

IV.A.1m Preparation and Reactions of Complex Hydrides for Hydrogen Storage: Metal Borohydrides and Aluminum Hydrides

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Objectives

ORNL is conducting research to develop the chemistry for a reversible hydrogen storage system based on complex hydrides, chosen mostly from the borohydrides, amine borohydrides, amides/imides, alane or the alanates of the light elements in the periodic table that will achieve the DOE/FreedomCAR performance targets for 2010.

Technical Barriers

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

- (A) System Weight and Volume
- (P) Lack of Understanding of Hydrogen Chemisorption and Physisorption

Technical Targets

ORNL is investigating high wt% materials, and efforts are directed toward making the release and uptake of hydrogen reversible. Percentages in Table 1 are for H₂ release only.

TABLE 1. Progress towards Meeting Technical Targets for Reversible Hydrogen Storage

Characteristic/ System	Units	2010/2015 DOE Targets/ Theoretical	ORNL observed
System Gravimetric Capacity	wt% (kg H₂/kg system x 100)	6%/9%	—
Al(BH ₄) ₃	—	16.92%	14.5%
Al(BH ₄) ₃ (NH ₃) ₂	—	17.19%	15.2%
Al(BH ₄) ₃ (NH ₃) ₃	—	17.26%	16.0%
Mg(BH ₄) ₂ (NH ₃) ₂	—	16.0%	14.6%

Accomplishments

Progress was made toward preparing new materials and understanding the mechanism of hydrogen release from metal borohydrides:

- Initiated a study of ammine metal borohydride (AMBH) complexes: synthesis, structure, and potential as hydrogen storage materials.
- Mg- and Ca-AMBH were prepared via a solvent-free synthesis route.
- The solvent free reaction of anhydrous ammonia with Al(BH₄)₃ gives the product Al(BH₄)₃(NH₃)₂; reaction of ammonia with aluminum borohydride in toluene and ether solvents gives different products.
- Investigated ionic liquids as a reaction medium for regenerating alane. The AlH₄⁻ anion appears to react with the imidazolium cation of the ionic liquid. Further work on ionic liquids will be discontinued.



Introduction

The focus of work at ORNL is the development of new materials, synthetic methods for materials, and studies of chemical reactions and processes that will lead to materials that will achieve the DOE/FreedomCAR performance targets for 2010. ORNL generally develops synthetic methods based on methodology that offers the most potential for scaling to kilogram and greater lot size. Synthetic methods are being developed and reactions are being studied for two types of target materials for hydrogen storage: complex anionic materials (Metal Hydride Center of Excellence [MHCoe] Project B) and amide/imide (M-N-H) systems (MHCoe Project C). For both types of materials ORNL is seeking (a) methods to scale up synthesis of

known materials or new materials identified by MHCoe partners (b) development of new materials. ORNL is also collaborating with scientists at Brookhaven National Laboratory in MHCoe Project D, the alane focus group, with an emphasis on using the methods of solution inorganic and organometallic chemistry in an effort to develop or improve processes to regenerate alane.

Approach

Our research involves materials from both known synthesis as well as those from newly designed synthetic procedures. The primary method used to follow the progress of reactions which release hydrogen is by temperature programmed pressure measurements where gaseous reaction products other than hydrogen are analyzed using a mass spectrometer or by infrared spectroscopy. Hydrogen desorption and uptake are investigated in a traditional Sieverts apparatus. Fourier transform infrared spectroscopy, X-ray diffraction (XRD), and elemental analysis by inductively coupled plasma-atomic emission spectroscopy as well as solution nuclear magnetic resonance (NMR) are available at ORNL to characterize solid reaction products, and Raman and solid NMR are available through collaboration with MHCoe partners. Structural determination using high resolution synchrotron-based XRD is available through internal collaboration at ORNL. Each material will initially be examined in a dehydrogenation study, both with and without catalysts. Those materials found to be suitable hydrogen storage material candidates will then be examined for regenerative (hydrogen absorption) capability. From these results, chemical (and-or procedural) adjustment to the most promising of the materials will be made in order to obtain the optimal in hydrogen de/absorption capacity.

