Metal Borohydrides, Ammines, and Aluminum Hydrides as Hydrogen Storage Materials

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Oak Ridge National Laboratory
Oak Ridge, Tennessee

June 7-11, 2010

Project ID # ST068

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Overview

Timeline

- Start: March 1, 2005
- End: Sept 30, 2010
- 91% complete

Barriers Addressed

- B. Weight and volume
- M. Hydrogen capacity and reversibility
- N. Lack of understanding of hydrogen chemisorption and physisorption

Budget

- Total project funding to date - $2470K (DOE 100%)
- Funding for FY09 - $700K
- Planned Funding for FY10 - $300K

Partners/Collaborators

- Participant in the MHCoE
- Ohio State University
- JPL and Cal Tech (NMR)
- Brookhaven National Lab (AlH_3 chemistry)

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Relevance/Program Objectives

The program objective is to develop the chemistry for a *reversible* **Hydrogen** storage system based on **Boron, Nitrogen** (ammine/amide/imide) and **Aluminum**. ORNL focuses on high hydrogen content materials (>10 wt %).

Focus of research during the review period was the preparation, structural determination, and hydrogen desorption reactions of ammine aluminum borohydrides, formed by the reaction of NH_3 with $Al(BH_4)_3$. A greater understanding of desorption reactions will help overcome the reversibility barriers in select H_2 storage materials.

Materials Investigated by ORNL during review period

Compound	Formula Weight	Theory % hydrogen
$Al(BH_4)_3$	**71.508**	**16.92%**
$Al(BH_4)_3 \cdot 2NH_3$	**105.570**	**17.19%**
$Al(BH_4)_3 \cdot 3NH_3$	**122.601**	**17.26%**

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Approach

Research at ORNL 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. Collaborations provide structural characterization of new materials by XRD or solid MAS-NMR

Quantity of hydrogen evolved from aluminum amine borohydrides confirms that ammonia protons contribute to hydrogen evolution. This begins to **address weight and volume technical barriers**. Identification of reaction intermediates has contributed to an **increased understanding of the hydrogen desorption process**.

Main Milestones for FY10 and Progress

- Investigate ammine metal borohydrides as hydrogen storage materials – good progress, on schedule
- Determine structure of aluminum amine borohydride reaction intermediate – structure completed

Technical Accomplishments and Progress

Overview of Important Results for the Review Period

- NH_3 adducts of $Al(BH_4)_3$ are formed in both in solution and under solvent-free conditions
- Products depend on reaction conditions (solvent/solvent-free)
- Product formed in toluene solvent, $Al(BH_4)_3 \bullet 3NH_3$, evolves as much hydrogen as a function of temperature as ammonia borane, NH_3BH_3
- Structure of product formed during reaction of $Al(BH_4)_3$ with NH_3 in diethyl ether gives insight into the reaction mechanism for hydrogen desorption
- Quantity of hydrogen desorbed from aluminum ammine borohydrides indicates both NH_3 and BH_4^- contribute to hydrogen evolution reaction
- Use of deuterated ammonia (ND_3) shows first hydrogen evolved is HD (indicating equal contributions from from ND_3 and BH_4^-)
- Solid state MAS-NMR spectroscopy of the hydrogen desorption reaction products
  - Al metal is **not** a product
  - Boron-nitride polymer **is** formed

$$Al(BH_4)_3 + n\ NH_3 \rightarrow Al(BH_4)_3 \cdot nNH_3 \rightarrow Al(BHNH)_3 + 7\tfrac{1}{2}\ H_2$$

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Formation of Ammine Aluminum Borohydrides

A rapid, solvent-free reaction occurs between $Al(BH_4)_3$ and NH_3

$$Al(BH_4)_3 + 2\ NH_3 \rightarrow Al(BH_4)_3 \bullet 2NH_3$$

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

Formation of a 2:1 NH_3:$Al(BH_4)_3$ adduct in agreement with literature

Bird and Wallbridge, *J. Chem. Soc. A*, **1967**, 664

XRD shows structure different from previously reported and structurally characterized ammonia adducts of aluminum borohydride:

- $[Al(NH_3)_6](BH_4)_3$ - octahedral aluminum, ionic borohydride

  Semenenko, *et al*, *Izv. AN SSSR, Ser. Khim.*, **1974**, 1455-1460.

