



# 2007 DOE Hydrogen Program Review

## **Hydrogen Storage by Spillover**

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**Project ID: ST3**

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# Overview

## Timeline

- Project start date: FY05
- Project end date: FY10
- Percent complete: 45%

## Budget

- Total project funding
  - DOE share: \$939,356
  - Contractor share: \$280,000
- Funding received in FY06: \$225,000
- Funding for FY07: \$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

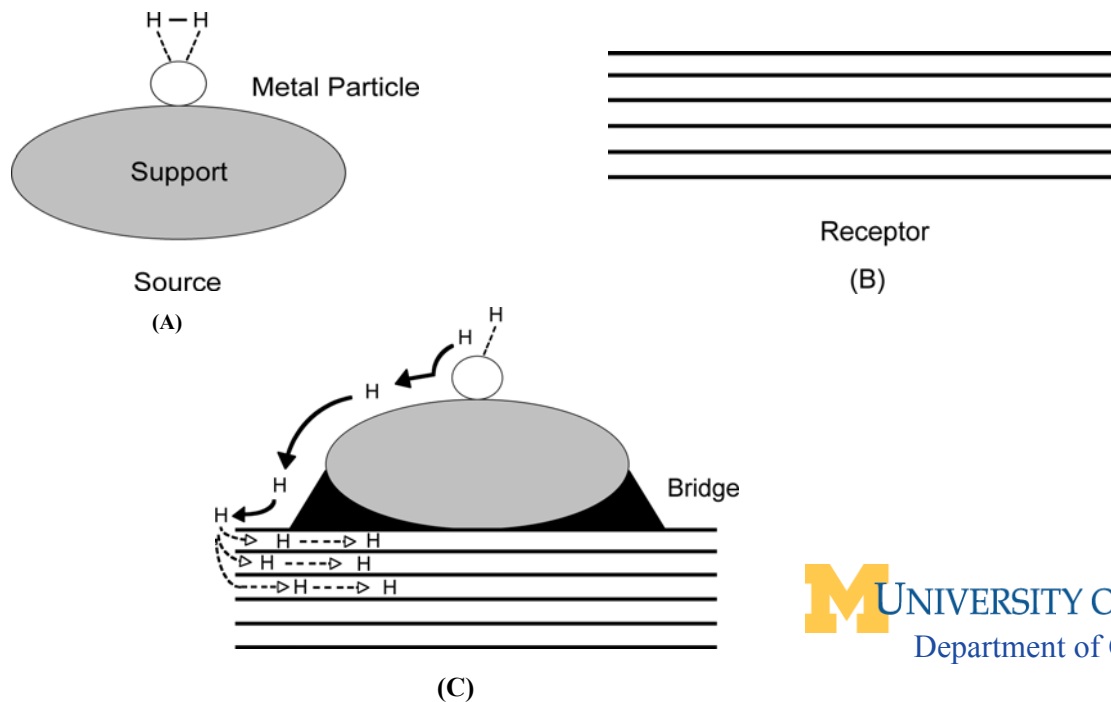
- Sample/adsorbed H Verification, Characterization & Mechanism  
**NREL, NIST, Rice U**
- Plan industrial collaboration after the initial phase of study and sorbent optimization

# Project Objectives

- To develop hydrogen storage materials with capacities in excess of 6 wt% (and 45 g/L) at room temperature by using the spillover mechanism
  - To develop and optimize our new Bridge-Building techniques for spillover to enhance hydrogen storage
  - To develop direct doping techniques for spillover
  - To obtain a mechanistic understanding for hydrogen spillover in nanostructured carbon-based materials for the purpose of hydrogen storage

