

Complex Hydrides for Hydrogen Storage Studies of the $\text{Al}(\text{BH}_4)_3$ System

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In Collaboration with the DOE Metal Hydride Center of Excellence

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(This presentation does not contain any proprietary information)



Overview

Timeline

- Start: March 1, 2005
- End: Sept 30, 2010
- 40% complete

Budget

- Total project funding \$1.9 M (DOE 100%)
- Funding for FY06 - \$300K
- Funding for FY07 - \$300K

Barriers Addressed

- Weight and volume
- Hydrogen capacity and reversibility
- Lack of understanding of hydrogen chemisorption and physisorption

Partners/Collaborators

- Participant in the MHCoe
- GE (diborane chemistry)
- Sandia (Raman)
- JPL (NMR)



Program Objectives

Develop the chemistry for a hydrogen storage system based on complex hydrides, chosen from the borohydrides, amides/imides, alane, or the alanates of the light elements in the periodic table.

- ORNL is developing new materials and methods for synthesis of new and known materials. The ORNL goal is to employ solvent-based procedures appropriate for scale-up to production and practical application.
- Two general tasks:
 - The discovery and characterization of new materials and processes.
 - The development of synthetic methods and processes in support of MHCoe collaborators.

Target Materials and Processes:

- complex anionic materials (MHCoe Project B)
- amide/imide (M-N-H) systems (MHCoe Project C)
- regeneration of alane (MHCoe Project D).

ORNL's Contribution

Research at ORNL takes advantage of expertise in synthesis (inorganic, organometallic and organic)

Synthetic Capabilities: Synthetic methods in solution – vacuum line, Schlenk line, cannula, and glovebox methods to handle oxygen and water sensitive materials, reactions in liquid ammonia.

Characterization Methods: Temperature programmed decomposition, reaction products determined with mass spectrometry, in-situ X-ray diffraction, IR and Raman spectroscopy, NMR spectroscopy, Sievert's apparatus for P-T-C determination, high pressure reactor (2000 psi)



Results in Prior Years

Focus of work in FY05 and first quarter FY 06 was LiAlH_4 and sodium-magnesium amide systems

Investigated effect of additives on the decomposition of LiAlH_4

Preparation of organometallic compounds of Ti for use as catalysts for liberation and uptake of hydrogen from LiAlH_4 .

Preparation of Ti catalyst by reaction of $\text{Ti}(\text{NR}_2)_4$ with liquid ammonia

Transition of work to focused projects within MHCoE in second quarter of FY06

ORNL participated in:

Project B – Complex Anionic Materials (borohydrides and alanates)

Project C – Amides/Imides (M-N-H systems)

Attention directed to covalent borohydrides in last quarter of FY 06

Technical Achievements – MHCoE Project B – Complex Anionic Materials (borohydrides and alanates):

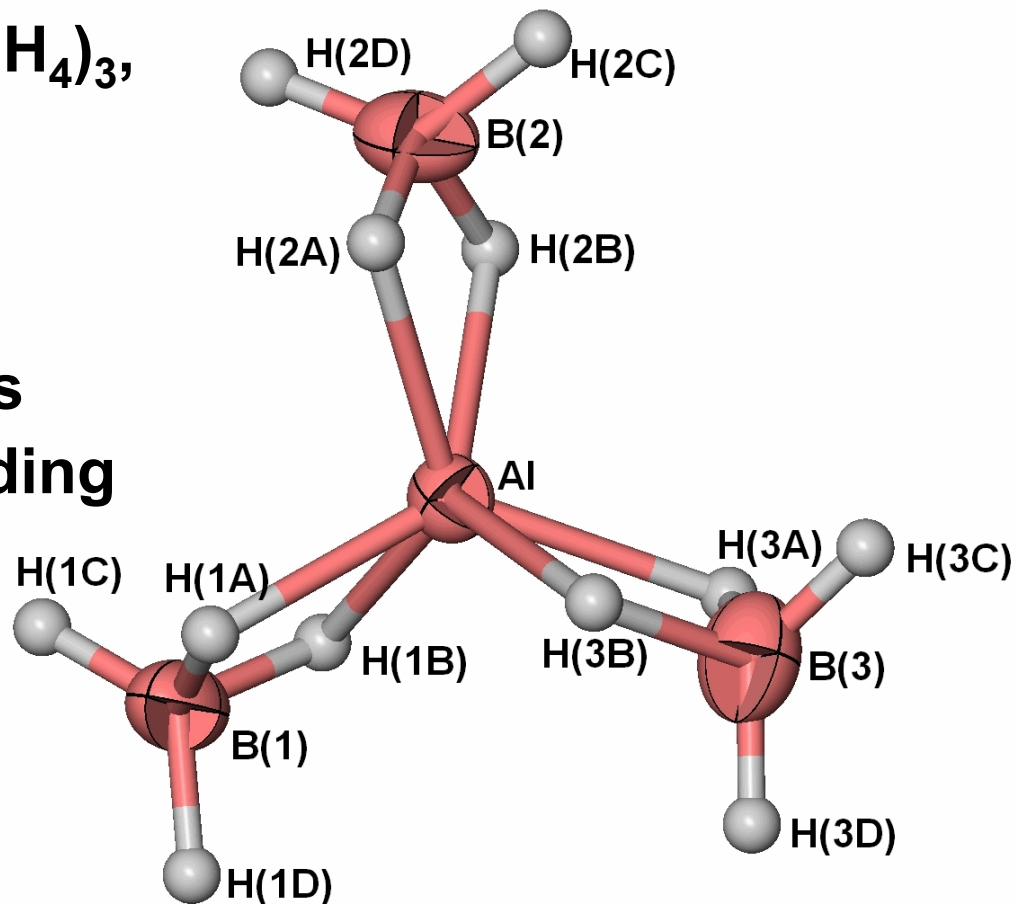
Covalent metal borohydrides are high hydrogen content materials which decompose to give hydrogen.

