A Synergistic Approach to the Development of New Hydrogen Storage Materials, Part I

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Overview

Timeline
- Project start: 12/1/04
- Project end: 11/30/09
- Percent complete: 70%

Budget
- Total funding expected: $2.9M
  - $1.8M from DOE to UC Berkeley
  - $600k from DOE to LBNL
  - $500k in cost-sharing
- Funding FY08: $600k
- Funding FY09: $567k

Barriers
- Identify new materials enabling a hydrogen storage system achieving:
  - 2 kWh/kg (6 wt %)
  - 1.5 kWh/L (0.045 kg/L)
  - 4 $/kWh

Partners
- ChevronTexaco
- General Motors Corporation
- Electric Power Research Institute
Overall Program

Synthesis of porous polymers (Fréchet)
Synthesis of porous coordination solids (Long)
Calculations of H₂ binding energies (Head-Gordon)
Synthesis of destabilized hydrides (Richardson)
H₂ storage characterization instrumentation (Mao)
Metal/metal hydride nanocrystals (Alivisatos)
Synthesis of nanostructured boron nitrides (Zettl)
Theory for boron nitride materials (Cohen and Louie)

*Note that the results presented here are solely from Part I, which is funded through EERE.
H₂ Adsorption in a Hypercrosslinked Polymer

\[ \text{poly(chloromethylstyrene-co-divinylbenzene)} \]

- Surface area: 2,200 m²/g
- Sorption capacity: 3.8 wt %

77 K

Excess H₂ Adsorbed, wt %

Pressure, MPa

[Graph showing the adsorption isotherm at 77 K]
Hypercrosslinked Polyaniline

<table>
<thead>
<tr>
<th>Polyaniline</th>
<th>Reagent</th>
<th>Reactions</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><img src="image1.png" alt="Br-Bromo" /></td>
<td>Ullman 1 [K_2CO_3\text{ and CuBr in NMP} ]</td>
<td>Crosslinked polyaniline</td>
</tr>
<tr>
<td></td>
<td><img src="image2.png" alt="I-Iodo" /></td>
<td>Ullman 2 [Cu(PPh_3)_3 \text{ and } CsCO_3 \text{ in NMP, Toluene and DMF} ]</td>
<td></td>
</tr>
<tr>
<td></td>
<td><img src="image3.png" alt="Br-Bromo" /></td>
<td>Buchwald [Pd(dbu)_2 \text{ and tBuONa and DPPF in NMP, Toluene and DMF} ]</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Surf. area, m²/g</th>
<th>Pore volume, mL/g</th>
<th>Nano</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ullman 1 (dibromo)</td>
<td>156</td>
<td>0.13</td>
<td>0.03</td>
</tr>
<tr>
<td>Ullman 2 (diiodo)</td>
<td>96</td>
<td>0.04</td>
<td>0.01</td>
</tr>
<tr>
<td>Buchwald (diiodo)</td>
<td>343</td>
<td>0.25</td>
<td>0.13</td>
</tr>
<tr>
<td>Buchwald (tribromo)</td>
<td>368</td>
<td>0.25</td>
<td>0.11</td>
</tr>
</tbody>
</table>
Size Exclusion of Gases in Ultrananopores

<table>
<thead>
<tr>
<th></th>
<th>BET/N₂</th>
<th>Langmuir/H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Buchwald (tribromo)</td>
<td>157</td>
<td>354</td>
</tr>
</tbody>
</table>

H₂ adsorption only

Surface area, m²/g

Gas adsorbed, cm³ liquid equiv/g

Pressure, MPa

N₂ nanopore volume
Nanoporous Nitrogen-Containing Polymers

1,4-Diaminobenzene

Reagent Reaction Product

Crosslinked aromatic rings

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Surf. area, m²/g</th>
<th>Pore volume, mL/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Langmuir</td>
<td>Total</td>
</tr>
<tr>
<td>Diiodobenzene</td>
<td>192</td>
<td>0.01</td>
</tr>
<tr>
<td>Tribromobenzene</td>
<td>384</td>
<td>0.13</td>
</tr>
</tbody>
</table>
Stronger $\text{H}_2$ Adsorption

