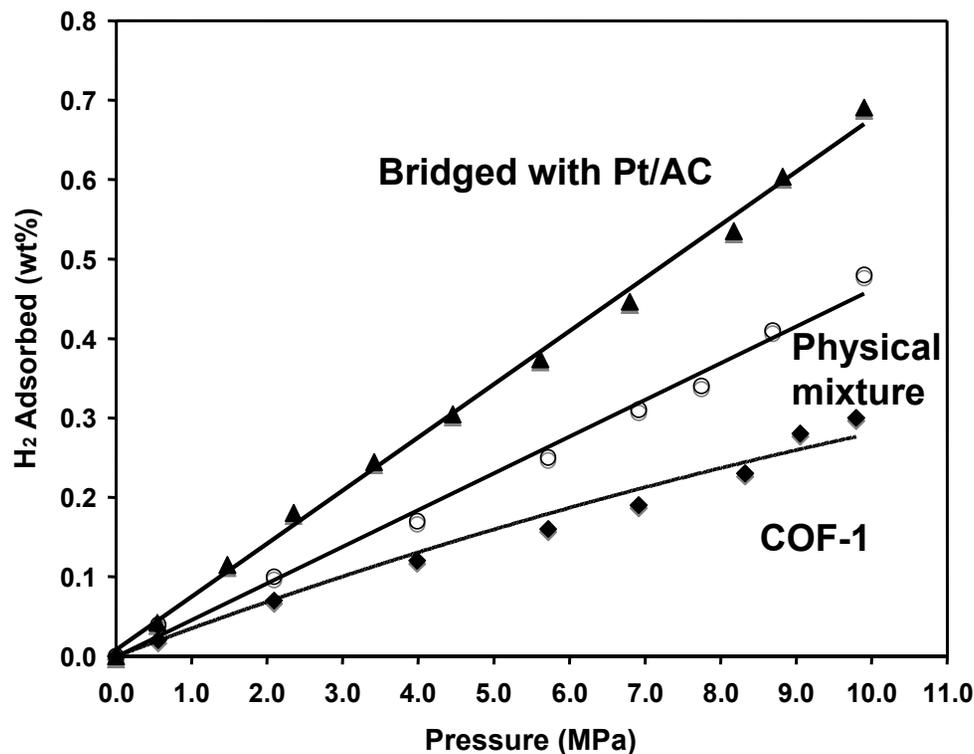
Technical Approach

- Use our bridge-building technique to significantly enhance spillover and storage at ambient temperature for MOFs (US & Foreign Patent applications filed, Yang et al., US20070082816A1 & WO2007046881A2, 2006)
- Synthesis of nanostructured carbons with ultra-high surface areas ($>3400 \text{ m}^2/\text{g}$) and develop effective, direct metal-doping techniques for spillover-storage at ambient temperature
- Apply deuterium isotope tracer techniques to obtain an understanding for spillover storage

Results following these three approaches are summarized as follows.

Technical Accomplishments/ Progress/Results

High-pressure Hydrogen Isotherms at 298K on COF-1 (C_3H_2BO) bridged with 10% added Catalyst (5%Pt/AC) (80% COF-1 + 10% catalyst + 10% bridges)



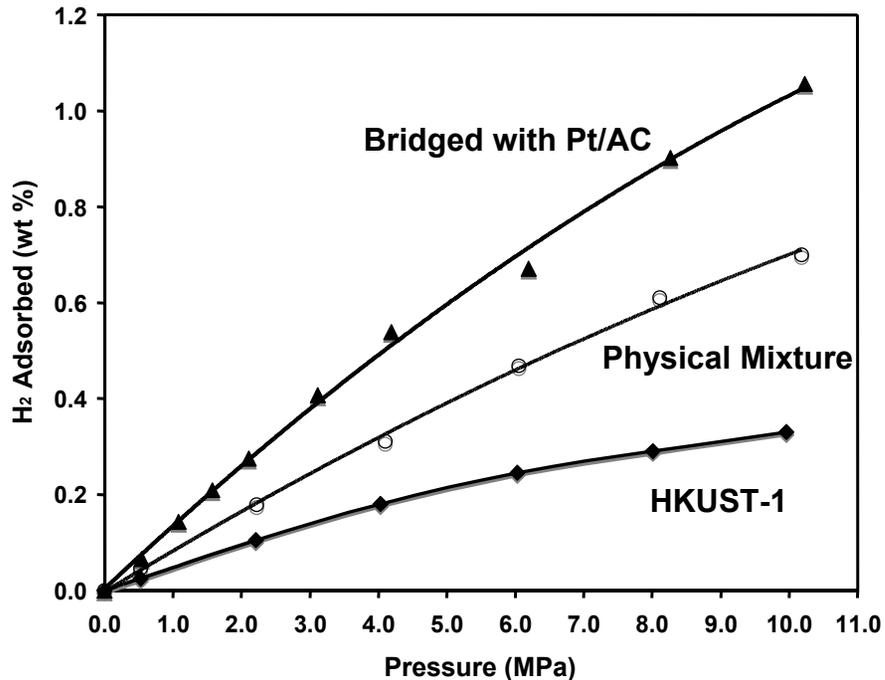
Courtesy of Cole, Yaghi, et al., Science, 310:1166 (2005)

- Hydrogen uptake can be significantly increased by spillover at 298K, and the isotherms are nearly linear; i.e., far from being saturated at 10 MPa.
- *All H_2 uptake values in this work are excess capacities.*

