An overview of liquid hydrogen carrier R&D supported by the DOE Fuel Cell Technologies Office

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Fuel Cell Technologies Office
Hydrogen Storage Program Manager
• Definition of an ideal liquid hydrogen carrier
• How liquid hydrogen carriers could fit in the infrastructure
• Overview of key properties needed for an effective carrier
• Overview of DOE supported R&D on liquid carriers
  – Air Products and Chemicals Inc.
  – Hawaii Hydrogen Carriers
  – University of Oregon/Boston College
• \( \text{H}_2 \) Infrastructure – potential areas liquid carriers could offer advantages
What is not being covered

• Solid or gaseous carriers

• “One-way” carriers – e.g., ammonia, hydrocarbon reformation

• Slurries – solid carrier suspended in a slurring agent – e.g., ammonia borane or alane (AlH$_3$) in AR 20 silicon oil
What’s an ideal liquid H₂ carrier?

- Stable with little to no release of hydrogen under the range of ambient conditions

  \[\text{LQ} + \text{H}_2 \xleftrightarrow{\text{catalyst}} \text{LQ}^*\text{H}_2 + \text{heat}\]

- Rapidly able to release hydrogen using available “waste” heat and temperature (e.g., PEM fuel cell)
- Remains in liquid phase throughout all stages of hydrogenation/dehydrogenation and temperature range
- Low volatility and able to be separated from the released hydrogen easily
- Little degradation on cycling (i.e., minimal side reactions and loss of volatile components) – long cycle life
Operation scheme for “2-way” liquid hydrogen carriers

Estimate: ~72 liters of hydrogenated liquid carrier could reversibly store 5 kg of hydrogen at 7 wt.% and 1g/cc density.

~ 50% of the volume required for 700 bar compressed H₂ at ambient temperatures!

Liquid Carrier Pathway

Carrier Production

Carrier Regeneration

Energy & Raw Materials

Hydrogen Production

Delivery

Fueling Station

On-Board Vehicle Process

Hydrogen Generator

Return

Vehicle

- - - Carrier Present for All Options

--- Carrier for Round Trip Options

----- Carrier for On-Board H₂ Production

--- H₂
Potential for use onboard vehicles

Currently not a focus area for the DOE-EERE Fuel Cell Technologies Office

LQ = liquid carrier
Δ = heat
Liquid Hydrogen Carrier Development
Calculated dehydrogenation enthalpy, $H_D^\circ$ (kJ/mole $H_2$), for three series of polyaromatic hydrocarbons as a function of the number of rings. The PM3 semi-empirical method was used for the calculations. (Air Products, Final Report, DOE Award # DE-FC36-04GO14006)
The aromatic stabilization energy of polyaromatic hydrocarbons is determined by the relative number of aromatic sextet structures in the molecules. (Clar, E. in “Polycyclic Hydrocarbons”, Academic Press, NY, 1964, Chapter 16)
Effect of heteroatoms in the rings

Calculated dehydrogenation enthalpy, $H_D^\circ$ (kJ/mole $H_2$) for N-heterocycles and the corresponding polyaromatic hydrocarbons (PM3 method) (*Air Products, Final Report, DOE Award # DE-FC36-04GO14006*)
Impact of *cis-trans* isomerization

*Cis-trans* isomerism in naphthalene and the relative energetics (*Air Products, Final Report, DOE Award # DE-FC36-04GO14006*)
Standard enthalpies of formation, Hf° and standard dehydrogenation enthalpies, HD°, (kcal/mole H2) of N-heterocyclic aromatic and cycloaliphatic molecule pairs. (Air Products, Final Report, DOE Award # DE-FC36-04GO14006)
## Alkylated carbazoles

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Formula</th>
<th>Melting Point</th>
<th>Theoretical Capacity (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbazole</td>
<td>C$<em>{12}$H$</em>{9}$N</td>
<td>250°C</td>
<td>6.7</td>
</tr>
<tr>
<td>N-methylcarbazole</td>
<td>C$<em>{12}$H$</em>{9}$N-CH$_{3}$</td>
<td>90°C</td>
<td>6.2</td>
</tr>
<tr>
<td>N-ethylcarbazole</td>
<td>C$<em>{12}$H$</em>{9}$N-CH$<em>{2}$CH$</em>{3}$</td>
<td>70°C</td>
<td>5.7</td>
</tr>
</tbody>
</table>

Yields of nickel-catalyzed hydrogenation and N-alkylation of carbazole.