- Heat of adsorption, kJ/mol
- Hydrogen adsorbed, wt%

Diaminobenzene + tribromobenzene

Polyaniline + diiodobenzene
Hypercrosslinked Polypyrrole

Crosslinking with alkyl groups:

\[
\text{N} \begin{array}{c}
\text{H} \\
\end{array} + \text{CH}_2\text{I}_2 \xrightarrow{\text{Cs}_2\text{CO}_3} \text{N} \begin{array}{c}
\text{H} \\
\end{array} \text{CH}_2 \text{N} \begin{array}{c}
\text{H} \\
\end{array} \text{CH}_2 \text{N} \begin{array}{c}
\text{H} \\
\end{array} \text{CH}_2 \text{N} \begin{array}{c}
\text{H} \\
\end{array} \text{CH}_2 \text{N} \begin{array}{c}
\text{H} \\
\end{array}
\]

DMSO

Crosslinking with boron:

\[
\text{N} \begin{array}{c}
\text{H} \\
\end{array} + \text{Bi}_3 \xrightarrow{\text{Cs}_2\text{Co}_3 \text{ (fine powder)}} \text{B}
\]

Toluene
Increased H₂ Adsorption Capacity

Temperature: $T = 77 \text{ K}$

<table>
<thead>
<tr>
<th></th>
<th>Surface Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET/N₂</td>
<td>Ppy 738 m²/g</td>
</tr>
<tr>
<td></td>
<td>Pani 630 m²/g</td>
</tr>
</tbody>
</table>
Size Exclusion of Gases in Ultrananopores

No ultrananopores

Ultrananopores

Gas Adsorbed, cm$^3$/g liquid equiv.

Pressure, MPa

\[ \text{H}_2 \]

\[ \text{N}_2 \]

Gas Adsorbed, cm$^3$/g liquid equiv.

Pressure, MPa

\[ \text{H}_2 \]

\[ \text{N}_2 \]

Chemical structures of possible ultrananopores.
Hydrogen Storage in Completely-Activated MOF-5

• Currently best known material for cryogenic hydrogen storage at 77 K

• Performance at 298 K is poor owing to weak interaction of H₂ with surface
A Beryllium-Based Metal-Organic Framework

\[
\text{Be(NO}_3\text{)}_2 (\text{aq}) + \text{H}_3\text{BTB} \xrightarrow{\Delta \text{ DMSO/DMF}} \text{Be}_{12}(\text{OH})_{12}(\text{BTB})_4
\]

- Unprecedented structure with Be\textsubscript{12}(OH)\textsubscript{12} rings and 12 and 15 Å channels
- Nitrogen adsorption isotherm affords BET surface area of 4020 m\textsuperscript{2}/g
Low-Pressure H$_2$ Uptake in Be$_{12}$(OH)$_{12}$(BTB)$_4$

- Weak interaction of H$_2$ with surface, as desired for cryogenic storage
- At pressures up to 100 bar, expect gravimetric storage above MOF-5
Strong $\text{H}_2$ Binding in MOF-5 Functionalized with Cr$^0$

- Orbital interactions lead to strongly-bound $\text{H}_2$ complex that is too stable
- Need to generate charge-induced dipole interaction of 15-20 kJ/mol

$\Delta H = 78$ kJ/mol
(Head-Gordon et al.)
Exposed Mn$^{2+}$ sites lead to isosteric heat of adsorption of up to 10.1 kJ/mol

Need to increase strength of binding and concentration of open metal sites

*GM-supported research
Paddlewheel Frameworks

$M_3(BTC)_2$ (M = Cr, Cu, Zn, Mo)

- Preparation of $Cr_3(BTC)_2$ is new and activation of $Mo_3(BTC)_2$ is improved
- Enables comparison of $H_2$ binding at the open $M^{	ext{II}}$ coordination sites

<table>
<thead>
<tr>
<th></th>
<th>surface area ($m^2/g$)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>BET</td>
</tr>
<tr>
<td>$Cr_3(BTC)_2$</td>
<td>2340</td>
</tr>
<tr>
<td>$Cu_3(BTC)_2$ $^a$</td>
<td>1944</td>
</tr>
<tr>
<td>$Zn_3(BTC)_2$</td>
<td>collapsed</td>
</tr>
<tr>
<td>$Mo_3(BTC)_2$ $^b$</td>
<td>1280</td>
</tr>
<tr>
<td>$Mo_3(BTC)_2$</td>
<td>1800</td>
</tr>
</tbody>
</table>

$^a$ J. Am. Chem. Soc. 2006, 128, 3494
$^b$ J. Mater. Chem. 2006, 16, 2245
**H₂ Uptake in M₃(BTC)₂ (M = Cr, Mo)**

- First assessment of strength of H₂ binding to a Cr²⁺ center
- Expect better results for Co²⁺ and Ni²⁺ owing to a smaller ionic radius
- Attempts to synthesize analogues with other metal ions are underway
H₂ Uptake in Mg₂(DOBDC)