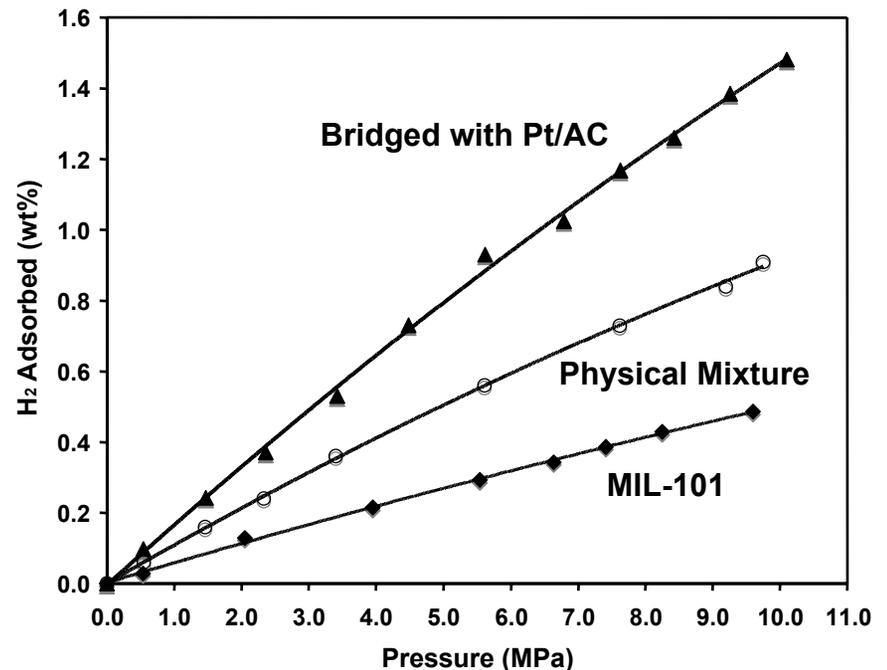
Accomplishments Slides (con't)

H₂ Isotherms at 298 K on MOFs bridged with 10% added catalyst (5%Pt/AC)

HKUST-1 [Cu₂(C₉H₃O₆)_{4/3}]



MIL-101 (Cr₃F(H₂O)₂O[(O₂C)C₆H₄(CO₂)₃])

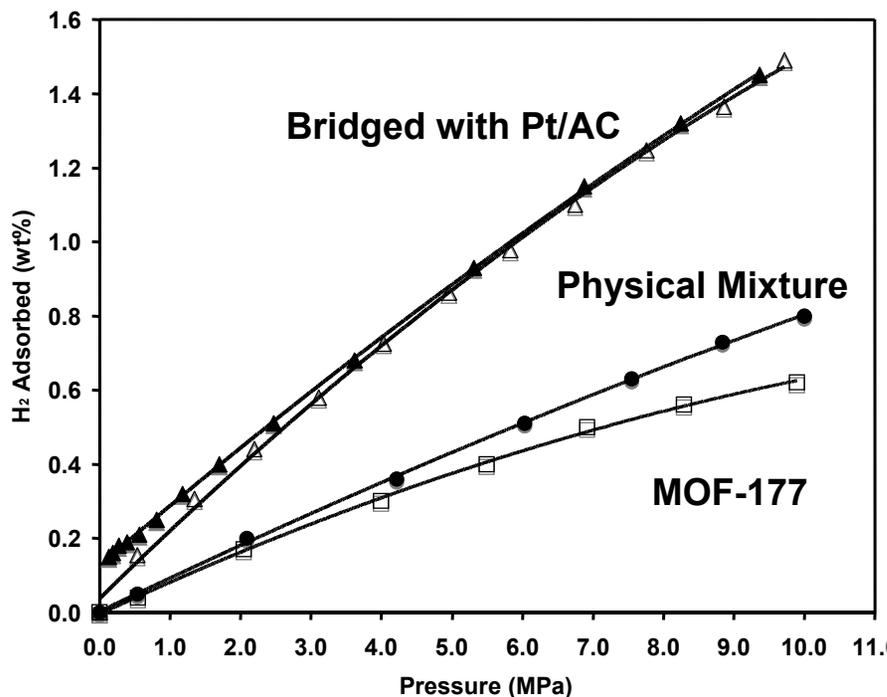


- MIL-101 is a promising candidate for spillover storage, as 1.5 wt% storage is achieved at 10 MPa on the bridged sample (due to its large surface area).

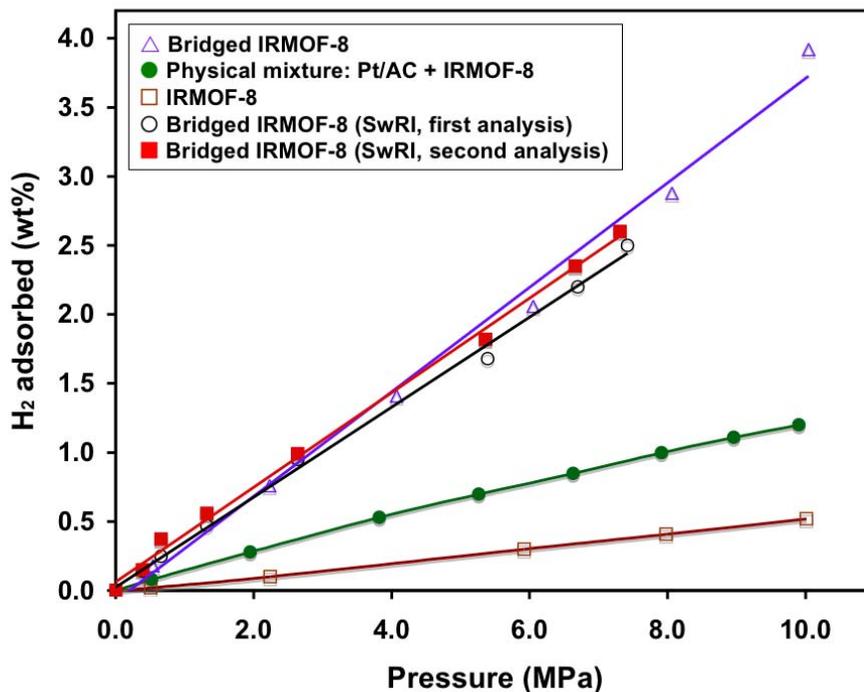
Accomplishments Slides (con't)

