2008 DOE Hydrogen Program Review
Hydrogen Storage by Spillover

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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 m²/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 (C₃H₂BO) bridged with 10% added Catalyst (5%Pt/AC) (80% COF-1 + 10% catalyst + 10% bridges)

- 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 H₂ 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)
Summary Results on Pure and Bridged MOFs
(Bridged MOFs: 10% Pt/AC + 80% MOF with 10% carbon bridges)

<table>
<thead>
<tr>
<th>MOF</th>
<th>BET Surface Area m²/g</th>
<th>( H_2 ) at 77K, 1 atm, wt%</th>
<th>( H_2 ) at 298K, 100 atm, wt%</th>
<th>Bridged Sample, ( H_2 ) 298K, 100 atm, wt%*</th>
<th>( \Delta H ) (Bridged), kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>IRMOF-8</td>
<td>548</td>
<td>1.4</td>
<td>0.4</td>
<td>2.2 - 4.0 (Vol. Capacity: 22.4-40.8 g/L*)</td>
<td>-21</td>
</tr>
<tr>
<td>COF-1</td>
<td>628</td>
<td>1.1</td>
<td>0.3</td>
<td>0.7</td>
<td>-7</td>
</tr>
<tr>
<td>HKUST-1</td>
<td>1296</td>
<td>2.2</td>
<td>0.3</td>
<td>1.1</td>
<td>-9</td>
</tr>
<tr>
<td>MIL-101</td>
<td>2930</td>
<td>1.8</td>
<td>0.5</td>
<td>1.5</td>
<td>-13</td>
</tr>
<tr>
<td>MOF-177</td>
<td>3100</td>
<td>1.5</td>
<td>0.6</td>
<td>1.5</td>
<td>-10</td>
</tr>
</tbody>
</table>

- 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.
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)

H₂ isotherms at 298 K on TC (templated carbon) & 6wt% metal-doped (ultrasound assisted) M/TC. All M/TC were H₂-reduced at 300°C except Ru/TC-T was thermally reduced (in N₂) at 900°C (1 hr) (Metal particle size: 2 - 4 nm)

- Storage on nanostructured carbons is far from reaching theoretical limit: >2wt% per 1000 m²/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$_2$ Isotopic Tracer - Accomplishments Slides (con’t)

TPD Result for 6 wt% Pt on Templated Carbon (3400 m$^2$/g) after dosing with 0.4 atm H$_2$ or D$_2$ at 298 K for 5 min (followed by quench, gas phase removal and TPD)

**H$_2$ followed by D$_2$**

- 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.