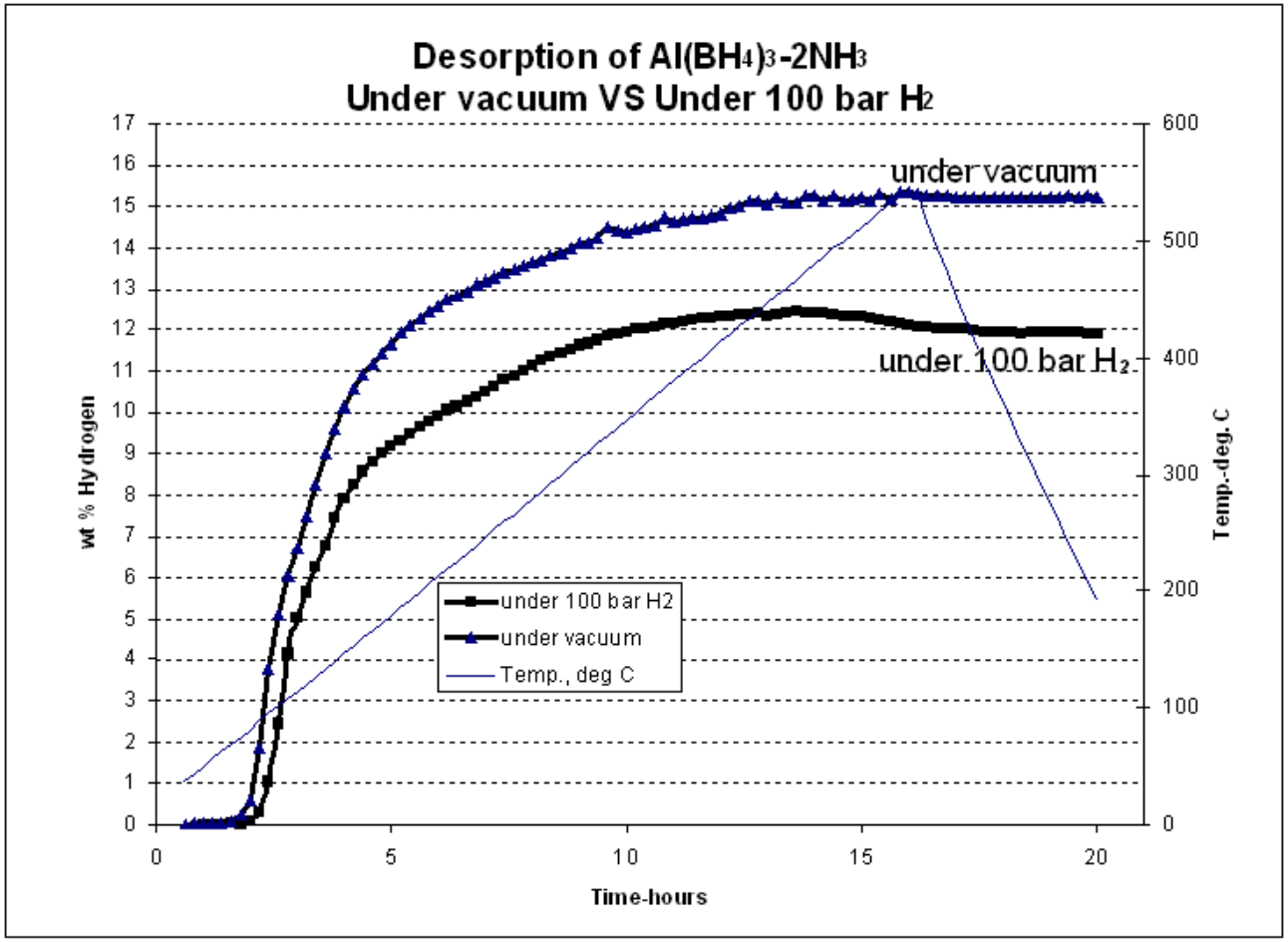
- $Al(BH_4)_3NH_3$ - tetrahedral aluminum

  Lobkovskii, *et al*, *Zh. Strukt. Khim.*, **1974**, *15*, 70-73.

NH_3 adduct of $Al(BH_4)_3$ desorbs H_2 at a lower temperature than parent compound

Thermal Desorption of H_2 from $Al(BH_4)_3 \bullet 2(NH_3)$

Quantity of H_2 released indicates NH_3 is decomposing as well as BH_4^-



Catalysts ($RuCl_3$ and $TiCl_3$) have no influence on desorption temperature; consistent with forming Al-H and BH_3 in rate determining step

Decreased H_2 evolution under 100 bar hydrogen pressure indicates potential reversibility