H₂ Isotherms at 298 K on MOFs bridged with 10% added catalyst (5%Pt/AC)

MOF-177 [Zn₄O(BTB)₂, BTB = benzenetribenzoate]



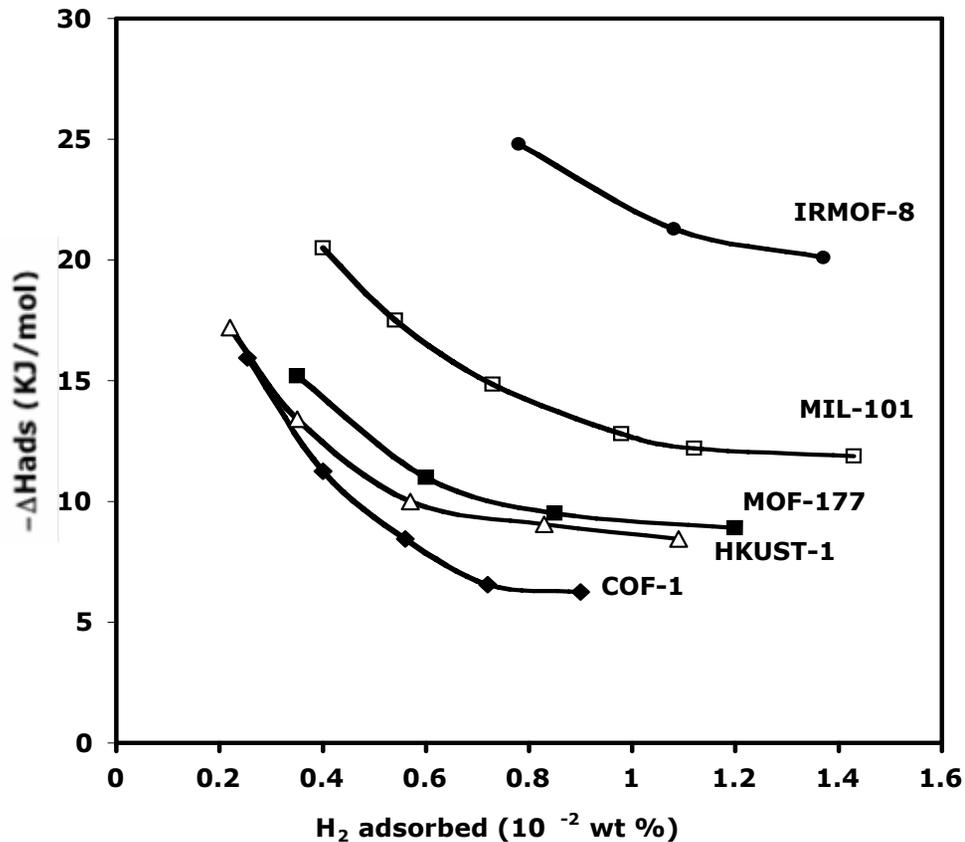
IRMOF-8 [Zn₄O(C₁₂H₆O₄)₃], SwRI: SwRI Validation
(Results from last year's annual Review)



- Spillover-storage is fully reversible at 298K (via full desorption by evacuation at 298K). (▲ indicates desorption branch down to 1.2 bar)
- MOF-177 and IRMOF-8 are similar; they are formed by [Zn₄O]⁶⁺ clusters and organic linkers, i.e., Zn₄O(C₂₇H₁₇O₆)₂ (MOF-177) vs. Zn₄O(C₁₂H₆O₄)₃ (IRMOF-8). A possible explanation is that a higher metal cluster content favors uptake of spillover hydrogen.

Accomplishments Slides (con't)

Isosteric heats of adsorption of H₂ on bridged metal-organic frameworks with Pt/carbon (based on isotherms at 298K and 323K)



Heats of adsorption approximately follow metal-oxide contents.
(ΔH levels off around 1-2% coverage)

Accomplishments Slides (con't): Summary Table

Summary Results on Pure and Bridged MOFs

(Bridged MOFs: 10% Pt/AC + 80% MOF with 10% carbon bridges)

