

IV.B.11 Chemical Hydrogen Storage Using Polyhedral Borane Anions and Aluminum-Ammonia-Borane Complexes

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Project End Date: March 2010

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency

Technical Targets

Phase II - Al-AB Complexes:

- This project is directed towards evaluating Al-AB complexes as candidates for hydrogen storage. The hydrogen release studies on these complexes coupled with Center's efforts on other AB materials will be targeted towards the design and synthesis of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:
 - Cost: \$4/kWh net
 - Specific energy: 1.5 kWh/kg
 - Energy density: 0.9 kWh/L

(Note: the specific energy and energy density are the revised DOE 2010 hydrogen storage targets.)

Objectives

Phase I

- Develop heterogeneous catalysts for the controlled generation of hydrogen from the hydrolysis of salts of $B_{12}H_{12}^{2-}$, $B_{10}H_{10}^{2-}$ and $B_{11}H_{14}^{-}$ ions.
- Determine the kinetics and mechanism of these catalyzed borane anion hydrolysis reactions to provide design data for large-scale hydrogen generation devices.

Phase II

- Synthesize and evaluate aluminum-ammonia-borane (Al-AB) complexes as hydrogen storage candidates.
- Carry out hydrogen release studies on Al-AB complexes by thermal dehydrogenation process.
- Investigate the regeneration of the spent material.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

Accomplishments

- Synthesized various Al-AB complexes. These include $Al(NH_2BH_3)_3$, $LiAl(NH_2BH_3)_4$ and their ammonia adducts.
- Conducted initial hydrogen release experiments on these complexes by thermal dehydrogenation process. $Al(NH_2BH_3)_3$ complex starts releasing hydrogen at 60°C. The $LiAl(NH_2BH_3)_4$ complex and ammonia adduct of $Al(NH_2BH_3)_3$ generate hydrogen at 100°C.
- Discovered that ammonia adduct of $Al(NH_2BH_3)_3$ also releases NH_3 when heated above 80°C.
- Preliminary differential scanning calorimetric (DSC) studies on $Al(NH_2BH_3)_3$ indicate that the hydrogen release from this complex is exothermic and will require off-board regeneration.



Introduction

The phase I of the University of Missouri efforts were directed towards investigating catalytic hydrolysis of polyhedral borane anions for hydrogen generation. This project was down-selected in year 2008. The phase II of the project is directed towards evaluating Al-AB complexes as chemical hydrogen candidates.

The AB molecule is a demonstrated source of chemically stored hydrogen, which can meet DOE performance parameters except for its regeneration from spent AB and elemental hydrogen. Our project is focused on the synthesis and evaluation of AB derivatives containing aluminum as a structural component since some direct reactions of aluminum and its derivatives with dihydrogen are known processes which yield Al-H intermediates and products. Consequently, the presence of an aluminum center bonded to multiple AB residues might combine the efficiency of AB dehydrogenation with an aluminum mediated hydrogenation process leading to reversibility. Other modifications could also be used to test for reversible regeneration such as the introduction of transition metal catalysts and the use of ionic liquid solvation. Figure 1 illustrates hydrogen capacity of AB and metal ammonia-borane (M-AB) complexes.

Approach

In the phase II of the project the center has focused its efforts on developing amino boranes and M-AB complexes as candidates for chemical hydrogen storage. The project at the University of Missouri is focused upon developing Al-ABs as sources for hydrogen fuel generation, specifically their synthesis, dehydrogenation and regeneration studies. Initially we have concentrated our efforts on the synthesis of $\text{Al}(\text{NH}_2\text{BH}_3)_3$, $\text{LiAl}(\text{NH}_2\text{BH}_3)_4$ and their ammonia adducts. Figure 1 shows the theoretical hydrogen wt% capacity for AB and various metal amido boranes. The Al-AB complexes have comparable hydrogen capacity with other M-ABs and have potential to meet DOE's 2010 and 2015 targets for system wt%.

