



Metal Borohydrides and Aluminum Hydrides

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Project ID #:
ST35

Timeline

- **Start: March 1, 2005**
- **End: Sept 30, 2010**
- **60% complete**

Budget

- **Total project funding to date - \$1470K (DOE 100%)**
- **Funding for FY07 - \$300K**
- **Funding for FY08 - \$670K**

Barriers Addressed

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

Partners/Collaborators

- **Participant in the MHCoe**
- **Ohio State University**
- **GE (diborane chemistry)**
- **JPL and Cal Tech (NMR)**

Develop the chemistry for a reversible hydrogen storage system based on borohydrides, amides/imides, alane, or the light alanates

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 uses expertise in synthesis and characterization of materials: inorganic-organometallic-organic chemistry.
 - The discovery and characterization of new materials and processes.
 - The development of synthetic methods and processes in support of MHCoE collaborators.
 - The ORNL goal is to employ solvent-based procedures appropriate for scale-up to production and practical application.
 - Focus on high hydrogen content materials (> 10 wt% hydrogen)

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

Inorganic, Organometallic, and Organic Synthetic Capabilities:

Synthetic methods in solution – vacuum line, Schlenk line, cannula, and glovebox methods.

Experimental: Temperature programmed thermal decomposition (TPD) on a vacuum system (1) Volatile compounds allowed to react with heated zone at constant temperature (2) Non-volatile materials heated by ramping temperature at constant rate (variable) to $>400\text{ }^{\circ}\text{C}$

Gases separated by fractionation for spectroscopic identification



Glass vacuum line, teflon stopcocks, viton o-rings

Outline of Activities by Target Material

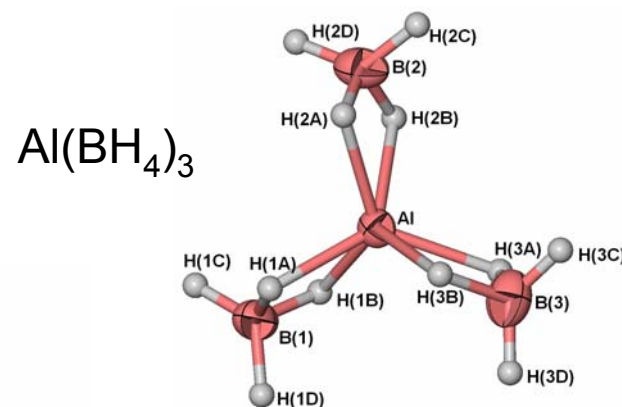
- **Complex anionic materials (MHCoE Project B)**
 - Investigated dehydrogenation of $\text{Al}(\text{BH}_4)_3$, measured temperature dependent product distribution; prepared $\text{AlB}_4\text{H}_{11}$ from reaction of $\text{Al}(\text{BH}_4)_3$ with B_2H_6
 - Used $\text{Al}(\text{BH}_4)_3$ as a synthon for preparation of solvent free $\text{Mg}(\text{BH}_4)_2$; investigated dehydrogenation of $\text{Mg}(\text{BH}_4)_2$
 - Observed diborane as product of alkali metal borohydrides; will discuss implications for reaction mechanism
 - Prepared and studied dehydrogenation of BH_4^- eutectic mixtures
 - Prepared B_3H_8^- bound to $\text{Mg}(\text{II})$; investigate boron hydride clusters
- **Amide/imide (M-N-H) systems (MHCoE Project C)**

Developed method for analysis of NH_3 by mass spectrometry during dehydrogenation of imide/amide compounds under vacuum
- **Regeneration of alane (MHCoE Project D)**
 - Investigating ionic liquids as a reaction medium for alane regeneration – imidazolium and quaternary ammonium tetrahydroaluminates
 - Investigating alane formation stabilized by hindered amines
 - Preparing alternative transition metal catalysts for study by BNL

