



# 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 H<sub>2</sub> 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 H<sub>2</sub> storage by spillover as to be explained)
  - To obtain a mechanistic understanding for hydrogen spillover in nanostructured materials for the purpose of hydrogen storage

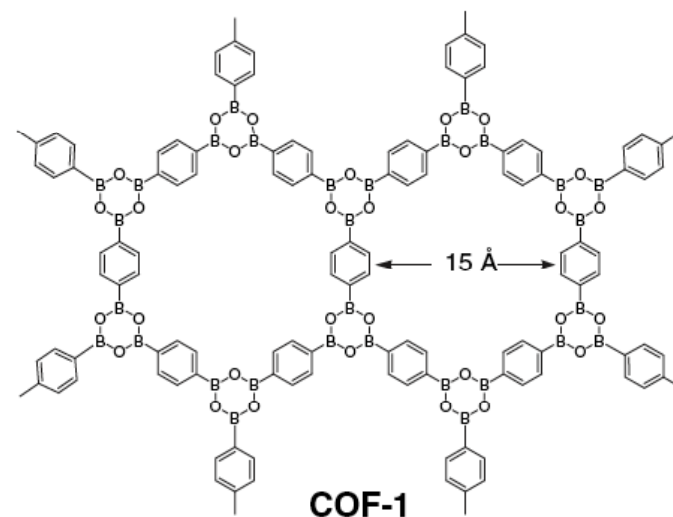
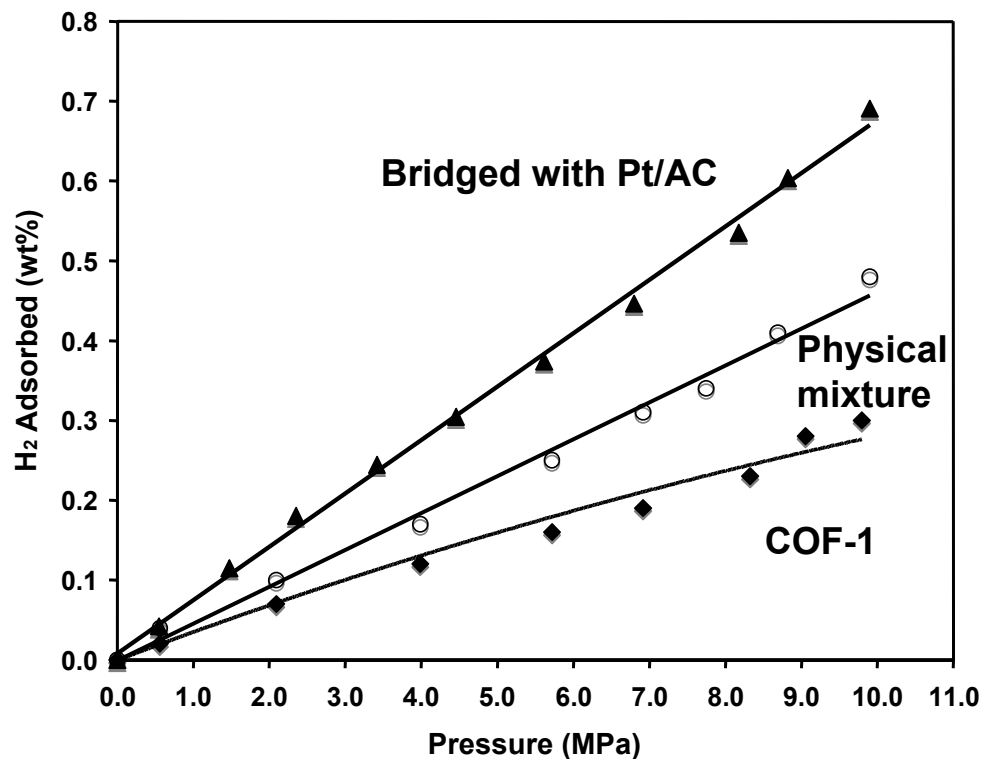
# Technical Approach

- 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)



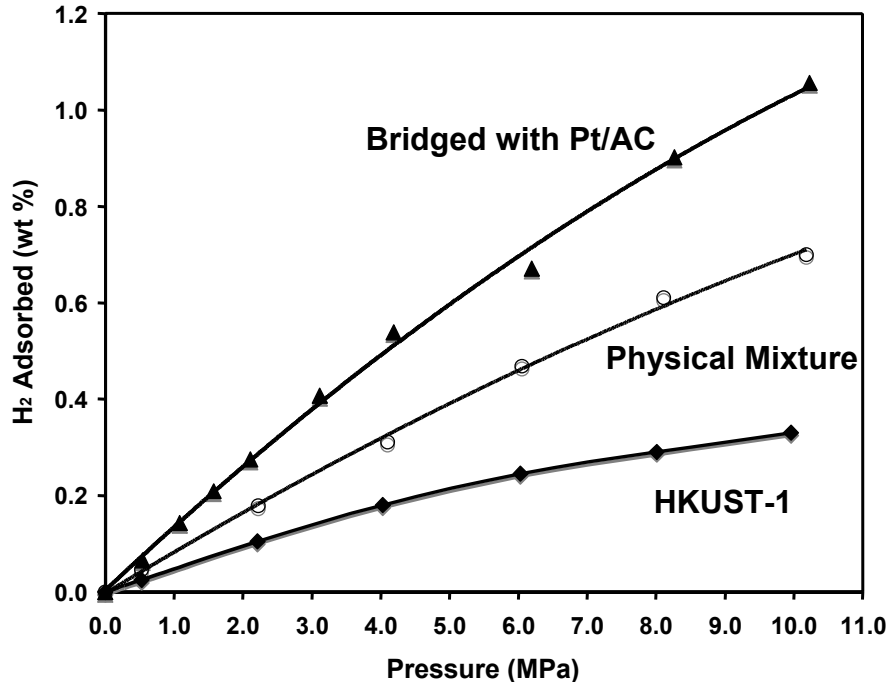
Courtesy of Cole, Yaghi, et al., Science, 310:1166 (2005)

