

IV.A.1i Metal Borohydrides, Ammines, and Aluminum Hydrides as Hydrogen Storage Materials

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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 metal borohydrides and ammine/amides/imides of metal borohydrides, with particular emphasis on the aluminum complexes of these materials. These materials are expected to achieve the DOE/FreedomCAR performance targets for 2010 as well as 2015. Research at ORNL focuses on high hydrogen content materials (>10 wt%).

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan for Fiscal Year (FY) 2010 and FY 2015:

- (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. The materials in Table 1 are related materials for reference or materials that have been investigated by ORNL in the last year (percentages

in table below are for H₂ release only). The DOE system targets to which we want to compare are 4.5% hydrogen for 2010 and 5.5% hydrogen for 2015. The material of interest must allow for a weight penalty for the container.

TABLE 1. Progress towards Meeting Technical Targets

Compound	Formula Weight	% Hydrogen (calc)	% Hydrogen Evolved (500°C)
Al(BH ₄) ₃	71.508	16.92%	12.7%
Al(BH ₄) ₃ ·2NH ₃	105.570	17.19%	15.1%
Al(BH ₄) ₃ ·3NH ₃	122.601	17.26%	15.9%
NH ₃ BH ₃	30.865	19.59%	~12%

Accomplishments

Progress was made toward defining the structure and understanding the mechanism of hydrogen release from aluminum ammine borohydrides:

- NH₃ adducts of Al(BH₄)₃ are formed both in solution and under solvent-free conditions and the products depend on reaction conditions (solvent/solvent-free).
- Quantity of hydrogen desorbed from aluminum ammine borohydrides indicates both NH₃ and BH₄⁻ contribute to hydrogen evolution reaction, and the product formed in toluene solvent, Al(BH₄)₃·3NH₃, evolves as much hydrogen as a function of temperature as ammonia borane, NH₃BH₃.
- Structure of product formed during reaction of Al(BH₄)₃ with NH₃ in diethyl ether gives insight into the reaction mechanism for hydrogen desorption, and the use of deuterated ammonia (ND₃) shows first hydrogen evolved is deuterium hydride (indicating equal contributions from ND₃ and BH₄⁻).
- Solid state magic angle spinning-nuclear magnetic resonance (MAS-NMR) spectroscopy (collaboration with the California Institute of Technology [Caltech] and Jet Propulsion Laboratory [JPL]) of the hydrogen desorption reaction products show definitively that (1) Al metal is not a product and (2) a boron-nitride polymer is formed.



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 2015. ORNL is developing new materials, developing synthetic methods to prepare materials, and studying chemical reactions that will lead to materials that reversibly store hydrogen. Our research takes advantage of expertise in handling oxygen and moisture sensitive reagents, knowledge of reaction pathways in solution, and insight into mechanisms of reactions and catalytic pathways. The research at ORNL emphasizes high hydrogen content materials (>10 wt% hydrogen).

In past work the thermal decomposition of $\text{Al}(\text{BH}_4)_3$ was studied in some detail in an effort to determine the dehydrogenation mechanism. In these studies we concluded that $\text{Al}(\text{BH}_4)_3$ follows a step-by-step loss of BH_3 during pyrolysis, ultimately producing AlH_3 and diborane (or higher borohydride clusters) which undergo their own thermal decomposition to form hydrogen, aluminum and a $(\text{BH})_n$ polymeric residue. At 150°C, diborane is the predominant product but hydrogen becomes the dominant product as the temperature is increased. At 300°C and higher, the rate of decomposition of AlH_3 and diborane to form products (H_2) is fast compared to loss of BH_3 from $\text{Al}(\text{BH}_4)_3$.

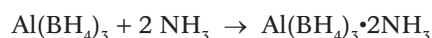
Approach

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 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 (FTIR) spectroscopy, X-ray diffraction (XRD), and elemental analysis by inductively coupled plasma atomic emission spectroscopy as well as solution NMR are available at ORNL to characterize solid reaction products, and Raman and solid-state NMR are available through collaboration with Metal Hydride Center of Excellence partners. During this year ORNL obtained a thermogravimetric analyzer (TGA) which is housed in a glove box (<1 ppm H_2O and O_2) with capability of analysis of the evolved gas by mass spectrometry. 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

Most of the experimental work in the last year has been concerned with characterization of the products of the reaction of ammonia with aluminum borohydride. We have previously reported that a rapid, solvent-free reaction occurs between $\text{Al}(\text{BH}_4)_3$ and NH_3



The structure of the product is not known with certainty but it is thought to be a trigonal bipyramid with axial NH_3 ligands and equatorial BH_4^- ligands. The reaction of ammonia with aluminum borohydride in solvents gives different products from the solvent-free reaction. $\text{Al}(\text{BH}_4)_3$ was previously reported by Bird and Wallbridge [1] to react with anhydrous ammonia in a 1:2 ratio in the absence of solvent to form $\text{Al}(\text{BH}_4)_3(\text{NH}_3)_2$ which is believed to have a trigonal bipyramidal geometry about the Al(III) center with axial NH_3 groups. The theoretical hydrogen content of this material is 17.2 wt% and we have observed that hydrogen is evolved at a lower temperature than from the parent compound, $\text{Al}(\text{BH}_4)_3$. The total hydrogen evolved is 15.2 wt% upon heating to 550°C. From the large amount of H_2 evolved it is apparent that both the BH_4^- and NH_3 groups are reactive.

