Advanced Concepts for Hydrogen Storage

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Advanced Concepts Topics

• The following topics were identified by me through an in-depth review of the recent technical literature to search out new materials areas that might, with more research, have potential for improved hydrogen storage:
  – Advanced hydride materials
  – Hydride “alcoholysis”
  – BN nanotubes
  – Zeolites
  – Mesoporous materials
  – Nanosize metal powders
  – Hydrogen from iron hydrolysis

• These and other contributed ideas will be discussed by the Advanced Concepts Working Group
A. Zuttel, et.al., “Hydrogen Desorption From Lithiumtetrahydroboride (LiBH₄),
Hydrogen Generation from LiBH₄

- LiBH₄ (lithium tetrahydroboride)
  - Salt-like, hygroscopic, crystalline material
  - Density 0.68 g/cm³
  - Melting point 275°C

- LiBH₄ = LiH + B + 1.5H₂(g)
  - DG becomes negative at 450°C
  - Endothermic reaction
  - 13.8 wt.% H₂ released

- A low temperature H₂ release has been observed
  - 2.3 wt.% H₂ released at 118°C
  - May be related to an orthorhombic-to-tetragonal crystallographic change

- Is this a reversible process?

Hydrolysis of LiBH$_4$-Organics

Organics combined with LiBH$_4$ to reduce the severity and heat of the hydrolysis reaction

$$\text{[L]}\text{BH}_4 + 4\text{xH}_2\text{O} \rightarrow 4\text{xH}_2 + \text{xMOH} + \text{xB(OH)}_3 + \text{xL}$$

- **Compound 1:**
  - $[\text{HC(3,5-Me}_2\text{pz})_3]\text{LiBH}_4$
- Molecular weight of organics in the range of 300 g/mol

**Table 2. Heats of hydrolysis reaction of the novel hydrides**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\text{NaBH}_4$</th>
<th>$\text{LiBH}_4$</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>LJ mol hydride</td>
<td>2437</td>
<td>2311</td>
<td>74</td>
<td>65</td>
<td>-36</td>
<td>-54</td>
<td>-54</td>
</tr>
<tr>
<td>LK mol H$_2$ produced</td>
<td>2431</td>
<td>2311</td>
<td>650</td>
<td>477</td>
<td>699</td>
<td>898</td>
<td>1000</td>
</tr>
<tr>
<td>LK kg reactants</td>
<td>2496</td>
<td>2379</td>
<td>-692</td>
<td>-509</td>
<td>-753</td>
<td>-995</td>
<td>-1200</td>
</tr>
</tbody>
</table>

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<th>4</th>
<th>5</th>
<th>6</th>
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<td>LK kg reactants</td>
<td>-2496</td>
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<td>692</td>
<td>509</td>
<td>753</td>
<td>995</td>
<td>1200</td>
</tr>
</tbody>
</table>

**Table 3. Hydrogen yields and maximum temperatures**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\text{NaBH}_4$</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Yield*</td>
<td>89, 96</td>
<td>88, 100</td>
<td>98</td>
<td>56, 68</td>
<td>84</td>
<td>76, 87</td>
<td>104, 101</td>
</tr>
<tr>
<td>(C)*</td>
<td>97, 98</td>
<td>52, 67</td>
<td>63</td>
<td>84, 54</td>
<td>60</td>
<td>45, 45</td>
<td>55, 36</td>
</tr>
</tbody>
</table>

- **2.5 wt.% H$_2$ produced from Compound 1**

Chemical Reactions of Hydrides With Alcohols (Alcoholysis)