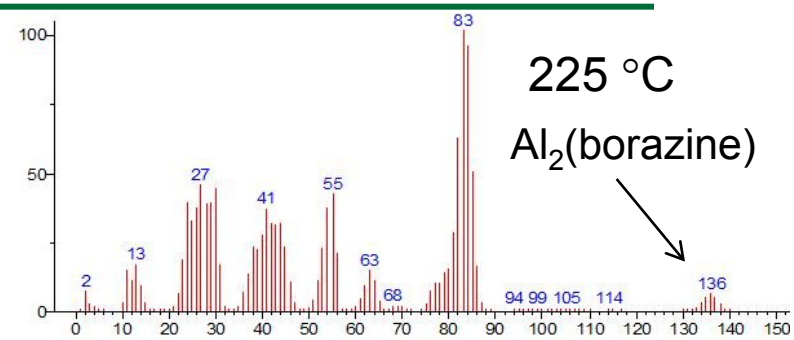
Deuterium Labeled Mechanistic Study

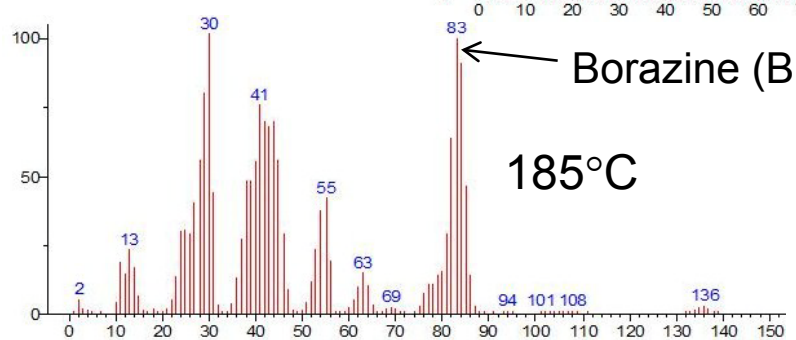
Prepared $Al(BH_4)_3 \bullet 2(ND_3)$ in a solvent free reaction using ND_3 ammonia

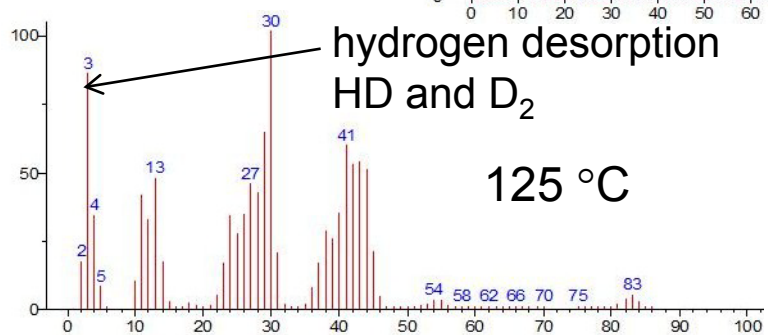
Determined mass spectra of evolved gas as a function of temperature

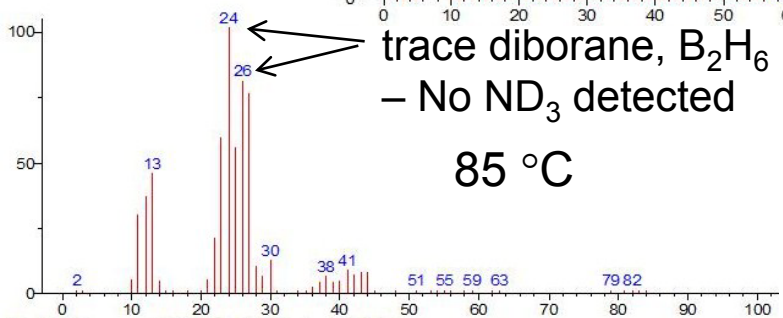
Detection of HD indicates source of hydrogen is both BH_4^- and ND_3.

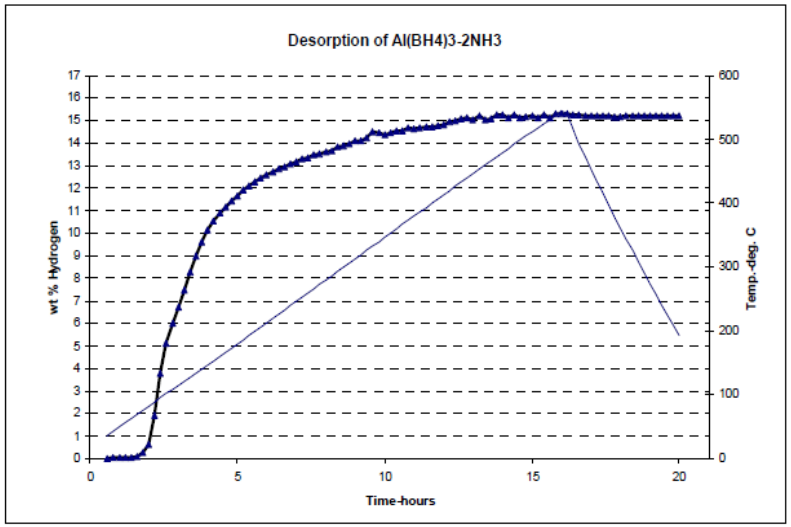
Presence of D_3-borazine is evidence of reaction between BH_3 and ND_3.