- Borohydride complexes of Al, Ti, and Zr have been shown to be precursors for the CVD of metal borides with the evolution of H₂ as a by-product.
- Volatile or liquid hydrogen storage material will have some engineering advantages for scale-up – heat and mass transfer.
- M(BH₄)₃ where M = Al, Ti are known to react with LiBH₄ to make non-volatile salts Li[M(BH₄)₄].

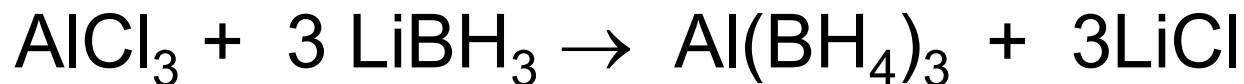
Chemistry of Liquid and/or Volatile Metal Borohydrides

Thermal decomposition of $\text{Al}(\text{BH}_4)_3$,
 $\text{Ti}(\text{BH}_4)_3$, and $\text{Zr}(\text{BH}_4)_4$ under
investigation for H_2 storage

Covalent molecular compounds
have double bridge M-H-B bonding
as illustrated for $\text{Al}(\text{BH}_4)_3^*$



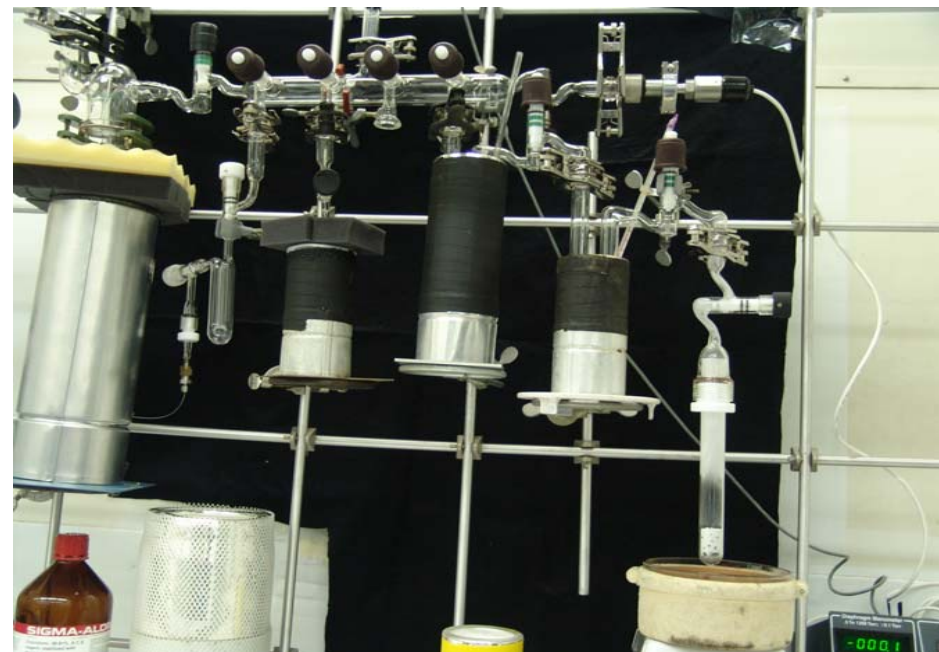
Preparation and Reactions of $\text{Al}(\text{BH}_4)_3$



A 50 - 130 °C, stepwise replacement reaction.*

The product is a volatile, pyrophoric liquid (120 torr at 0 °C, $\rho = 0.55$ g/mL) that can be isolated and purified on a high vacuum line.

