Overview

Timeline
• Start: FY 05
• End: FY 09
• 25% complete

Budget
• Total funding
  – $1.1 M DOE share
  – $ 0.28 M cost share
• DOE FY05: $155K(partial)
• DOE FY06: $ 200 K

Barriers
• Weight and volume
• Efficiency
• Regeneration Processes

Amineboranes offer high H$_2$ storage capacity in principle, but thermal H$_2$ release is slow and inefficient. Effective catalysts for dehydrogenation/hydrogenation of BN compounds are needed.

Partners
DOE Center of Excellence for Chemical Hydrogen Storage
Objectives

• To understand the interaction of BN compounds with transition metals
• To develop Platinum group metal (PGM) based catalysts for dehydrogenation and rehydrogenation of BN compounds
• To determine thermodynamic parameters for hydrogenation/dehydrogenation
• To develop non PGM catalysts
Ammonia Borane as a H₂ Storage Material

**Appropriate Thermodynamics**

\[ n \text{H}_3\text{NBH}_3 \rightarrow [\text{H}_2\text{NBH}_2]_n + n \text{H}_2 \quad \Delta H_{\text{calc}} = 8 \text{ kcal.mol}^{-1} \]

\[ [\text{H}_2\text{NBH}_2]_n \rightarrow [\text{HNBH}]_n + n \text{H}_2 \quad \Delta H_{\text{calc}} = -3 \text{ kcal.mol}^{-1} \]

\[ [\text{HNBH}]_n \rightarrow [\text{NB}]_n + n \text{H}_2 \quad \Delta H_{\text{calc}} = -9 \text{ kcal.mol}^{-1} \]

Near thermoneutral reactions important for reversibility.

Ammonia Borane as a $H_2$ Storage Material

**DOE Storage Targets**

<table>
<thead>
<tr>
<th>Target wt%</th>
<th>2010</th>
<th>2015</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6.0</td>
<td>9.0</td>
</tr>
</tbody>
</table>

**Storage Potential of Ammonia Borane**

<table>
<thead>
<tr>
<th>$H_2$ Released</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt% $H_2$</td>
<td>6.5</td>
<td>13.0</td>
<td>19.6</td>
</tr>
<tr>
<td>Product</td>
<td>$[H_2NBH_2]_n$</td>
<td>$[HNBH]_n$</td>
<td>$[NB]_n$</td>
</tr>
</tbody>
</table>
Dehydrogenation of Ammonia Borane

Thermal

\[ \text{H}_3\text{NBH}_3 \xrightarrow{-\text{H}_2} \text{borazine} \]


Catalyzed

\[ \text{H}_3\text{NBH}_3 \xrightarrow{[\text{Rh}]} \text{borazine} + 2\text{H}_2 \]


0.6 mol% catalyst

48 – 84 hours at 45 °C
Approach

• We seek to develop catalysts to accelerate dehydrogenation/rehydrogenation of amine boranes, eg.

\[ n \text{ NH}_3\text{BH}_3 \underset{[\text{catalyst}]}{\xleftrightarrow{}} [\text{NH}_2\text{BH}_2]_n + n \text{ H}_2 \]
Results: Catalyst Choice

\[ n \text{NH}_3\text{BH}_3 \xrightarrow{[\text{catalyst}] \text{THF, rt}} [\text{NH}_2\text{BH}_2]^n + n \text{H}_2 \]

- (POCOP)Ir(H)\textsubscript{2} already known to be an effective alkane (transfer) dehydrogenation catalyst.

- Amineboranes are isoelectronic with alkanes.

Evolution of Hydrogen

$$n \text{H}_3\text{NBH}_3 \xrightarrow{[\text{Ir}]} [\text{H}_2\text{NBH}_2]_n + n \text{H}_2$$

<table>
<thead>
<tr>
<th>Equivalents of H₂</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25 mol%</td>
<td>30</td>
</tr>
<tr>
<td>0.5 mol%</td>
<td></td>
</tr>
<tr>
<td>1.0 mol%</td>
<td></td>
</tr>
</tbody>
</table>
Characterization of Solid Product

\[ n \text{NH}_3\text{BH}_3 \xrightarrow{[\text{catalyst}] \ \text{THF, rt}} [\text{NH}_2\text{BH}_2]^n + n \text{H}_2 \]

- Single well characterized non-volatile product
- All other reported reactions of this type lead to mixtures including borazine

Comparison with Previous Best Catalyst

<table>
<thead>
<tr>
<th></th>
<th>[Rh(1,5-COD)(µ-Cl)]₂</th>
<th>[H₂NBH₂]₅</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Catalyst Loading</strong></td>
<td>0.6 mol%</td>
<td>0.5 mol%</td>
</tr>
<tr>
<td><strong>Temperature (°C)</strong></td>
<td>45</td>
<td>25</td>
</tr>
<tr>
<td><strong>H₂ evolved (equiv.)</strong></td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td><strong>Products</strong></td>
<td>Borazine</td>
<td>[H₂NBH₂]₅</td>
</tr>
<tr>
<td><strong>Time</strong></td>
<td>48 – 84 hr</td>
<td>&lt; 15 min</td>
</tr>
</tbody>
</table>

At least 200 fold increase in reaction rate over previous best.