Results

During the last year we investigated a number of routes to synthesize Al-AB complexes. Of these routes, the reaction of $\text{M}(\text{NH}_2\text{BH}_3)_n$ where $\text{M} = \text{Li}, \text{Na}$ or K with AlCl_3 gave the desired $\text{Al}(\text{NH}_2\text{BH}_3)_3$ complex. The $\text{M}(\text{NH}_2\text{BH}_3)_n$ were prepared from the reaction of NH_3BH_3 with corresponding metal hydrides. The reaction of $\text{Li}(\text{NH}_2\text{BH}_3)$ with AlCl_3 at low temperature gives $\text{Al}(\text{NH}_2\text{BH}_3)_3$ in good yield, but the isolation of the pure product is complicated. Alternatively, the reaction

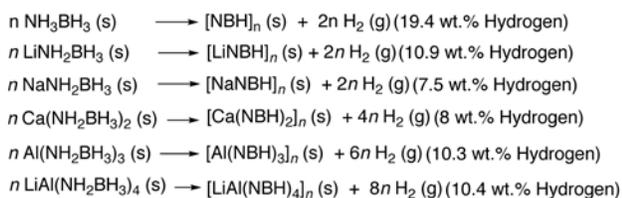
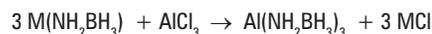


FIGURE 1. Hydrogen Capacity for AB and M-AB

of $\text{Na}(\text{NH}_2\text{BH}_3)$ with AlCl_3 proceeded well to give Al-AB in 70% yield. The purity of the material was confirmed by ^{11}B and ^{27}Al nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy.

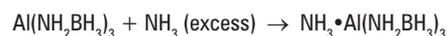


General Procedure for the Synthesis of $\text{Al}(\text{NH}_2\text{BH}_3)_3$

The reaction was carried out by adding a solution of AlCl_3 in glyme to a solution of M-AB ($\text{M} = \text{Li}, \text{Na}$ or K) at -10°C over a period of 30 minutes. The reaction was further stirred for 4 h at -10°C . The reaction was monitored by observing the ^{11}B NMR spectrum of a sample of the reaction mixture. Completion of the reaction is indicated by the disappearance of M-AB peak at 20.2 ppm. The reaction mixture was filtered and the solvent was removed under vacuum. The resulting solid was washed with a mixture of glyme and diethyl ether to give $\text{Al}(\text{NH}_2\text{BH}_3)_3$ in approximately 70% yield. The product $\text{Al}(\text{NH}_2\text{BH}_3)_3$ was characterized by ^{11}B , ^1H and ^{27}Al NMR and IR spectroscopy (Figure 2).

Synthesis of $\text{NH}_3 \cdot \text{Al}(\text{NH}_2\text{BH}_3)_3$ Adduct

The ammonia adduct of $\text{Al}(\text{NH}_2\text{BH}_3)_3$ was synthesized by reacting $\text{Al}(\text{NH}_2\text{BH}_3)_3$ with excess of ammonia in tetrahydrofuran and isolated as an insoluble precipitate.



The complex was characterized by solid-state ^{11}B NMR and IR spectroscopy. A powder X-ray diffraction study showed that the ammonia adduct is structurally similar to the parent $\text{Al}(\text{NH}_2\text{BH}_3)_3$ complex and suggests that the ammonia is incorporated in the unit cell by hydrogen bonding. To gain more insight into the structure of this ammonia adduct we are synthesizing various amine complexes of $\text{Al}(\text{NH}_2\text{BH}_3)_3$ which will be soluble in common organic solvents and will be more

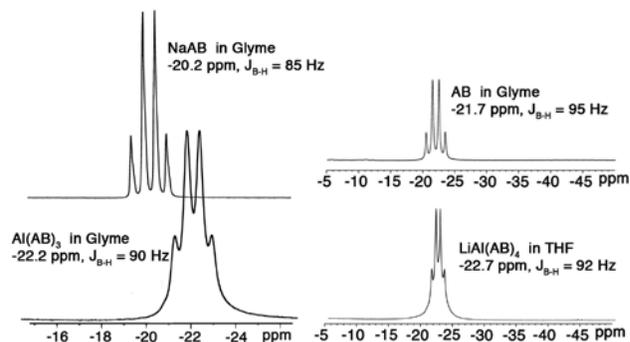
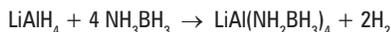


FIGURE 2. ^{11}B NMR Characterizations of Al-AB Complexes

suitable for structural characterization studies including single crystal X-ray diffraction analysis.