- Open Mg²⁺ sites lead to an isosteric heat of adsorption as high as 12.8 kJ/mol
- Neutron diffraction (Craig Brown, NIST) shows Mg···D₂ distance of 2.5 Å
Calculation of Substituent Effects

Metal chosen as Cr$^0$

<table>
<thead>
<tr>
<th></th>
<th>OMe</th>
<th>OH</th>
<th>NH$_2$</th>
<th>F</th>
<th>CH$_3$</th>
<th>H</th>
<th>COH</th>
<th>COOH</th>
<th>CF$_3$</th>
<th>NO$_2$</th>
<th>CN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy, kJ/mol</td>
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Legend:
- Electrostatics
- Back-donation
- Forward donation
Effect of Substituent (R)

- Electron-donating groups enhance binding, while electron-withdrawing groups reduce binding
  - Tunability is 7% of binding
  - Energies are for three bound H$_2$ molecules

- Correlates with back-donation, electrostatics

- Quantitative information; qualitative insight
  - BDC$^{2-}$ substituents can fine-tune binding
  - Coarse-tuning must come from different metals
Effect of Metal Substitution

- Heavier isoelectronic elements:
  - \((C_6H_6)Cr(H_2)_3\) binding per \(H_2\) of 68 kJ/mol
  - \((C_6H_6)Mo(H_2)_3\) binding per \(H_2\) of 84 kJ/mol

- Lighter transition elements:
  - \((C_6H_6)Cr(H_2)_3\) binding per \(H_2\) of 68 kJ/mol
  - \((C_6H_6)Ti(H_2)_4\) binding per \(H_2\) of 32 kJ/mol

- Shows coarse tuning is possible
  Still need to examine synergy of these effects
Computational Study of H$_2$ Binding in Cu-BTT

Measurements of H$_2$ binding energy within \( \text{HCu}[(\text{Cu}_4\text{Cl})_3(\text{BTT})_8] \) underway

- We will attempt to synthesize \( \text{HCu}[(\text{Cu}_4\text{Br})_3(\text{BTT})_8] \)

\( \omega \text{B97X-D/6-31G}^* \) calculations:

<table>
<thead>
<tr>
<th>X</th>
<th>E (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>-10.9</td>
</tr>
<tr>
<td>Cl</td>
<td>-10.9</td>
</tr>
<tr>
<td>Br</td>
<td>-13.0</td>
</tr>
<tr>
<td>I</td>
<td>--</td>
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</tbody>
</table>
Computational Study of H₂ Binding in “Zn-BTT”

[B97X-D/6-31G* calculations:

<table>
<thead>
<tr>
<th>X</th>
<th>(E_{Cu}/\text{kJ/mol})</th>
<th>(E_{Zn}/\text{kJ/mol})</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>-10.9</td>
<td>-13.8</td>
</tr>
<tr>
<td>Cl</td>
<td>-10.9</td>
<td>-15.9</td>
</tr>
<tr>
<td>Br</td>
<td>-13.0</td>
<td>-16.3</td>
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- Suggests significant improvement in binding energy for Zn-BTT frameworks
- We will therefore attempt to synthesize \(\text{Zn}_3[(\text{Zn}_4\text{Cl})_3\text{(BTT)}_8]_2\)
Destabilization of Metal Hydrides

- Attempts at alloying of Mg in order to reduce $\Delta H$
- Success in partial substitution to form $\text{Mg}_{1-x}\text{A}_x$ ($\text{A} = \text{Mn, Fe, Ni}$)
- Some increases in plateau pressures, but poor kinetics
- Attempts to substitute Na and Li for Mg are underway
Addition of MgF₂ Enhances Utilization of MgH₂

- MgF₂ slows desorption, but increases amount desorbed despite added weight
- Fluoride is distributed over particle surface; no evidence for bulk substitution (XRD)
Fluoride Effect Persists through Repeated Cycling

- Best results are for 3 mol% MgF$_2$ added

High-resolution TEM shows sharp faceting and marked inhibition of Mg grain growth in fluoride-containing samples.

Without fluoride, sintering and coarsening reduce surface area and contribute to Mg isolation.

MgH$_2$ + 3 mol% MgF$_2$ after 2nd desorption @ 300° C
Metal Catalyst Activity not Inhibited by Fluoride

Activity of added vanadium not inhibited by the presence of fluoride

Good utilization at 250 °C

Still below 1 wt % at 200 °C

- Future work: higher energy milling and alternative fluoride sources

- In addition, the effect of fluoride addition on ternary hydrides will be studied