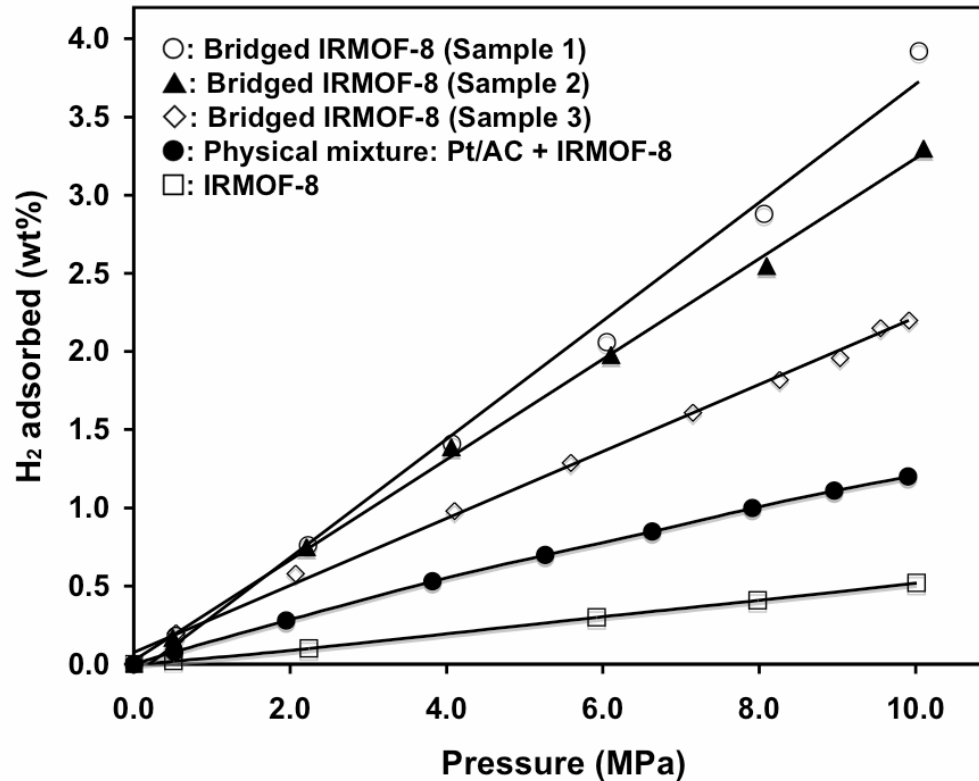
# Technical Approach

**Strategy for storage by spillover: (A) Supported metal catalyst for H<sub>2</sub> dissociation; (B) Sorbent as receptor for H; (C) Building carbon bridges (by carbonization of a precursor) for spillover, resulting in a composite sorbent. (Yang et al., U.S. Patent application filed, 2005)**



# Technical Accomplishments/ Progress/Results

Isotherms measured at 298K on Pt/AC catalyst (10%) and IRMOF-8 (80 or 90%)

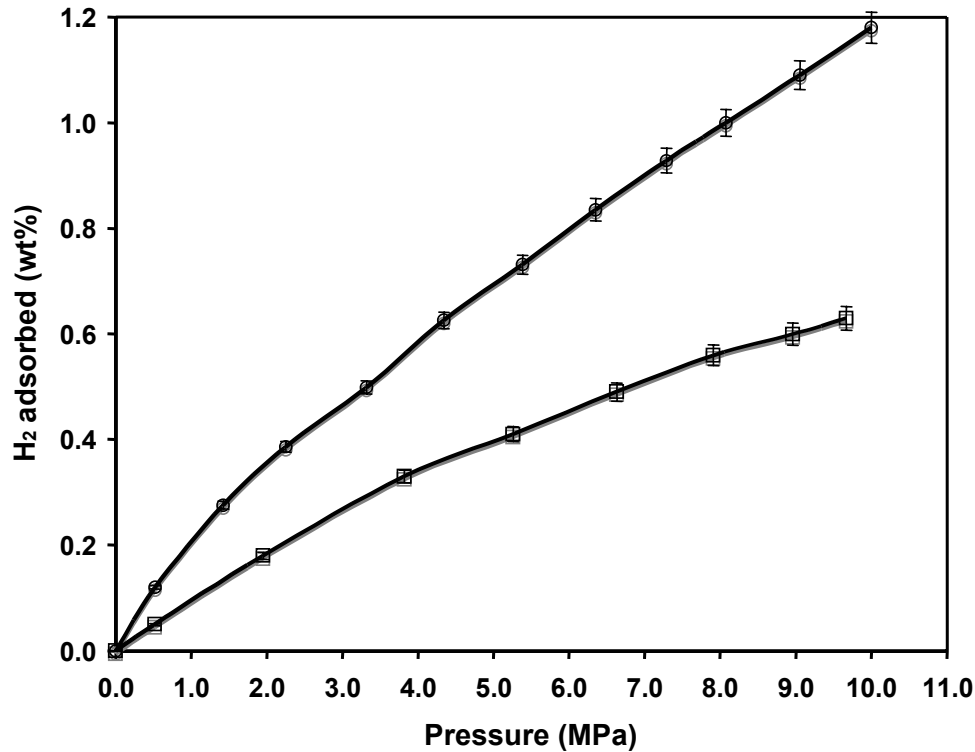


- Spillover can significantly enhance H<sub>2</sub> capacity.
- Bridge building can further increase H<sub>2</sub> capacity.
- MOFs are unstable as they decompose in ambient air (by hydrolysis), and are difficult to reproduce as shown by Samples 1-3 (by the same procedure).