Synthesis of $\text{LiAl}(\text{NH}_2\text{BH}_3)_4$

The synthesis of $\text{LiAl}(\text{NH}_2\text{BH}_3)_4$ was achieved by reacting LiAlH_4 with AB at room temperature for 24 h. The product was characterized by ^{11}B and ^{27}Al NMR spectra and IR spectroscopy.



The reaction of this $\text{LiAl}(\text{NH}_2\text{BH}_3)_4$ with liquid ammonia gave a white precipitate. Further structural characterization of this precipitate is currently underway.

Thermal Dehydrogenation Studies on Al-AB Complexes

Figure 3 shows the thermogravimetric analysis-mass spectrometer (TGA-MS) analysis of Al-AB complexes.

These studies done at Los Alamos National Laboratory show that $\text{Al}(\text{NH}_2\text{BH}_3)_3$ releases hydrogen at 60°C and the ammonia adduct $\text{NH}_3 \cdot \text{Al}(\text{NH}_2\text{BH}_3)_3$ generates hydrogen at 100°C . The ammonia adduct also releases ammonia at 100°C . The $\text{LiAl}(\text{NH}_2\text{BH}_3)_4$ complex starts releasing hydrogen at 110°C and peaks at around 170°C . A DSC analysis on $\text{Al}(\text{NH}_2\text{BH}_3)_3$ indicates that the hydrogen release process is exothermic and therefore will require an off-board regeneration process.

Hydrogen release experiments on $\text{Al}(\text{NH}_2\text{BH}_3)_3$ and $\text{LiAl}(\text{NH}_2\text{BH}_3)_4$ complexes were carried out by heating the complexes to 190°C in the absence of solvent or a catalyst. A plot of moles of hydrogen released vs. temperature is shown in Figure 4. In the case of $\text{Al}(\text{NH}_2\text{BH}_3)_3$ complex, approximately 4.1 moles of hydrogen is released at 190°C , which corresponds to about 6 wt% hydrogen based on material wt%. The $\text{LiAl}(\text{NH}_2\text{BH}_3)_4$ complex under similar experimental conditions released approximately 5.2 moles of hydrogen