- 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.*

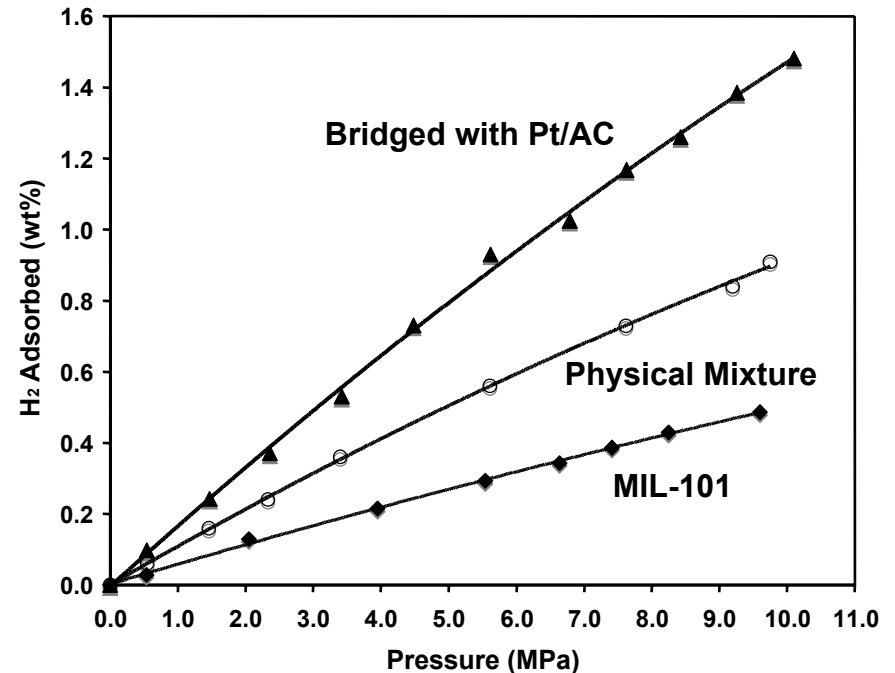
# Accomplishments Slides (con't)

## H<sub>2</sub> Isotherms at 298 K on MOFs bridged with 10% added catalyst (5%Pt/AC)

### HKUST-1 [Cu<sub>2</sub>(C<sub>9</sub>H<sub>3</sub>O<sub>6</sub>)<sub>4/3</sub>]



### MIL-101 (Cr<sub>3</sub>F(H<sub>2</sub>O)<sub>2</sub>O[(O<sub>2</sub>C)C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>)<sub>3</sub>])

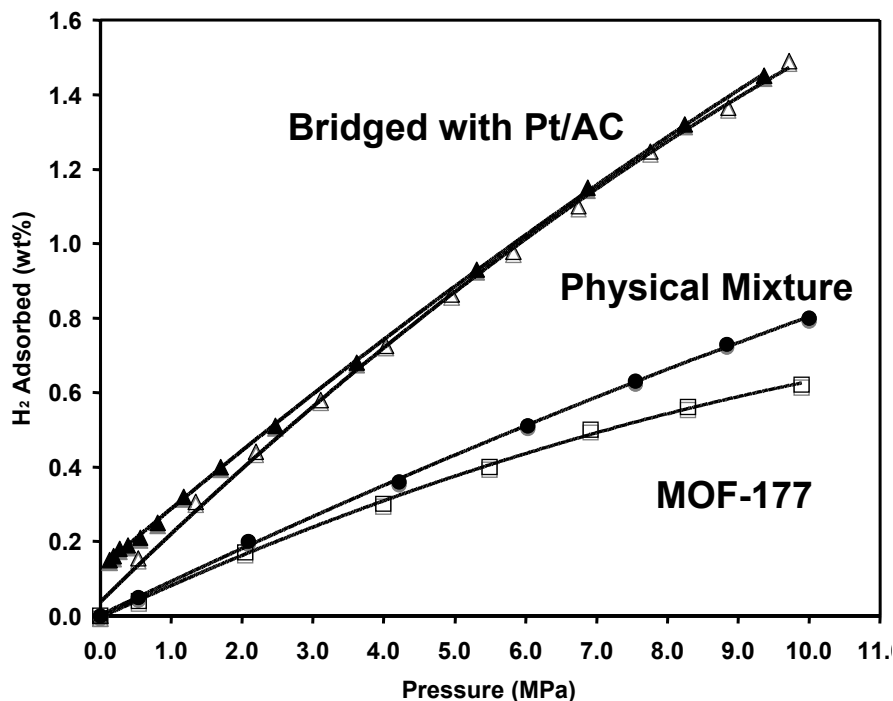


- MIL-101 is a promising candidate for spillover storage, as 1.5 wt% storage is achieved at 10 MPa on the bridged sample (due to its large surface area).

