Hydrogen Storage by Reversible Hydrogenation of Liquid-phase Hydrogen Carriers

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5/17/06

This presentation does not contain any confidential or otherwise restricted information
Overview

Timeline
• 2/04 – 2/08
• 80% complete

Budget
• Total project $6,121,242
  – DOE share $4,346,082 (71%)
• FY06 funding $1,000,000
• FY07 funding $1,025,000

Barriers
• Technical Barriers- Hydrogen Storage:
  A. System Weight and Volume
  C. Efficiency
  E. Charging/Discharging Rates
  R. Regeneration Processes

Interactions
• Current interactions: Auto OEM’s, Argonne National Laboratory
• Anticipated interactions: Chemical hydrides COE
Objectives

• Development of liquid-phase hydrogen storage materials (liquid carriers) with capacities and thermodynamic properties that enable hydrogen storage systems meeting 2010 DOE system-level targets. Optimization of dehydrogenation and hydrogenation catalysts.
  – Selective, reversible catalytic hydrogenation and dehydrogenation. Multiple cycles of use with no significant degradation of the materials.
  – Optimal heat of dehydrogenation (10-13 kcal/mole H₂), enabling the catalytic dehydrogenation at unprecedented temperatures (<200 °C).
  – Multi-functional liquid carriers that enable autothermal dehydrogenation.
  – Low volatility (b.p. > 300 °C), enabling the use of these liquids in simplified systems onboard vehicles and reducing exposure to vapors.
  – Enhanced rates of catalytic dehydrogenation with wash coat catalysts.
Approach: A regenerable organic liquid carrier for hydrogen storage onboard vehicles and stationary H₂ delivery

- 19 gallons of hydrogenated liquid carrier will reversibly store 5 kg hydrogen at 7 wt. % and 1g/cc density
Maximum energy efficiency: by (a) recovering the exothermic (-ΔH) of hydrogenation and (b) utilizing the waste heat from the power source to supply the ΔH for the endothermic dehydrogenation.

Autothermal hydrogen storage: Organic liquid carrier provides hydrogen to the power source and supplies the necessary heat of dehydrogenation via selective, H₂-reversible oxidation.
Experimental Discovery Approach

- **Carrier Selection**
  - Selection based upon structure/property relationships

- **Computational Modeling**
  - Must use proper models

- **Organic Synthesis**
  - High purity compounds

- **Selective Hydrogenation**
  - 99+% selective!
  - Many different types of molecules

- **Dehydrogenation Testing**
  - Large variation in rates between catalysts
  - Must also be 99+% selective
Technical Accomplishments/ Progress/Results

• Dehydrogenation catalyst development
  – Development of wash coated catalysts with high activity

• Organic liquid carrier discovery and testing
  – Towards lowering dehydrogenation temperatures
  – Investigation of new carrier candidates with increased available H₂ capacity

• A new concept: Autothermal hydrogen storage with organic liquid carriers
  – “Bi-functional” liquid carriers
  – Highly selective catalytic oxidation
Improved Catalyst Efficiency

• Our high-throughput catalyst testing is performed with slurry catalysts in small stirred tank reactors. However, dehydrogenation catalyst must be utilized in a stationary form in end-use application onboard vehicles.

• Dehydrogenation catalysts in pelletized form (eg. in a packed bed reactor) are limited by mass transfer
  – Effectiveness factor (% of available active metal catalyst) only 0.08 (reported last year)

• Thin catalyst coatings (10-20 μm) on a surface should improve effectiveness

• Thin coatings (wash coats) are catalysts used in practical reactors (eg. microreactors and monoliths)
Efficient Wash Coat Catalyst Developed

• Slurry reactors measure intrinsic catalyst activity
• Circulating flow reactor measures wash coat catalyst activity
• Model relates intrinsic activity to wash coat on a monolith
• High catalyst efficiency demonstrated (8X higher than pellets)

Hydrogen flow vs. conversion for dehydrogenation of perhydro-N-ethylcarbazole in a circulating flow reactor
Energetics of stepwise heat of dehydrogenation (kcal/mol H₂)

