Chemical Hydrogen Storage Using Aluminum Ammonia-borane Complexes

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Overview

Timeline

- Project start date
  Fiscal year 2005
- Project end date
  Fiscal year 2010
- Percent complete 80%

Budget

- Total project funding
  - DOE share $ 1,250,000 (proposed)
  - Contractor share $ 312,000
- Funding received in FY08
  $ 349,927
- Funding for FY09
  $ 349,339

Barriers

- Barriers addressed
  - Weight and Volume
  - Flow Rate
  - Energy Efficiency
  - Cost
  - Regeneration Process

Partners

- DOE Center of Excellence for Chemical Hydrogen Storage
  - LANL
  - PNNL

Los Alamos NATIONAL LABORATORY

Pacific Northwest NATIONAL LABORATORY

Project Objectives

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

- In collaboration with Center Partners, develop efficient thermal dehydrogenation methods for hydrogen release from aluminum amidoborane derivatives.

$$n\,Al(NH_2BH_3)_3\ (s) \longrightarrow [Al(NB)_3]_n\ (s) + 7.5n\,H_2\ (g)\ (12.8\ wt.\%\ Hydrogen)$$

$$n\,NH_3Al(NH_2BH_3)_3\ (s) \longrightarrow [Al(NB)_3]_n\ (s) + 9n\,H_2\ (g)\ (13.4\ wt.\%\ Hydrogen)$$

$$n\,LiAl(NH_2BH_3)_4\ (s) \longrightarrow [LiAl(NB)_4]_n\ (s) + 10n\,H_2\ (g)\ (13\ wt.\%\ Hydrogen)$$

$$n\,NH_4[Al(NH_2BH_3)_4]\ (s) \longrightarrow [(Al(NB)_4NH]_n\ (s) + 11.5n\,H_2\ (g)\ (14\ wt.\%\ Hydrogen)$$

- In collaboration with Center Partners, determine a suitable route for the regeneration of the spent material.

Milestones

Synthesize Al-AB complexes and their ammonia adducts	100% Complete
Conduct hydrogen release studies by thermal dehydrogenation process	100% Complete
Find a suitable route for the regeneration of Al-AB spent material.	80% Complete

Approach

Aluminum Amidoboranes

- Ammonia borane (AB) is a demonstrated source of chemical hydrogen storage and has material capacity of 20 wt. % hydrogen. It can potentially meet DOE performance parameters except for its regeneration from spent materials.

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

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

- 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 - Amidoboranes

Amidoboranes System Capacity:

1. NH_3BH_3 (s) $\longrightarrow$ BNH_n (s) + 3 H_2 (g) (19.4 wt.% Hydrogen)

2. $n\,LiNH_2BH_3$ (s) $\longrightarrow$ $[LiNB]_n$ (s) + 2.5n H_2 (g) (13.5 wt.% Hydrogen)

   $n\,LiNH_2BH_3$ (s) $\longrightarrow$ $[LiNBH]_n$ (s) + 2n H_2 (g) (10.9 wt.% Hydrogen)

3. $n\,NaNH_2BH_3$ (s) $\longrightarrow$ $[NaNB]_n$ (s) + 2.5n H_2 (g) (9.4 wt.% Hydrogen)

   $n\,NaNH_2BH_3$ (s) $\longrightarrow$ $[NaNBH]_n$ (s) + 2n H_2 (g) (7.5 wt.% Hydrogen)

4. $n\,Ca(NH_2BH_3)_2$ (s) $\longrightarrow$ $[Ca(NB)_2]_n$ (s) + 5n H_2 (g) (10 wt.% Hydrogen)

   $n\,Ca(NH_2BH_3)_2$ (s) $\longrightarrow$ $[Ca(NBH)_2]_n$ (s) + 4n H_2 (g) (8 wt.% Hydrogen)

5. $n\,NH_3Al(NH_2BH_3)_3$ (s) $\longrightarrow$ $[Al(NB)_3]_n$ (s) + 9n H_2 (g) (13.4 wt.% Hydrogen)

6. $n\,Al(NH_2BH_3)_3$ (s) $\longrightarrow$ $[Al(NB)_3]_n$ (s) + 7.5n H_2 (g) (12.8 wt.% Hydrogen)