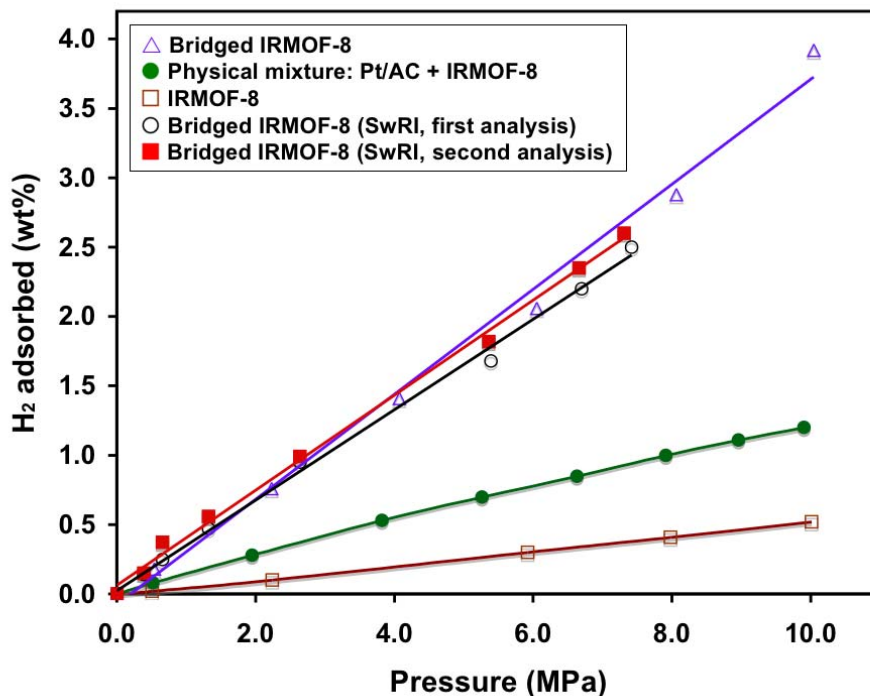
# Accomplishments Slides (con't)

## H<sub>2</sub> Isotherms at 298 K on MOFs bridged with 10% added catalyst (5%Pt/AC)

MOF-177 [Zn<sub>4</sub>O(BTB)<sub>2</sub>, BTB = benzenetribenzoate]



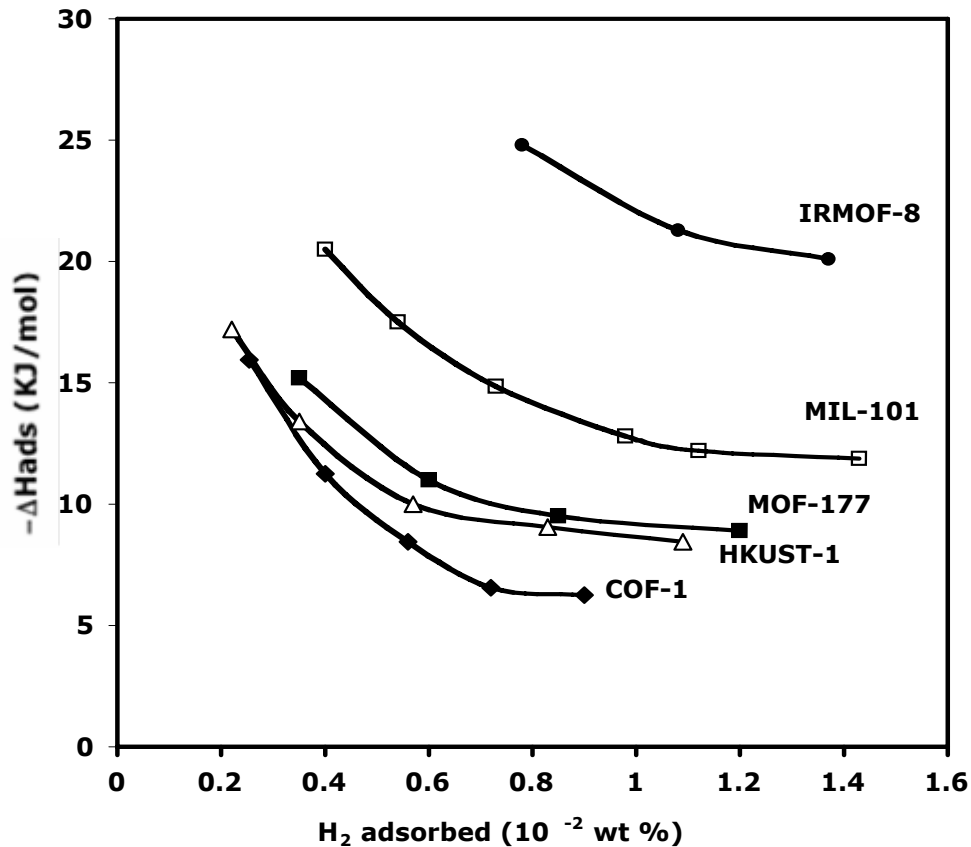
IRMOF-8 [Zn<sub>4</sub>O(C<sub>12</sub>H<sub>6</sub>O<sub>4</sub>)<sub>3</sub>], SwRI: SwRI Validation  
(Results from last year's annual Review)



- 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 [Zn<sub>4</sub>O]<sup>6+</sup> clusters and organic linkers, i.e., Zn<sub>4</sub>O (C<sub>27</sub>H<sub>17</sub>O<sub>6</sub>)<sub>2</sub> (MOF-177) vs. Zn<sub>4</sub>O(C<sub>12</sub>H<sub>6</sub>O<sub>4</sub>)<sub>3</sub> (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 H<sub>2</sub> on bridged metal-organic frameworks with Pt/carbon (based on isotherms at 298K and 323K)