- Average β-carboline ΔH = 10.4 (cf. N-ethylcarbazole average ΔH =11.3)
  - Lower ΔH enables substantial conversion at lower temperatures than N-ethylcarbazole; closer to PEM FC waste heat temperature (Desirable ΔH range is 10-13 kcal/mol H₂)
Dehydrogenation of β-carboline

- Clean dehydrogenation observed (no byproducts), but only partial conversion – limiting the hydrogen storage capacity
- Temperatures required for dehydrogenation are higher than predicted by calculated dehydrogenation energetics

Conclusion: Catalyst activity is limited at very low temperatures (<150 °C)
- Testing of new catalysts necessary to improve performance
Comparison of Naphthyridine Isomers (Theoretical capacity 7.2 wt. % H₂)

![Chemical structures]

<table>
<thead>
<tr>
<th>Isomer</th>
<th>Calc. avg. ΔH (kcal/mol)</th>
<th>Melting point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1,5]</td>
<td>13.7</td>
<td>60-62</td>
</tr>
<tr>
<td>[1,6]</td>
<td>13.6</td>
<td>25-27</td>
</tr>
<tr>
<td>[1,7]</td>
<td>13.8</td>
<td>64-65</td>
</tr>
<tr>
<td>[2,6]</td>
<td>13.8</td>
<td>118-120</td>
</tr>
</tbody>
</table>

Large melting point differences between isomers. Average heat of dehydrogenation similar, but....
Energetics of stepwise heat of dehydrogenation

1,6-Naphthyridine, $\Delta H$ (kcal/mol)

Large differences in heats within possible reaction pathways for this isomer
Dehydrogenation of 1,6-Naphthyridine

Calculation

\[
\text{H}_2 \rightarrow \text{N} \rightarrow \text{H} \rightarrow \text{N} \rightarrow \text{H}
\]

• >7 wt. % hydrogen evolution, but reaction pathway goes through non-preferred intermediate (high temperature for second step)

• This carrier is not optimal for complete endothermic dehydrogenation, but may be suitable for autothermal dehydrogenation

Experiment

\[
\text{H}_2 \rightarrow \text{N} \rightarrow \text{H} \rightarrow \text{N} \rightarrow \text{H}
\]

-3 H\(_2\) 5% Pd/C 225 °C 1 atm. H\(_2\)

-2 H\(_2\) 5% Pd/C 275 °C 1 atm. H\(_2\)
• High conversion of 4,4’-Bipiperidine with ~5 wt. % H₂ evolved; significant amount of dimer formation.
Potential hydrogen carriers with >7 wt. % H₂

- 9.87 wt. % H₂
- Avg. ΔH = ca. 16.7 kcal/mol H₂

- 8.77 wt. % H₂
- Avg. ΔH = ca. 16.0 kcal/mol H₂

- Hydrogenation of nitriles can be achieved with high selectivity using “base modified” catalysts

- Dehydrogenation will require higher temperatures than other liquid carriers (ΔH above preferred 10-13 kcal/mol range)
Dehydrogenation of 1,3-bis(methylamino)cyclohexane

- ca. 3 wt. % H₂ evolved under catalytic dehydrogenation conditions
- Undesired coupling of imine (CH=NH) intermediates leads to cyclization and formation of oligomers
- Other isomers may be less prone to oligomerization and/or cyclization
Autothermal H₂ storage: a new concept for organic liquid H₂ carriers

- 5.4 wt.% H₂ (material basis) with no external input of heat
- Only partial conversion to the fully oxidized product is necessary for autothermal operation
- Highly selective catalytic chemistry is known for all of these steps
Autothermal H₂ storage: a new concept for organic liquid H₂ carriers
## Selectively oxidizable functional groups for liquid carriers