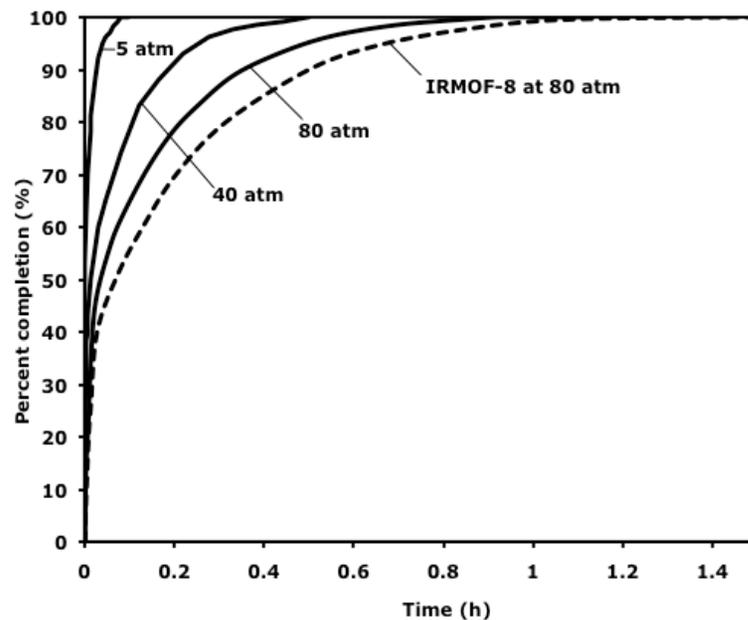
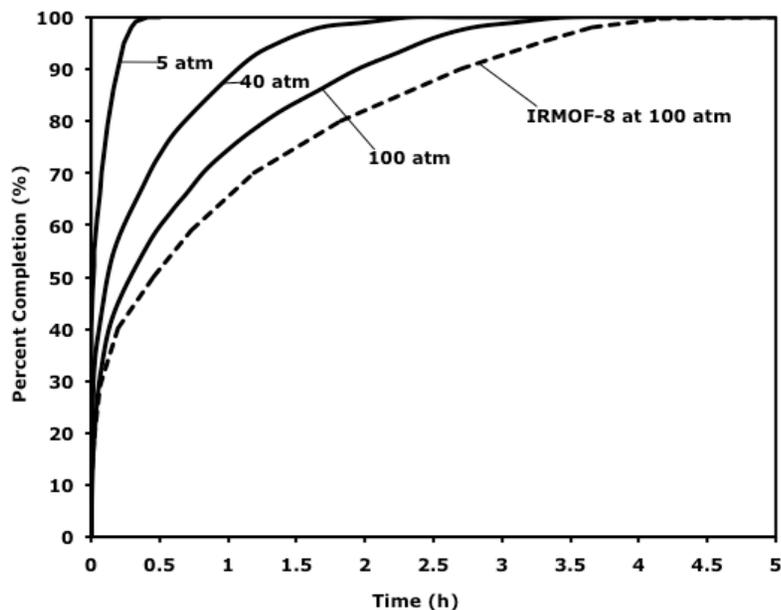
	<i>BET</i> Surface Area <i>m</i> ² / <i>g</i>	<i>H</i> ₂ at 77K, 1 atm, wt%	<i>H</i> ₂ at 298K, 100 atm, wt%	Bridged Sample, <i>H</i> ₂ 298K, 100atm, wt%*	ΔH (Bridged), kJ/mol
IRMOF-8	548	1.4	0.4	2.2 - 4.0 (Vol. Capacity: 22.4- 40.8 g/L*)	<u>-21</u>
COF-1	628	1.1	0.3	0.7	-7
HKUST-1	1296	2.2	0.3	1.1	-9
MIL-101	<u>2930</u>	1.8	0.5	1.5	-13
MOF-177	<u>3100</u>	1.5	0.6	1.5	-10

- Both surface area and heat of adsorption (binding energy) are important in determining hydrogen storage by spillover.

* Gravimetric and volumetric capacities are based on material only, not system values. Volumetric capacity is based on a bulk density of 1.02 g/cm³ for MOF-8.

Accomplishments Slides (con't)

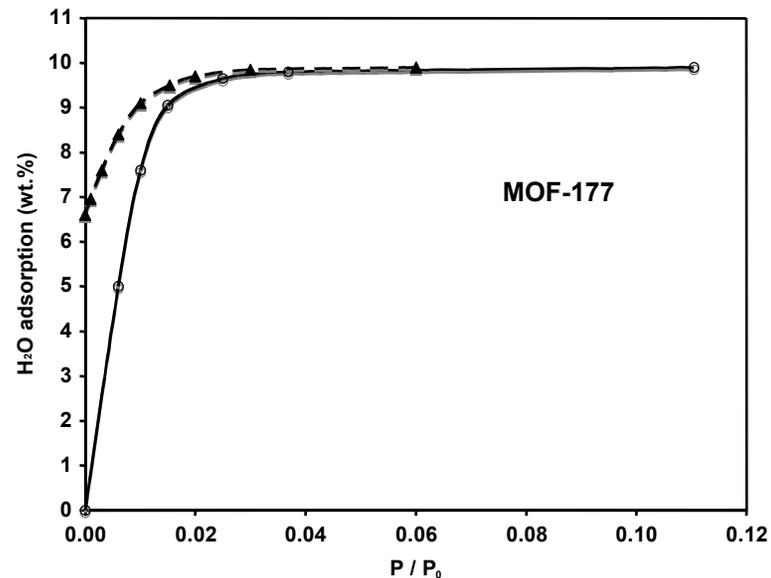
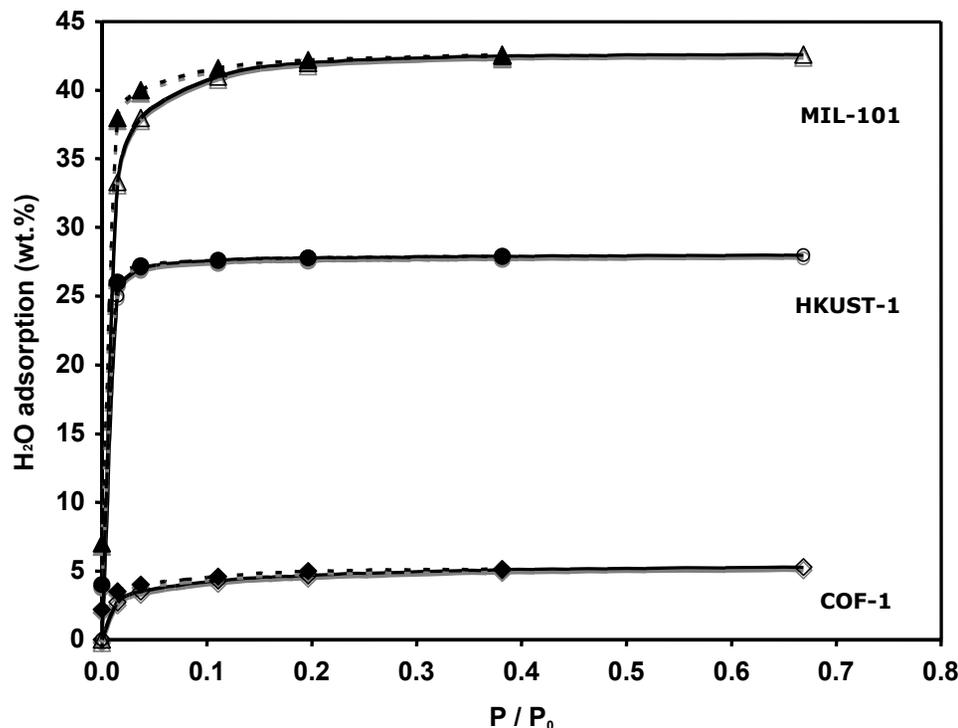
Rates of Adsorption (l), and Desorption (r) at Different *End Pressures* on Bridged MIL-101 ($T = 298\text{ K}$). Pressure steps (atm): 0→5→20→40→60→80→100 & Reverse