   $n\,Al(NH_2BH_3)_3$ (s) $\longrightarrow$ $[Al(NBH)_3]_n$ (s) + 6n H_2 (g) (10.3 wt.% Hydrogen)

7. $n\,NH_4[Al(NH_2BH_3)_4]$ (s) $\longrightarrow$ $[(Al(NB)_4NH]_n$ (s) + 11.5n H_2 (g) (14 wt.% Hydrogen)

8. $n\,LiAl(NH_2BH_3)_4$ (s) $\longrightarrow$ $[LiAl(NB)_4]_n$ (s) + 10n H_2 (g) (13 wt.% Hydrogen)

Approach

Synthesis of Aluminum-AB Complexes

- Our initial targets for Al-AB complexes are $Al(NH_2BH_3)_3$, its ammonia adduct $NH_3 \bullet Al(NH_2BH_3)_3$, $LiAl(NH_2BH_3)_4$ and $NH_4[Al(NH_2BH_3)_4]$. A number of routes are available for their synthesis.

- Metathesis reaction of $AlCl_3$ with M-AB (M = Li, Na or K) should give Al-AB. Further reaction of Al-AB with liquid NH_3 will give the desired $NH_3 \bullet Al(NH_2BH_3)_3$.

- Similarly the reaction of $LiAlH_4$ with AB Should give $LiAl(AB)_4$. Cation exchange to NH_4 will give the desired $NH_4[Al(NH_2BH_3)_4]$ complex.

Synthesis of Aluminum AB Complexes (Continued)

$Al(NH_2BH_3)_3$ from Aluminum Hydride

$$Al(NH_2)_3 + BH_3 \cdot THF \xrightarrow{\times} Al(NH_2BH_3)_3$$

$Al(NH_2)_3$ is difficult to isolate in pure form and easily forms polymeric $[Al(NH_2)NH]n$ which does not react with $BH_3 \cdot THF$ complex.