Multinuclear MAS NMR Characterization of Ammine Aluminum Borohydrides

Summary of results and conclusions collaboration with JPL/CalTech

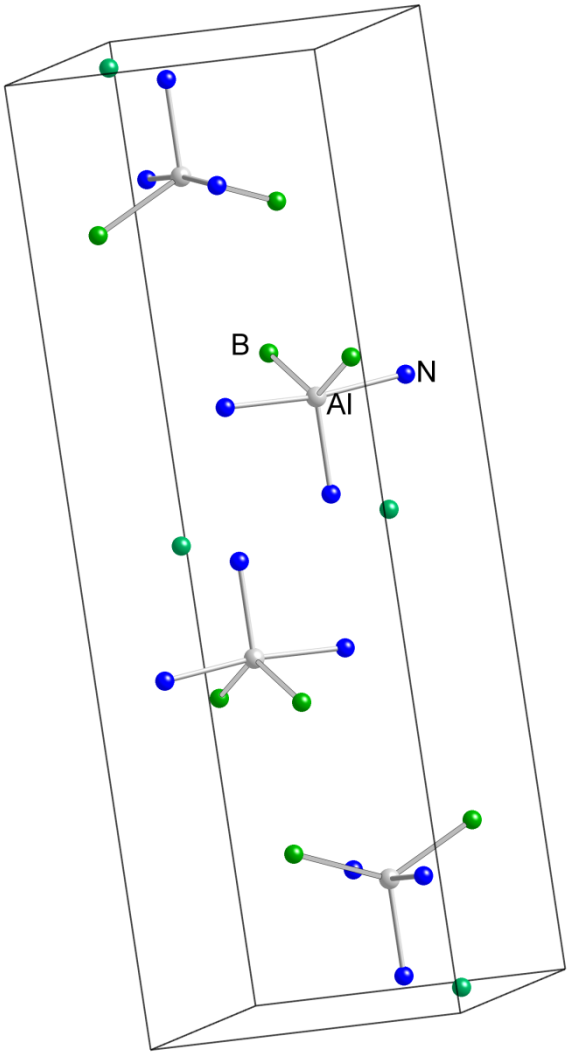
- Determined ^{27}Al, ^{11}B, ^{1}H, and ^{15}N NMR spectra of $Al(BH_4)_3 \bullet 2(NH_3)$ prepared by solvent free reaction
- Determined spectra of hydrogen desorption products
- Used samples prepared from normal isotopic composition ammonia and ^{15}N-ammonia
- ^{11}B and ^{27}Al spectra of as prepared materials indicate nuclei are in two different sites (8:1 ratio), one having asymmetry – from preparative route we can speculate that $[Al(NH_3)_6](BH_4)_3$ may be present in minor amount

More Multinuclear MAS NMR

- ^{27}Al NMR of material desorbed at 135 °C or 200 °C shows overlap of broad resonance, one disappearing upon desorption at 500 °C – chemical shift indicates coordination number of Al has decreased at higher T – spectra clearly show that Al metal is not a product
- ^{11}B NMR of material desorbed at 100 °C,135 °C, 200 °C, and 500 °C show progression from boron hydride species to a boron nitride polymer as the chemical form of the hydrogen desorption species
- ^{1}H NMR of material desorbed at 200 °C and recharged with 100 bar hydrogen shows no evidence of hydrogen uptake
- ^{15}N NMR of desorption products inconclusive

