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
- PNNL

Los Alamos NATIONAL LABORATORY Pacific Northwest NATIONAL LABORATORY

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.

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

$$n\ LiAl(NH_2BH_3)_4\ (s) \longrightarrow [LiAl(NBH)_4]_n\ (s) + 8n\ H_2\ (g)\ \text{(10.4 wt.\% Hydrogen)}$$

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

Approach-Relevance
Aluminum Amidoboranes

- 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. NH_3BH_3 (s) $\longrightarrow$ BNHn (s) + 2.5 H_2 (g) (19 wt% hydrogen)

b. $n\, LiNH_2BH_3$ (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)

c. $n\, NaNH_2BH_3$ (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)

d. $n\, Ca(NH_2BH_3)_2$ (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)

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

f. $n\, Al(NH_2BH_3)_3$ (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)

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

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

Approach
Synthesis of Al-AB Complexes

- For this study we focused our efforts on the synthesis of $Al(NH_2BH_3)_3$ and $LiAl(NH_2BH_3)_4$ [referred to as $Al(AB)_3$ and ($LiAl(AB)_4$ respectively].

- Metathesis reaction of $AlCl_3$ with M-AB (M = Li, Na or K) should give $Al(AB)_3$. Further reaction of $Al(AB)_3$ with liquid NH_3 will give the ammonia adduct, NH_3•$Al(AB)_3$.

- Similarly the reaction of $LiAlH_4$ 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 $AlCl_3$ 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)

$Al(NH_2BH_3)_3$ from $AlCl_3$

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

M = Li, Na or K

$$Al(NH_2BH_3)_3 + NH_3\ (\text{excess}) \longrightarrow NH_3 \bullet Al(NH_2BH_3)_3$$

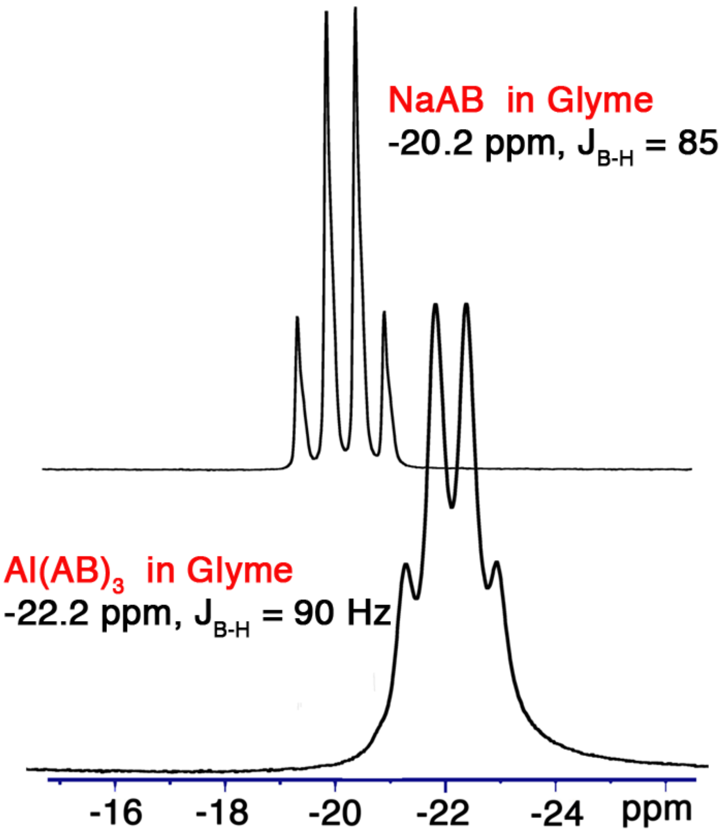
$LiAl(AB)_4$ was synthesized in quantitative yield by reacting $LiAlH_4$ with AB at room temperature.

