Chemical Hydrogen Storage Using Polyhedral Borane Anion Salts

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Overview

Timeline

• Project start date
  Fiscal year 2005
• Project end date
  Fiscal year 2009
• Percent complete 45%

Budget

• Total project funding
  – DOE share $ 1,250,000 (proposed)
  – Contractor share $ 312,000
• Funding received in FY06
  $ 250,000 (DOE share)
• Funding for FY07
  $ 250,000 (DOE share)

Barriers

• Barriers addressed
  – System Weight and Volume
  – Efficiency
  – Regeneration Processes
  – By-Product/Spent Material Removal

Partners

• DOE Center of Excellence for Chemical Hydrogen Storage
  – LANL
  – Penn State
Objectives

• Develop heterogeneous catalysts for the controlled release of hydrogen from the hydrolysis of salts of $\text{B}_{12}\text{H}_{12}^{2-}$, $\text{B}_{10}\text{H}_{10}^{2-}$ and $\text{B}_{11}\text{H}_{14}^{-}$ ions to meet DOE system targets for capacity, efficiency and cost.

• Determine the kinetics and mechanisms of these catalyzed polyhedral borane anion hydrolysis reactions to provide design data for large-scale hydrogen storage devices.

• Optimize existing processes for the conversion of diverse BH sources to $\text{B}_{12}\text{H}_{12}^{2-}$ and $\text{B}_{10}\text{H}_{10}^{2-}$ salts for direct use in hydrogen storage without extensive purification.

• Develop BO to BH regeneration process.
Approach - Technical Strategy

Polyhedral Hydridoborates - Electron Reservoirs

The University of Missouri-Columbia (MU) team will provide the overall program focal point for the investigation of polyhedral borane anions $\text{B}_n\text{H}_n^{2-}$ ($n = 10$ and $12$), $\text{B}_{11}\text{H}_{14}^{-}$ and their derivatives as reservoirs for stored electrons available for proton reduction and hydrogen release upon catalyzed hydrolysis.

\[
\begin{align*}
\text{B-OH} & \xrightarrow{2 \text{ e}^-} \text{B-H} & \text{R}_3\text{N} & \xrightarrow{150 \, ^\circ\text{C}} \\
2 \text{H}_2\text{O} & & \text{B}_{12}\text{H}_{12}^{2-} + 2 \text{ R}_3\text{NH}^+ & \text{B}_{10}\text{H}_{10}^{2-} + 2 \text{ R}_3\text{NH}
\end{align*}
\]

Properties of $\text{B}_{12}\text{H}_{12}^{2-}$ and $\text{B}_{10}\text{H}_{10}^{2-}$:
- Very $\text{H}_2\text{O}$ soluble alkali metal salts
- Non-toxic ($\text{LD}_{50} = 1.2 \text{g Na}_2\text{B}_{12}\text{H}_{12}/\text{Kg body weight in mice}$)
- Thermally stable $>500\, ^\circ\text{C}$
- No decomposition on storage in $\text{H}_2\text{O}$ solution at elevated temperatures
The $\text{B}_{12}\text{H}_{12}^{2-}$ ion is readily formed in excellent yield by heating $>\text{B-H}$ containing species with a base (R$_3$N).

Crude materials containing $>\text{B-H}$ may be converted to a $\text{B}_{12}\text{H}_{12}^{2-}$ salt which is extracted with water and used directly for catalytic generation of hydrogen.

Useful $>\text{B-H}$ sources obtainable from many different routes can be exploited.

Tetrahydridoborate salts of any purity are easily converted to Na$_2\text{B}_{12}\text{H}_{12}$.

Both Na$_2\text{B}_{10}\text{H}_{10}$ and NaB$_{11}\text{H}_{14}$ can be easily obtained from NaBH$_4$.

System Efficiency and Cost:
Polyhedral borane applications

Transition metal catalyst is need to generate hydrogen from Na$_2\text{B}_{12}\text{H}_{12}$ and Na$_2\text{B}_{10}\text{H}_{10}$ and will slower than in the case of NaBH$_4$.