*(Air Products, Final Report, DOE Award # DE-FC36-04GO14006)*

<table>
<thead>
<tr>
<th>Alkyl group</th>
<th>Yield of perhydro-N-alkylcarbazole</th>
<th>Yield of partially hydrogenated N-alkylcarbazole</th>
<th>Hydrogenated carbazole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl</td>
<td>98%</td>
<td>2%</td>
<td>0%</td>
</tr>
<tr>
<td>Ethyl</td>
<td>97%</td>
<td>3%</td>
<td>0%</td>
</tr>
<tr>
<td>n-propyl</td>
<td>97.5%</td>
<td>2.5%</td>
<td>0%</td>
</tr>
<tr>
<td>iso-propyl</td>
<td>59%</td>
<td>7%</td>
<td>34%</td>
</tr>
</tbody>
</table>
Dehydrogenation conditions

- Typical dehydrogenation experimental conditions for perhydro-N-alkylcarbazole performed by Air Products:
  - the dehydrogenation catalyst was slurried (1-5 wt.%) in liquid perhydro-N-alkylcarbazole
  - 1 atm. initial hydrogen pressure
  - temperature ramped at a controlled rate up to 150-200 °C
  - slurry stirred at 500-800 rpm
  - rate of hydrogen release from the reactor measured with a flow meter

GC-MS analysis of intermediates indicate hydrogen released in steps of 2 hydrogen molecules. Scheme above includes calculated electronic energy change (DE; kJ/mol H2) for the stepwise dehydrogenation of perhydro-N-ethylcarbazole
Stability with cycling

Five sequential dehydrogenation steps of hydrogenation/dehydrogenation cycling experiments of N-ethylcarbazole. (Air Products, Final Report, DOE Award # DE-FC36-04GO14006)
Effect of catalyst on dehydrogenation performance

Overlay of perhydro-N-ethylcarbazole hydrogenationation data for a range of catalysts.

(Air Products, Final Report, DOE Award # DE-FC36-04GO14006)
Effect of catalyst, H$_2$ release rate and temperature on H$_2$ purity

Dehydrogenation of perhydro-N-ethylcarbazole with palladium/platinum on alumina. The table shows the temperature and hydrogen flow rate at the time when the samples were analyzed.

<table>
<thead>
<tr>
<th>Pd on alumina</th>
<th>Pt on alumina</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temp (°C)</strong></td>
<td><strong>H$_2$ Flow (sccm)</strong></td>
</tr>
<tr>
<td>144</td>
<td>5.0</td>
</tr>
<tr>
<td>147</td>
<td>6.4</td>
</tr>
<tr>
<td>149</td>
<td>7.3</td>
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<tr>
<td>152</td>
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<tr>
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<td>5.0</td>
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<td>197</td>
<td>4.6</td>
</tr>
<tr>
<td>197</td>
<td>4.4</td>
</tr>
<tr>
<td>197</td>
<td>4.1</td>
</tr>
<tr>
<td>197</td>
<td>3.9</td>
</tr>
</tbody>
</table>

*Air Products, Final Report, DOE Award # DE-FC36-04GO14006*
How to supply the heat of enthalpy without consuming stored hydrogen?

Potential solution – Development of an Autothermal concept

A general schematic of one autothermal carrier cycle

Air Products, Final Report, DOE Award # DE-FC36-04GO14006
Autothermal dehydrogenation reactor system schematic.
Autothermal concept

- 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 concept

The perhydrofluorene/fluorene/fluorenone, dehydrogenation, selective oxidation and re-hydrogenation cycle.

Air Products, Final Report, DOE Award # DE-FC36-04GO14006
For packed-bed reactor designs, two different reaction rate limitations were anticipated:

1) incomplete catalyst utilization caused by “drying out” of the catalyst surface, and

2) a reduction of the intrinsic reaction rate due to the effect of diffusion through the porous catalyst to the active metal sites, as measured by the effectiveness factor.