Heats of adsorption approximately follow metal-oxide contents.  
( $\Delta H$  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)*

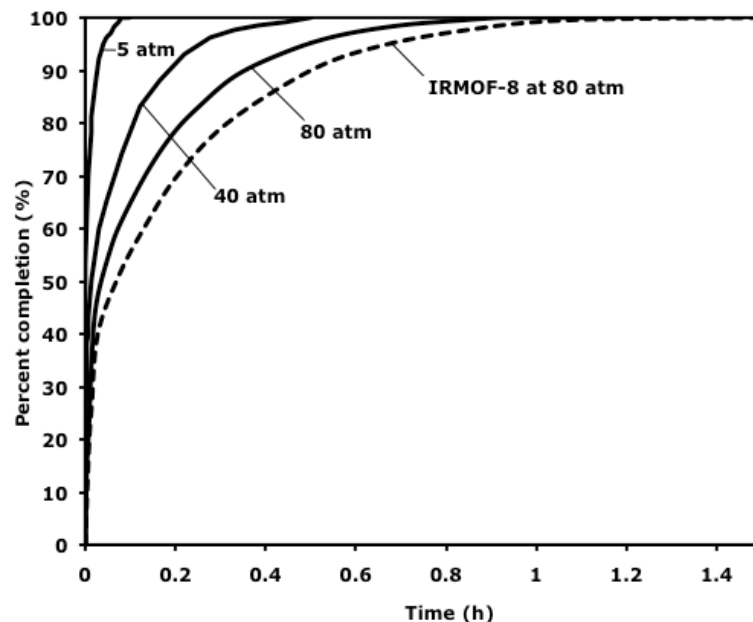
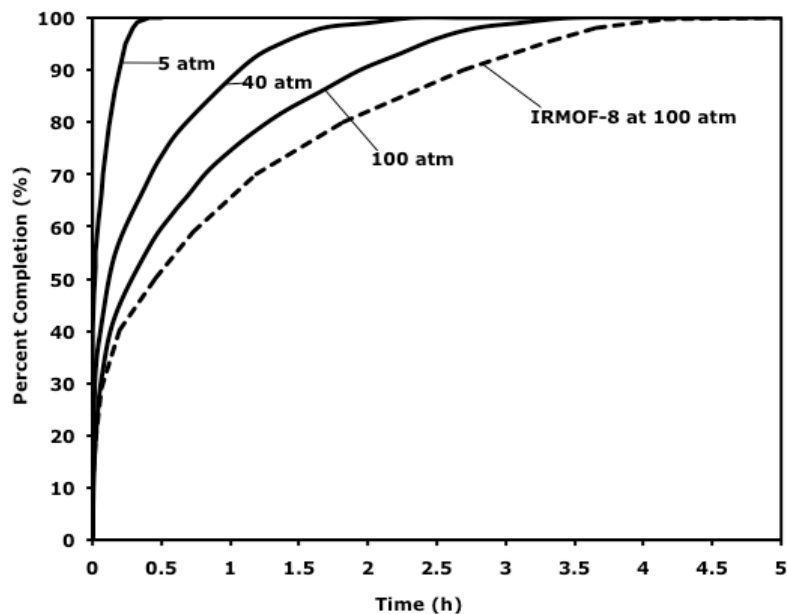
	<i>BET Surface Area m<sup>2</sup>/g</i>	<i>H<sub>2</sub> at 77K, 1 atm, wt%</i>	<i>H<sub>2</sub> at 298K, 100 atm, wt%</i>	<i>Bridged Sample, H<sub>2</sub> 298K, 100atm, wt%*</i>	<i>ΔH (Bridged), kJ/mol</i>
<b>IRMOF-8</b>	<b>548</b>	<b>1.4</b>	<b>0.4</b>	<b>2.2 - 4.0</b> (Vol. Capacity: 22.4- 40.8 g/L*)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

- **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/cm<sup>3</sup> for MOF-8.*