Blends of NaBH$_4$ and/or NaB$_{11}\text{H}_{14}$ with Na$_2\text{B}_{12}\text{H}_{12}$, etc. will yield hydrogen just as blends of hydrocarbons provide gasoline.

Polyhedral hydridoborate salts would be ideal for supplying hydrogen to large fixed installations or small and disposable devices when great safety and reliable hydrogen release after prolonged storage times (years) are required.
Approach—Technical Strategy
Hydrogen Release

- Material system wt% calculated for material consumed in the reaction vessel.
- DOE targets for system wt. **2005**: 4.5%; **2010**: 6.0%; **2015**: 9.0%

Material System weights %
(wt. H₂ / wt. Boranes + wt. H₂O) x 100

<table>
<thead>
<tr>
<th>Material System</th>
<th>Li salts</th>
<th>NH₄ salts</th>
<th>Na salts</th>
<th>K salts</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₁₂H₁₂²⁻ + 38 H₂O</td>
<td>6.46 %</td>
<td>6.28</td>
<td>6.20 %</td>
<td>5.96 %</td>
</tr>
<tr>
<td>B₁₀H₁₀²⁻ + 32 H₂O</td>
<td>6.54 %</td>
<td>6.34 %</td>
<td>6.24 %</td>
<td>5.95 %</td>
</tr>
</tbody>
</table>

- Reaction rates and efficiency can be measured by ¹¹B NMR of the reaction mixtures and by hydrogen evolution as a function of time.
• Metal catalyst is needed to hydrolyze $\text{B}_{11}\text{H}_{14}^-$, $\text{B}_{12}\text{H}_{12}^{2-}$ and $\text{B}_{10}\text{H}_{10}^{2-}$ anion salts.

• In each case the rate of hydrogen release depends upon the following variables:

  - Choice of polyhedral borane anion
  - Choice of metal catalyst
  - Concentration of polyhedral borane anion
  - Temperature
  - Concentration of the catalyst
  - $\text{pH}$ of the reaction mixture
Technical Accomplishments: Summary

• Identified an active Rh metal catalyst for the hydrolysis of borane anion salts.

• The rate of hydrolysis is first-order with respect to the concentration of borane anion salts and concentration of Rh metal catalyst.

• Hydrogen ion concentration and the identity of the cation accompanying the polyhedral ions has insignificant effect on the rate of hydrogen generation.
Technical Accomplishments:
Search for System for Optimal Capacity, Performance and Cost

• In our search for optimal system for hydrogen generation, we investigated various polyhedral borane anions including \( \text{NaB}_{11}\text{H}_{14} \), \( \text{KB}_{11}\text{H}_{14} \), \( \text{(NH}_4\text{)}_2\text{B}_{12}\text{H}_{12} \), \( \text{K}_2\text{B}_{12}\text{H}_{11} \), \( \text{Cs}_2\text{B}_{12}\text{H}_{12} \), \( \text{(NH}_4\text{)}_2\text{B}_{10}\text{H}_{10} \) and \( \text{K}_2\text{B}_{10}\text{H}_{10} \).

• Transition metal ions, such as cobalt, nickel, palladium and rhodium are known to form catalytically active metal borides in the presence of reactive borane species.

• Transition metals are good first choice catalysts since these could possibly be converted to the respective borides during the hydrolysis reactions.
Technical Accomplishments: Search for Optimal Catalyst for the Hydrolysis of Polyhedral Borane Anion Salts

• For purposes of initial exploration, Rh, Ni, Co, Pd, Ru, Ir and Pt catalysts of various types were examined for their catalytic activity in the hydrolysis of NaB\textsubscript{11}H\textsubscript{14}, (NH\textsubscript{4})\textsubscript{2}B\textsubscript{12}H\textsubscript{12}, K\textsubscript{2}B\textsubscript{12}H\textsubscript{12}, (NH\textsubscript{4})\textsubscript{2}B\textsubscript{10}H\textsubscript{10} and K\textsubscript{2}B\textsubscript{10}H\textsubscript{10}.