$Al(NH_2BH_3)_3$ from Aluminum Chloride

$$3\ M(NH_2BH_3) + AlCl_3 \longrightarrow Al(NH_2BH_3)_3 + 3\ MCl$$

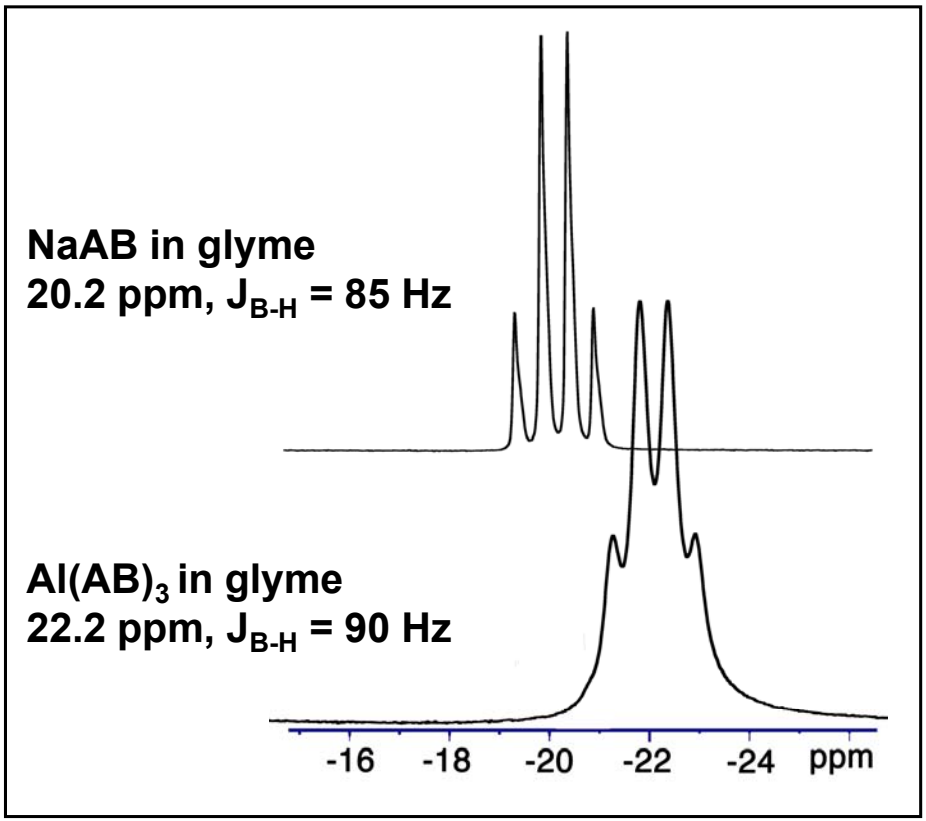
M = Li, Na or K

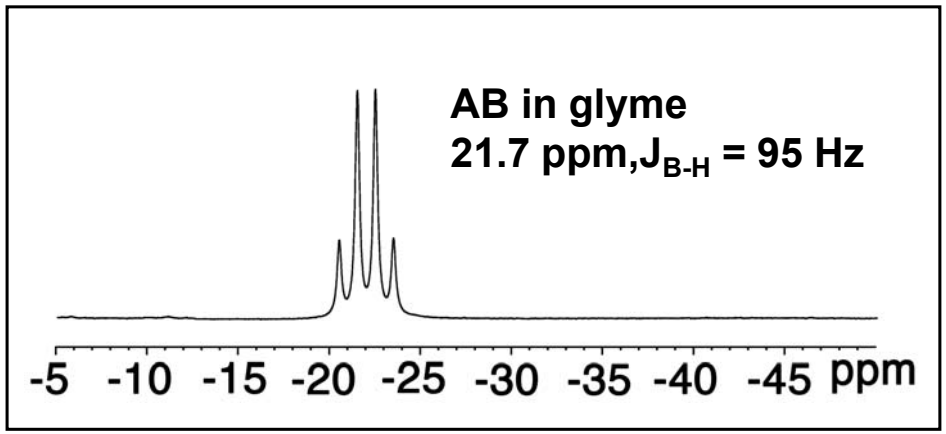
$$Al(NH_2BH_3)_3 + NH_3\ (excess) \longrightarrow NH_3 \cdot Al(NH_2BH_3)_3$$

The reaction of $AlCl_3$ with M-AB gives desired product. Milestone complete.