Final product can be characterized by MS, IR, and NMR analysis.



The key component in this reaction is to use a two fold excess of finely ground LiBH_4 , which is necessary in order to achieve a 94 % yield.

Thermal Decomposition of $\text{Al}(\text{BH}_4)_3$

Reaction Conditions

- ~1.5 to 3.0 mmol of $\text{Al}(\text{BH}_4)_3$ material was collected in a liquid N_2 cold trap adjacent to the reaction tube.
- $\text{Al}(\text{BH}_4)_3$ vapor (vapor pressure = 359 torr at 25 °C) was allowed to flow into the reaction tube which was constantly heated at selected temperatures.
- H_2 and B_2H_6 levels were examined and removed from the reaction tube at regular (15 – 60 min.) intervals.

Thermal Decomposition of $\text{Al}(\text{BH}_4)_3$ – theory 16.8 % H_2

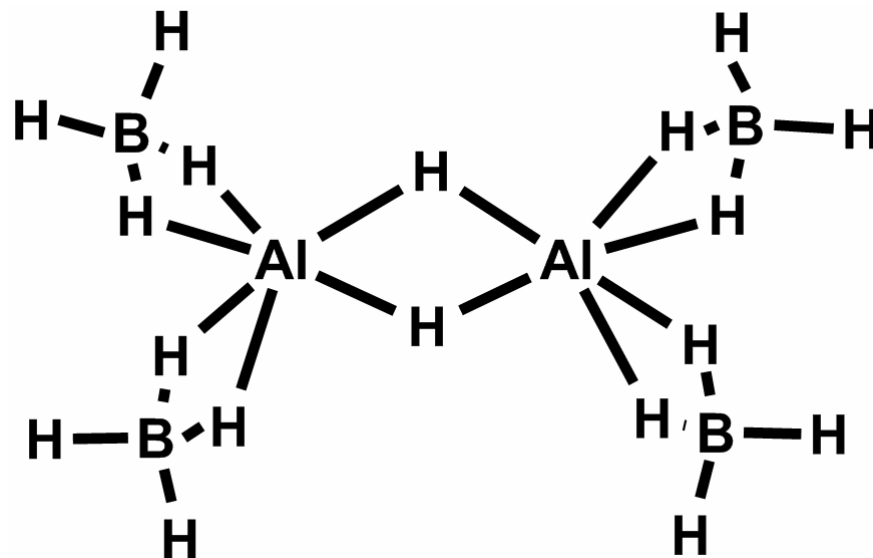
Product distribution is temperature dependent – 3 to 6 hr reaction time

Temperature ° C	H_2 per $\text{Al}(\text{BH}_4)_3$ (wt % H_2)	B_2H_6 per $\text{Al}(\text{BH}_4)_3$	Residue
175	1.4 (3.9 wt %)	0.68	Colorless, sublimable residue, likely composition $[\text{AlH}(\text{BH}_4)_2]_2$
200	1.3 (3.8 wt %)	0.36	Both light brown and colorless residue
250	3.5 (10.0 wt %)	0.16	Dark brown residue with a trace of colorless residue
300	5.0 (13.8 wt %)	0.41	Dark brown residue
350	5.4 (15.3 wt %)	trace	Dark brown residue
400	4.5 (12.7 wt %)	trace	Dark brown residue

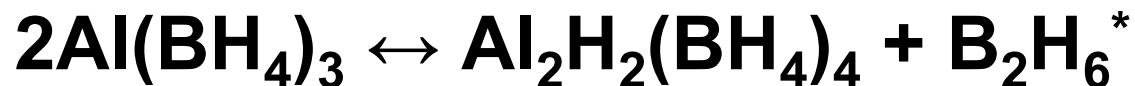
Product Formation Offer Clues to the $\text{Al}(\text{BH}_4)_3$ Pyrolysis Mechanism and Its Potential for Reversible Hydrogen Storage:

- Elemental analysis of the residue formed at the higher temperature indicates only AlB_3 remains.
- The colorless residue found at low temperatures is suspected to be the $[\text{AlH}(\text{BH}_4)_2]_2$ dimer.
- The first step in the $\text{Al}(\text{BH}_4)_3$ pyrolysis appears to be the release of diborane, followed by its own thermal decomposition to form H_2 .