Results

The majority of research at ORNL during the review period involved a study of AMBH, obtained from the reaction of ammonia with a metal borohydride. Although other researchers are investigating these materials as well, a unique feature in our study is our use of a solvent-free reaction system in which anhydrous ammonia is directly reacted with a metal borohydride. Our study has included the reaction of ammonia with Mg, Ca, and Al borohydrides, and for all three metals we can easily form the AMBH as a completely solvent-free product by direct reaction. This amination of the metal borohydrides was also shown to provide very important and desirable material properties as well as an increase in the amount of hydrogen desorbed in the case of Mg and Al borohydrides.

The Mg-AMBH is a quite promising material that was previously reported by Soloveichik, et al. [1]. Our innovation is the preparation of this compound by the direct (solvent free) reaction of anhydrous ammonia with magnesium borohydride. This material exhibits a remarkably low temperature for desorption compared to its parent metal borohydride, and our work shows it undergoes a fairly clean hydrogen desorption reaction, lacking any trace of by-products such as ammonia or diborane as observed by mass spectrometry. The quantity of hydrogen produced in the desorption indicates the ammonia is serving as a source of hydrogen as well as the borohydride. Interestingly, although $\text{Mg}(\text{BH}_4)_2$ was found to undergo a completely solid state desorption, the Mg-AMBH melts just prior to the H_2 desorption ($\sim 97^\circ\text{C}$). The solid magnesium:nitrogen:boron product following desorption of the hydrogen is amorphous to XRD and remains unidentified. To assist in the identification of the residue, we obtained ^{15}N -labeled ammonia and prepared a sample of $\text{Mg}(\text{BH}_4)_2(^{15}\text{NH}_3)_2$. This sample was given to our collaborators at the Jet Propulsion Laboratory and Caltech for analysis of the reaction product residue by high resolution ^{15}N -magic angle spinning-NMR (MAS-NMR). This experiment is still in progress.

The temperature programmed desorption of the Ca-AMBH yielded disappointing results. Although this material was easily synthesized (as either a mono or diammine species) via the solvent-free method, it was found that this material loses the NH_3 at a much lower temperature than that for hydrogen desorption. Several studies with a Sievert's apparatus proved that the material easily transformed back into $\text{Ca}(\text{BH}_4)_2$ prior to H_2 desorption, and then simply followed the usual desorption path previously shown for solvent free calcium borohydride. On a positive note, we found that even the solvated $\text{Ca}(\text{BH}_4)_2$ -tetrahydrofuran (THF) (as purchased from Aldrich) can be easily transformed into $\text{Ca}(\text{BH}_4)_2\cdot 2\text{NH}_3$ and then subsequently converted to the solvent-free $\text{Ca}(\text{BH}_4)_2$ as the ammonia is released. This reaction could be potentially useful for preparing $\text{Ca}(\text{BH}_4)_2$ in the pores of a carbon scaffold. The $\text{Ca}(\text{BH}_4)_2$ could be deposited in the pores in THF solution, the THF removed by formation of the NH_3 adduct, and the NH_3 removed by thermal treatment. The ammonia adduct of LiBH_4 was also observed to evolve ammonia prior to loss of hydrogen from the borohydride [2].

Aluminum borohydride was found to readily react with anhydrous ammonia in a 1:2 ratio in the absence of solvent to form $\text{Al}(\text{BH}_4)_3 \cdot 2\text{NH}_3$. The formation of this Al-AMBH resulted in a greatly increased material stability relative to the parent metal borohydride. While the volatile $\text{Al}(\text{BH}_4)_3$ (a liquid at room temperature) is explosive in air, its ammine counterpart is a white solid that only slowly decomposes in air and gently bubbles hydrogen as water is added. This same increase of

material stability has been noted with the ammination of the magnesium and calcium borohydrides as well. The H_2 desorption study of this Al ammine metal borohydride demonstrate that the added ammonia is actually contributing to the wt% hydrogen desorbed from the material as was observed for the Mg-AMBH. The temperature programmed desorption data is shown in Figure 1. Mass spectrometry analysis of the gas desorbed from the Al-AMBH has revealed trace amounts of ammonia, diborane, and borazine, $B_3H_3N_3H_3$, suggesting that the desorption reaction involves reaction of BH_3 and NH_3 components, facilitated by the Al(III), to form ammonia borane or another BHNH species. The decrease in hydrogen evolution at 100 bar H_2 pressure offers some hope that the system can be at least partially regenerated.

