Applied Research on the Use of Amine-Borane Materials for Hydrogen Storage

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A project that is part of
DOE Chemical Hydrogen Storage Center of Excellence

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

Timeline
- Project start date - FY05
- Project end date - FY09
- Percent complete - 40%

Budget
- Total funding* - $420K (requested)
  - DOE share - $332K
  - Contractor share - $88K
- Funding received FY06 - $50K
- Funding for FY07 - $89K
  (*over 5 years)

Barriers
- System Gravi. Capacity
- System Volu. Capacity
- Fuel Cost

Partners
- LANL
- PNNL
- Rohm & Haas
- U of Washington
- U of Pennsylvania
Objectives

- Overall safety analysis of amine-borane compounds and dissemination of this information throughout the Chemical Hydrogen Storage Center (completed in 2006).

- Ongoing development of improved processes for low cost and high yield preparation of ammonia-borane and N-substituted amine-borane compounds and liquid fuel mixtures to enable a more easily engineered overall system.

- Collaboration with center partners on evaluation of hydrogen on-board release and off-board regeneration capability and capacity of N-substituted amine-borane materials and liquid fuel mixtures to determine if a system can be developed that safely meets the DOE 2010 storage system target of 6-wt% hydrogen.
Approach

Process Development -- Preparation of Ammonia-Borane and N-substituted Amine-Borane Materials

• Evaluation of sodium borohydride plus ammonium salt compounds as route to amine-borane materials.

• Evaluation of internally and externally produced active borane complexes plus ammonia or amine as route to amine-borane materials.

• Evaluation of mixtures of ammonia-borane plus amine-borane compounds as a route to “liquid fuel” formulations.

• Supply of ammonia-borane and amine-borane materials to center partners for evaluation.
<table>
<thead>
<tr>
<th>Ammonium Salt</th>
<th>Solvent &amp; conditions</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH₄)₂CO₃</td>
<td>• THF</td>
<td>• 70% yield</td>
</tr>
<tr>
<td></td>
<td>• Rm Temp then heat</td>
<td>• mp 115 -120 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• clean NMR</td>
</tr>
<tr>
<td>(NH₄)HCO₃</td>
<td>• THF</td>
<td>• 64% yield</td>
</tr>
<tr>
<td></td>
<td>• Rm Temp then heat</td>
<td>• mp 120 -125 °C</td>
</tr>
<tr>
<td></td>
<td>• Difficult to stir</td>
<td>• clean NMR</td>
</tr>
<tr>
<td>NH₄OCHO</td>
<td>• THF</td>
<td>• 60% yield</td>
</tr>
<tr>
<td></td>
<td>• Rm Temp then heat</td>
<td>• mp 100 -105 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• impurities in NMR</td>
</tr>
<tr>
<td>NH₄OAc</td>
<td>• THF</td>
<td>• 70% crude yield</td>
</tr>
<tr>
<td></td>
<td>• Rm Temp then heat</td>
<td>• very impure</td>
</tr>
<tr>
<td></td>
<td>• Difficult filtration</td>
<td></td>
</tr>
</tbody>
</table>
NaBH₄ + NH₄X → NH₃-BH₃ + NaX + H₂

<table>
<thead>
<tr>
<th>Ammonium Salt</th>
<th>Solvent &amp; conditions</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄Br</td>
<td>THF, Rm Temp then heat</td>
<td>31% yield, clean NMR</td>
</tr>
<tr>
<td>NH₄Br</td>
<td>THF plus additive, Rm Temp then heat</td>
<td>45% yield, clean NMR</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>THF plus additive, Rm Temp then heat</td>
<td>4% yield</td>
</tr>
<tr>
<td>NH₄F</td>
<td>THF plus additive, Rm Temp then heat</td>
<td>low yield, very impure by NMR</td>
</tr>
</tbody>
</table>
BH₃ complex + NH₃ → NH₃-BH₃ + Lewis base