<table>
<thead>
<tr>
<th>Class of Selectively Oxidizable Functional Group</th>
<th>Functional Group in a Representative Molecule</th>
<th>Oxidative Dehydrogenation Product</th>
<th>Calorific Value per FW of Functional Group (kcal/gram)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary alcohols</td>
<td>a. Ar-CH$_2$OH</td>
<td>Ar-CHO</td>
<td>1.37</td>
</tr>
<tr>
<td></td>
<td>b. Ar-CH$_2$OH</td>
<td>Ar-COOH</td>
<td>3.33</td>
</tr>
<tr>
<td></td>
<td>c. R-CH$_2$OH</td>
<td>R-CHO</td>
<td>1.34</td>
</tr>
<tr>
<td>Secondary alcohols</td>
<td>R-CH(OH)-R’</td>
<td>RR’C=O</td>
<td>1.48</td>
</tr>
<tr>
<td></td>
<td>Ar-CH-OH-R</td>
<td>Ar-CO-R</td>
<td>1.69</td>
</tr>
<tr>
<td>Primary amines</td>
<td>R-CH$_2$NH$_2$</td>
<td>R-C≡N</td>
<td>2.79</td>
</tr>
<tr>
<td>Cyclic secondary amines</td>
<td>![Cyclic secondary amine structure]</td>
<td></td>
<td>0.53</td>
</tr>
<tr>
<td>N-Methyl tertiary amines</td>
<td>RR’N-CH$_3$</td>
<td>RR’CH(O)</td>
<td>6.53</td>
</tr>
<tr>
<td>Sulfides to Sulfoxides</td>
<td>R-S-R’</td>
<td>![Sulfide to Sulfoxide structure]</td>
<td>0.84</td>
</tr>
<tr>
<td>Sulfoxides to Sulfones</td>
<td>R-S(O)-R’</td>
<td>R(SO$_2$)R’</td>
<td>1.10</td>
</tr>
</tbody>
</table>
Experimental example (non-optimized): Catalytic dehydrogenation and selective oxidation of 4,7-phenantrholene

\[
\text{NH} \quad \text{NH} \quad \text{NH}
\]

\[
\rightarrow \quad \text{catalyst 1} \quad 230 \, ^\circ \text{C} \quad 1 \, \text{atm. H}_2
\]

\[
\quad \text{+ 5 H}_2
\]

\[
\rightarrow \quad \text{catalyst 2} \quad 230 \, ^\circ \text{C} \quad 1 \, \text{atm. air}
\]

\[
\quad \text{+ 2 H}_2\text{O}
\]

\[
\text{hydrogenation catalyst} \quad 170 \, ^\circ \text{C, 50 atm. H}_2
\]
Experimental example (non-optimized): Catalytic dehydrogenation and selective oxidation of 1-(Carbazolyl)-2-Hydroxypropane

\[
\begin{align*}
\text{N} & \quad \text{H}_3\text{C} \\
\text{N} & \quad \text{H}_3\text{C} \\
\text{OH} & \quad \text{OH} \\
5\% \text{Ru/Al}_2\text{O}_3 & \quad 1 \text{ atm. air} \\
190 \degree \text{C} & \quad \text{H}_3\text{C} \\
\end{align*}
\]

- Very high selectivity (>99%) observed for oxidation of alcohol to ketone
Future Work

- Development of new, improved liquid carriers
  - High dehydrogenation conversion < 120 °C (e.g., using carbolines)
    - Need: Better catalyst activity at very low temperatures
  - Complete amine → nitrile dehydrogenation studies
    - Increase selectivity for amine → nitrile dehydrogenation (e.g., activated nitriles)

- Complete demonstration of autothermal dehydrogenation concept
  - Investigate multiple functional group transformations
    - alcohol → ketone
    - alcohol → carboxylic acid

- Additional improvement of surface-supported catalysts
  - Higher dehydrogenation rates
  - Characterization of hydrogen quality

- We seek input from DOE AMR reviewers and the FreedomCAR tech. team on the potential value of the autothermal dehydrogenation concept
Project Summary

• **Relevance**: Development of practical hydrogen storage technology with desirable capacity, safety characteristics, efficiency and integration with hydrogen production/delivery

• **Approach**: Reversible, selective hydrogenation of organic liquid carriers. Multiple concepts to provide heat to liberate hydrogen onboard vehicle.

• **Technical Accomplishments**: Development of new liquid carriers with >7 wt. % capacity, Initial demonstration of autothermal hydrogen storage concept

• **Future Research**: Demonstrate complete autothermal dehydrogenation cycle with sufficient selectivity, rates. Complete testing of carriers with >7 wt. % capacity or dehydrogenation <120 °C.