• In these preliminary studies, Rh metal was found to be a superior catalyst for the hydrolysis of polyhedral borane anions.
# Catalytic Activity of Various Catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$\text{B}<em>{11}\text{H}</em>{14}^-$</th>
<th>$\text{B}<em>{10}\text{H}</em>{10}^{2-}$</th>
<th>$\text{B}<em>{12}\text{H}</em>{12}^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh Metal</td>
<td>Very Active</td>
<td>Very Active</td>
<td>Very Active</td>
</tr>
<tr>
<td>Rh/Co 3:1</td>
<td>Activity</td>
<td>Activity</td>
<td>Activity</td>
</tr>
<tr>
<td>Rh/Co 1:1</td>
<td>Corresponds to Rh Content</td>
<td>Corresponds to Rh Content</td>
<td>Corresponds to Rh Content</td>
</tr>
<tr>
<td>Rh/Co 1:3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoB$_2$</td>
<td>Active</td>
<td>Inactive</td>
<td>Inactive</td>
</tr>
<tr>
<td>NiB$_2$</td>
<td>Active</td>
<td>Inactive</td>
<td>Inactive</td>
</tr>
<tr>
<td>Ru Metal</td>
<td>Inactive</td>
<td>Inactive</td>
<td>Inactive</td>
</tr>
<tr>
<td>Ir sponge</td>
<td>Inactive</td>
<td>Inactive</td>
<td>Inactive</td>
</tr>
<tr>
<td>Pd Metal</td>
<td>Inactive</td>
<td>Inactive</td>
<td>Inactive</td>
</tr>
<tr>
<td>Pt Metal</td>
<td>Inactive</td>
<td>Inactive</td>
<td>Inactive</td>
</tr>
</tbody>
</table>
Hydrolysis of Borane Anions in the Presence of a Rhodium Metal Catalyst

- Of the various transition metal catalysts investigated, only rhodium metal catalyzed the hydrolysis of the generally less reactive \( \text{B}_{12}\text{H}_{12}^{2-} \) and \( \text{B}_{10}\text{H}_{10}^{2-} \) ions. These ions were inert to nickel boride and cobalt boride catalysts.

- Elemental analysis of the Rh catalyst proved that the catalyst is pure Rh metal having a BET surface area of \( \sim 55 \text{ m}^2 / \text{g} \).

- The majority of the catalyst is monodisperse with a particle size of approximately 240 nm. However, the presence of a few larger particles in the sample makes the average particle size approximately \( \sim 1 \mu \text{m} \).

- All hydrolysis reactions proceed to completion giving quantitative hydrogen and boric acid production.
Kinetic Data Obtained for Rh Metal-Catalyzed Borane Anion Hydrolysis

- The rates of hydrolysis of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ can be expressed by this differential rate equation:
  \[
  \frac{d[H_2]}{dt} = k [\text{Borane anion}] [\text{Rh catalyst}] + k' [H^+] \quad ???
  \]

- The rate of hydrolysis of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ is first-order with respect to the concentration of borane salts.

- The rate of hydrolysis of borane anions is first-order with respect to the effective Rh metal catalyst surface.

- Change of cations accompanying the polyhedral borane ions has no effect on the rate of hydrolysis.

- All polyhedral anion hydrolysis rates are essentially independent of hydrogen ion concentration.
Representative Kinetic Data: Rh Metal-catalyzed Hydrolysis of $\text{K}_2\text{B}_{10}\text{H}_{10}$

Effect of Borane Anion Concentration on the Initial Rate of Hydrolysis of $\text{K}_2\text{B}_{10}\text{H}_{10}$

Reaction conditions: 5 mol% Rh catalyst at 80 °C. The plot shows the initial 5% of hydrogen generation data.