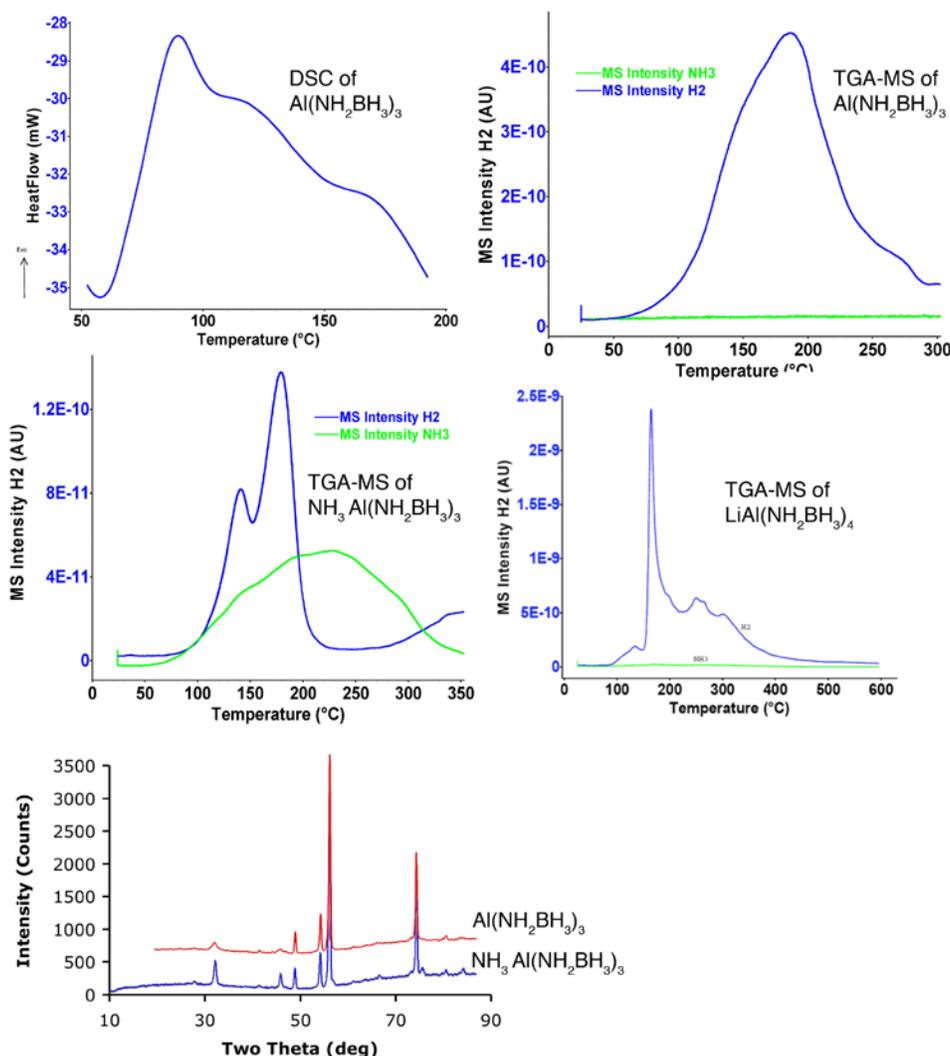


FIGURE 3. TGA-MS, DSC and Powder X-ray Study of Al-AB Complexes

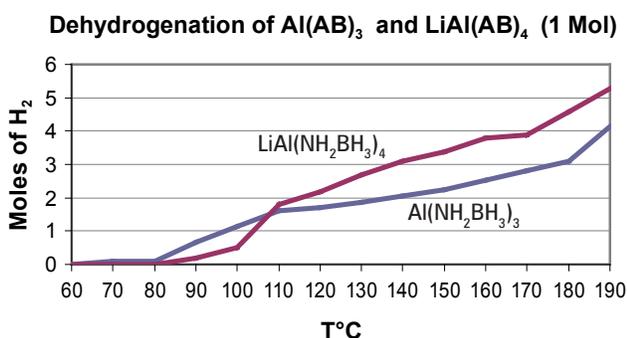


FIGURE 4. Thermal Dehydrogenation of $\text{Al}(\text{NH}_2\text{BH}_3)_3$ and $\text{LiAl}(\text{NH}_2\text{BH}_3)_4$ Complexes

which corresponds to around 7 wt% hydrogen based on material wt%. Further detailed quantitative hydrogen release measurements in the presence of a catalyst as well as kinetic studies on these Al-AB complexes are currently being carried out in our laboratories.

Conclusions and Future Directions

Al-AB complexes are viable candidates for chemical hydrogen storage. Our preliminary studies show that they can be easily synthesized from AB precursors and they are capable of generating hydrogen at lower temperature than AB alone.

- Synthesis of Al-AB complexes was achieved.
- Dehydrogenation in the absence of a catalyst show that they can generate hydrogen up to 7 wt%.

- TGA-MS analysis on the ammonia adduct of $\text{Al}(\text{NH}_2\text{BH}_3)_3$ showed that ammonia is also released when the complex is heated above 100°C.

Future Studies

- Carry out detailed hydrogen release experiments and conduct kinetic studies on the dehydrogenation process.
- Improve the hydrogen generation rate at lower temperature.
- Identify a suitable catalyst for dehydrogenation process.
- Identify spent material and investigate metal hydride mediated regeneration of the spent material.
- Structurally characterize Al-AB complexes.

FY 2009 Publications/Presentations

1. Poster presentation at DOE annual merit review, Washington, D.C., May 2009.