\* All H<sub>2</sub> uptake values in this work are excess capacities.

# Accomplishments Slides (con't)

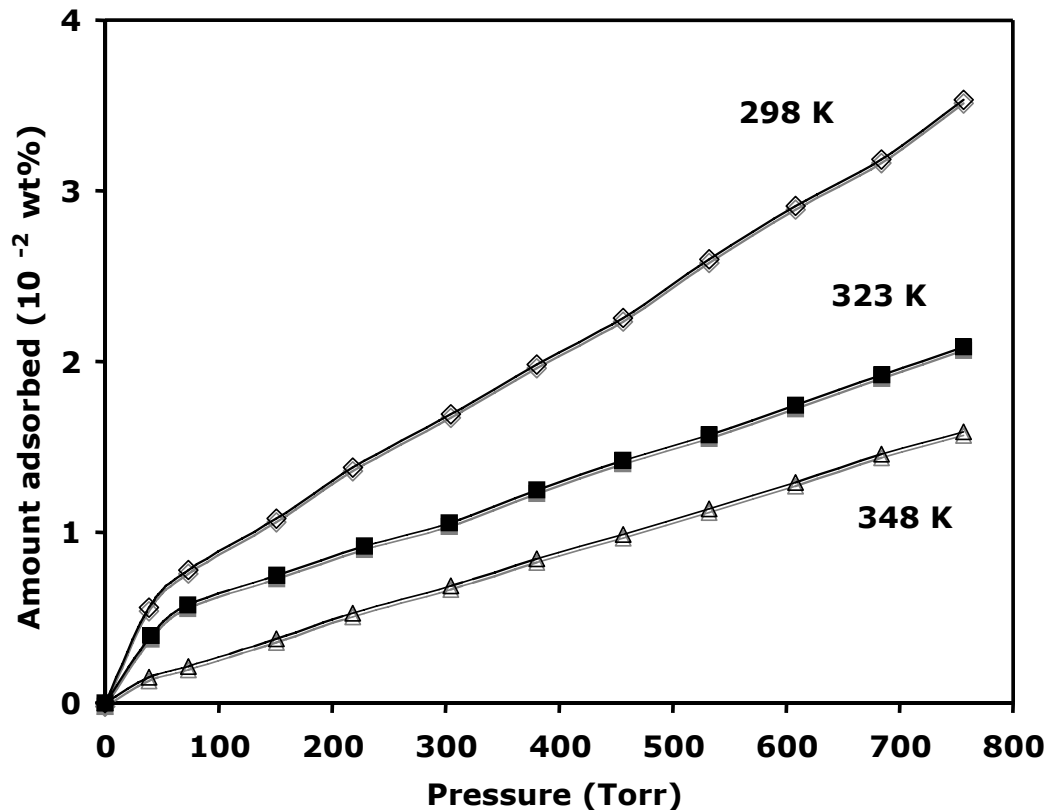
High-pressure Hydrogen Isotherms at 298 K on 6 wt%Pt/AX-21 by a new (direct) doping technique (error bars based on  $1\sigma$  of 4 samples)



- Spillover can significantly enhance H<sub>2</sub> capacity on AX-21
- Unlike MOFs, AX-21 is more stable and the H<sub>2</sub> capacities are reproducible.
- The data on Pt/AX-21 have been validated by DOE.
- Kinetics of spillover are slow; understanding of kinetics and mechanism is crucial for further development.