Preparation of Al-AMBH was investigated by reaction of ammonia with aluminum borohydride in toluene and in ether, and the products were different than that formed in the solvent free reaction as shown by XRD and elemental analysis. In toluene, the composition is very close to that prepared under solvent free conditions, and the composition is $Al(BH_4)_3(NH_3)_3$. The reaction in diethyl ether is quite different and involved loss of one BH_3 group prior to precipitation of the Al-AMBH. The structures of the materials prepared in solution were determined using high resolution XRD data collected at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. Although the $Al(BH_4)_3 \cdot 2NH_3$ material formed in the solvent free reaction has enhanced stability to air and water over the parent borohydride, we have discovered that the initially formed Al-AMBH slowly decomposes in the solid state into another phase (as detected by powder XRD). For this reason we were unable to determine the structure of this material during our experimental run at NSLS. The solvent-free Al-AMBH product was slowly transformed into two phases over time at room temperature with the

evolution of gas which included some diborane. One of the reaction products seems to be identical to the product formed in ether solution

The product formed in toluene has the structure shown in Figure 2 in which the Al centers have trigonal bipyramidal geometry with axial ammonia groups coordinated to the Al(III) sites. A view of the unit cell shows an additional ammonia group loosely associate with one of the borohydrides. We presume that the structure of the solvent-free product $Al(BH_4)_3(NH_3)_2$ has coordination about the Al site analogous to that shown in Figure 2. The temperature programmed desorption of $Al(BH_4)_3(NH_3)_3$ is shown in Figure 3. The total amount of hydrogen desorbed by this material at $550^\circ C$ is 16%, a value that rivals such chemical hydrides as NH_3BH_3 . Furthermore the mass spectrometry of the evolved gases from the stoichiometrically balanced $Al(BH_4)_3(NH_3)_3$ compound does not show evidence for even trace amounts of ammonia, diborane, or borazine. Formation of a borane ammonia adduct is likely occurring but the residue is amorphous, and vibrational spectroscopy and

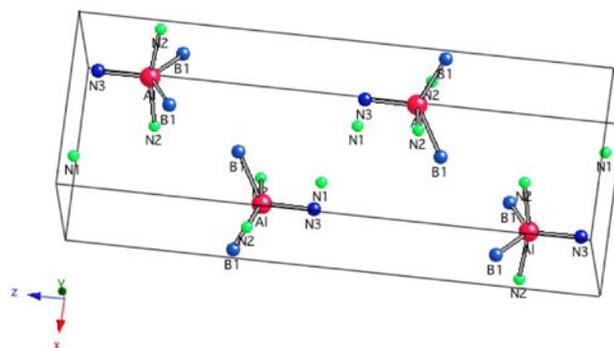


FIGURE 2. Structure of $Al(BH_4)_3(NH_3)_3$ prepared in toluene solution determined from high resolution XRD indicating trigonal bipyramidal coordination of the Al site. Aluminum, red; boron, blue; nitrogen, green. The positions of hydrogen atoms were not resolved.

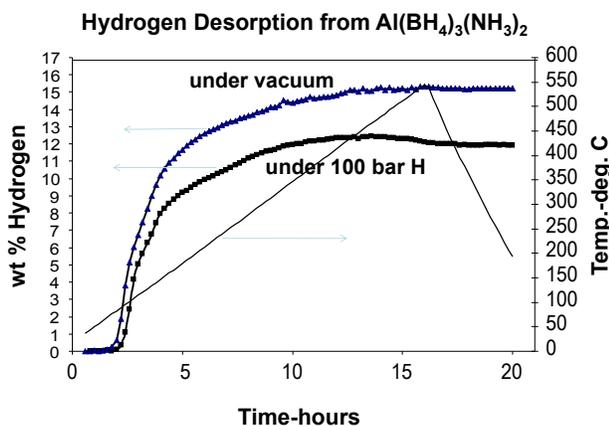


FIGURE 1. Temperature programmed desorption of hydrogen from $Al(BH_4)_3(NH_3)_2$ prepared by solvent free reaction under vacuum and under 100 Bar H_2 pressure.

