Hydrogen Storage by Reversible Hydrogenation of Liquid-phase Hydrogen Carriers

Alan Cooper, Aaron Scott, Donald Fowler, Frederick Wilhelm, Vyriil Monk, Hansong Cheng, Guido Pez
Air Products and Chemicals, Inc.
June 9, 2008

STP 25

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

Timeline
• 2/04 – 9/08
• ~95% complete

Budget
• Total project $6,121,242
  – DOE share $4,346,082 (71%)
• FY07 funding $1,025,000
• FY08 funding $738,082

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
Objectives – H$_2$ Storage (2007-2008)

- 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 H$_2$), enabling the catalytic dehydrogenation at unprecedented temperatures (<200$^\circ$C).
Objectives (cont.) – H₂ Storage (2007-2008)

- Multi-functional liquid carriers that enable autothermal dehydrogenation (primary project focus in 2007-2008)

- 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.
Autothermal Dehydrogenation Reactor System Schematic

Endothermic dehydrogenation of the carrier thermally coupled to an exothermic selective oxidation of the dehydrogenated carrier → no external heat input requirement
Autothermal Cycle Development Using Fluorene – Energetics

Step 1:
- Offboard: + 7 H₂
- Onboard: - H₂O

Step 2:
- Onboard: - 6 H₂, +84 kcal/mol* (endothermic)

Step 3:
- Offboard: O₂ (from air), - H₂O, -81 kcal/mol* (exothermic)

*Calculated using ΔH_f°
Step 1: Regeneration of oxidized carrier (fluorenone) back to perhydrofluorene

1) Pd/SiO₂ catalyst, 70°C, 8 bar H₂
2) Ru/Al₂O₃ Catalyst, 160°C, 60 bar H₂

>99% conversion and selectivity

Fluorenone
Solid m.p. 83°C
b.p. ~350°C

+ H₂O
>99% cis,cis conformer
Liquid b.p. 253°C

Other catalysts (e.g., Pd, Rh) are equally selective, but yield mixtures with other conformers that have higher dehydrogenation temperatures.
Step 2: Dehydrogenation of *cis,cis*-perhydrofluorene to fluorene (endothermic)

\[
\text{H}_2\text{H} \\
5\% \text{Pt/Al}_2\text{O}_3 \\
1 \text{ bar H}_2, \\
235^\circ\text{C} \\
\text{H}_2\text{H}
\]

\[\text{+ 6 H}_2 (6.7 \text{ wt. } \%)\]

>99% conversion and selectivity at 235°C

Not possible with a “natural” e.g., *cis*, *trans* mixture of conformers.
Step 3: Selective oxidation (exothermic) of fluorene to fluorenone

- Gas phase oxidation
- Very high selectivity and conversion

\[ \text{Iron/Vanadium oxide} \quad 350^\circ C \quad \text{>99\% conversion} \quad \text{>99\% selectivity} \]
## Selectively oxidizable functional groups for liquid carriers (I)

<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>Activated hydrocarbon groups</td>
<td><img src="image" alt="activated hydrocarbon group" /></td>
<td><img src="image" alt="oxidation product" /></td>
<td><img src="image" alt="calorific value" /></td>
</tr>
<tr>
<td>a. Ar-CH₃</td>
<td>Ar-CH₂OH</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>b. Ar-CH₃</td>
<td>Ar-CH(O)</td>
<td>5.2</td>
<td></td>
</tr>
<tr>
<td>c. Ar-CH₃</td>
<td>Ar-COOH</td>
<td>9.3</td>
<td></td>
</tr>
<tr>
<td>d. Ar-CH₂-Ar</td>
<td><img src="image" alt="oxidation product" /></td>
<td>5.9</td>
<td></td>
</tr>
<tr>
<td>e. <img src="image" alt="activated hydrocarbon group" /></td>
<td><img src="image" alt="oxidation product" /></td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>Primary alcohols</td>
<td>a. Ar-CH₂OH</td>
<td>Ar-CHO</td>
<td>1.4</td>
</tr>
<tr>
<td>b. Ar-CH₂OH</td>
<td>Ar-COOH</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>c. R-CH₂OH</td>
<td>R-CH(O)</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>Secondary alcohols</td>
<td>R-CH(OH)-R'</td>
<td>RR’C=O</td>
<td>1.5</td>
</tr>
<tr>
<td>Ar-CH-OH-R</td>
<td>ArRC=O</td>
<td>1.7</td>
<td></td>
</tr>
</tbody>
</table>
## Selectively oxidizable functional groups for liquid carriers (II)

<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 amines</td>
<td>CH$_3$-CH$_2$NH$_2$</td>
<td>R-C≡N</td>
<td>2.8</td>
</tr>
<tr>
<td>Cyclic secondary amines</td>
<td><img src="CyclicSecondaryAmines.png" alt="Image" /></td>
<td><img src="CyclicSecondaryAmines.png" alt="Image" /></td>
<td>0.5</td>
</tr>
<tr>
<td>N-Methyl tertiary amines</td>
<td>(CH$_3$)$_2$N-CH$_3$</td>
<td>(CH$_3$)$_2$N-CH(O)</td>
<td>6.5</td>
</tr>
<tr>
<td>Sulfides to Sulfoxides</td>
<td>R-S-R' (R,R'=CH$_3$)</td>
<td><img src="SulfidesToSulfoxides.png" alt="Image" /></td>
<td>0.8</td>
</tr>
<tr>
<td>Sulfoxides to Sulfones</td>
<td>R-S(O)-R' (R,R'=CH$_3$)</td>
<td>R(SO$_2$)R'</td>
<td>1.1</td>
</tr>
</tbody>
</table>
Potential Autothermal Cycle using N-methylcarbazole

Excess heat available from oxidation of methyl group to aldehyde
Summary

• An autothermal hydrogen storage cycle is possible using perhydrofluorene with:
  – ~95% conversion on dehydrogenation (net 6.3 wt. %)
  – 100% conversion during selective oxidation

• We have demonstrated all three steps of an autothermal hydrogen storage cycle with >99% selectivity.
  – Hydrogenation of fluorenone to perhydrofluorene
  – Dehydrogenation of perhydrofluorene to fluorene
  – Selective oxidation of fluorene to fluorenone

• A range of functional groups is available for exothermic selective oxidation reactions in designing new carriers.