- Rates for both adsorption and desorption are fast at low loadings but become slower at higher loadings.
- Desorption is faster than adsorption, and the desorption rates at 298K exceed the DOE discharge rate target (of 0.02 g/s/kW).
- Rates of both adsorption and desorption are higher than that on bridged IRMOF-8, which is consistent with the lower heats of adsorption for MIL-101. (Note: surface diffusion is the rate-limiting step in adsorption and desorption.)

Accomplishments Slides (con't)

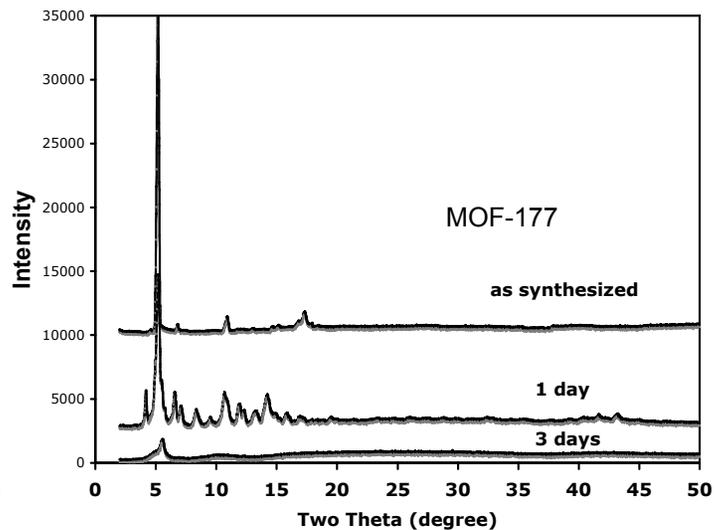
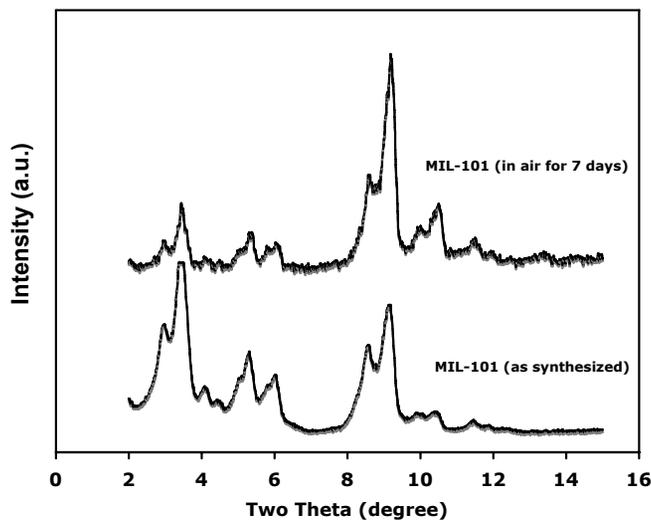
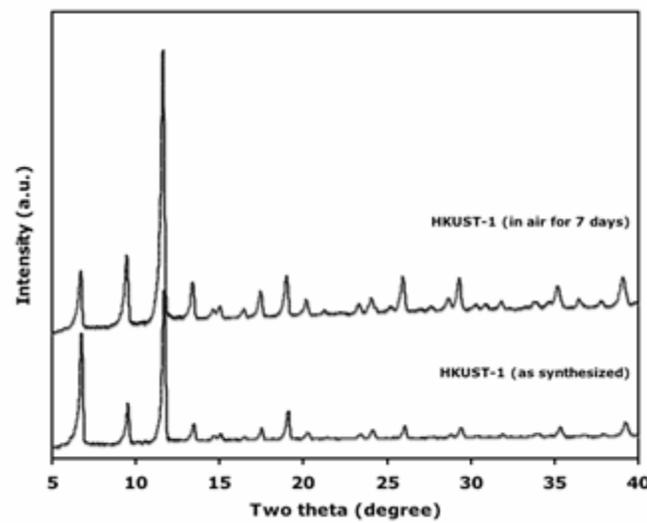
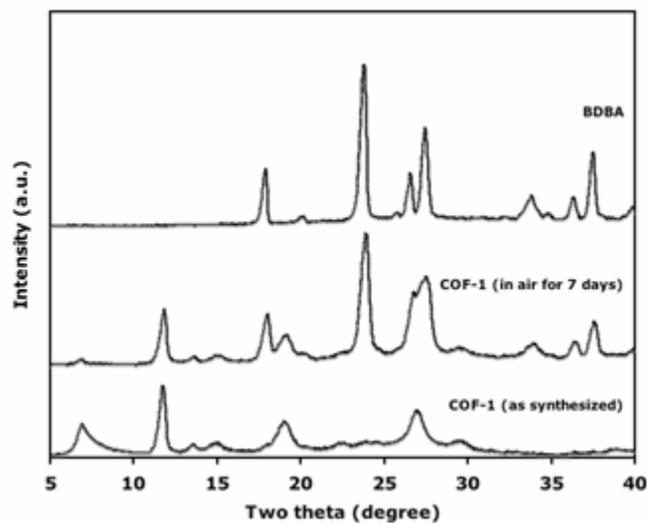
Water vapor adsorption isotherms at 298 K. P/P_0 is the ratio of H_2O vapor pressure (P) to saturation pressure at 298 K (P_0). Filled symbols: desorption branch.