## Accomplishments Slides (con't)

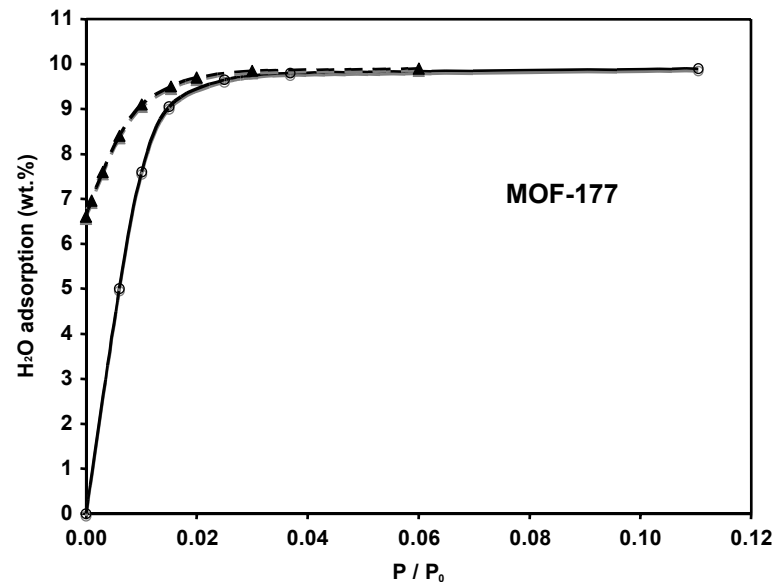
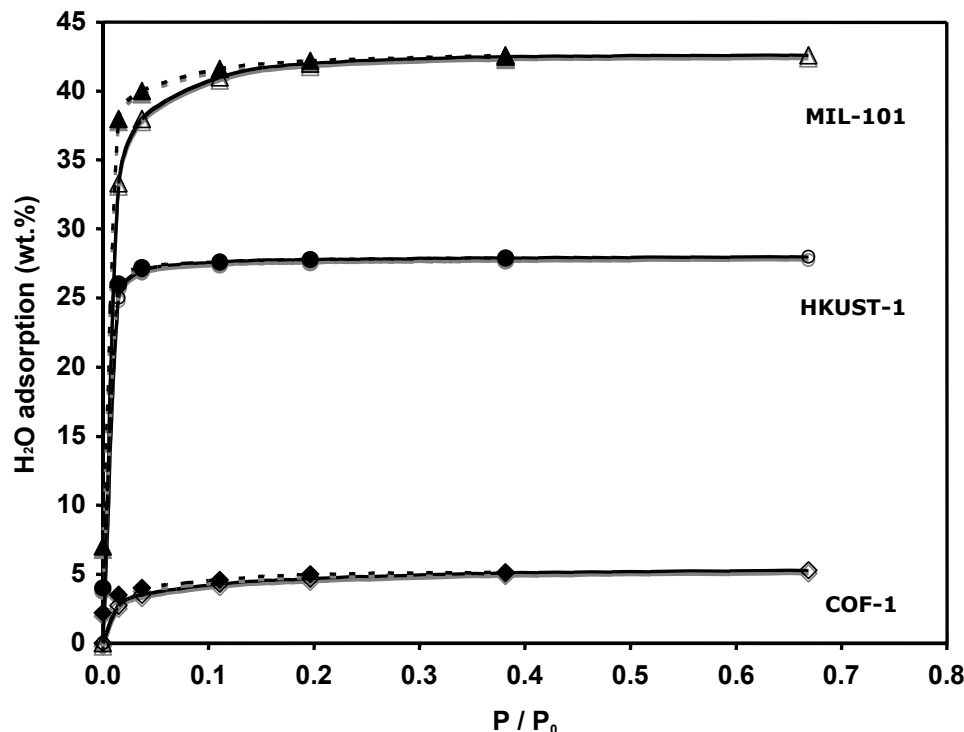
Rates of Adsorption ( $l$ ), and Desorption ( $r$ ) at Different *End Pressures* on Bridged MIL-101 ( $T = 298\text{ K}$ ). Pressure steps (atm): 0→5→20→40→60→80→100 & Reverse



- 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)

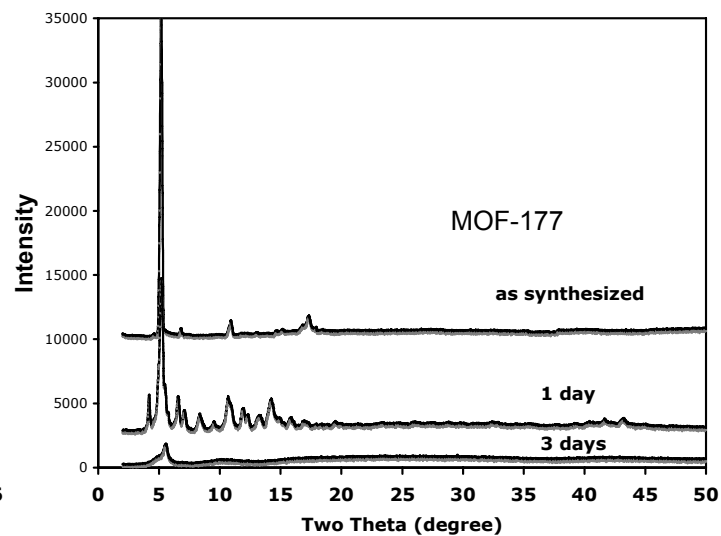
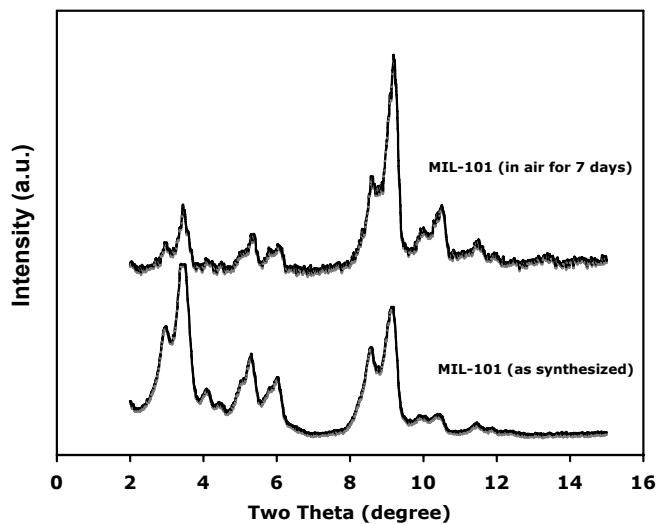
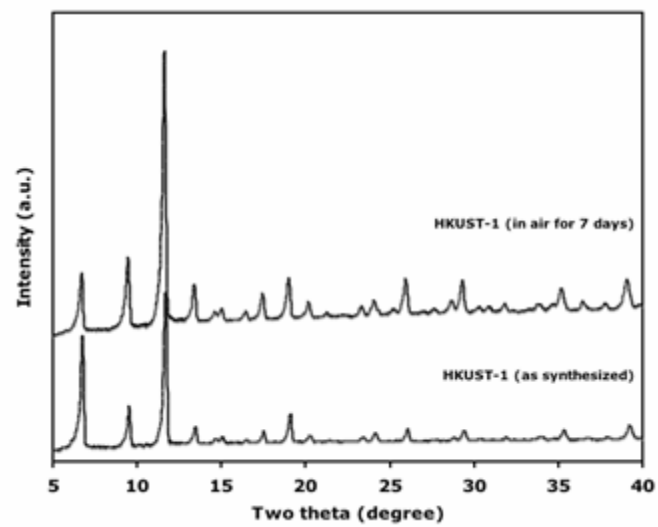
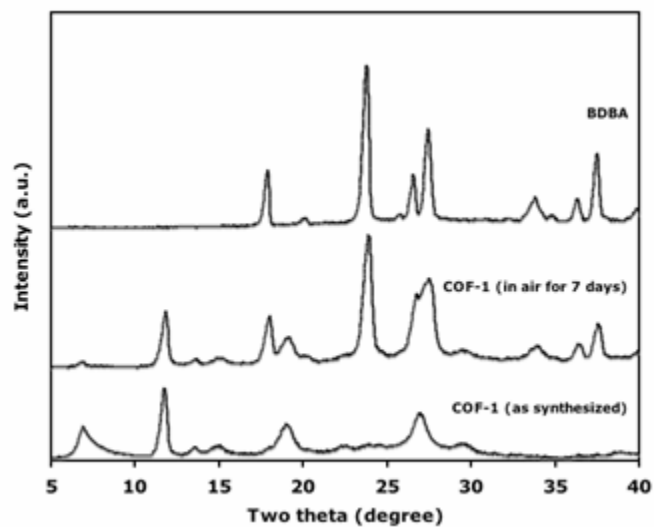
Water vapor adsorption isotherms at 298 K.  $P/P_0$  is the ratio of  $H_2O$  vapor pressure ( $P$ ) to saturation pressure at 298 K ( $P_0$ ). Filled symbols: desorption branch.