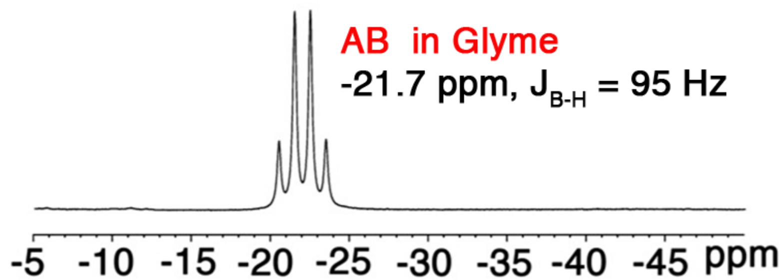
$Li[Al(NH_2BH_3)_4]$ from $LiAlH_4$

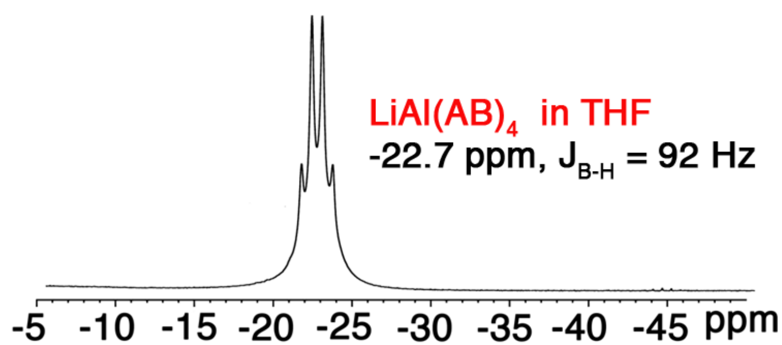
$$LiAlH_4 + 4\,NH_3BH_3 \longrightarrow LiAl(NH_2BH_3)_4 + 4\,H_2$$

Technical Accomplishments and Progress- Characterization of Al-AB Complexes

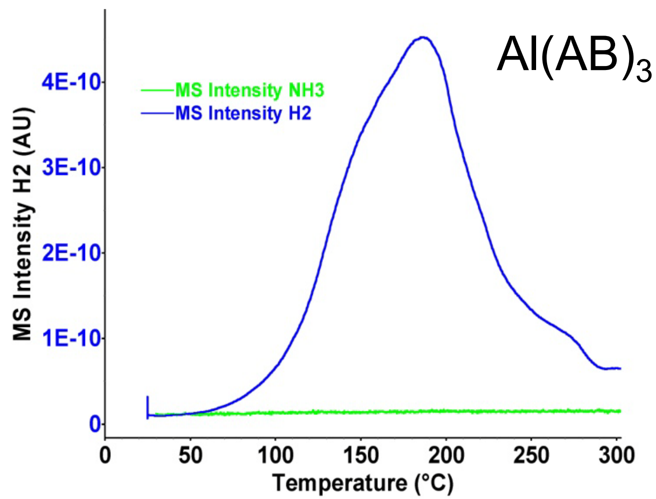
Both $Al(AB)_3$ and $LiAl(AB)_4$ are colorless solids. $LiAl(AB)_4$ is thermally more stable than $Al(AB)_3$. Amine adducts of $Al(AB)_3$ are colorless polymeric compounds insoluble in common organic solvents. (Milestone)