This $\text{Al}(\text{BH}_4)_3(\text{NH}_3)_2$ compound was also prepared using N-15 enriched ammonia, $^{15}\text{NH}_3$, and deuterated ammonia, ND_3 . The normal isotopic composition ammonia and N-15 enriched compounds was supplied to our collaborators at JPL and CalTech for analysis by solid-state NMR. Solid-state NMR measurements of ^1H , ^{11}B , and ^{27}Al as well as the ^{15}N resonances were determined for the starting diammine as well as at various stages of dehydrogenation. At complete dehydrogenation the ^{11}B MAS-NMR signal is clearly consistent with the formation of a $(\text{BH}-\text{NH})_n$ polymer, and there do not appear to be any clearly distinguishable intermediates with distinctly different resonances between the starting material and the final product. The ^{27}Al NMR indicates that Al metal is not a product of thermal degradation under the circumstances of gas evolution into a vacuum. Unfortunately the ^{15}N NMR of the enriched ammonia adduct was not definitive.

Mass spectrometry of the evolved gas from the ND_3 derivative is particularly helpful in assigning observed peaks to individual chemical species. The initial hydrogen which is evolved has mass 3, indicating one hydrogen atom originates from ND_3 and one originates from BH_4^- . We observe trace amounts of borazine, a cyclic six membered ring species in which three of

the hydrogen atoms are deuterium, (ND-BH)₃. It is interesting that up to approximately 200°C, there is no definitive evidence for exchange of hydrogen between B and N. The challenge of future work is stop the reaction at a stage that will allow the reaction to be reverse, and that will be the focus of work in the latter part of FY 2010.

The reaction of Al(BH₄)₃ with NH₃ in toluene gives a product which has an XRD pattern different from the ammonia adduct in the solvent free reaction; the elemental analysis of the product suggest the composition is Al(BH₄)₃•3NH₃. Bird and Wallbridge [1] indicate two moles of NH₃ react with aluminum borohydride in the stoichiometric ratio. However, the species [Al(NH₃)₆](BH₄)₃ in which aluminum is octahedrally coordinated by six ammonia ligands, is formed with excess ammonia. Both the FTIR spectrum and the XRD pattern of our product show the hexamine is not formed. High resolution XRD of this compound was obtained at the National Synchrotron Light Source at Brookhaven National Laboratory. A preliminary solution of the structure which was reported at the annual merit review meeting last year is now believed to be in error. The correct structure is now believed to have two coordinated borohydride groups and three coordinated ammonia groups along with one ionic borohydride group, [Al(BH₄)₂(NH₃)₃]BH₄. The tentative structure is shown in Figure 1. Preliminary calculations by B. P. Hay [2] confirm that this structure is an energy minimum with additional stabilization provided by hydrogen bonding between the ionic borohydride group and the coordinated amines.

The infrared spectra of the compounds we prepared from reaction of NH₃ with Al(BH₄)₃ either in the absence of solvent or using toluene as the solvent are roughly in agreement with the spectrum which was reported in the literature by Bird and Wallbridge for Al(BH₄)₃(NH₃)₂ or for Al(BH₄)₃NH₃. Figure 2 shows the normalized FTIR spectra of our two compounds along with the difference spectrum. As a first approximation, the spectra of the two compounds have a lot of peaks in common, and we anticipate that the structures of the two compounds are not vastly different. The infrared spectrum of [Al(NH₃)₆](BH₄)₃ as reported by both Bird and Wallbridge and by Semenenko is quite different from what we have observed, and along with the XRD serve as definitive evidence to prove that our compounds are not [Al(NH₃)₆](BH₄)₃. The spectrum of the material synthesized from toluene, Al(BH₄)₃(NH₃)₃, has less bands than the solvent free preparation. The high resolution XRD structure determination shown in Figure 1 has the chemical composition [Al(BH₄)₂(NH₃)₃](BH₄). It is anticipated that if this structure is correct, distinctive B-H stretching vibrations characteristic of uncoordinated borohydride will be observed, but these vibrations appear to be absent. Thus further