# Accomplishments Slides (con't)

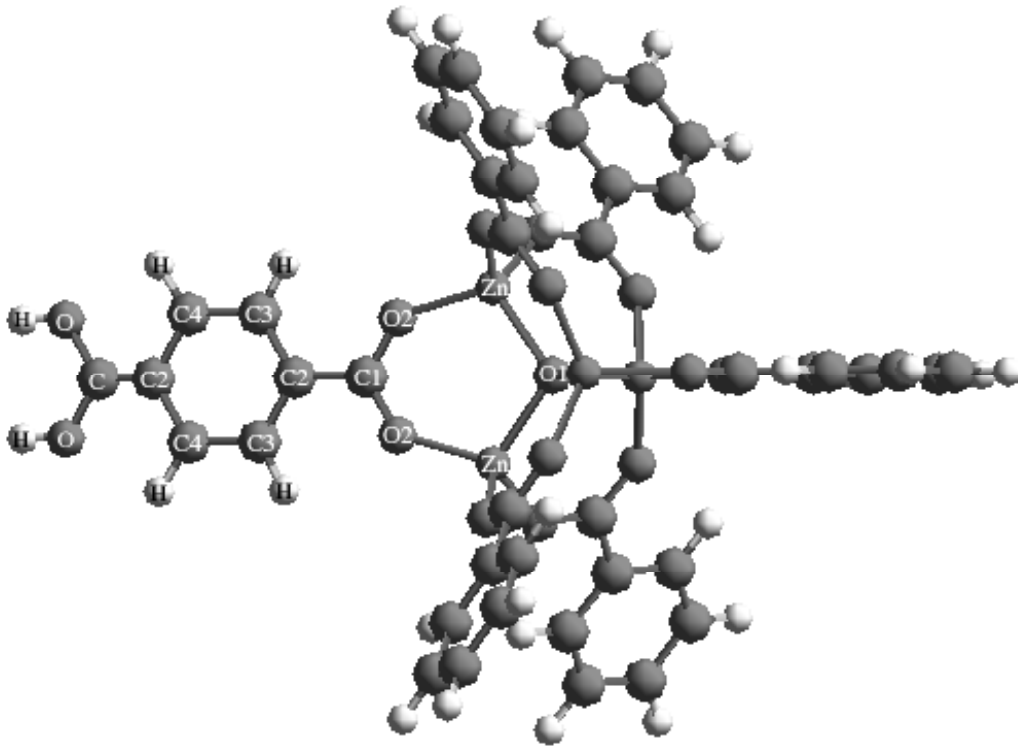
Low-P H<sub>2</sub> Adsorption Isotherms on Bridged IRMOF-8 (with Pt/AC Catalyst)



- Hydrogen storage capacity by spillover is temperature dependent
- From the temperature dependence, **the binding energies (isosteric heats of adsorption) are in the ideal range for storage: -24.8 kJ/mol (at 0.0078wt%), -21.3 kJ/mol (at 0.0108wt%) and -20.1 kJ/mol (at 0.0137wt%).**

# Accomplishments Slides (con't)

IRMOF-8 Model used for Molecular Orbital Computation (*left*) and Energy of Adsorption ( $E_{\text{ads}}$ ) for 1 H Atom on Each Site of IRMOF (*right*)