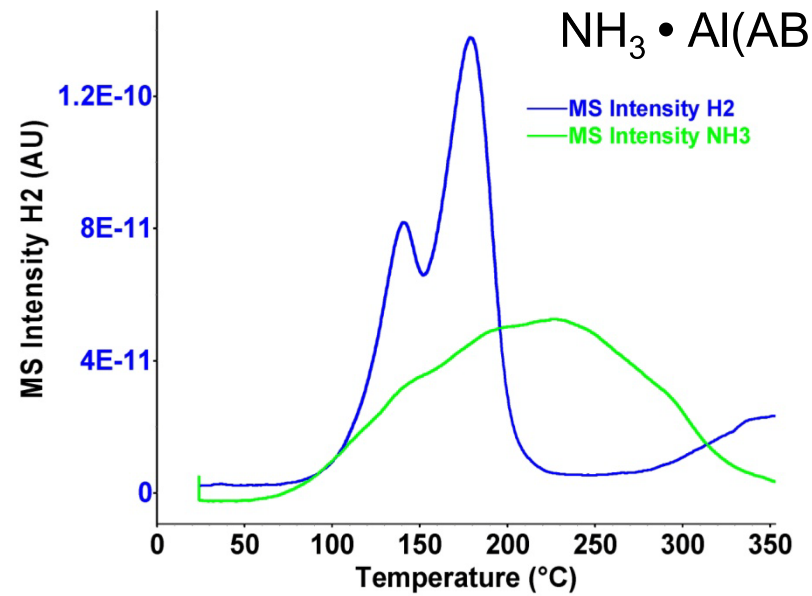


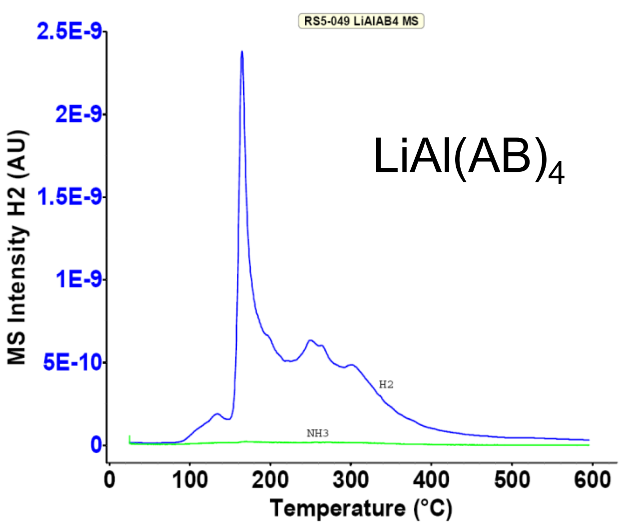




Technical Accomplishments and Progress- Thermal Dehydrogenation Studies TGA-MS



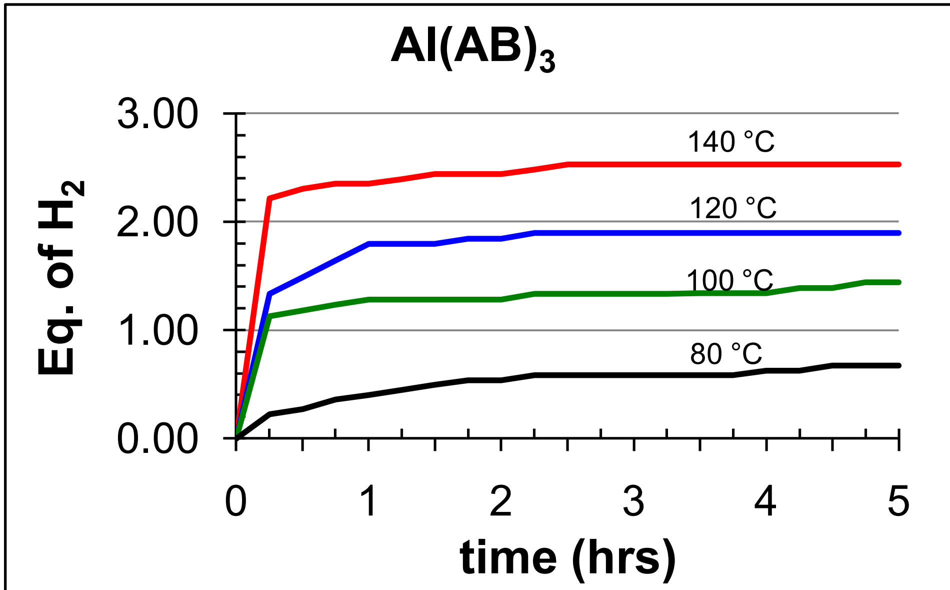


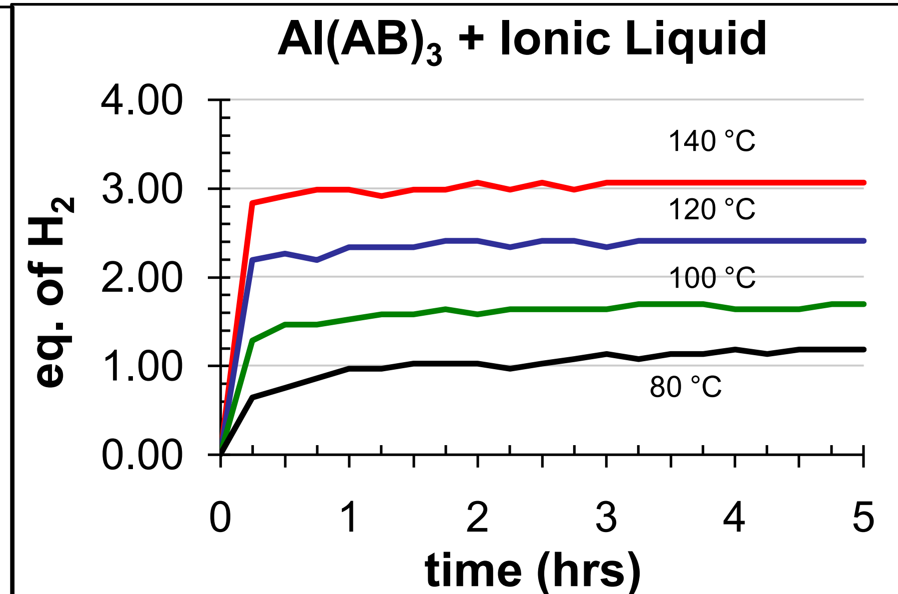


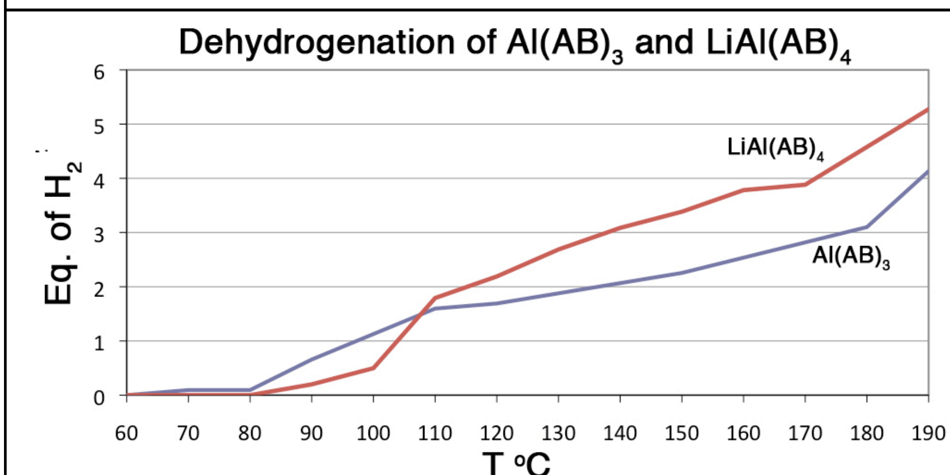
- $Al(AB)_3$ starts releasing hydrogen at 60 °C.
- $NH_3 \bullet Al(AB)_3$ releases ammonia when heated.
- $LiAl(AB)_4$ releases hydrogen at higher temperatures.
- Preliminary DSC analysis indicates the $Al(AB)_3$ has exothermic hydrogen release therefore will require off board regeneration. (milestone)

Partner - LANL

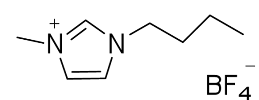
Technical Accomplishments and Progress- Dehydrogenation of $Al(AB)_3$