Alternative reactor designs investigated included:

1) Metal catalyst monoliths prepared from corrugated 0.05 mm iron/chromium foils coated with a tightly-adhering gamma alumina washcoat

2) Wicking microchannel reactor

3) Suspended slurry microchannel reactor – considered the most promising
H₂ liquid carrier economics are considered to be favorable, in the range of $0.85 – $4.50/kg H₂ delivery cost, provided that certain targets can be achieved. Specific recommendations include:

- reducing the liquid carrier cost to less than $10/gallon,
- lowering the carrier melting point,
- meeting a catalyst productivity target of >1,000,000 kg LOHC processed per kg of catalytic metal,
- and reducing the carrier loss rate to <2% per year.
Homogeneous Catalyst Development
Use of Homogeneous catalysts

- First homogenous aliphatic dehydrogenation catalyst
- 3 orders of magnitude higher activity than heterogeneous catalyst temperatures as low 100 °C
- Two-way catalyst

Homo- vs heterogeneous catalysts

Dehydrogenation of N-ethylperhydrocarbazole using homogeneous Ir PCP pincer catalyst gives higher rates of dehydrogenation at 2 orders of magnitude lower loadings than heterogeneous catalysts.

Alternative liquid carriers

- Fixed reactor geometry and conditions
- Require near 100% conversion
- 5x improvement in H₂ production

MPHI gives higher throughput

Liquid Hydrogen Carrier Development through B-N substituted heterocycles
B-N substituted heterocycles

Research objectives:
- liquid-phase
- gravimetric density (> 6 wt. %)
- volumetric density (> 4.5 vol. %)
- favorable thermodynamics (H₂ absorption and desorption)
- efficient and easy regeneration (reversibility)
- Couple exothermic H₂ desorption from BN with endothermic H₂ desorption from CC

Ease of hydrogenation for CBNs

\[ \text{N-t-Bu} \quad 10 \text{ mol\% Pd black} \quad \rightarrow \quad \text{no reaction} \]

\[ \begin{align*}
\text{N BH} & \rightarrow \text{35 psi H}_2 \\
& \rightarrow \text{80 °C} \\
& \rightarrow \text{Benzene-d}_6
\end{align*} \]

\[ \begin{align*}
\text{N-t-Bu} & \quad 10 \text{ mol\% Pd/C} \\
& \rightarrow \text{35 psi H}_2 \\
& \rightarrow \text{80 °C} \\
& \rightarrow \text{Benzene-d}_6 \text{ solvent} \\
& \rightarrow >90\% \text{ conversion}
\end{align*} \]

\[ \text{BH N-t-Bu} \]

\[ \text{t-Bu} \quad \rightarrow \text{no reaction} \]

\[ \text{BH t-Bu} \]

Benzene-d\textsubscript{6} is not hydrogenated!

VS.

\[ \text{Rh/Al}_2\text{O}_3 \quad 1200 \text{ psi H}_2 \\
\rightarrow \text{160 °C} \]

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

\[ \text{University of Oregon presentation at the 2009 Hydrogen and Fuel Cells Technologies Annual Merit Review and Peer Evaluation Meeting, #ST-016, 21 May 2009} \]
### Series of CBNs investigated

1) **Liquid phase**

<table>
<thead>
<tr>
<th></th>
<th>Formula</th>
<th>Mw</th>
</tr>
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<tbody>
<tr>
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<td>B</td>
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<tr>
<td>C</td>
<td><img src="image" alt="Structure C" /></td>
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</tr>
<tr>
<td>D</td>
<td><img src="image" alt="Structure D" /></td>
<td>85</td>
</tr>
</tbody>
</table>

2) **Potentially reversible**

<table>
<thead>
<tr>
<th></th>
<th>Formula</th>
<th>Mw</th>
</tr>
</thead>
<tbody>
<tr>
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<tr>
<td>F</td>
<td><img src="image" alt="Structure F" /></td>
<td>99</td>
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</table>

3) **High capacity**

<table>
<thead>
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<th></th>
<th>Formula</th>
<th>Mw</th>
</tr>
</thead>
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<tr>
<td>I</td>
<td><img src="image" alt="Structure I" /></td>
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<tr>
<td>J</td>
<td><img src="image" alt="Structure J" /></td>
<td>85</td>
</tr>
<tr>
<td>K</td>
<td><img src="image" alt="Structure K" /></td>
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</tr>
<tr>
<td>L</td>
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<td>145</td>
</tr>
</tbody>
</table>