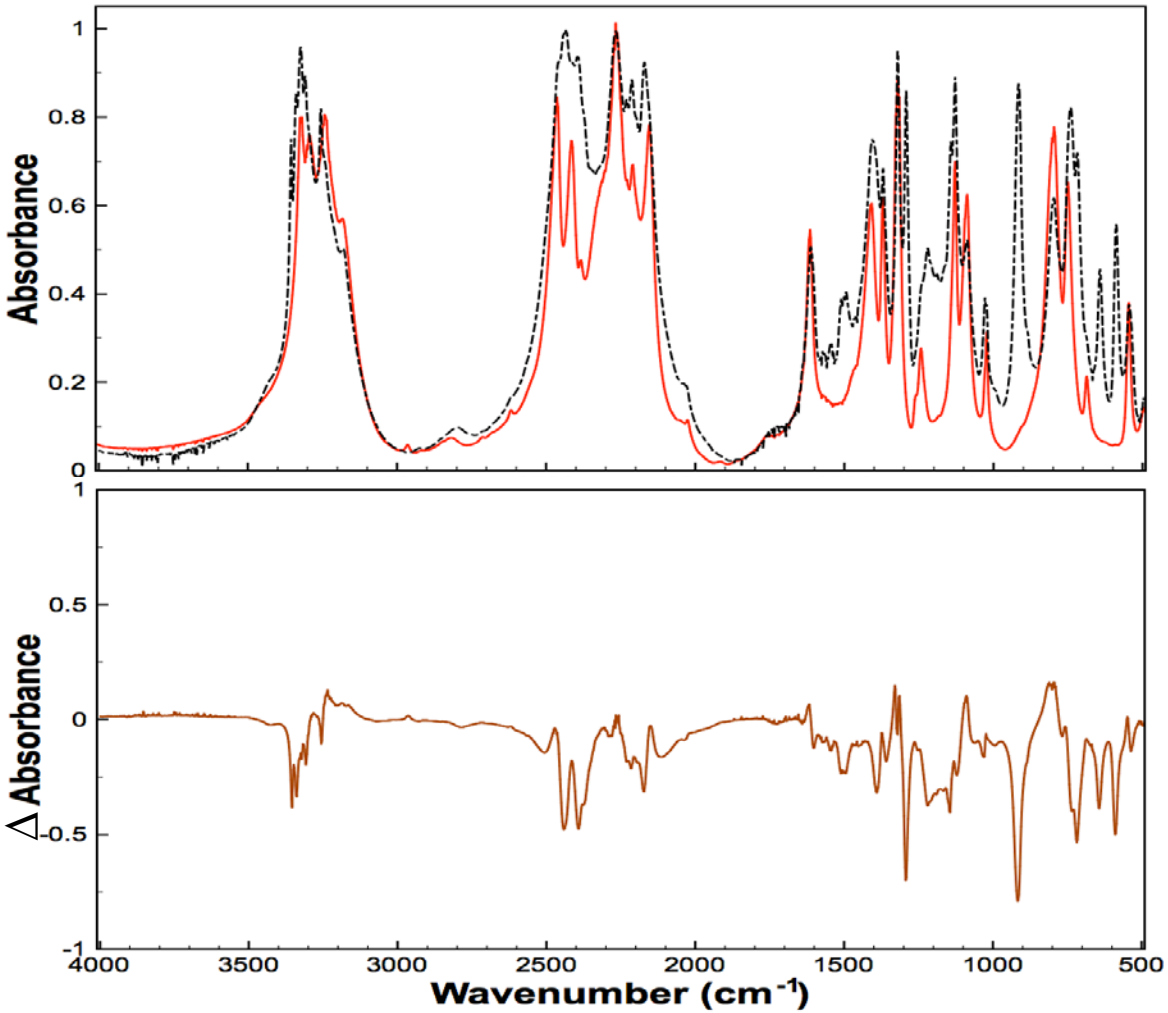
Reaction of $Al(BH_4)_3$ with NH_3 in Toluene

- The reaction of $Al(BH_4)_3$ with NH_3 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 $Al(BH_4)_3 \bullet 3NH_3$
- Bird and Wallbridge (*J. Chem. Soc. A*, **1967**, 664) indicate two moles of NH_3 react with the stoichiometric ratio but the species $[Al(NH_3)_6](BH_4)_3$ is formed with excess ammonia – the FTIR spectrum and the XRD pattern of our product shows the hexamine is not formed
- High resolution XRD obtained at NSLS. Preliminary structure which was reported at the AMR last year (shown to right) is now believed to be in error; work is in progress to resolve structure