Loss of Diborane Results in the Formation of the $\text{Al}_2\text{H}_2(\text{BH}_4)_4$ Dimer:

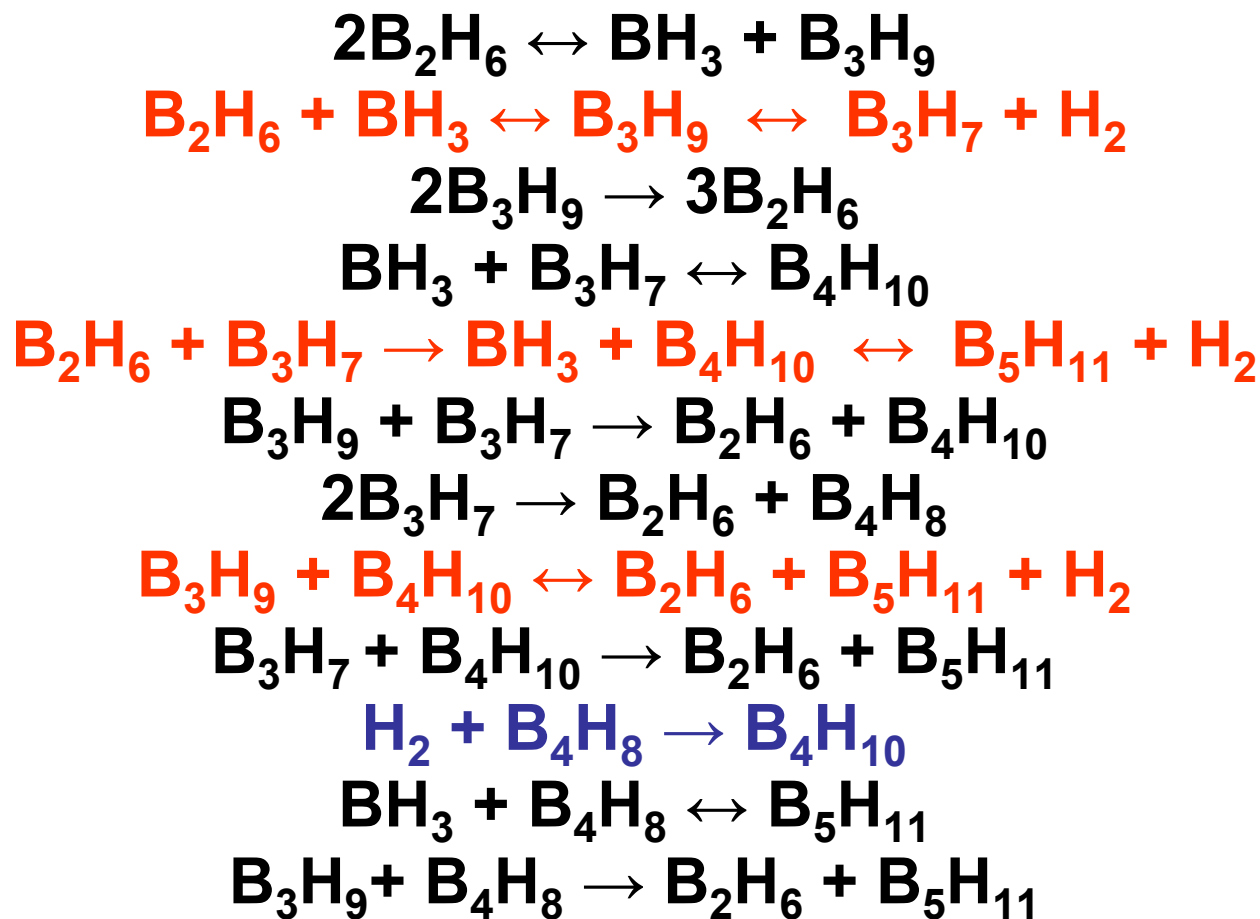


At the lower temperatures (<200° C), an equilibrium was established between $\text{Al}(\text{BH}_4)_3$ and $\text{Al}_2\text{H}_2(\text{BH}_4)_4$ as shown in:



* (a) Maybury, P. C.; Larrobu, J. C.; *Inorg. Chem.*, 2, 885, 1963. (b) Noth, H.; Rurlander, R.; *Inorg. Chem.*, 20, 1063, 1981. (c) Demachy, I.; Volatron, F.; *Inorg. Chem.*, 33, 3965, 1994.