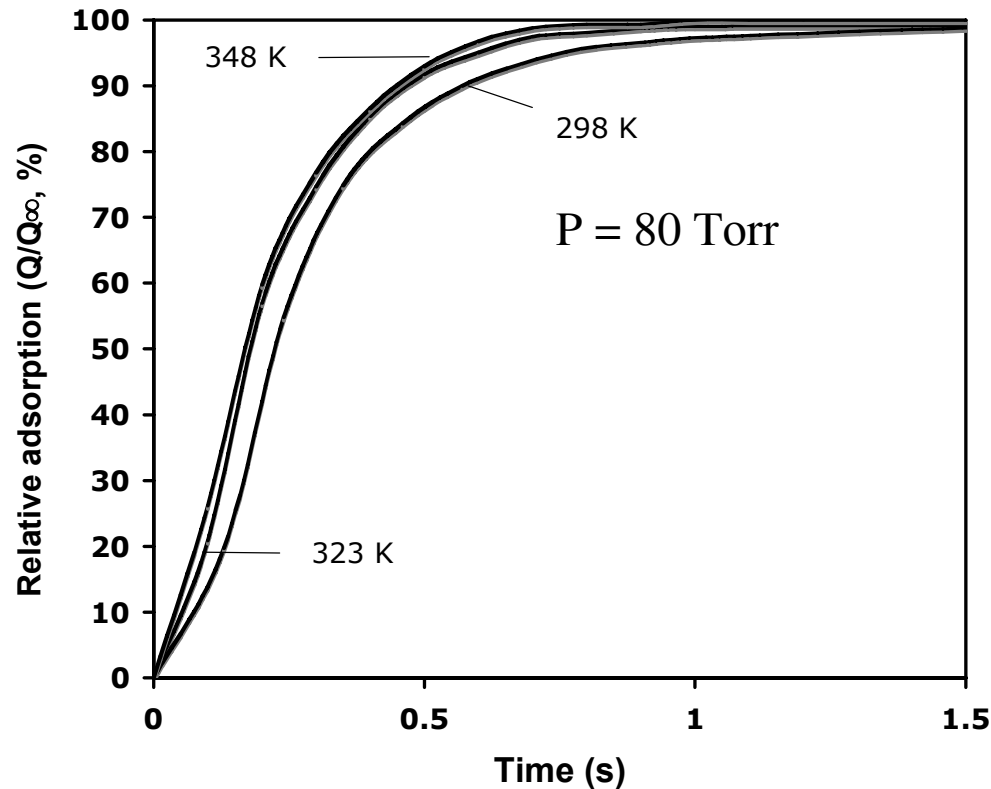
MOF Model Site	$E_{\text{ads}}$ (kJ/mol H)
O1	-3.60
O2	-40.33
C1	-7.66
C2	-15.15
C3	-49.62
C4	-41.82
Zn	-3.26

- Spillover H can form weak bonds with all sites of MOF.
- Two H atoms could bond with each O site.
- The bond energies agree with the **experimental heats of adsorption**.
- The **theoretical maximum amount** for IRMOF-8 by spillover is **7wt%** (or **71.4 g/L by volume**), which are promising for meeting 2010 DOE system wt. & vol. targets of **6wt% & 45g/L**.



# Accomplishments Slides (con't)

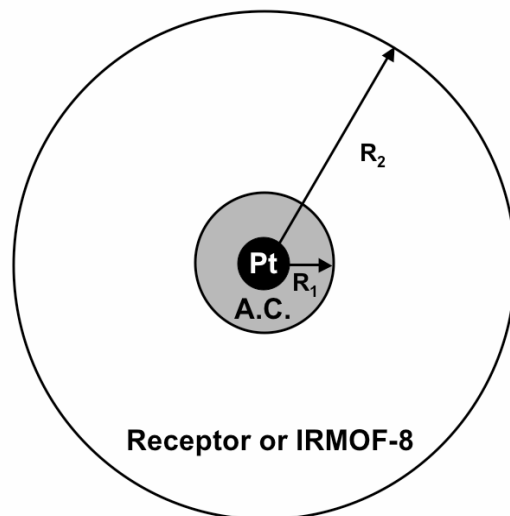
## Hydrogen Adsorption Kinetics on Bridged IRMOF-8 ( $Q_{\infty}$ = Equilibrium Amount)



- Spillover is very fast at low pressures
- The activation energy for surface diffusion is **9.3 kJ/mol** for H on bridged IRMOF-8,  $\sim 1/2$  to  $1/3$  of the binding energies
- Surface diffusion time constant,  $D/R^2$ , can be calculated from the uptake rate.  
But what is R?