Technical Accomplishments and Progress

^{11}B NMR and IR Studies on Al(AB)$_3$ Complexes

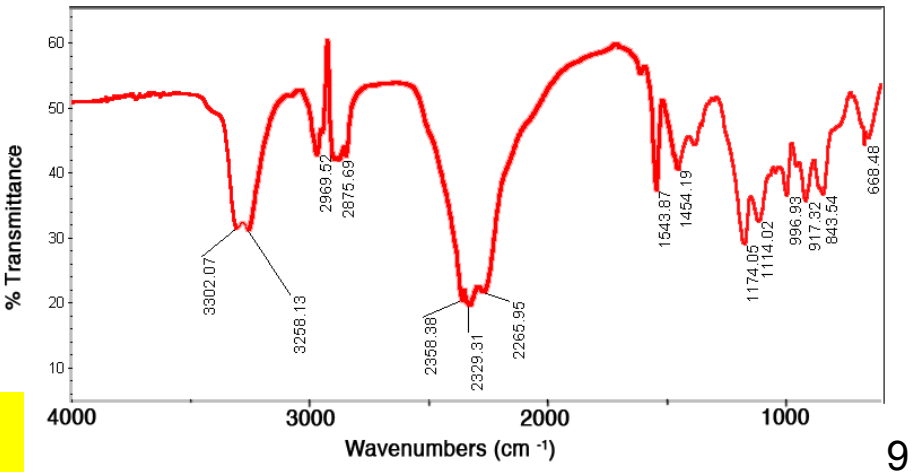




$3\ M(NH_2BH_3) + AlCl_3 \longrightarrow Al(NH_2BH_3)_3 + 3\ MCl$

M = Li, Na or K

$Al(NH_2BH_3)_3 + NH_3$ (excess) $\longrightarrow NH_3 \cdot Al(NH_2BH_3)_3$



IR spectrum of $NH_3 \cdot Al(AB)_3$ in Nujol

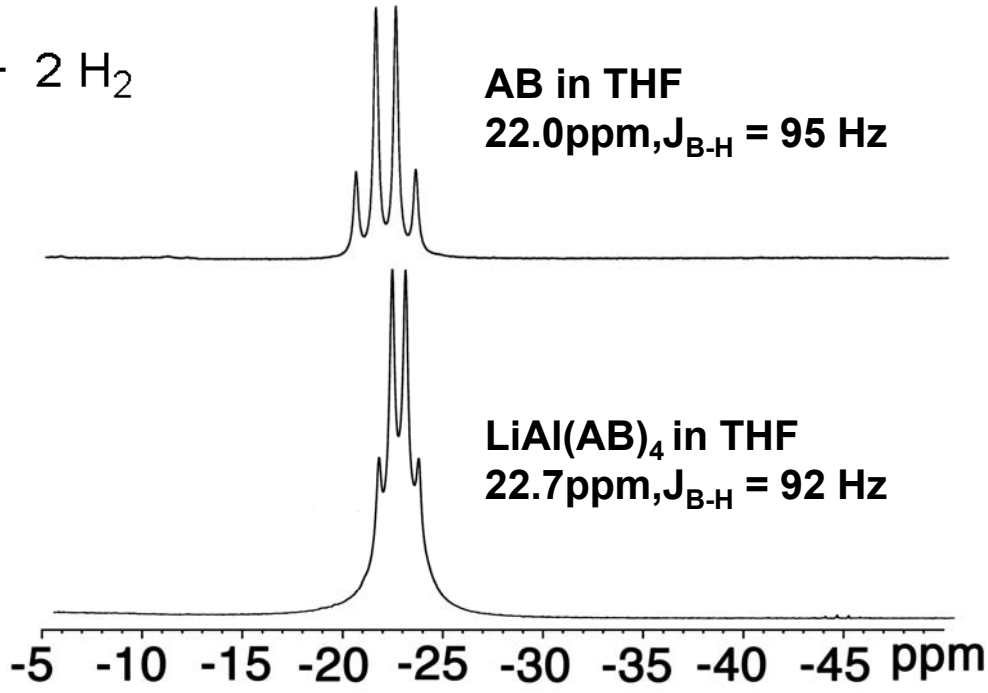
M-AB Derivatives are well-characterized.

Technical Accomplishments and Progress

^{11}B NMR Studies on $LiAl(AB)_4$ Complex

$Li[Al(NH_2BH_3)_4]$

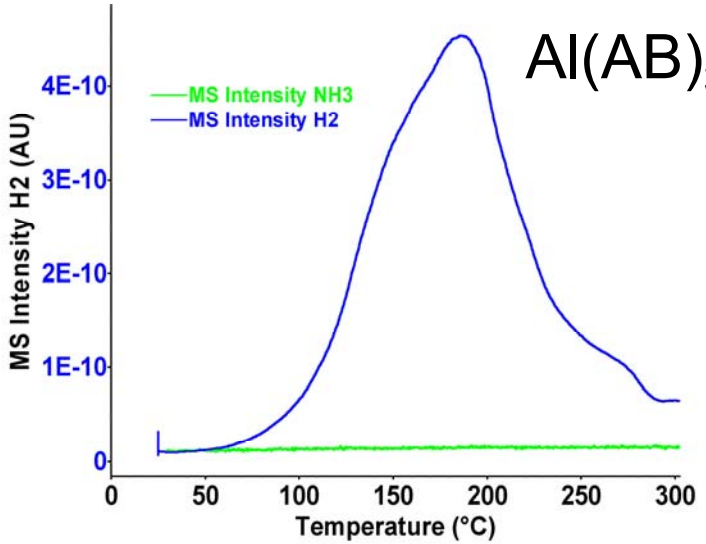
$$LiAlH_4 + 4\,NH_2BH_3 \longrightarrow LiAl(NH_2BH_3)_4 + 2\,H_2$$