<table>
<thead>
<tr>
<th>Borane complex</th>
<th>Solvent &amp; conditions</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>BH₃-THF</td>
<td>• THF</td>
<td>• 68% yield</td>
</tr>
<tr>
<td></td>
<td>• BH₃-THF added to NH₃</td>
<td>• mp 120 - 125 °C</td>
</tr>
<tr>
<td></td>
<td>• -78 °C then Rm temp</td>
<td>• clean NMR</td>
</tr>
<tr>
<td>BH₃-SMe₂</td>
<td>• THF</td>
<td>• 62% crude yield</td>
</tr>
<tr>
<td></td>
<td>• -20 °C then Rm temp</td>
<td>• strong sulfur odor</td>
</tr>
</tbody>
</table>
## Progress (continued)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equations</th>
<th>Conditions</th>
<th>Results</th>
</tr>
</thead>
</table>
| **CH₃NH₂ + BH₃-THF** | \( \text{CH}_3\text{NH}_2 + \text{BH}_3\text{-THF} \rightarrow \text{CH}_3\text{NH}_2\text{-BH}_3 \) | • THF solvent  
• CH₃NH₂ added to BH₃-THF  
• -20 °C then Rm temp | • 91% yield  
• mp 55 - 56 °C  
• clean NMR |
| **CH₃NH₃Cl + NaBH₄** | \( \text{CH}_3\text{NH}_3\text{Cl} + \text{NaBH}_4 \rightarrow \text{CH}_3\text{NH}_2\text{-BH}_3 + \text{NaCl} + \text{H}_2 \) | • THF solvent plus additive  
• Rm temp then heat | • 51% yield |
| **(CH₃)₂NH + BH₃-THF** | \( (\text{CH}_3)_2\text{NH} + \text{BH}_3\text{-THF} \rightarrow (\text{CH}_3)_2\text{NH-BH}_3 \) | • THF solvent  
• (CH₃)₂NH added to BH₃-THF  
• -5 °C then Rm temp | • 88% yield  
• mp 36 - 38 °C  
• clean NMR |
\[
\begin{align*}
\text{NH}_3 + \text{BH}_3\text{-THF} & \rightarrow \text{NH}_3\text{-BH}_3 (\text{AB}) \\
\text{CH}_3\text{NH}_2 + \text{BH}_3\text{-THF} & \rightarrow \text{CH}_3\text{NH}_2\text{-BH}_3 (\text{MeAB})
\end{align*}
\]

- co-synthesis
- 35:65 AB:MeAB
- THF solvent
- NH3 added to BH3-THF
- (CH3)2NH added to BH3-THF
- -45 °C then Rm temp
- oil at 30 °C
- solid at 25 °C
- minor impurities by NMR
Accomplishments

• Various processes were evaluated for the laboratory preparation of ammonia-borane (AB). Borane-THF plus ammonia gave the best yield and purity.

• Various processes were evaluated for the laboratory preparation of methylamine-borane (MeAB). Borane-THF plus methylamine gave the best yield and purity.

• As a first attempt to a “Liquid Fuel”, melting points were measured for nine AB/MeAB mixtures over the range: (90-10%) AB/ (10-90%) MeAB. The 30-40% AB mixtures had the lowest melting point of 35-37 °C.

• Co-synthesis of a 35% AB/ 65% MeAB mixture gave a product oil at 30 °C which crystallized at 25 °C giving a near “Liquid Fuel”.

• AB and MeAB samples were provided to the University of Washington and Pacific Northwest National Lab partners in the CHSCoE.
Future Work

• Continued process improvement for the laboratory preparation of ammonia-borane (AB) and methylamine-borane (MeAB). The use of “in-situ” generated borane-THF will be evaluated as a means to lower the cost of a potential fuel.

• Co-synthesis of the 35:65 AB:MeAB mixture will be studied in the presence of a few % of various inert high-boiling additives as a means to possibly give a fuel that is a liquid at room temperature.

• Stability of various low melting 35:65 AB:MeAB mixtures will be evaluated to make sure pressure build-up is not a problem.

• The best AB:MeAB “liquid” mixture candidate will be supplied to other Center partners to see if safe decomposition can be achieved at a reasonable temperature and if a non-volatile N-B-H product is produced that can be readily converted back to the liquid fuel.

• Laboratory quantities of AB, MeAB and other amine-borane materials will continue to be provided to all interested partners in the Chemical Hydrogen Storage Center.
Project Summary

• A document entitled, "Ammonia-Borane and Related N-B-H Compounds and Materials: Safety Aspects, Properties and Applications" was completed in 2006 and was supplied to the DOE and all the partners in the Chemical Hydrogen Storage Center of Excellence. A copy of the complete survey can be supplied to anyone interested.

• A mixture of ammonia-borane and methylamine-borane appears to have great promise as a potential “liquid” formulation for chemical hydrogen storage, please see the posters from University of Washington and Los Alamos National Lab for some recent results on the AB/MeAB system.

• Laboratory quantities of this liquid fuel mixture will be evaluated in collaboration with interested partners in the Chemical Hydrogen Storage Center to determine if this material can be used in a system to safely meet the DOE 2010 storage system target of 6-wt% hydrogen.