## Accomplishments Slides (con't)

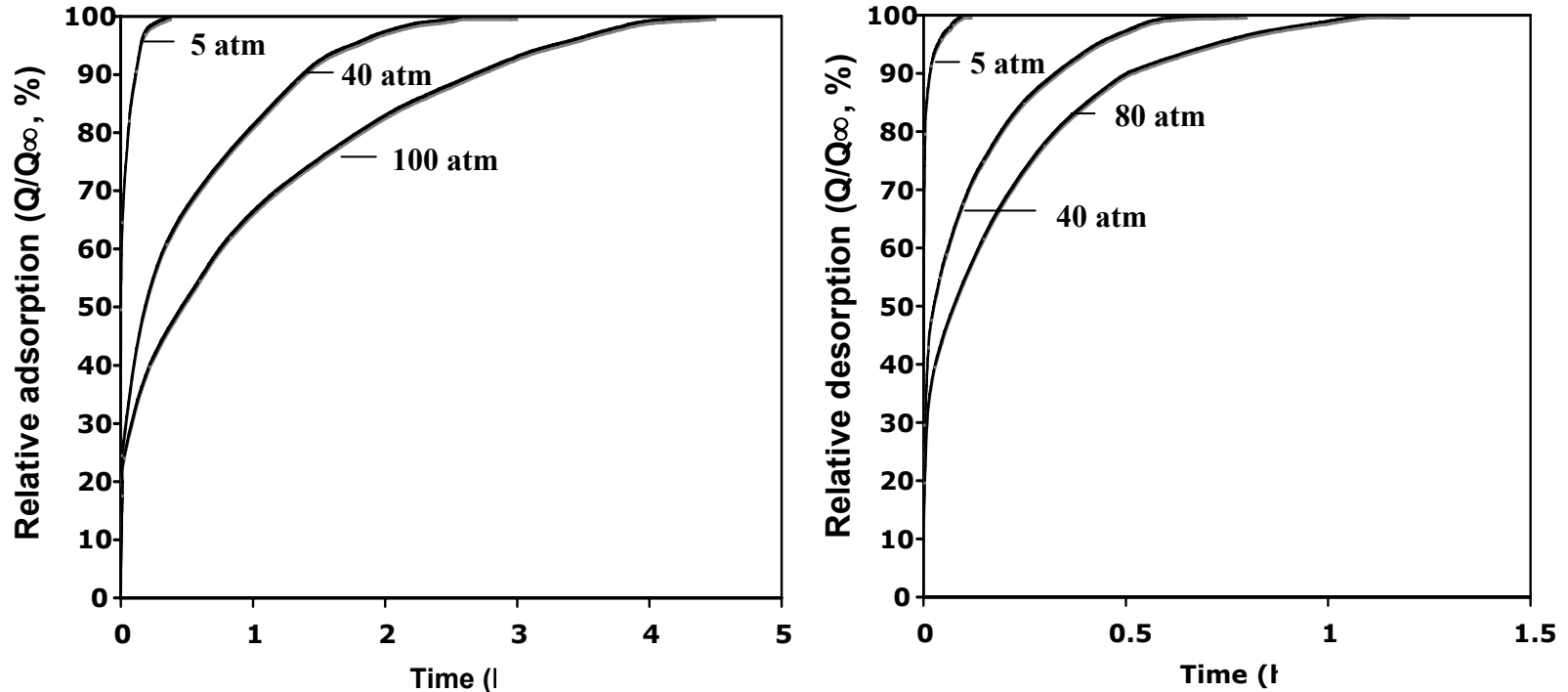
Simple 2-D Model for Hydrogen Spillover on Bridged IRMOF-8 including Pt/AC Catalyst (AC: Activated Carbon)



- Spillover is rate-limited by surface diffusion of H on receptor (not  $H_2$  dissociation on Pt)
- $R_2$  is the radius of diffusion for  $D/R^2$
- R depends on connectivity between receptor particles, and is increased by bridge building

# Accomplishments Slides (con't)

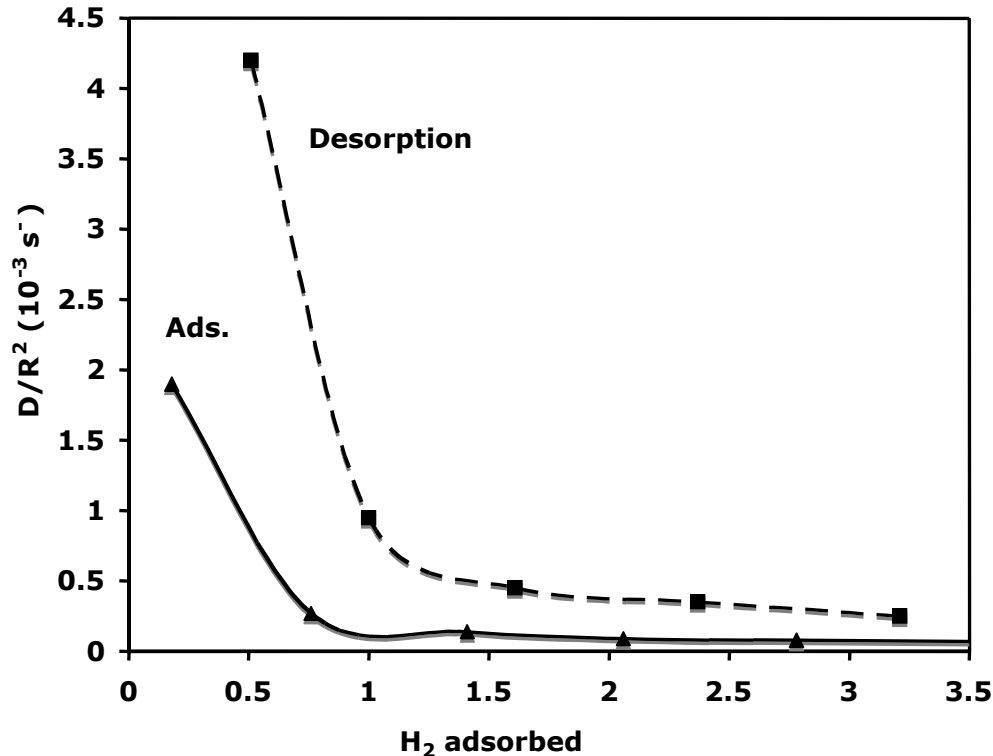
Rates of Adsorption ( $l$ ), and Desorption ( $r$ ) at Different Pressures on Bridged IRMOF-8 (T = 298 K).  $Q_{\infty}$  = Equilibrium Adsorption (a) or Desorption (b) Amount at Each Pressure