- “**2007 DOE Technical Plan- Storage**, *Reversible Materials-Based Storage Systems* (p. 15): An understanding of chemical reactivity is needed particularly ...exposure to air and moisture....”
- All MOFs studied here adsorb moisture very strongly (at low concentrations).
- Some hysteresis is seen due to strongly adsorbed H_2O .

Accomplishments Slides (con't)

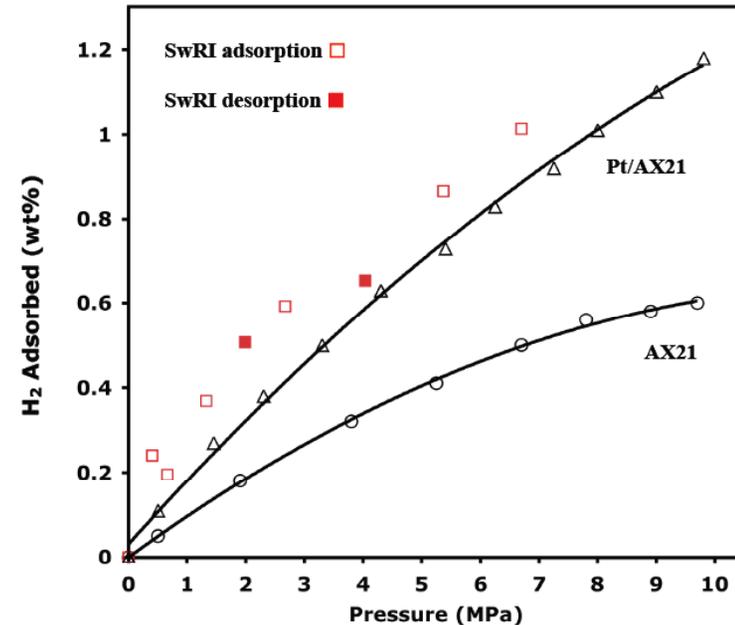
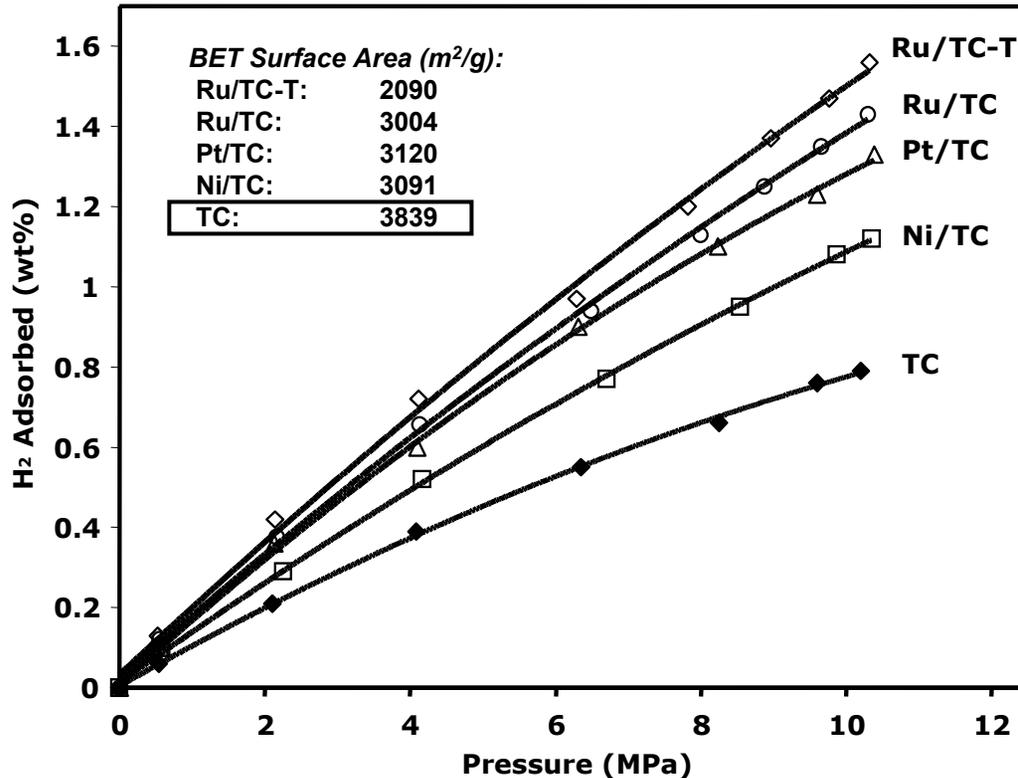
XRD of MOFs before and after exposure to ambient air (*BDBA*:1,4-benzene diboronic acid)



Among these MOFs, MOF-177 and COF-1 decompose completely in ambient air (by moisture), while MIL-101 and HKUST-1 are relatively more stable.