Hydrogen atoms were not refined

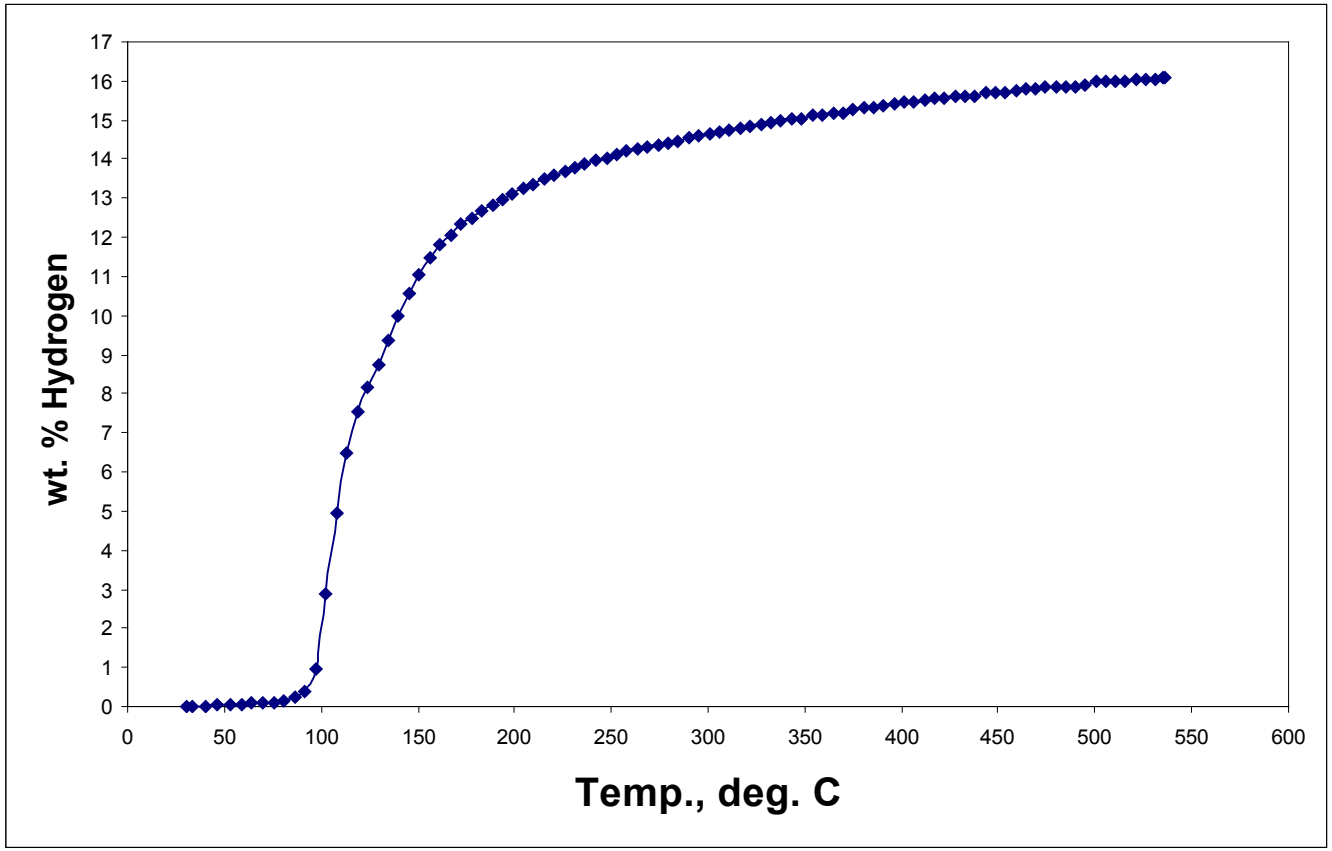
FTIR Spectra of Ammine Aluminum Borohydrides



- **Top**: The FTIR spectra of the solvent free preparation (- -) and the synthesis from toluene (–) are shown (KBr pellets, protected from air)
- **Bottom**: Calculated difference spectrum. Both figures share a common x axis.
- Spectra are very close in N-H, Al-H, and B-H stretching vibration regions
- Hydrogen desorption reactions differ mainly in quantity of H_2 evolved

Two reaction products have similar chemical composition

Hydrogen TPD of $Al(BH_4)_3 \bullet 3NH_3$



MS analysis of evolved gas indicates that less diborane is evolved by the three ammonia adduct compared to the two ammonia adduct

Hydrogen desorption takes place in three stages, beginning at < 100 °C

Objective of further research is to make first two stages of reaction reversible

Aluminum Amine Borohydrides Release Large Amounts of H_2

Compound	Formula Weight	% hydrogen (calc)	% hydrogen (500 C)
$Al(BH_4)_3$	**71.508**	**16.92%**	**12.7%**
$Al(BH_4)_3 \cdot 2NH_3$	**105.570**	**17.19%**	**15.1%**
$Al(BH_4)_3 \cdot 3NH_3$	**122.601**	**17.26%**	**15.9%**
NH_3BH_3	**30.865**	**19.59%**	**~12%***

Both the diammonia and the triammonia compounds release such a large amount of H_2 that ammonia must be losing hydrogen as well as borohydride

We don't know the exact composition of the product after the second stage (~150 °C), but the amount of hydrogen is consistent with the reaction

$$Al(BH_4)_3 \cdot 3NH_3 \rightarrow Al + 3(BHNH) + 7\tfrac{1}{2}\, H_2 \quad 12.33\% \text{ hydrogen}$$

MAS NMR indicates a BN polymer is the thermal decomposition product

Ammonia borane (potential 19.6% hydrogen) going to $(BHNH)_n$ is 13.06%

Quantity of H_2 evolved from $Al(BH_4)_3 \bullet 3NH_3$ is competitive with that evolved from ammonia borane at the same temperature.