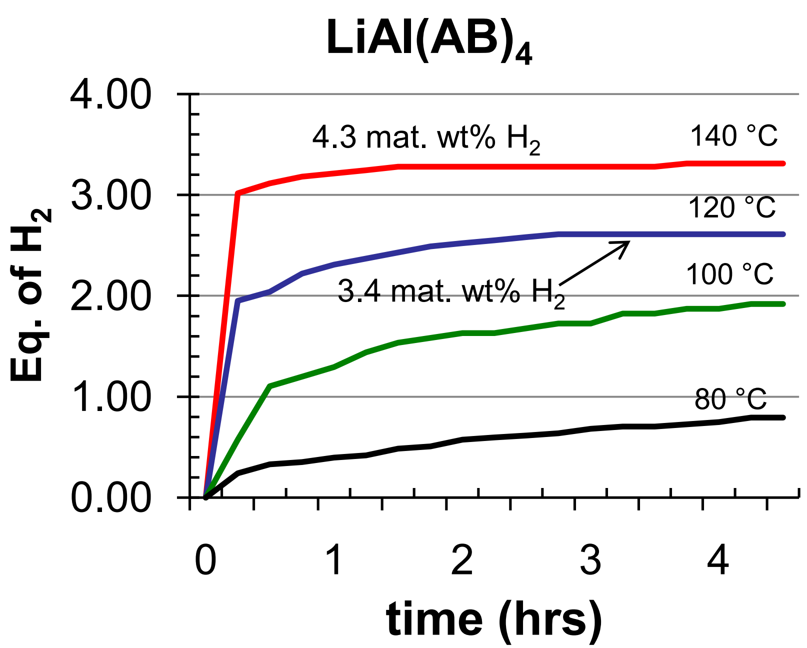
$Al(AB)_3$ releases more hydrogen in the presence of a ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate

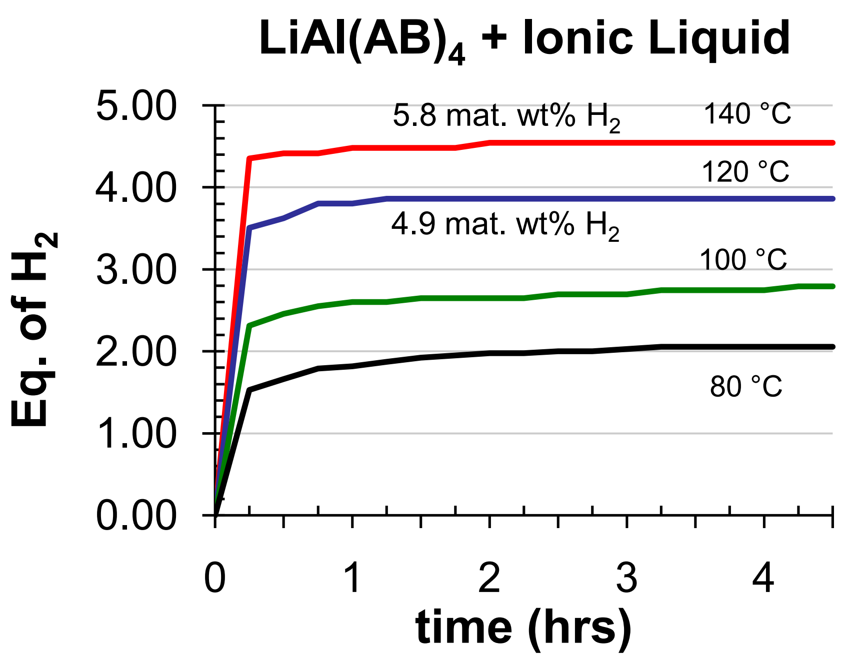


(Milestone)

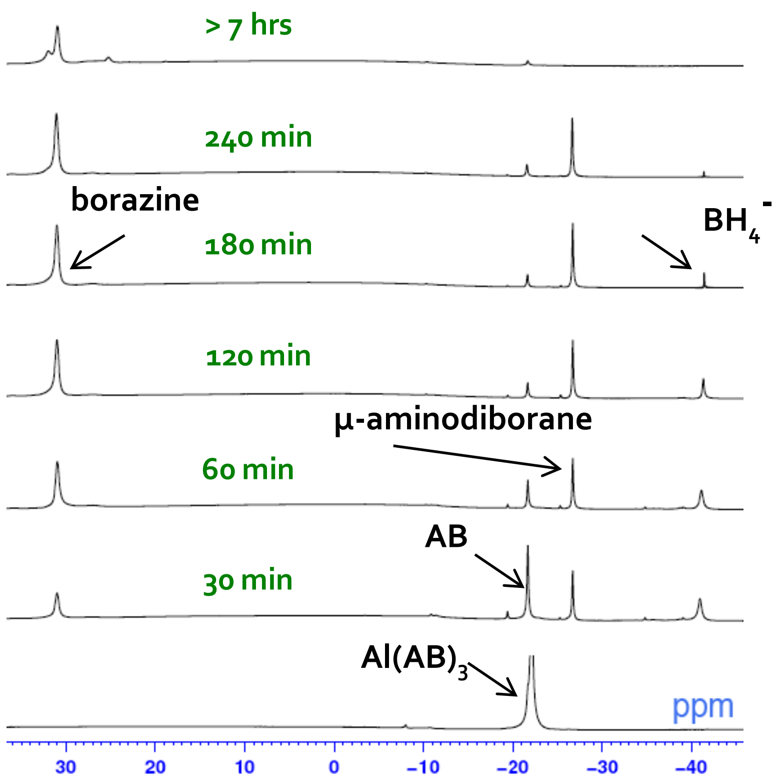
Technical Accomplishments and Progress- Dehydrogenation of $LiAl(AB)_4$