Accomplishments Slides (con't)

H_2 isotherms at 298 K on TC (templated carbon) & 6wt% metal-doped (ultrasound assisted) M/TC. All M/TC were H_2 -reduced at 300°C except Ru/TC-T was thermally reduced (in N_2) at 900°C (1 hr) (Metal particle size: 2 - 4 nm)



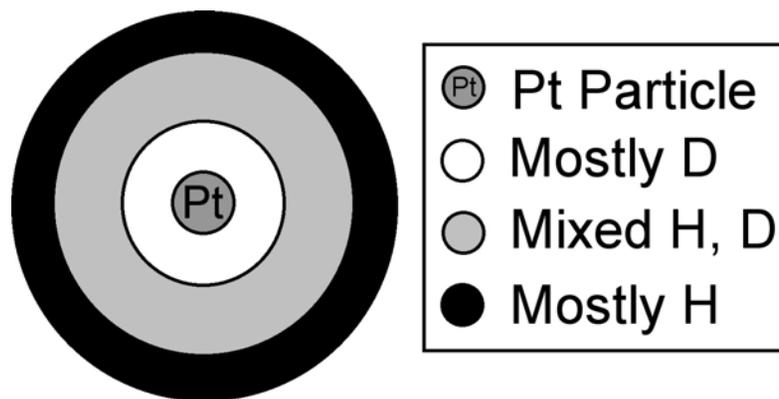
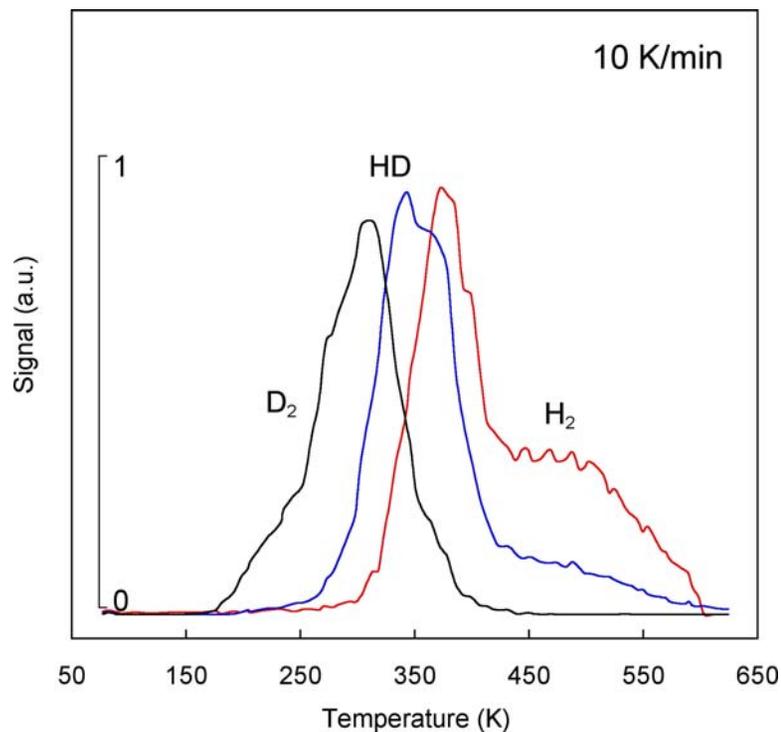
Results from last year's annual Review

- Storage on nanostructured carbons is far from reaching theoretical limit: >2wt% per 1000 m^2/g .
- The effect of metal is directly related to the equilibrium amounts adsorbed on the metal.
- Thermal reduction is most effective in anchoring metal particles, leading to more spillover.

Mechanistic Studies of Spillover with D₂ Isotopic Tracer - Accomplishments Slides (con't)

TPD Result for 6 wt% Pt on Templated Carbon (3400 m²/g) after dosing with 0.4 atm H₂ or D₂ at 298 K for 5 min (followed by quench, gas phase removal and TPD)

H₂ followed by D₂

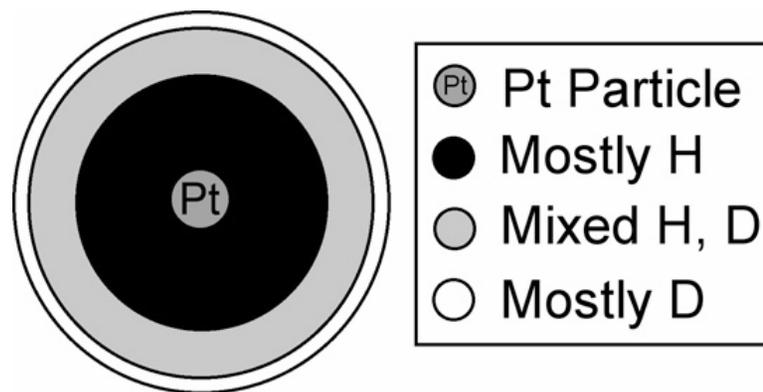
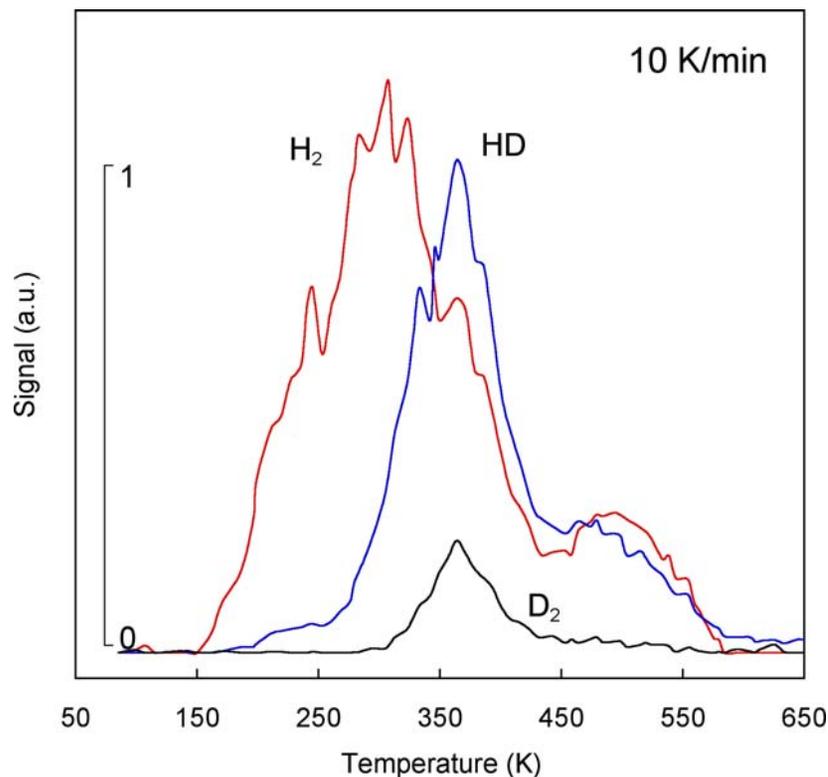