<table>
<thead>
<tr>
<th>Hydride</th>
<th>wt. % of H₂ (in respect to the hydride weight)</th>
<th>Litres of H₂ obtained per 1 kg of hydride</th>
<th>Total H₂ capacity (including the weight of the hydride and the alcohol - methanol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiH</td>
<td>25.4</td>
<td>2845</td>
<td>5.0</td>
</tr>
<tr>
<td>LiAlH₄</td>
<td>13.2</td>
<td>1478</td>
<td>7.2</td>
</tr>
<tr>
<td>Li₂AlH₆</td>
<td>16.8</td>
<td>1882</td>
<td>6.1</td>
</tr>
<tr>
<td>LiBH₄</td>
<td>23.1</td>
<td>2592</td>
<td>9.4</td>
</tr>
<tr>
<td>NaH</td>
<td>8.3</td>
<td>933</td>
<td>3.6</td>
</tr>
<tr>
<td>NaAlH₄</td>
<td>9.3</td>
<td>1045</td>
<td>5.9</td>
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<td>Na₂AlH₆</td>
<td>8.9</td>
<td>996</td>
<td>4.6</td>
</tr>
<tr>
<td>NaBH₄</td>
<td>13.3</td>
<td>1490</td>
<td>7.3</td>
</tr>
<tr>
<td>Li₂BeH₄</td>
<td>22.0</td>
<td>2460</td>
<td>7.1</td>
</tr>
<tr>
<td>Li₂BeH₆</td>
<td>22.5</td>
<td>2516</td>
<td>6.7</td>
</tr>
<tr>
<td>MgH₂</td>
<td>15.3</td>
<td>1716</td>
<td>4.5</td>
</tr>
<tr>
<td>CaH₂</td>
<td>9.6</td>
<td>1074</td>
<td>3.8</td>
</tr>
<tr>
<td>FeTiH₂</td>
<td>5.7</td>
<td>641</td>
<td>2.6</td>
</tr>
<tr>
<td>ZrH₂</td>
<td>4.3</td>
<td>484</td>
<td>2.6</td>
</tr>
<tr>
<td>TiH₂</td>
<td>8.1</td>
<td>905</td>
<td>3.5</td>
</tr>
<tr>
<td>MgAlH₆</td>
<td>11.7</td>
<td>1307</td>
<td>6.7</td>
</tr>
<tr>
<td>LiAlH₄</td>
<td>11.9</td>
<td>1329</td>
<td>8.1</td>
</tr>
<tr>
<td>ZrAlH₆</td>
<td>6.6</td>
<td>737</td>
<td>4.6</td>
</tr>
</tbody>
</table>

\[ MH_x + x \text{ROH} \rightarrow M(\text{OR})_x + x \text{H}_2 \uparrow \]

\[ \text{LiH} + \text{CH}_3\text{OH} \rightarrow \text{LiOCH}_3 + \text{H}_2 \]

\[ \text{NaH} + \text{CH}_3\text{OH} \rightarrow \text{NaOCH}_3 + \text{H}_2 \]

\[ \text{LiH} + 2\text{C}_2\text{H}_5\text{OH} \rightarrow \text{LiOOC}_2\text{H}_5 + \text{H}_2 \]

\[ \text{MgH}_2 + 2\text{C}_2\text{H}_5\text{OH} \rightarrow \text{Mg(OOC}_2\text{H}_5)_2 + 2\text{H}_2 \]

Controlled and convenient production of H₂ at room temperature and below room temperature

Hydrogen Adsorption by Boron Nitride Nanotubes

BN nanotubes synthesized through a chemical vapor deposition process by pyrolyzing a B-N-O precursor at 1730°C in a N₂/NH₃ atmosphere

Zeolite Structures

“Zeolite” is the Greek word for “boiling stone”

Comparison of Carbon and Zeolite Hydrogen Physisorption

- Physisorption at 77°K and 1 bar pressure
- Activated carbon Norit 990293
  - BET surface area 2030 m²/gm
  - 2.1 wt.% hydrogen adsorbed
    • Highest level of all carbon materials that were examined
- Zeolite ZSM-5
  - BET surface area 430 m²/gm
  - 0.7 wt.% hydrogen adsorbed
    • Highest level of all silica-based materials that were examined

Modeling suggests that Zeolite A can store at least 2 wt.% H₂ if all cage sites are filled.
Large Pore Zeolite UTD-1

- High silica zeolite
  - SiO$_2$/Al$_2$O$_3$ ratio ~ 70
- 14-ring channel
- One-dimensional channel along [001]
- Channel dimensions of 1.0 x 0.75 nm

Hydrogen storage in large pore zeolites has never been examined

Synthesis of Ordered Carbon Molecular Sieves by Templating

- Mesoporous silica molecular sieve MCM-48 impregnated with sucrose
- Sucrose converted to carbon by heating to 800-1100°C in vacuum or inert atmosphere
- Silica framework dissolved in aqueous solution of NaOH and ethanol

What are the hydrogen storage capabilities of this ordered carbon molecular sieve material?