$LiAl(AB)_4$ releases more hydrogen in the presence of a ionic liquid – 1-butyl-3-methylimidazolium tetrafluoroborate

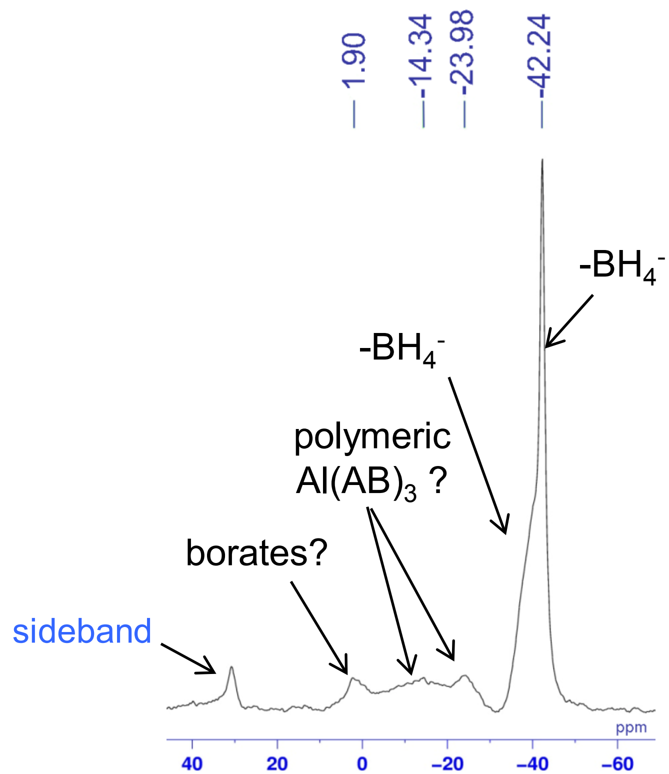




Technical Accomplishments and Progress- NMR Studies on $Al(AB)_3$ Dehydrogenation

