Chemical Hydrogen Storage Using Aluminum Ammonia-Borane Complexes

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ST059
Overview

Timeline
• Project start date 01/01/2005
• Project end date 06/30/2010
• Percent complete 100%

Barriers
• Barriers addressed
  – System weight and volume
  – Efficiency

Budget
• Total project funding
  – DOE share $1,387,420
  – Contractor share $346,855
• Funding received in FY09 $340,493
• Funding for FY10 – N/A

Partners
• DOE center of excellence for chemical hydrogen storage
• LANL
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Project Objectives

• Evaluate aluminum amidoborane derivatives as hydrogen storage candidates that can achieve DOE storage targets.

• Develop efficient thermal dehydrogenation methods for hydrogen release from aluminum amidoborane derivatives.

\[
n \text{Al(NH}_2\text{BH}_3\text{)}_3 (s) \xrightarrow{} [\text{Al(NBH)}_3]_n (s) + 6n \text{H}_2 (g) (10.3 \text{ wt.\% Hydrogen})
\]

\[
n \text{LiAl(NH}_2\text{BH}_3\text{)}_4 (s) \xrightarrow{} [\text{LiAl(NBH)}_4]_n (s) + 8n \text{H}_2 (g) (10.4 \text{ wt.\% Hydrogen})
\]

• In collaboration with Center Partners, determine a suitable route for the regeneration of the spent material.
Ammonia borane (AB) is a demonstrated source of chemical hydrogen storage and has the material capacity of 20 wt. % hydrogen. It can potentially meet DOE performance parameters except for its regeneration from spent materials.

Aluminum amidoborane complexes (Al-AB) and their derivatives have high hydrogen capacity and are capable of meeting DOE storage targets.

The presence of an Al center bonded to multiple AB might combine the efficiency of AB dehydrogenation with an Al mediated hydrogenation process leading to better rates and reversibility.

It is presumed that Al-AB complexes will decrease the enthalpy of hydrogen loss and undergo dehydrogenation at a lower temperature than AB alone.
Approach – Relevance
Amidoboranes System Capacities:

a. $\text{NH}_3\text{BH}_3$ (s) $\rightarrow$ BNH$n$ (s) + 2.5 $\text{H}_2$ (g) (19 wt% hydrogen)

b. $n \text{LiNH}_2\text{BH}_3$ (s) $\rightarrow$ [LiNB]$_n$ (s) + 2.5$n$ $\text{H}_2$ (g) (13.5 wt.% Hydrogen)
   $n \text{LiNH}_2\text{BH}_3$ (s) $\rightarrow$ [LiNBH]$_n$ (s) + 2$n$ $\text{H}_2$ (g) (10.9 wt.% Hydrogen)

c. $n \text{NaNH}_2\text{BH}_3$ (s) $\rightarrow$ [NaNB]$_n$ (s) + 2.5$n$ $\text{H}_2$ (g) (9.4 wt.% Hydrogen)
   $n \text{NaNH}_2\text{BH}_3$ (s) $\rightarrow$ [NaNBH]$_n$ (s) + 2$n$ $\text{H}_2$ (g) (7.5 wt.% Hydrogen)

d. $n \text{Ca(NH}_2\text{BH}_3)_2$ (s) $\rightarrow$ [Ca(NB)$_2$]$_n$ (s) + 5$n$ $\text{H}_2$ (g) (10 wt.% Hydrogen)
   $n \text{Ca(NH}_2\text{BH}_3)_2$ (s) $\rightarrow$ [Ca(NBH)$_2$]$_n$ (s) + 4$n$ $\text{H}_2$ (g) (8 wt.% Hydrogen)

e. $n \text{NH}_3\text{Al(NH}_2\text{BH}_3)_3$ (s) $\rightarrow$ [Al(NB)$_3$]$_n$ (s) + 9$n$ $\text{H}_2$ (g) (13.4 wt.% Hydrogen)

f. $n \text{Al(NH}_2\text{BH}_3)_3$ (s) $\rightarrow$ [Al(NB)$_3$]$_n$ (s) + 7.5$n$ $\text{H}_2$ (g) (12.8 wt.% Hydrogen)
   $n \text{Al(NH}_2\text{BH}_3)_3$ (s) $\rightarrow$ [Al(NBH)$_3$]$_n$ (s) + 6$n$ $\text{H}_2$ (g) (10.3 wt.% Hydrogen)

g. $n \text{NH}_4[\text{Al(NH}_2\text{BH}_3)_4]$ (s) $\rightarrow$ [(Al(NB)$_4$NH]$_n$ (s) + 11.5$n$ $\text{H}_2$ (g) (14 wt.% Hydrogen)

h. $n \text{LiAl(NH}_2\text{BH}_3)_4$ (s) $\rightarrow$ [LiAl(NB)$_4$]$_n$ (s) + 10$n$ $\text{H}_2$ (g) (13 wt.% Hydrogen)
Approach
Synthesis of Al-AB Complexes

• For this study we focused our efforts on the synthesis of Al(NH₂BH₃)₃ and LiAl(NH₂BH₃)₄ [referred to as Al(AB)₃ and (LiAl(AB)₄ respectively].

• Metathesis reaction of AlCl₃ with M-AB (M = Li, Na or K) should give Al(AB)₃. Further reaction of Al(AB)₃ with liquid NH₃ will give the ammonia adduct, NH₃•Al(AB)₃.