SiO₂ Xerogels and Aerogels

- **Xerogels**
  - Produced by conventional drying of wet silica gel

- **Aerogels**
  - Produced by liquid-to-gas drying of wet silica gel
    - Supercritical fluid drying

**Structural Properties of SiO₂ Aerogels**

- Bulk density: 0.003-0.500 g/cm³
- Porosity: 80% - 99.8%
- Mean pore diameter: 20-150 nm
- BET surface area: 100-1600 m²/gm

No studies of hydrogen storage in SiO₂ xerogels and aerogels in the literature

Mesoporous Metal-Organic MOF-5

- Chemical formula $\text{Zn}_4\text{O} \cdot (\text{BDC})_3 \cdot (\text{DMF})_8 \cdot (\text{C}_6\text{H}_5\text{Cl})$
  - BCD = 1,4 - benzenedicarboxylate
  - DMF = dimethylformamide
- $\text{ZnO}_4$ tetrahedral clusters linked together by $\text{C}_6\text{H}_4\text{-C-O}_2$ “struts”
- Cubic crystal structure
- 1.294 nm spacing between centers of adjacent clusters
- **What are the hydrogen storage characteristics of this material?**

Mesoporous Organosilica Material

benzene-silica hybrid material
Hydrogen storage behavior?

Nanosize Metal and Ceramic Powders

- Nanosize metal and ceramic powders are commercially available
  - 10 - 100 nm diameters
- Nanosize metal powders
  - Au, Ag, Ni, Ti, Mo, Pt, W
- Nanosize ceramic powders
  - $\text{Al}_2\text{O}_3$, $\text{ZrO}_2$, $\text{CeO}_2$, $\text{CuO}$, $\text{MgO}$
  - $\text{SiO}_2$, $\text{TiO}_2$
Gold-Thiol Single Molecule Electrical Junctions


Can this approach be applied to hydrogen storage on nanosized metal powders?
Hydrogen Production by Grinding of Powders

“In wet grinding in liquid media including water or alcohol, it has been confirmed that a considerable amount of hydrogen is generated and causes an abnormal increase in pressure of a closed mill pot, even when the feed materials hardly react with them.”

Steel milling balls used to mill ceramic materials react with water to form hydrogen

\[3 \text{Fe} + 4 \text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 4 \text{H}_2\]

– 3.3 wt.% \(\text{H}_2\) including both Fe and \(\text{H}_2\text{O}\)

Hydrogen Storage in Modified Iron Oxides

H₂ Storage:  \[ \text{Fe}_3\text{O}_4 + 4\text{H}_2 = 3\text{Fe} + 4\text{H}_2\text{O} \]

H₂ Recovery:  \[ 3\text{Fe} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 4\text{H}_2 \]

- Additives accelerate reduction and oxidation reactions at lower temperatures
  - Al, Cr, Zr, Ga, V the most effective

Hydrogen Production by the Optimized Milling of Iron Powders

Concept:

- Cartridges filled with Fe powder, water, and Al$_2$O$_3$ balls (or powder)

- Mechanically vibrating the cartridge produces hydrogen gas
  - $3\text{Fe} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 4\text{H}_2$
  - Possibility of using ultrasonic agitation

- Replace cartridge when Fe is exhausted

- Recycle spent cartridges by heating in hydrogen gas
  - $\text{Fe}_3\text{O}_4 + 4\text{H}_2 = 3\text{Fe} + 4\text{H}_2\text{O}$
Advanced Concepts Summary

• A number of new approaches for hydrogen storage can be identified from the recent technical literature
  – Advanced hydride materials
  – Hydride “alcoholysis”
  – BN nanotubes
  – Zeolites
  – Mesoporous materials
  – Nanosize metal powders
  – Hydrogen from iron hydrolysis

• Additional study is required to establish the viability of these approaches for achieving the goal of significant improvements in hydrogen storage