- “**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<sub>2</sub>O.

## Accomplishments Slides (con't)

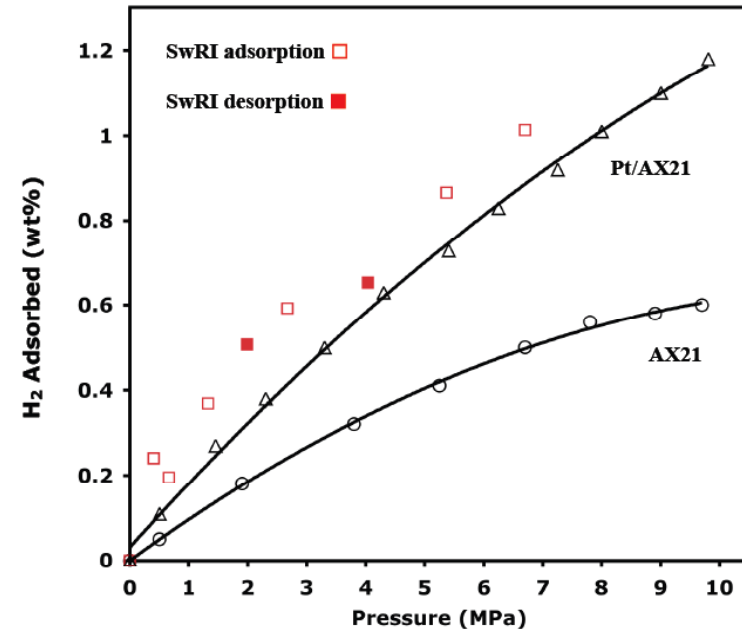
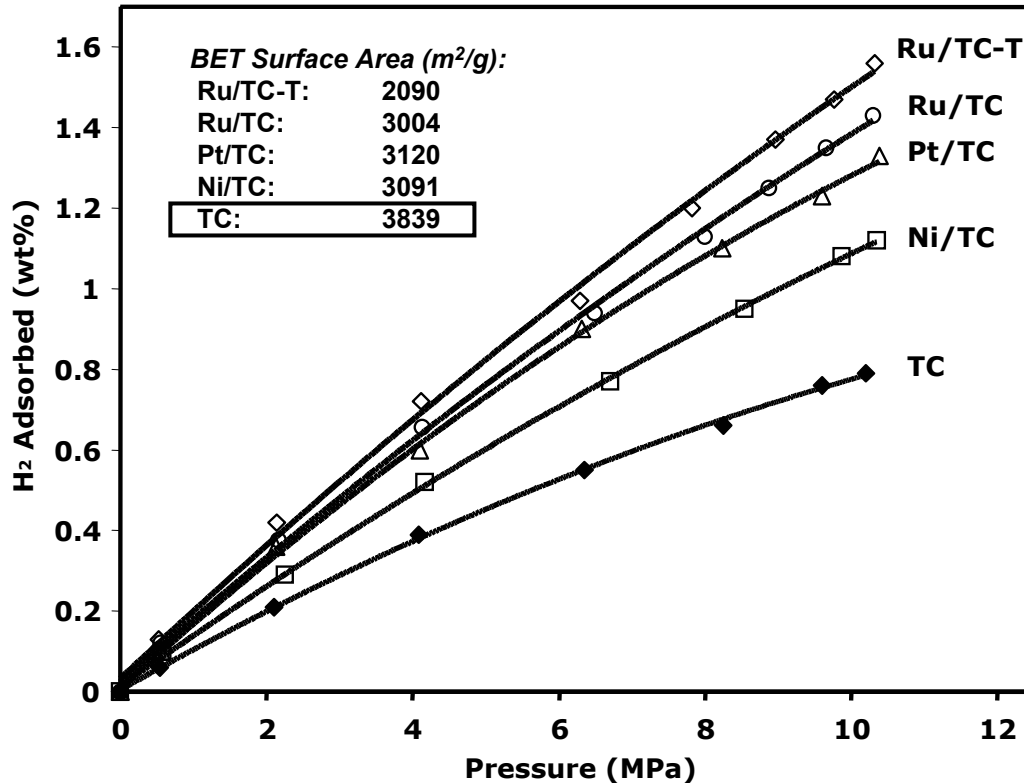
XRD of MOFs before and after exposure to ambient air (*BDBA*:1,4-benzene diboronic acid)