• Eventually, the Ir catalyst converts to a dormant form:
Future Work

• In collaboration with PNNL, use calorimetry to accurately measure the heat of reaction for the dehydrogenation reaction. This is critical to validate computational work and to evaluate reversibility.
• Explore ligand variations with Ir for better catalysis.
• Define the mechanism of the reaction; use mechanistic insight to guide catalyst development
• Study rehydrogenation reactions.
• Develop non PGM catalysts with less expensive metals such as Fe, Co and Ni.
Summary

- We have developed an extraordinarily active dehydrogenation catalyst with activity orders of magnitude greater than the prior art.
- The catalyst is well defined and active indefinitely in the presence of hydrogen.
- In contrast to previous reports of complex mixtures, our Ir catalyst gives a single non-volatile BN containing product.
Backup Data: Characterization of Solid Product

\[ n \text{NH}_3\text{BH}_3 \xrightarrow{\text{[catalyst]}} \text{THF, rt}} \xrightarrow{\text{[n catalyst]}} [\text{NH}_2\text{BH}_2]^n + n \text{H}_2 \]

- Solid state $^{11}\text{B}$ NMR.
- Infrared spectroscopy.
- Powder X-ray diffraction.

Fig. 5. $^{11}$B MAS NMR spectra of the three polymers recorded at 9.4 T.

Fig. 8. Schematic representation of the three polymers structures, based on NMR results.

Solid State $^{11}$B NMR of $[\text{BH}_2\text{NH}_2]_5$
IR of $[\text{BH}_2\text{NH}_2]_5$
XRD of $[\text{H}_2\text{NBH}_2]_5$
<table>
<thead>
<tr>
<th>Bond Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir(1)-B(1)        2.185(9)</td>
</tr>
<tr>
<td>Ir(1)-P(1)        2.3137(14)</td>
</tr>
<tr>
<td>Ir(1)-P(2)        2.3122(14)</td>
</tr>
<tr>
<td>Ir(1)-C(1)        2.032(4)</td>
</tr>
</tbody>
</table>
$^{31}$P = 171.6 ppm
$^{11}$B = 13 ppm

$^1$H NMR in THF-$d_8$

$J = 26$ Hz
$J = 7.7$ Hz
$J = 5.7$ Hz
$J = 8.0$ Hz
IR spectrum of (POCOP)IrH(BH₂)

Solution in C₆H₆
Initial Rates

Reaction appears to be ca. first order in $\text{NH}_3\text{BH}_3$ and (POCOP)Ir(H)$_2$.

Rate = $k_{\text{obs}}[\text{NH}_3\text{BH}_3]$

($k_{\text{obs}} = k[\text{IrH}_2(\text{POCOP})]$)

- $y = 0.0205x - 0.0283$
  - $R^2 = 0.9977$
- $y = 0.0113x + 0.0395$
  - $R^2 = 0.9933$
- $y = 0.0087x - 0.0148$
  - $R^2 = 0.985$

$\ln([\text{NH}_3\text{BH}_3]_0/[[\text{NH}_3\text{BH}_3]_0-\text{H}_2])$
At lower catalyst loadings, rate slows as (POCOP)Ir(H)$_2$ is converted to (POCOP)IrH(BH$_2$).
DORMANT

\[
\text{Ir}^0 \text{H}_2 \quad \text{Ir}^+ \text{H} \quad \text{Ir}^+ \text{H}_2
\]

ACTIVE

\[
\text{Ir}^+ \text{BH}_2 \quad \text{Ir}^+ \text{BH}_2 \quad \text{Ir}^+ \text{BH}_2
\]

ACTIVE

\[
\text{Ir}^+ \text{BH}_2 \quad \text{Ir}^+ \text{BH}_2
\]

\[
\text{Ir}^+ \text{BH}_2 \quad \text{Ir}^+ \text{BH}_2
\]

[\text{Ir}(\text{BH}_2)\text{H}]^-

start

5 atm H\_2; 2 hr

Sol\textsuperscript{n} degassed
Publications and Presentations

Critical Assumptions and Issues

• Computational work suggests that the hydrogenation/dehydrogenation of BN compounds is reversible. This needs to be verified by experiment. Thermodynamic data for these complexes is very limited.

• The formation of volatile borazine must be avoided for fuel cell applications. Most catalysts generate mixtures including borazine.

• The cost of amine borane must be brought down.