- Rates for both adsorption and desorption are fast at low loadings but become slower at higher loadings
- Desorption is faster than adsorption
- Desorption (or **discharge**) rate is **fast enough** for powering vehicle at **60 or 70 miles/hour**

## Accomplishments Slides (con't)

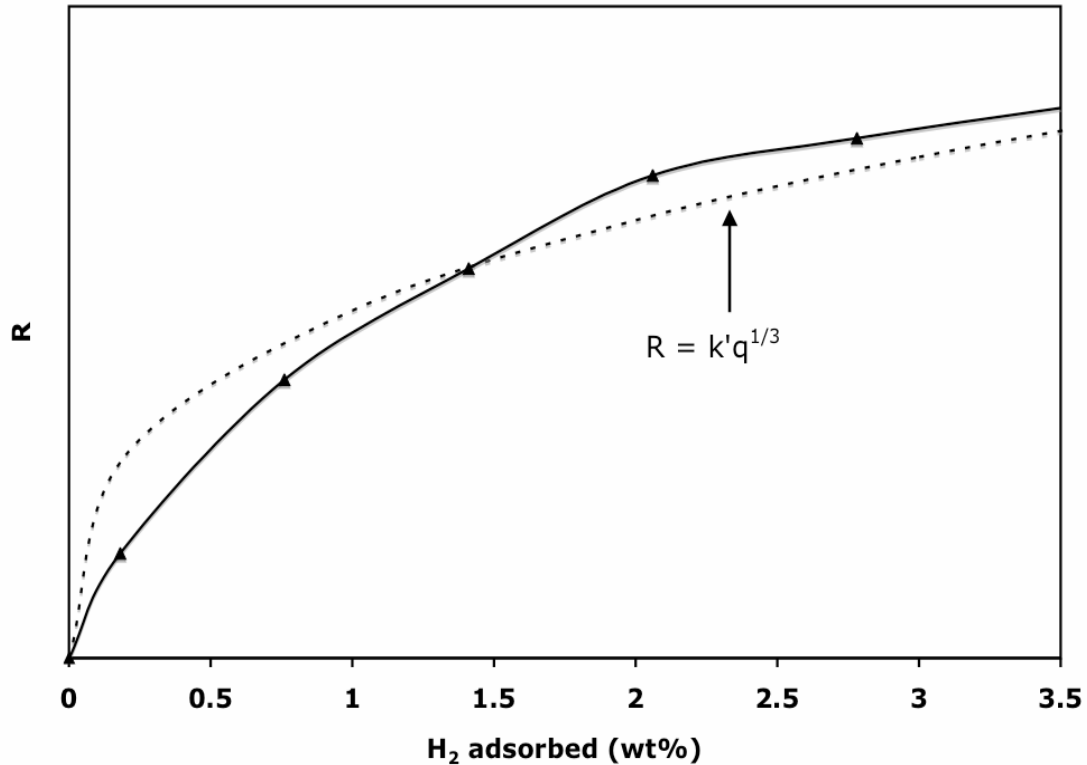
### $D/R^2$ as Function of $H_2$ Loading at 298 K for Bridged IRMOF-8