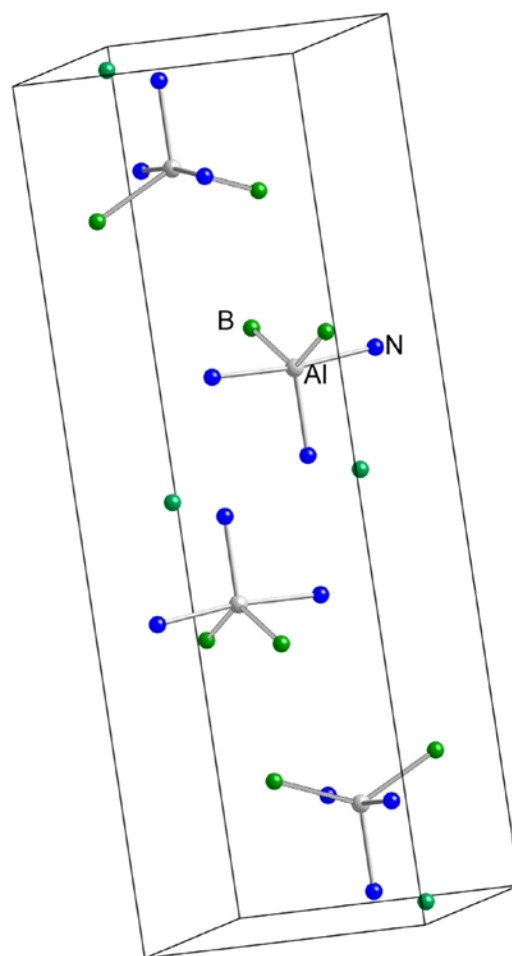


FIGURE 1. Structure of [Al(BH₄)₂(NH₃)₃](BH₄) with B and N atoms shown as green and blue spheres respectively. The position of H atoms was not refined.

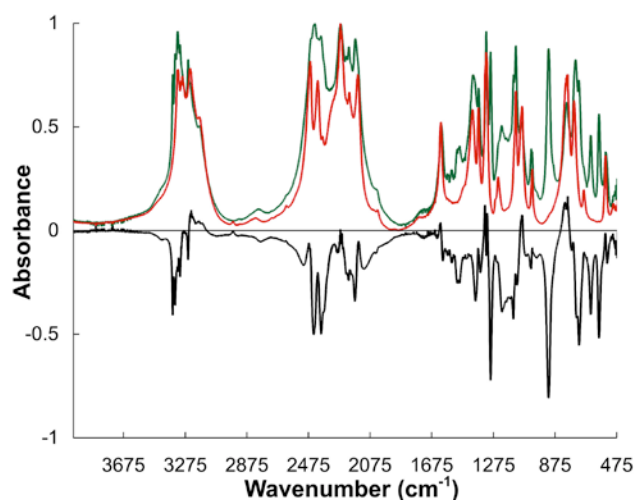


FIGURE 2. The FTIR spectra of the solvent free preparation Al(BH₄)₃•2(NH₃) (green) and the synthesis from toluene [Al(BH₄)₂(NH₃)₃]BH₄ (red) are shown (KBr pellets, protected from air) Calculated difference spectrum (black) is shown at the bottom as negative peaks.

characterization of this very interesting and high hydrogen content material is warranted.

Conclusions and Future Directions

The adducts of ammonia with aluminum borohydride are high hydrogen content materials in which both the ammonia and borohydride groups contribute to hydrogen evolution, but the product depends on the reaction conditions:

- Refine the elemental analysis of the aluminum ammine borohydrides and precisely determine the amounts of gaseous products in the reaction of ammonia with aluminum borohydride in solvents (toluene and ether).
- Multinuclear solution and solid MAS-NMR of aluminum ammine borohydrides will be used to identify intermediates in desorption reactions.
- TGA with evolved gas analysis by mass spectrometry will be implemented to follow reactions of ammine metal borohydrides and identify intermediates.
- Continue study of aluminoboranes in collaboration with J.-C. Zhao, Ohio State University.

FY 2010 Publications/Presentations

1. "Synthesis, Characterization, and hydrogen Sorption Properties of Complex Metal Boron Hydrides," D.A Knight, G.M. Brown, J.-C. Zhao, R. Bowman, J. Zan, J. Kulleck, C. Kim, and S.-J. Hwang, oral presentation, 238th ACS National Meeting, Washington, D.C., August 16–20, 2009.
2. "Structure and Characterization of two Novel Aluminum Borohydride Amines." A.M dos Santos, C.J. Rawn, J. Bai, D.A. Knight and G.M. Brown, oral presentation 2009 ACA Meeting, Toronto, July 25–30, 2009.
3. "Characterization Studies of Boron-Containing Compounds for Hydrogen Storage Applications," R.C. Bowman, S. Hwang, C. Kim, G.M. Brown, D.A. Knight, J.-C Zhao, J.W. Reiter, J.A. Zan, G.L. Soloveichik, S. Kniajanski, oral presentation, Materials Challenges in Alternative & Renewable Energy Sources 2010, Cocoa Beach FL, February 1, 2010.

References

1. Bird and Wallbridge, *J. Chem. Soc. A*, **1967**, 664.
2. B.P. Hay, unpublished results.