*University of Oregon presentation at the 2015 Hydrogen and Fuel Cells Technologies Annual Merit Review and Peer Evaluation Meeting, #ST-104, 10 June 2015*
Potential high capacity materials

Overview of materials and their properties:

- mp: 75-77 °C
- d: 1.00 kg/L

Overall (–6 H₂)

<table>
<thead>
<tr>
<th>Property</th>
<th>Gas Phase</th>
<th>Liquid Phase</th>
<th>THF</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔH(gas)</td>
<td>–83.1</td>
<td>+102.3</td>
<td></td>
</tr>
<tr>
<td>ΔH(liquid)</td>
<td>–59.6</td>
<td>+102.8</td>
<td></td>
</tr>
<tr>
<td>ΔG(gas)</td>
<td>–107.3</td>
<td>+49.4</td>
<td></td>
</tr>
</tbody>
</table>

Per mol H₂:

<table>
<thead>
<tr>
<th>Property</th>
<th>Gas Phase</th>
<th>Liquid Phase</th>
<th>THF</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔG(gas)</td>
<td>–17.8</td>
<td></td>
<td>–4.8</td>
</tr>
<tr>
<td>ΔH(liquid)</td>
<td>–10.0</td>
<td></td>
<td>+4.0</td>
</tr>
<tr>
<td>ΔG(THF)</td>
<td>–13.6</td>
<td></td>
<td>–3.6</td>
</tr>
</tbody>
</table>

Energies in kcal/mol @ 298K:

- Gas Phase: G3MP2
- Liquid Phase: G3MP2 (gas) + BP*0.025 (Trouton’s rule)

Overall potential: 9.4 wt.%; 94 g H₂/L, potential liquid phase starting material at operating T

University of Oregon presentation at the 2015 Hydrogen and Fuel Cells Technologies Annual Merit Review and Peer Evaluation Meeting, #ST-104, 10 June 2015
Exo/Endothermic reactions for CBNs

Exothermic Reaction

\[ \Delta H_{\text{rxn}} = -41.4 \text{ kJ/mol } \text{H}_2 \]

Endothermic Reaction

\[ \Delta H_{\text{rxn}} = 62.8 \text{ kJ/mol } \text{H}_2 \]

Thermodynamic Coupling Performed with Properties of Actual CBN Materials

3 \[ \begin{array}{c} \text{NH}_2 \\ \text{BH}_2 \end{array} \xrightarrow{-6\text{H}_2} \begin{array}{c} \text{N} \\ \text{B} \\ \text{N} \end{array} \]

4.7 wt% \text{H}_2

47 g \text{H}_2/L

\[
\begin{array}{c}
\text{J} \\
\text{X}
\end{array}
\]

\[
\begin{array}{c}
\text{Me} \\
\text{Me}
\end{array}
\]

University of Oregon presentation at the 2015 Hydrogen and Fuel Cells Technologies Annual Merit Review and Peer Evaluation Meeting, #ST-104, 10 June 2015
$H_2$ Infrastructure considerations
Can liquid hydrogen carriers address key cost and performance issues of the hydrogen infrastructure?

• Transport/delivery
  – Capital cost of delivery equipment
  – Payload for delivery

• Forecourt
  – Storage
  – Compression
Hydrogen Delivery Critical Costs

H₂ Compression, Storage and Dispensing (CSD) Cost Breakdown

- 2020 goal for H₂ cost at the pump is <$4/gge (production and delivery cost included)
- Compression and storage are 75% of the cost of H₂ station dispensing costs.

Compression is a key challenge for the cost of delivering and dispensing H₂

Total Cost: $2.36

*Based on the pipeline scenario
- Air Products’ reports available through the DOE Office of Science and Technology Information (www.osti.gov)
  - Design and Development of New Carbon-based Sorbent Systems for an Effective Containment of Hydrogen - DOE Award No. DE-FC36-04GO14006
  - Reversible Liquid Carriers for an Integrated Production, Storage and Delivery of Hydrogen - DOE Award Number DE-FC36-05GO15015

- FCTO Annual Progress Reports: http://energy.gov/eere/fuelcells/annual-progress-reports
Thank you!