- Diffusion time constant ( $D/R^2$ ) declines with loading
- Diffusivity ( $D$ ) does not decline with loading; thus,  $R$  increases with loading
- This result is strong evidence that the **spillover H** also serves as bridges

# Accomplishments Slides (con't)

## Concentration Dependence of R (in $D/R^2$ )



- The diffusion distance for spillover (  $R$  ) increases with loading (  $q$  )
- The dependence can be expressed as  $R = kq^{1/3}$

## Accomplishments Slides (con't)

### Model for Adsorption on Spillover Systems:

Equilibrium constant  $K_1$  that relates the surface concentration (C) of H on activated carbon support to that on Pt:

$$K_1 = \frac{C_{AC}}{C_{Pt}}$$

Likewise,  $K_2$  is the equilibrium constant between MOF and Pt:

$$K_2 = \frac{C_{MOF}}{C_{Pt}}$$

At equilibrium, the total amount adsorbed (on AC and MOF):

$$q = K_1 q_{Pt} + \left( \frac{R_2}{R_1} \right)^3 K_2 q_{Pt}$$

where the isotherm on Pt is given by Langmuir (1918):

$$q_{Pt} = \frac{k_1 \sqrt{P_{H_2}}}{1 + k_2 \sqrt{P_{H_2}}} \quad \text{and} \quad R_2 = k' q^{1/3}$$

## Accomplishments Slides (con't)

Substituting  $q_{Pt}$  and  $R_2$  into the isotherm, one gets:

$$q = \frac{K_1 k_1 \sqrt{P_{H_2}}}{1 + k_2 \sqrt{P_{H_2}} - K' k_1 \sqrt{P_{H_2}}}$$

where  $K' = \left(\frac{k'}{R_1}\right)^3 K_2$

***This is the equilibrium isotherm for the spillover system. It's shape can be concave, convex or linear.....***

At the limit of very high pressures:

$$q \cong \frac{K_1 k_1}{k_2 - K' k_1}$$

- The first model for equilibrium isotherm for spillover is developed and verified.

## Future work plan/Objectives

- Storage by spillover with bridge-building on other high surface area MOFs: MIL-101, COF-1 (Covalent organic framework), and MOF-177
- New direct doping techniques on AX-21 and other ultra-high-surface-area carbons
- Test other promising receptors (sorbents) (for sorbent candidates, see R. T. Yang, *Adsorbents: Fundamentals and Applications*, Wiley, New York, 2003)
- Test different catalysts and bridge-building precursors, as well as techniques for bridge building
- Obtain basic understanding of the spillover process including equilibrium and kinetics, using deuterium isotope
- To achieve the 4.5 wt% (36 g/L) DOE (interim) system target at 298K in FY2007
- 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.
- Bridge building facilitates spillover thereby enhances storage.
- The binding energies of the spiltover hydrogen are in the ideal range of 20-25 kJ/mol for storage applications.
- The discharge rates of the spiltover hydrogen at ambient temperature are fast enough for automotive applications, but the charging rates at ambient temperature are slow.
- The model developed in this work is useful to those performing atomistic calculations (e.g., Boris Yakobson)
- Further understanding for the mechanism of spillover/storage is needed.
- Further development for different sorbent/catalyst/bridges is needed.

# Summary Table

**All data are @ 298K (Room Temperature)**

## **On-Board Hydrogen Storage System Targets**

(\*Data based on material only, not system value)

(\*\* Based on a bulk density of 1.02 g/cm<sup>3</sup> for MOF-8)

<b>Sorbent</b>	<b>Storage Parameter</b>	<b>Units</b>	<b>2010 System Target</b>	<b>FY06 Result*</b>	<b>FY07 Result*</b>	<b>Notes</b>
Bridged IRMOF-8	Wt. Storage Capacity	wt % H <sub>2</sub>	6 wt%	4 wt%	2.2-4 wt%	Highly unstable; low reproducibility
	Vol. Storage Capacity	Kg H <sub>2</sub> /L	45 g/L	40.8 g/L**		
	Desorption Temperature			298K	298K	
Metal/Carbon (Pt/AX-21)	Wt. Storage Capacity				1.2 wt%	More stable; Reproducible; Validated by NREL
	Vol. Storage Capacity					
	Desorption Temperature				298K	