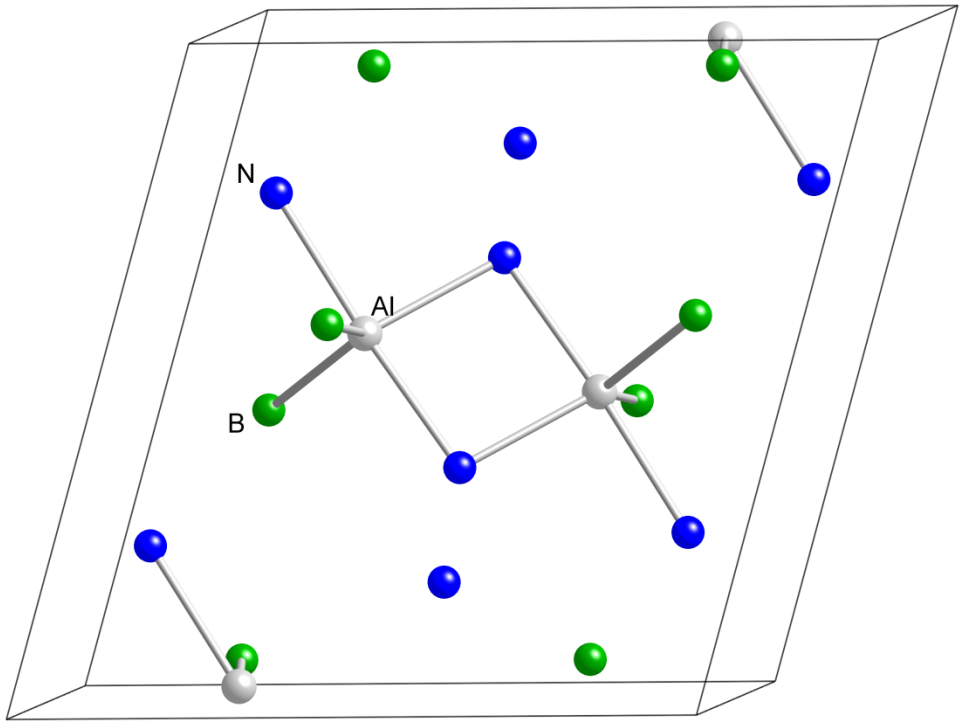
*G. Wolf, *et. al.*, *Thermochimica Acta*, **445**, *2*, 121-125.

Aluminum Borohydride-Ammonia in Ether

- Reaction of aluminum borohydride with ammonia was studied in diethyl ether solvent. This solvent forms a 1:1 adduct with aluminum borohydride having roughly tetrahedral geometry around the Al center.
- Gases (B_2H_6 and H_2) evolved during the reaction – products will be quantified in future work.
- XRD pattern and FTIR spectra distinctly different from solvent free reaction and reaction in toluene
- Chemical analysis shows Al:B ratio is 1:2, a loss of one borohydride from starting $Al(BH_4)_3$
- $Al(BH_4)_3 \bullet O(Et)_2 + 2\ NH_3 \rightarrow$

$$Al(NH_2)(BH_4)_2(NH_3) + \tfrac{1}{2}\ H_2 + \tfrac{1}{2}\ B_2H_6 + O(Et)_2$$

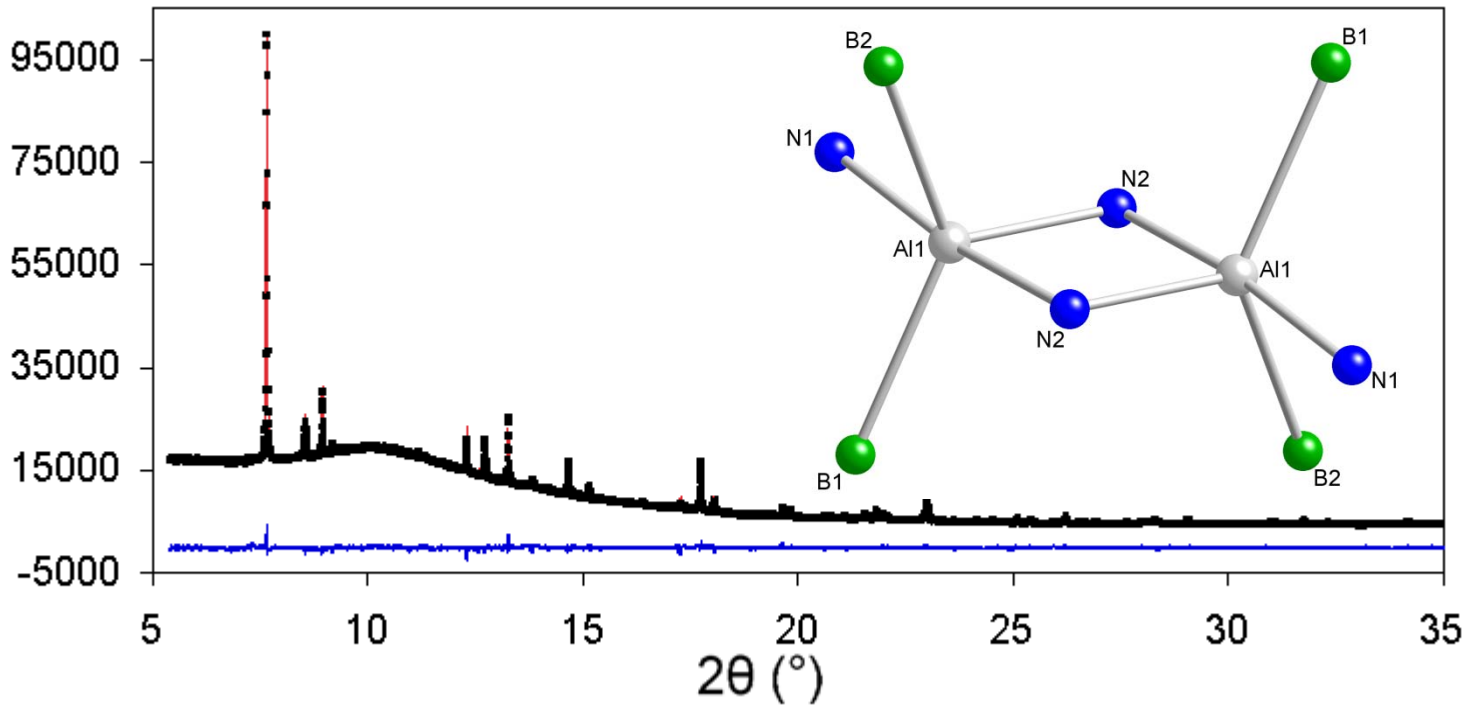
Structure of Aluminum Borohydride-Ammonia Synthesized in Ether