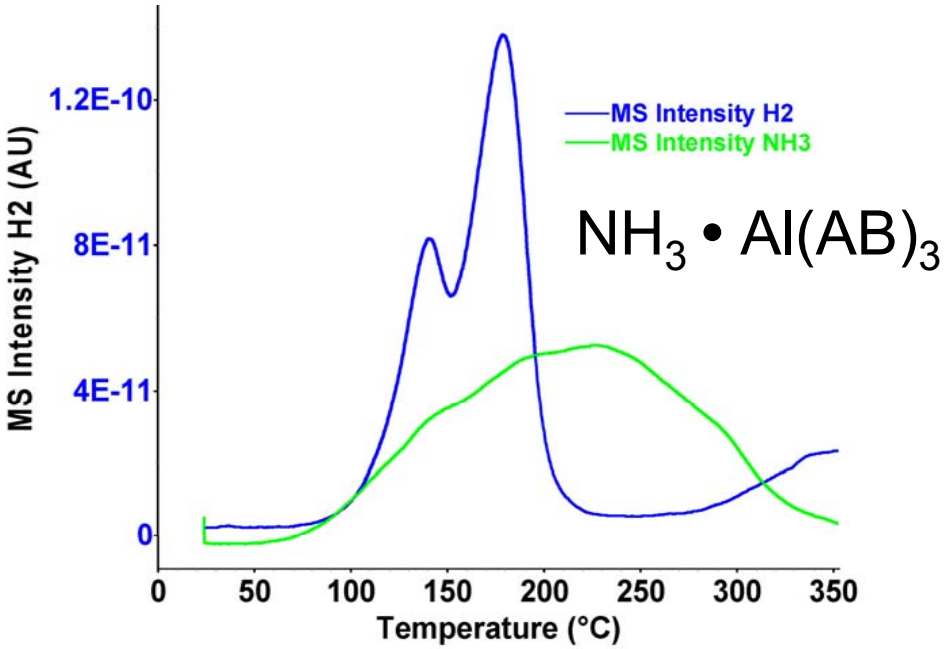


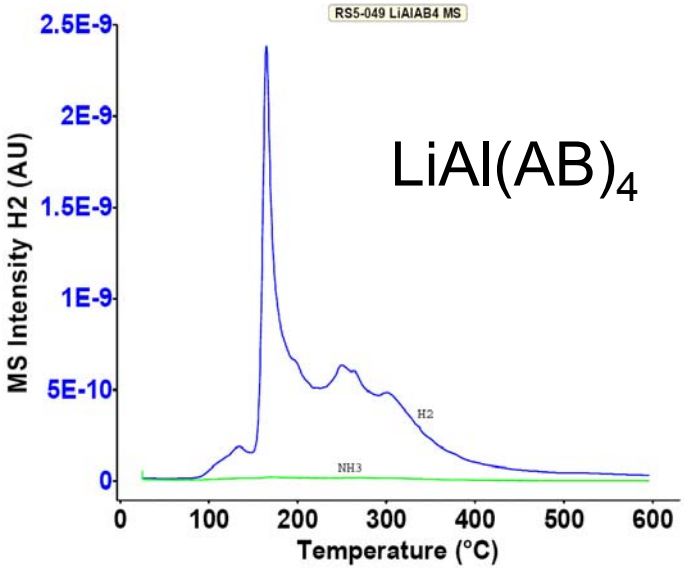
- The reaction of $LiAlH_4$ with AB in THF gives quantitative yield of $LiAl(NH_2BH_3)_4$.
- An unidentified precipitate was formed from the reaction of NH_3 with $LiAl(NH_2BH_3)_4$.

M-AB adducts are characterized.
Milestone complete.