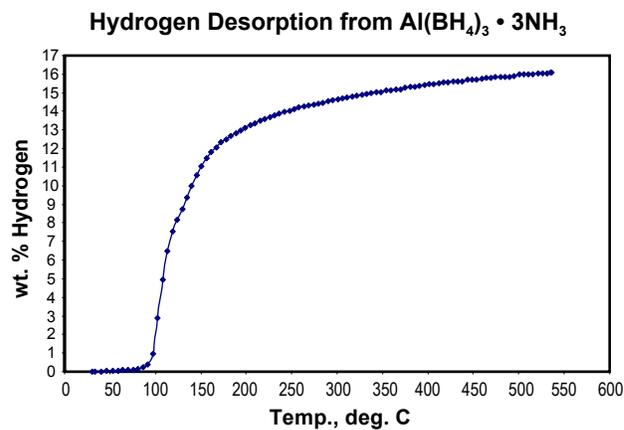


FIGURE 3. Temperature programmed desorption of hydrogen from $Al(BH_4)_3(NH_3)_3$ prepared in toluene solution under vacuum.

solid state MAS-NMR will be utilized to identify the product.

Reaction of $\text{Al}(\text{BH}_4)_3$ with NH_3 in ether solution led to the evolution of gas including diborane and possibly some hydrogen. The structure of the product which precipitated from solution was determined from high resolution XRD data, and the structure confirms chemical analysis which indicated the Al:B ratio was 1:2. The structure shown in Figure 4 indicates discrete Al dimers having double amide bridges between two Al(III) centers, each with two terminal borohydride groups and one ammonia filling out the coordination sphere. The composition is best described as $[\text{Al}(\text{BH}_4)_2(\text{NH}_3)(\text{NH}_2)]_2$. This structure is quite informative because it offers insight into the potential decomposition mechanism of Al-AMBH compounds leading to hydrogen formation. It has been our contention that the first step in the decomposition of metal borohydride compounds is the formation of a metal hydride and borane. The decomposition of $\text{Al}(\text{BH}_4)_3(\text{NH}_3)_2$ leads to initial formation of an aluminum hydride which reacts with the coordinated ammonia of another molecule leading to hydrogen evolution and formation of a bridged amide group.



Further evidence for this pathway comes from isotopic labeling studies in which the initial hydrogen

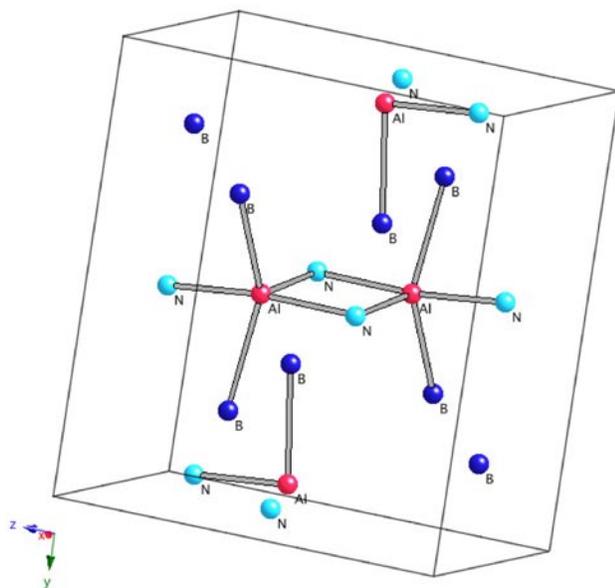


FIGURE 4. Structure showing the unit cell of $[\text{Al}(\text{BH}_4)_2(\text{NH}_3)(\text{NH}_2)]_2$, prepared in ether solution as determined from high resolution XRD indicating bridged amide ligands between Al sites. Aluminum, red; boron, blue; nitrogen, light blue. The positions of hydrogen atoms were not resolved

evolved from $\text{Al}(\text{BH}_4)_3(\text{ND}_3)_2$ is predominantly mass 3 indicating it is deuterium hydride, where the H originates from BH_4^- and D from ND_3 . Future work will include an attempt to prepare and study the decomposition of $\text{Al}(\text{NH}_2\text{BH}_3)_3$ to understand whether ammonia borane is a possible intermediate.