Hydrogen atoms were not refined

- Structure of the product of the reaction of aluminum borohydride with ammonia in diethyl ether was determined by high resolution XRD data taken at the NSLS
- Product is an amide (NH_2^-) bridged dimer with terminal ammonia and borohydride groups
- Structure offers insight into mechanism of hydrogen desorption from amine-borohydride complexes
- First step is reaction of Al-BH_4 to form Al-H and BH_3
- Second step is reaction of coordinated ammonia with Al-H to evolve H_2 and make Al - NH_2
- Consistent with ND_3 labeling results

High Resolution XRD and Refinement Results



Rietveld refinement (48 variables)
χ^2 =17.52
wRp = 4.74%
Rexp = 1.14%.

Bond	Length (Å)
Al – B1	2.307(6) Å
Al – B2	2.282(6) Å
Al – N1	2.017(7) Å
Al – N2	1.997(4), 2.014(7) Å

Technical Accomplishments and Progress

- We have identified a high yield synthesis of $HAl(BH_4)_2$
- This compound will react with diborane in part to reform $Al(BH_4)_3$
- Literature results indicate another product formed which is insoluble in hydrocarbon solvent
- Work is in progress to investigate reaction of diborane with $HAl(BH_4)_2$ at elevated diborane pressure; objective is to obtain a more readily characterized aluminoborane product

Collaboration with J.-C. Zhao at Ohio State University to investigate the chemistry of aluminoboranes such as AlB_4H_{11} continues

Collaborations

MHCoE Partners

- J.-C. Zhao, Ohio State University – Development of aluminoboranes such as AlB_4H_{11} as hydrogen storage materials and chemistry of ammine borohydrides
- Cal Tech and JPL – Structural characterization of materials by MAS NMR
- BNL – Chemistry of alane and Ti – catalyzed activated Al metal

Other Collaborators

- Claudia J. Rawn, MSTD, ORNL – Heated Stage X-ray diffraction (XRD); synchrotron based XRD for structural determination
- Jianming Bai and Antonio F. Moreira dos Santos, structure determination by synchrotron based XRD

Future Plans

- 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 MS 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 Univ.
- Investigate chemistry of alane ammines ($AlH_3 \bullet nNH_3$)

Summary Slide

Relevance/Program Objectives: ORNL is developing the chemistry for a reversible hydrogen storage system based on high hydrogen content (>10 wt %) materials

Plan and Approach: ORNL has expertise in handling oxygen and moisture sensitive reagents, knowledge of reaction pathways in solution, and insight into mechanisms of reactions and catalytic pathways which it uses in materials development.

Technical Accomplishments and Progress:

- Reaction of ammonia with aluminum borohydride give materials with high hydrogen content.
- Deuterium labeling experiments demonstrate that the first hydrogen evolved comes equally from the ammonia and the borohydride components.
- The reaction of ammonia with aluminum borohydride in ether yields a product that gives insight into the reaction mechanism of evolution from this class of materials.

Collaborations: Ohio State University, CalTech/JPL, BNL

Proposed Future Research: We will continue aluminum ammine borohydride studies with an emphasis on identifying BN product and making hydrogen desorption reversible, aluminoborane research will continue, and chemistry of AlH_3 with ammonia will be initiated if funding is available.

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