Thermal Dehydrogenation Studies TGA-MS



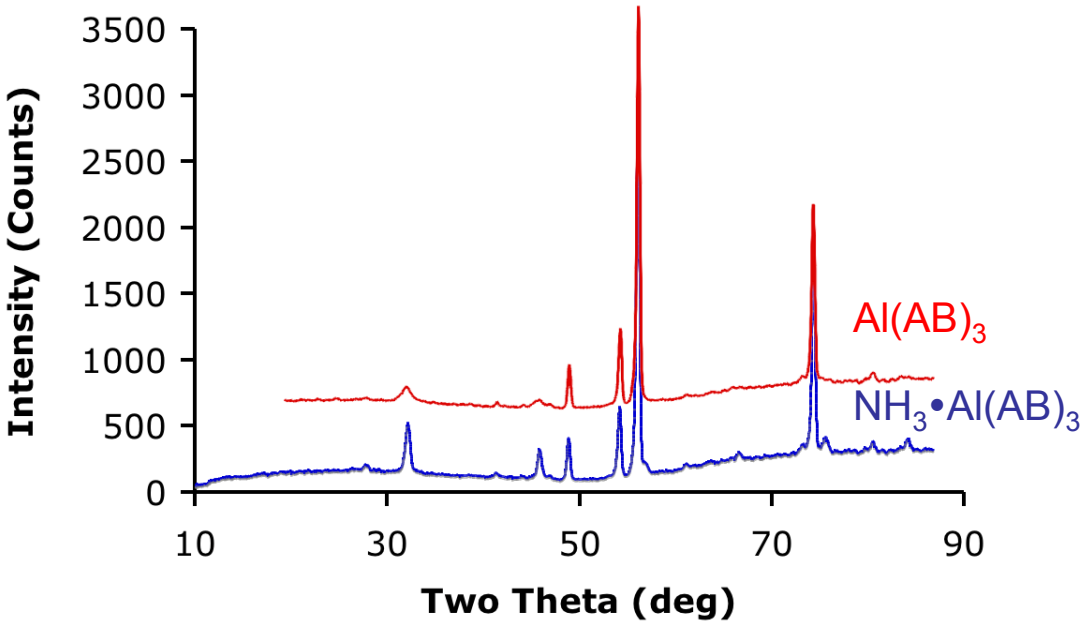


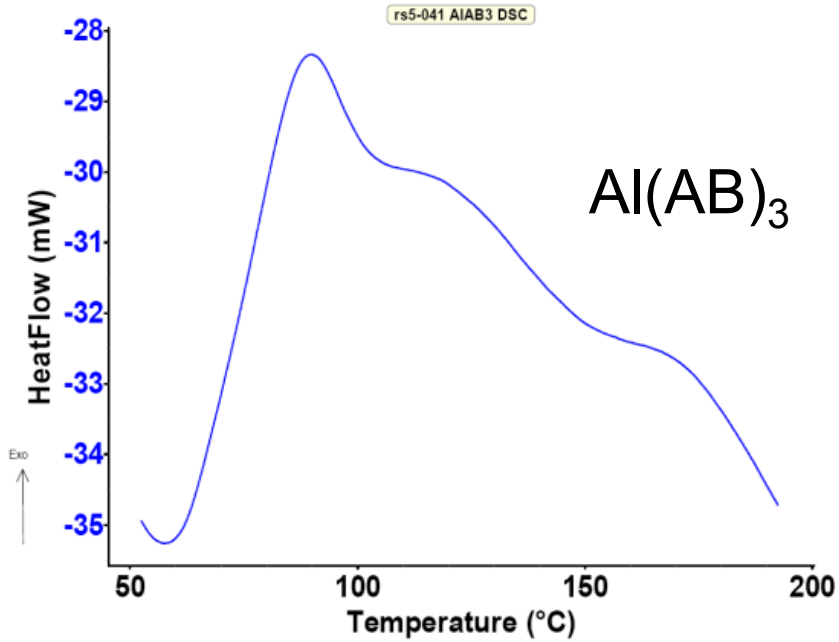


- $Al(NH_2BH_3)_3$ starts releasing hydrogen at 60 °C.
- NH_3•$Al(NH_2BH_3)_3$ releases ammonia when heated.
- $LiAl(AB)_4$ releases hydrogen at higher temperatures.

Thermal release studies are underway.
Milestone complete.

Powder X-ray Diffraction and DSC of Al-AB Complexes





The powder X-ray diffraction pattern of these complexes exhibit similar pattern suggesting that ammonia is incorporated in the unit cell via hydrogen bonding.

Preliminary DSC analysis indicates the $Al(AB)_3$ has exothermic hydrogen release therefore will require off-board regeneration. (milestone)

Collaboration

University of Missouri project is coordinated with Center Partners through frequent discussions, monthly conference calls, sample sharing and analytical instrumental support.

- Los Alamos National Laboratory
  - Dehydrogenation studies.
  - Regeneration efforts.
- Pacific National Laboratory
  - Solid state NMR studies.
  - Regeneration efforts.

Future Work

- Continue the analysis of hydrogen release from these new materials.
- Determine long term stability of new materials.
- Establish hydrogen release kinetics for new materials.
- Determine solid state structures.

Summary

Since last review – for year 2009

- Synthesized $Al(AB)_3$, $LiAl(AB)_4$ complexes and their ammonia adducts in good yields. The complexes were characterized by NMR and IR studies.

- Preliminary dehydrogenation studies indicate Al-AB complexes release hydrogen at 60 °C, lower than AB alone.

- TGA-MS studies show that the ammonia adduct of Al-AB complex also releases ammonia.