- Clear evidence is shown for the dissociation-spillover mechanism.
- The desorption step follows a reverse spillover process.

Accomplishments Slides (con't)

TPD Result for 6 wt% Pt on Templated Carbon (3400 m²/g) after dosing with 0.4 atm H₂ or D₂ at 298 K for 5 min (followed by quench, gas phase removal and TPD)

D₂ followed by H₂

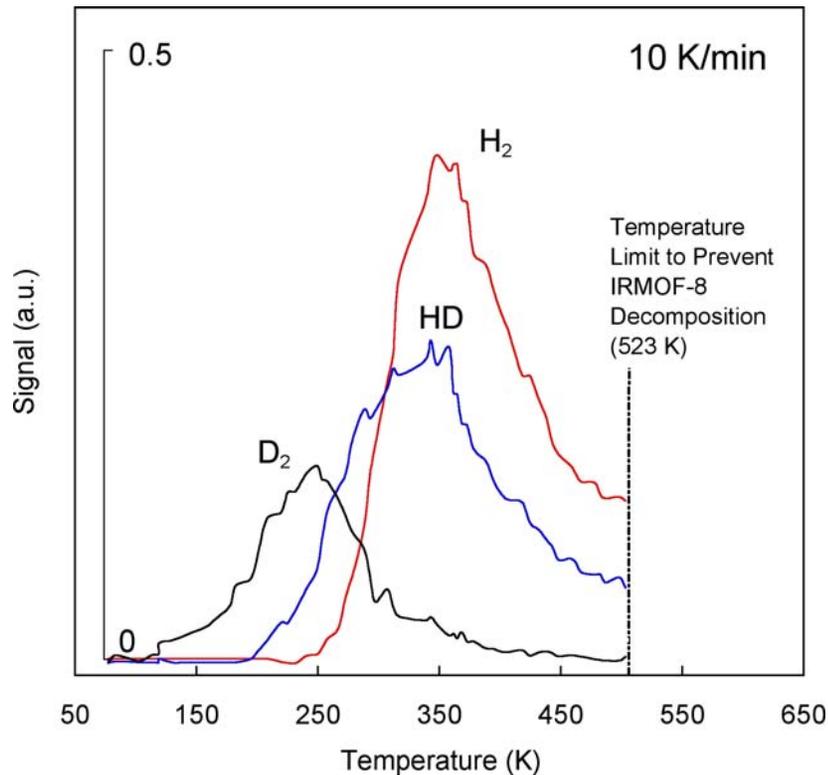


- Again, desorption follows reverse spillover.
- The small D₂ peak is possibly caused by premature recombination. Bond energy for D₂ > H₂, i.e., 106 vs. 104 kcal/mol.

Accomplishments Slides (con't)

TPD Result for IRMOF-8 (bridged to 5 wt% Pt/C) after dosing with 0.4 atm H₂ or D₂ at 298 K for 5 min (followed by quench, gas phase removal and TPD)

H₂ followed by D₂



- Clear evidence is shown for the dissociation-spillover mechanism on MOF.
- The desorption step also follows a reverse spillover process.

Future work plan/Objectives

- During FY 2008: Study kinetics of spillover for charge and discharge steps on both bridged MOFs and Metal/Carbon; provide further results on the rate-limiting steps in charge and discharge steps; perform isotope tracer studies on mechanism of spillover-storage.
- Storage by spillover with bridge-building on other high surface area MOFs: particularly PCN-type MOFs from our Center
- Syntheses of carbons with ultra-high surface areas, i.e., >3500 m²/g.
- Develop new direct metal-doping techniques on AX-21 and other ultra-high-surface-area carbons
- Obtain basic understanding of the spillover process including equilibrium and kinetics, using deuterium isotope tracers (D₂ and HD)
- To achieve the 6 wt% (48 g/L) DOE (interim) system target at 298K
- To address issues on fueling rates and other DOE targets

Summary

- H₂ dissociation and spillover can significantly increase the H₂ storage capacity at ambient temperature for all MOFs and nanostructured carbons.
- Spillover-storage on MOFs depends on both surface area and binding energy.
- Spillover-storage on nanostructured carbons depends on how metals are doped, and is far from reaching theoretical limits.
- Desorption rates at ambient temperature for both MOFs and carbon exceed DOE target for discharge rate.
- Deuterium isotope tracer studies showed direct evidence for hydrogen dissociation and spillover at 298K.
- Deuterium isotope tracer studies also showed that desorption followed a reverse spillover mechanism.