• Similarly the reaction of LiAlH₄ with AB Should give LiAl(AB)₄.
Technical Accomplishments and Progress-Synthesis of Al-AB Complexes

Al(AB)_3 is conveniently accessible by the reaction of AlCl₃ with M-AB (M=Li, Na or K) at low temperature. The choice of solvent and temperature are critical for isolation of pure material. (Milestone)

**Al(NH₂BH₃)₃ from AlCl₃**

\[
3 \text{M(NH₂BH₃)} + \text{AlCl₃} \rightarrow \text{Al(NH₂BH₃)₃} + 3 \text{MCl} \\
M = \text{Li, Na or K}
\]

\[
\text{Al(NH₂BH₃)₃} + \text{NH₃ (excess)} \rightarrow \text{NH₃} \cdot \text{Al(NH₂BH₃)₃}
\]

LiAl(AB)₄ was synthesized in quantitative yield by reacting LiAlH₄ with AB at room temperature.

**Li[Al(NH₂BH₃)₄] from LiAlH₄**

\[
\text{LiAlH₄} + 4 \text{NH₃BH₃} \rightarrow \text{LiAl(NH₂BH₃)₄} + 4 \text{H₂}
\]
Both $\text{Al(AB)}_3$ and $\text{LiAl(AB)}_4$ are colorless solids. $\text{LiAl(AB)}_4$ is thermally more stable than $\text{Al(AB)}_3$. Amine adducts of $\text{Al(AB)}_3$ are colorless polymeric compounds insoluble in common organic solvents. (Milestone)

**Graphs:**
- **NaAB in Glyme**
  - $-20.2$ ppm, $J_{B-H} = 85$ Hz
- **AB in Glyme**
  - $-21.7$ ppm, $J_{B-H} = 95$ Hz
- **$\text{Al(AB)}_3$ in Glyme**
  - $-22.2$ ppm, $J_{B-H} = 90$ Hz
- **Li$\text{Al(AB)}_4$ in THF**
  - $-22.7$ ppm, $J_{B-H} = 92$ Hz
Technical Accomplishments and Progress-
Thermal Dehydrogenation Studies TGA-MS

- Al(AB)₃ starts releasing hydrogen at 60 °C.
- NH₃•Al(AB)₃ releases ammonia when heated.
- LiAl(AB)₄ releases hydrogen at higher temperatures.
- Preliminary DSC analysis indicates the Al(AB)₃ has exothermic hydrogen release therefore will require off board regeneration. (milestone)

Partner - LANL
Technical Accomplishments and Progress-Dehydrogenation of Al(AB)₃

Al(AB)₃ releases more hydrogen in the presence of a ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate (Milestone)
Technical Accomplishments and Progress-
Dehydrogenation of LiAl(AB)₄

LiAl(AB)₄ releases more hydrogen in the presence of a ionic liquid—1-butyl-3-methylimidazolium tetrafluoroborate
Technical Accomplishments and Progress-
NMR Studies on Al(AB)_3 Dehydrogenation

Solution $^{11}$B NMR (160 MHz) of thermolysis products of Al(AB)_3 at 80 °C in glyme.

Solid state CPMAS $^{11}$B NMR (96 MHz) of thermolysis products of Al(AB)_3 after 4h at 120 °C.
Technical Accomplishments and Progress-NMR Studies on LiAl(AB)$_4$ Dehydrogenation

Solution $^{11}$B NMR (160 MHz) of thermolysis products of LiAl(AB)$_4$ at 80 °C in glyme.

Solid state CPMAS $^{11}$B NMR (96 MHz) of thermolysis products of LiAl(AB)$_4$ after 4h at 120 °C.
Collaborations

- This project is coordinated with Center Partners through frequent discussions, monthly conference calls, sample sharing and analytical instrument support.

- LANL – TGA MS, DSC, Support for dehydrogenation studies

- PNNL – Support for dehydrogenation studies
Proposed Future Work

2010 –

• Determine the solid state structure of Al(AB)₃, LiAl(AB)₄, and amine adducts of Al(AB)₃.

• Identify dehydrogenation products and intermediates.
Summary of Accomplishments

2009-2010-

- Synthesized Al(AB)$_3$ and LiAl(AB)$_4$ in good yields.
- The rate of hydrogen release is higher in the presence of an ionic liquid.
- Preliminary NMR studies indicate that the dehydrogenation of LiAl(AB)$_4$ and Al(AB)$_3$ follows AB and metal amidoborane dehydrogenation pattern due to release of AB from Al-AB complexes.
Project Summary

- Relevance: Aluminum amidoboranes (Al-AB) have high material wt capacity (13 wt%) and are capable of meeting DOE storage targets.
- Approach: Al-AB systems with their multiple AB bonded to an Al center might combine efficiency of AB dehydrogenation with an Al mediated hydrogenation process leading to better rates and reversibility.
- Technical Accomplishments and Progress: (Synthesis) Al(AB)₃ was synthesized in two steps starting from AB in good yields. LiAl(AB)₄ was synthesized in one step from AB in excellent yield. (Release) Dehydrogenation of both Al(AB)₃ and LiAl(AB)₄ in presence of an ionic liquid releases hydrogen at a higher rate and amount.
- Future Work: Identify dehydrogenation intermediates using solid state NMR studies. Determine the solid state structures of Al-AB complexes and their amine adducts.