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)



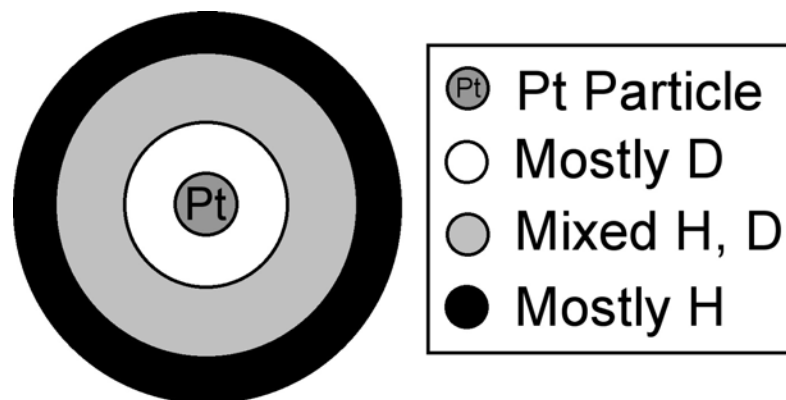
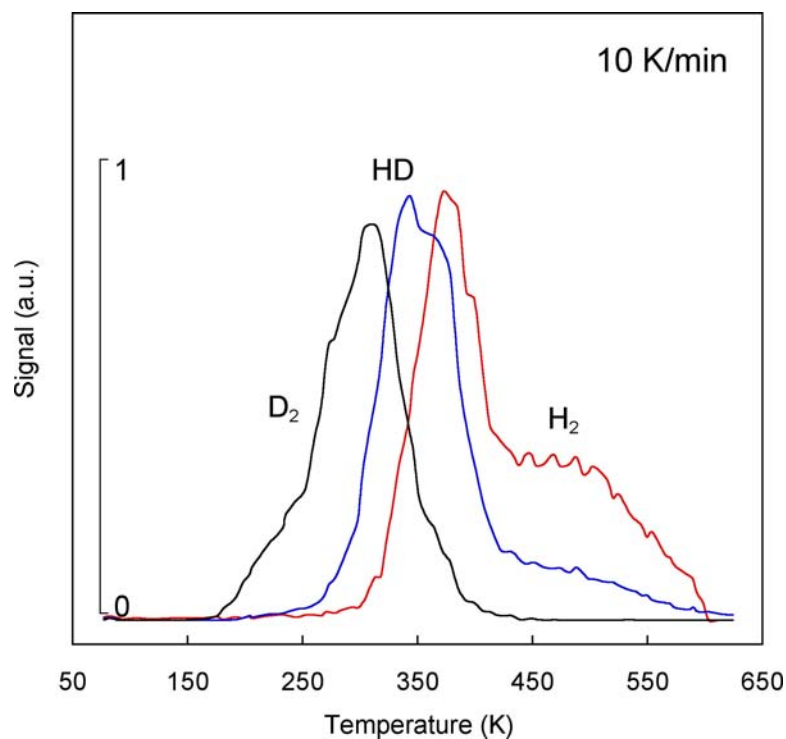
*Results from last year's annual Review*

- 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 D<sub>2</sub> Isotopic Tracer - Accomplishments Slides (con't)

TPD Result for 6 wt% Pt on Templated Carbon (3400 m<sup>2</sup>/g) after dosing with 0.4 atm H<sub>2</sub> or D<sub>2</sub> at 298 K for 5 min (followed by quench, gas phase removal and TPD)