The use of ionic liquids as a possible medium for the regeneration of alane was investigated since ionic liquids favor polar transition states. As a part of this work we attempted preparation of the ionic liquid 1,2-dimethyl-3-N-butylimidazolium tetrahydroaluminate. The AlH_4^- anion appears to react with the imidazolium cation of the ionic liquid. Further work on ionic liquids as a reaction medium will be discontinued.

Conclusions and Future Directions

Progress has been made in preparing ammonia metal borohydrides by a solvent free method, and progress has been made in understanding the mechanism by which hydrogen is evolved from metal borohydrides and ammonia metal borohydrides. The chemistry of aluminum borohydrides has proven to be quite rich, and preparation of $^{15}\text{NH}_3$ derivatives of Al-AMBHs will be productive for analysis of reaction products by ^{15}N MAS-NMR. We intend to continue study of aluminoboranes in collaboration with J.-C. Zhao, (Ohio State University).

- Determine the yield of the $\text{B}_{12}\text{H}_{12}^{2-}$ species in desorption of $\text{Mg}(\text{BH}_4)_2$ in borohydride eutectic melt, a continuation of work reported in Fiscal Year 2008. We want to prepare and study the decomposition of $\text{Mg}(\text{B}_3\text{H}_8)_2$ to understand how borohydride clusters form so that the hydrogenation process can be made reversible.
- Continue our study of the AMBHs, looking at how mixtures and catalysts might affect the desorption/absorption processes. As a part of that study we will develop a synthesis of titanium borohydride and titanium ammine borohydride and investigate stability and desorption characteristics of the latter.
- We will investigate the hydrogen desorption chemistry of alane amines ($\text{AlH}_3 \cdot n\text{NH}_3$) and the reactions of alane alkylamines AlH_3NR_3 as reducing agents.

FY 2009 Publications/Presentations

1. Ji-Cheng Zhao, Douglas A. Knight, Gilbert M. Brown, Chul Kim, Son-Jong Hwang, Joseph W. Reiter, Robert C. Bowman Jr., Jason A. Zan, and James G. Kulleck, "Study of Aluminoborane Compound $\text{AlB}_4\text{H}_{11}$ for Hydrogen Storage," *J. Phys. Chem. C*, **2009**, 113 (1), 2-11.
2. "Hydrogen Desorption/absorption Studies of Metal Boron Hydride Compounds" D.A. Knight, G.M. Brown, and J.H. Schneibel, oral presentation 236th National Meeting of the American Chemical Society in Philadelphia, PA August, 2008.

3. “Solvent-Free Synthesis and Hydrogen Sorption Properties of Ammine Metal Borohydrides,” G.M. Brown, D.A. Knight, J.H. Schneibel, C.J. Rawn, and J. Bai, oral presentation 237th National Meeting of the American Chemical Society in Salt Lake City, UT March 22–26, 2009.
4. “Ammine metal borohydrides as hydrogen storage materials,” D Knight, G. Brown, Claudia Rawn, oral presentation NHA Conference and Hydrogen Expo, March 30–April 3, 2009, Columbia, SC.

References

1. Grigorii Soloveichik, Jae-Hyuk Her, Peter W. Stephens, Yan Gao, Job Rijssenbeek, Matt Andrus, and J.-C. Zhao, Ammine Magnesium Borohydride Complex as a New Material for Hydrogen Storage: Structure and Properties of $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$, *Inorg. Chem.* **2008**, *47*, 4290-4298.
2. Simon R. Johnson, William I.F. David, David M. Royse, Marco Sommariva, Christina Y. Tang, Francesca P.A. Fabbiani, Martin O. Jones, Peter P. Edwards, “The Monoammoniate of Lithium Borohydride, $\text{Li}(\text{NH}_3)\text{BH}_4$: An Effective Ammonia Storage Compound,” *Chemistry - An Asian Journal*, *4*, 2009, 849-854.