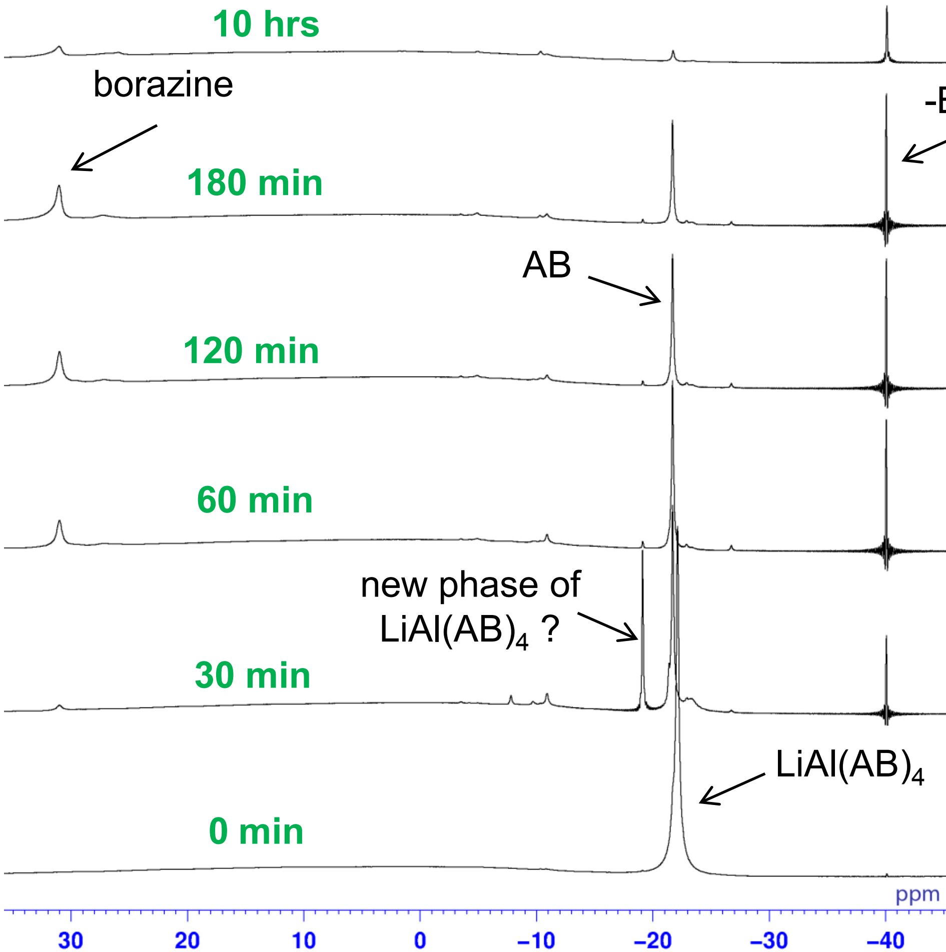


Solution [11]B NMR (160 MHz) of thermolysis products of $Al(AB)_3$ at 80 °C in glyme.



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



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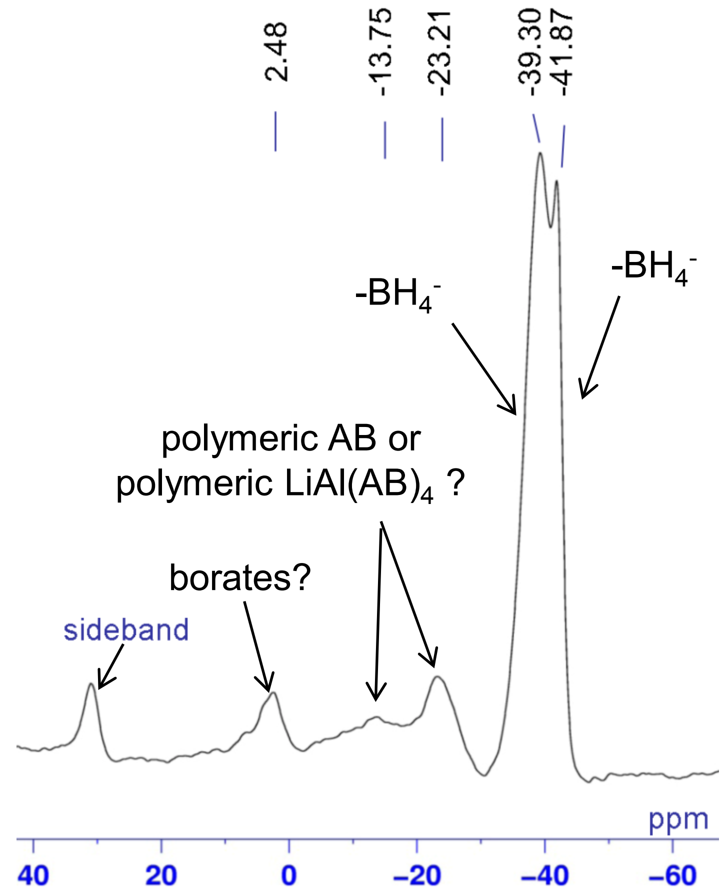

Solid state CPMAS [11]B NMR (96 MHz) of thermolysis products of $LiAl(AB)_4$ after 4h at 120 °C.

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.