Diborane Pyrolysis is a Complex Mechanism Forming H₂ in Several Steps:*



Product Formation Offer Clues to the $\text{Al}(\text{BH}_4)_3$ Pyrolysis Mechanism and Its Potential for Reversible Hydrogen Storage:

- The equilibrium observed between $\text{Al}(\text{BH}_4)_3$ and $\text{Al}_2\text{H}_2(\text{BH}_4)_4$ suggests one route of hydrogen storage reversibility.
- The complex diborane decomposition mechanism also indicates several points of reversibility.
- These two anomalies combined may be key factors leading to the viable regeneration of metal borohydride hydrogen storage materials.

Near Future Directions – FY07

- Continue investigation of $\text{Al}(\text{BH}_4)_3$ decomposition reactions under flash vacuum pyrolysis conditions; determine product ratio $[\text{H}_2]/[\text{B}_2\text{H}_6]$
- Determine conditions to make evolution of hydrogen from $\text{Al}(\text{BH}_4)_3$ reaction reversible
- Collaborate with E. Majzoub (Raman spectroscopy) and R. C. Bowman (NMR) for characterization of intermediate decomposition products of $\text{Al}(\text{BH}_4)_3$
- Prepare $\text{Ti}(\text{BH}_4)_3$ and determine decomposition products, reversibility
- Prepare known solid compounds $\text{LiM}(\text{BH}_4)_4$ where $\text{M} = \text{Al}, \text{Ti}$ by reaction of $\text{M}(\text{BH}_4)_3$ with LiBH_4 in solution; and examine the thermal decomposition reactions and reversibility of these materials.
- Collaborate with J. C. Zhao (GE) to study reactions of diborane.
- Use vacuum line and mass spectrometry facilities to determine yield of diborane as a product of decomposition of other metal borohydrides such as $\text{Ca}(\text{BH}_4)_2$ and $\text{Mg}(\text{BH}_4)_2$.

Future Directions – FY08 and beyond

Test Ti and Ti-Al catalysis of decomposition reaction of aluminum borohydrides, determine whether the reaction is reversible, and examine the influence of a catalyst on the product distribution.

Prepare $\text{Ca}[\text{M}(\text{BH}_4)_4]_2$ and $\text{Mg}[\text{M}(\text{BH}_4)_4]_2$ where M is Al, Ti and examine the thermal decomposition reactions and reversibility of these materials.

Understand medium dependence of reaction of diborane with metal hydrides in general

MHCoE Project C –Amides/Imides (M-N-H systems)

Future Directions – FY07 and FY08

Develop New Materials from Investigation of Ammonolysis Chemistry of Metal Dialkylamides in Liquid Ammonia:

- Prepare amides (and imides or nitriles) of Mg and Al in liquid ammonia from ammonolysis of $M(NR_2)_n$ precursors; incorporate Ti catalyst as “ Ti_3N_4 ” using the previously characterized product of the ammonolysis of $Ti(NR_2)_4$ in liquid NH_3 .
- Investigation, preparation, and decomposition reactions of $LiAl(NH_2)_4$; combine this material with LiH , MgH_2 , or CaH_2 – use the decomposition of $Al(NH_2)_3$ to AlN and NH_3 , the latter of which reacts with the metal hydride to produce hydrogen.
- Utilize high solubility of alkali metal borohydrides in liquid ammonia as a preparative route for mixed metal amides and borohydrides

Summary

- Pyrolysis of aluminum borohydride demonstrates how a substantial amount of hydrogen can be obtained from these complex borohydride materials.
- The equilibrium observed between $\text{Al}(\text{BH}_4)_3$ and $\text{Al}_2\text{H}_2(\text{BH}_4)_4$, in conjunction with the complex mechanism of the pyrolysis of diborane, suggests a route for reversible hydrogen storage.
- Further studies involving a variety of metal borohydrides are planned to identify those materials having the most favorable hydrogen evolution and regenerative capabilities.
- Focus of future chemistry is expected to be complex hydrides of Al, Mg, and Ti