<table>
<thead>
<tr>
<th>$\text{K}<em>2\text{B}</em>{10}\text{H}_{10}$ Concentration</th>
<th>100% Hydrogen Yield</th>
<th>Observed Rate mmole H$_2$ / sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.013 M</td>
<td>2.69 mmol</td>
<td>0.0040</td>
</tr>
<tr>
<td>0.050 M</td>
<td>10.50 mmol</td>
<td>0.021</td>
</tr>
<tr>
<td>0.10 M</td>
<td>21.00 mmol</td>
<td>0.055</td>
</tr>
</tbody>
</table>
Initial Rate of Hydrogen Generation with Respect to Concentration of $K_2B_{10}H_{10}$

- Determination of initial rates was carried out by linear approximation of first ~ 5% of kinetic data observed.
- Reaction conditions: 5 mol% Rh metal catalyst at 80 °C
Representative Kinetic Data:
Effect of Rh Metal Catalyst Added on the Hydrolysis of $\text{K}_2\text{B}_{10}\text{H}_{10}$

- Reaction conditions: 13 mM (0.025 g) of $\text{K}_2\text{B}_{10}\text{H}_{10}$ in presence of Rh metal catalyst at 80 °C; 100% hydrogen yield = 2.69 mmole
- The plot shows the initial 5% of hydrogen generation data.
Dependence of Initial Rates of Hydrogen Generation on Effective Added Rh Catalyst

Reaction conditions: 13 mM (0.025 g) of K₂B₁₀H₁₀ in presence of Rh metal catalyst at 80 °C.
Future Work

• The work in year ‘07 will focus on improving the system performance by increasing the hydrogen generation rate and reducing the cost of the system.

• Investigate alternative transition metal catalyst formulations, catalyst nanoparticles, zeolite composites and other solid-supported catalysts to reduce the material system cost and to increase the rate of hydrogen generation.

• Refine kinetic data for polyhedral anion hydrolysis reactions; determine activation energies and explore reaction mechanism.
Collaboration and Partners

- Electrochemical studies of reversible electron (hydrogen) storage mediated by electrochemical reactions of polyhedral borane anions and their derivatives (Penn State University) will be supported by MU as follows:
  - Through MU and Penn State consultation, promising candidate polyhedral borane derivatives will be identified for electrochemical studies at Penn State for BO to BH regeneration process.
  - Feasible polyhedral borane derivatives will be supplied to Penn State for study following their synthesis at MU.

- Polyhedral borane derivatives sought by the DOE Chemical Hydrogen Storage Center of Excellence for reversible hydrogen uptake and release will be supplied by MU.
Overall Result Summary

• Capacity
  – The polyhedral borane anion system was able to achieve material system capacity of ~ 6.5 wt% (0.056 g H₂ released / g laboratory vessel contents)

• Efficiency
  – Number of other transition metal catalysts were investigated and are being perused for the hydrolysis of polyhedral borane anions.
  – In our preliminary investigations, Rh metal catalyst was found to be best catalyst for the hydrolysis of polyhedral borane anions.
  – The hydrolysis of $\text{B}_{10}\text{H}_{10}^{2-}$ is faster than $\text{B}_{12}\text{H}_{12}^{2-}$ anions.
## Overall Result Summary: Quantitative Performance Metrics:

**Hydrolysis of 13mM $K_2B_{10}H_{10}$ with 50% mol of Rh catalyst at 80 ºC**

<table>
<thead>
<tr>
<th>DOE TARGET</th>
<th>Metrics</th>
<th>2010 Center Goal</th>
</tr>
</thead>
</table>
| **System Gravimetric Capacity** | 0.056 g H$_2$ released/g laboratory vessel contents “in laboratory vessel” [K$_2$B$_{10}$H$_{10}$+water consumed+catalyst] | > 6.0 wt %
Phase I: Material
Phase II: System-2010
Phase II: 9% Material-2015 |
| **System Volumetric Capacity**  | 0.083 kg H$_2$/L laboratory vessel contents “in laboratory vessel” [K$_2$B$_{10}$H$_{10}$+water consumed+catalyst] | > 0.045 kg/L
Phase I: Material
Phase II: System-2010
Phase II: 0.060 Material-2015 |
| **H$_2$ Flow Rate**             | 1821 ml laboratory reactor required for 0.80 mole H$_2$/sec              | Reactor volume
Amount of catalyst                                                |
| (0.02 (g/s)/kW) (80 kW stack)   |                                                                         |                                                                                  |