### H<sub>2</sub> followed by D<sub>2</sub>

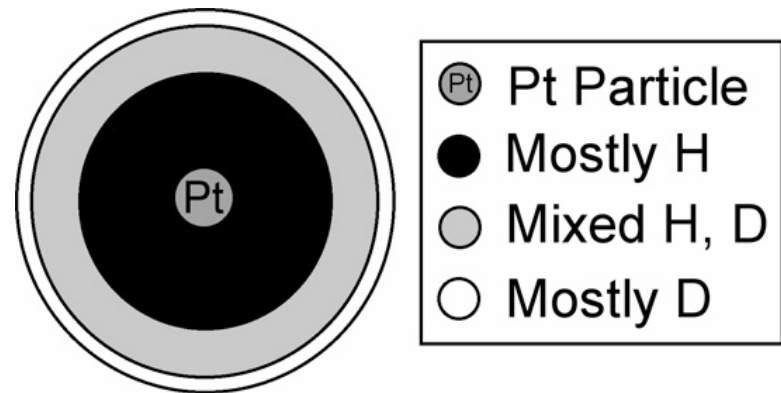
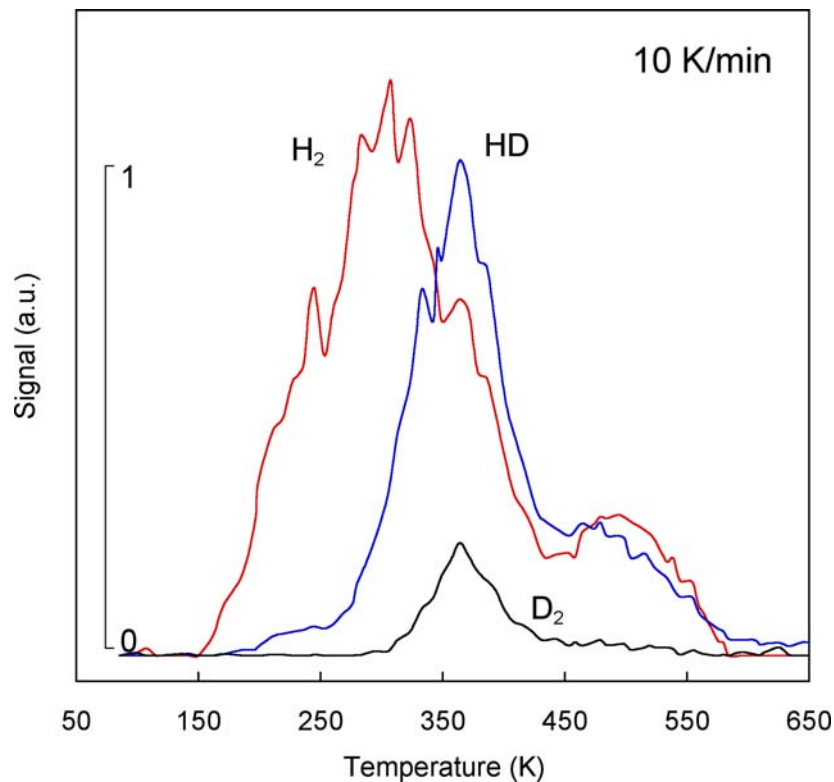


- Clear evidence is shown for the dissociation-spillover mechanism.
- The desorption step follows a reverse spillover process.

## Accomplishments Slides (con't)

TPD Result for 6 wt% Pt on Templated Carbon (3400 m<sup>2</sup>/g) after dosing with 0.4 atm H<sub>2</sub> or D<sub>2</sub> at 298 K for 5 min (followed by quench, gas phase removal and TPD)

### D<sub>2</sub> followed by H<sub>2</sub>

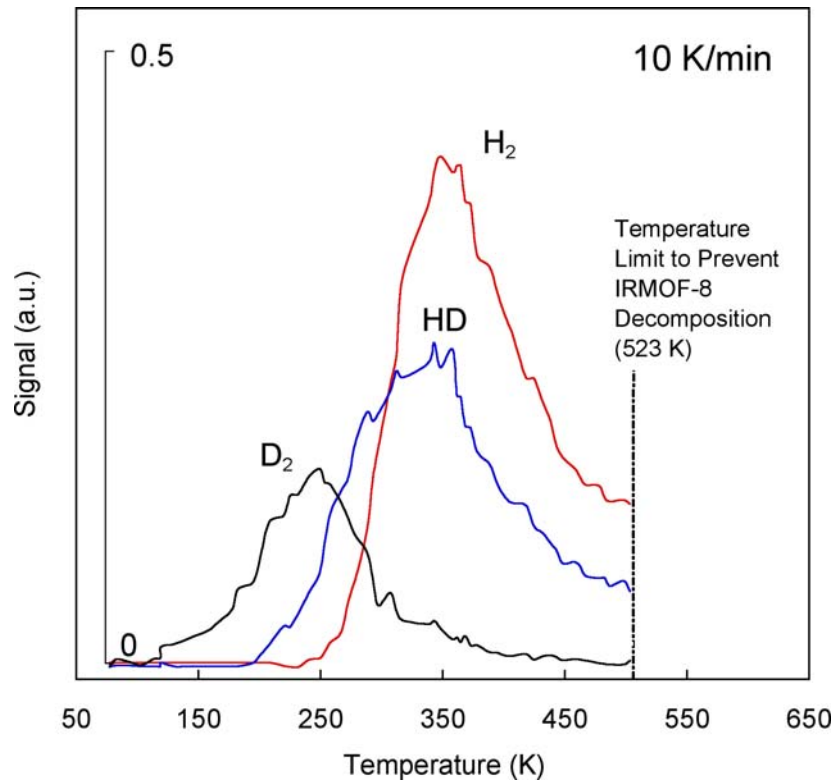


- Again, desorption follows reverse spillover.
- The small D<sub>2</sub> peak is possibly caused by premature recombination. Bond energy for D<sub>2</sub> > H<sub>2</sub>, i.e., 106 vs. 104 kcal/mol.

## Accomplishments Slides (con't)

TPD Result for IRMOF-8 (bridged to 5 wt% Pt/C) after dosing with 0.4 atm H<sub>2</sub> or D<sub>2</sub> at 298 K for 5 min (followed by quench, gas phase removal and TPD)

### H<sub>2</sub> followed by D<sub>2</sub>



- 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.,  $>3500$  m<sup>2</sup>/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 (D<sub>2</sub> 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

- H<sub>2</sub> dissociation and spillover can significantly increase the H<sub>2</sub> 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.