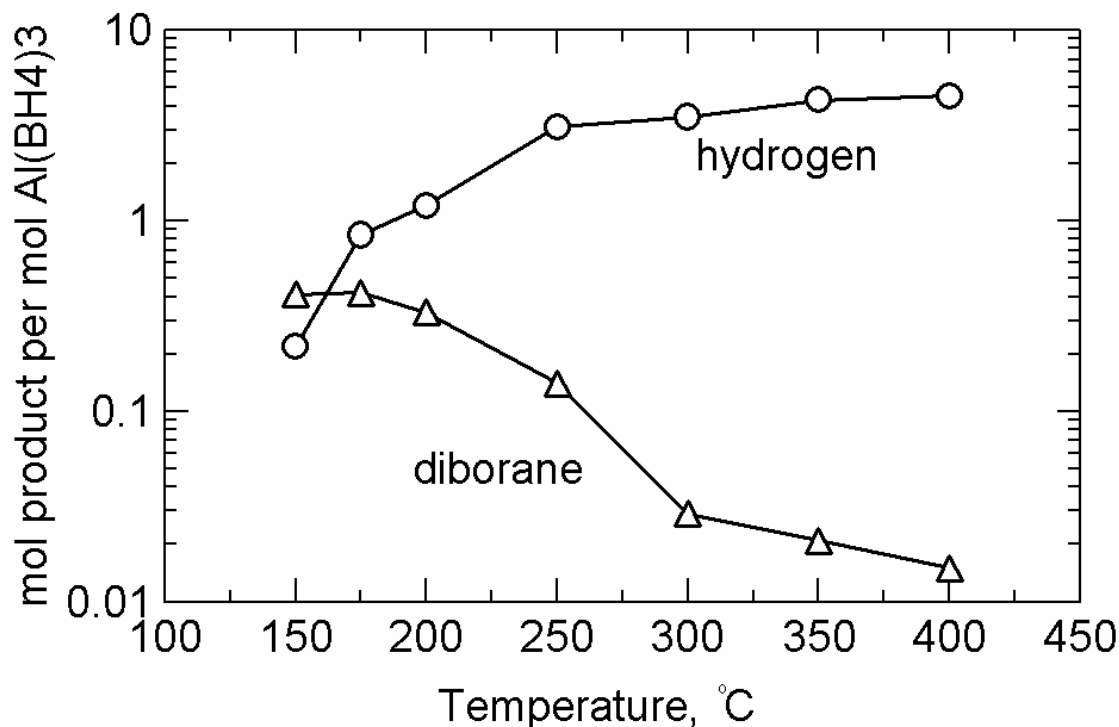
Liquid at room temperature - theory 16.8 wt % H_2

Covalent Al-H-B bonding

Reaction from the vapor phase – 3 to 6 hr reaction time



Product Distribution with Temperature

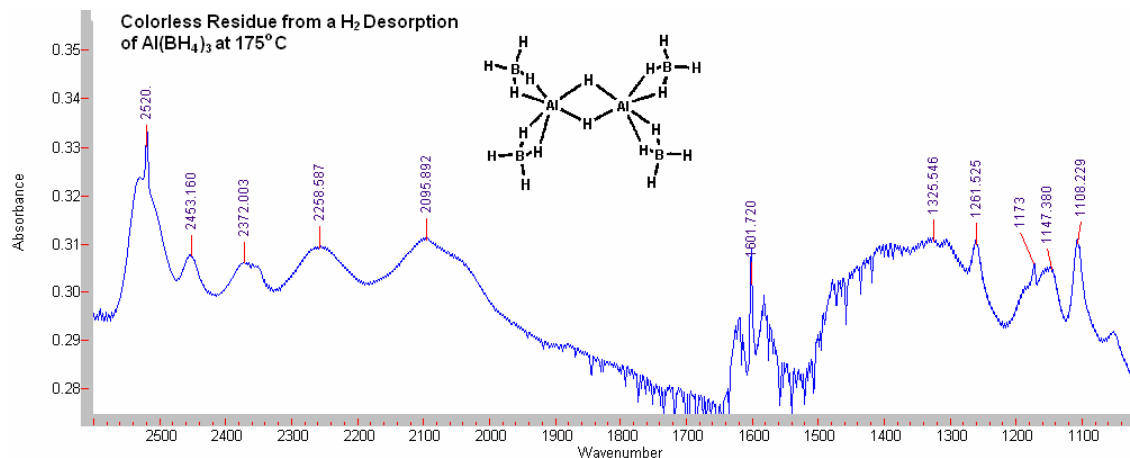


(D. A. Knight, et al, manuscript in preparation)

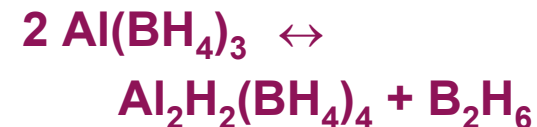
Product distribution is temperature dependent

Reaction studied under both static and flash vacuum pyrolysis conditions

– product distribution independent of mode



At $< 200^\circ\text{C}$, 0.5 eq. of B_2H_6 (identified by FTIR and MS) was formed:

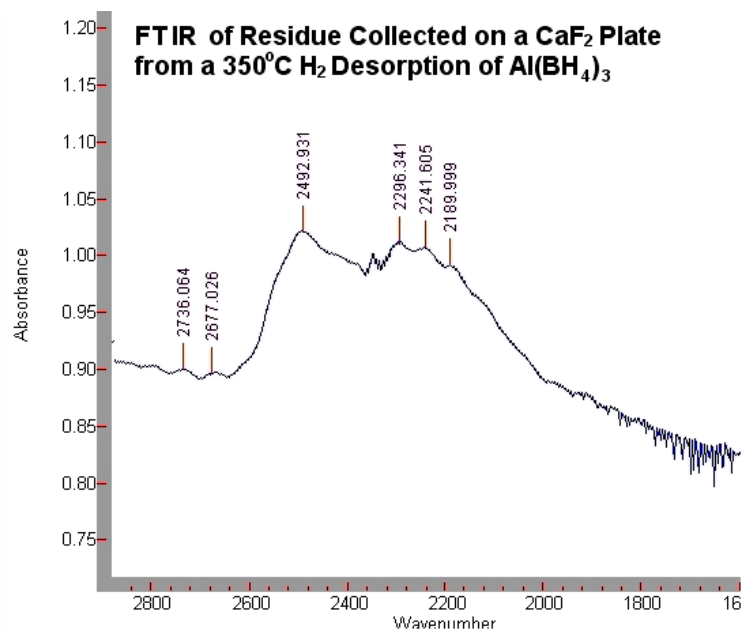
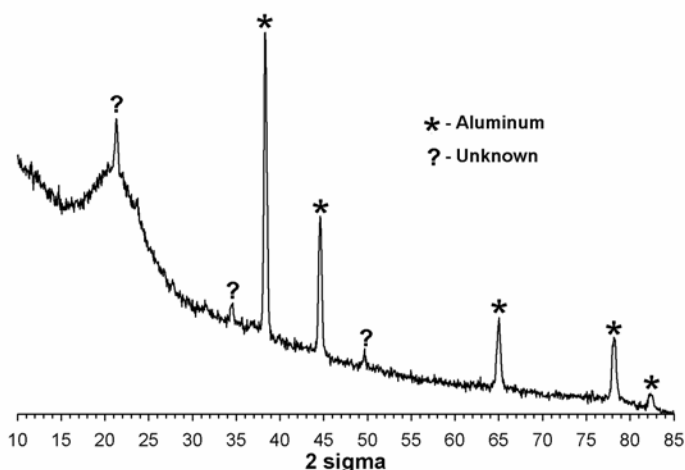


Product collected on CaF_2 plate

Between $300 - 400^\circ\text{C}$, 4.5 eq (12.7 wt %) H_2 was produced:



Residue from a H_2 Desorption of $\text{Al}(\text{BH}_4)_3$ at 350°C



XRD of solid shows Al metal instead of aluminum boride

FTIR shows distinctive B-H stretching vibrations

- 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 300 °C, rate of decomposition of AlH_3 and diborane to form products is fast compared to loss of BH_3 from AlBH_4
- No reaction of H_2 at 100 bar to hydrogenate reaction products in absence of catalyst
- We have prepared ammonia adduct – $\text{Al}(\text{BH}_4)_3 \cdot 2\text{NH}_3$ – solid at room temperature, dehydrogenation begins at 100 °C without melting or sublimation, diborane evolution suppressed.

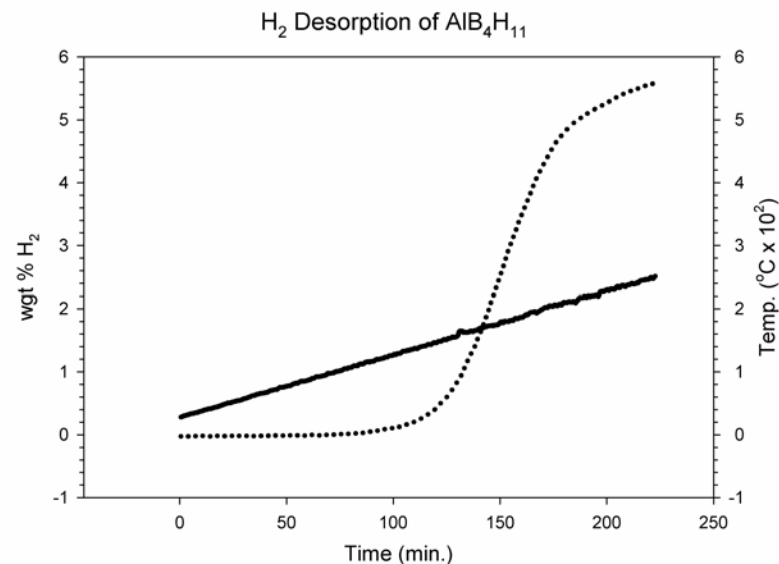
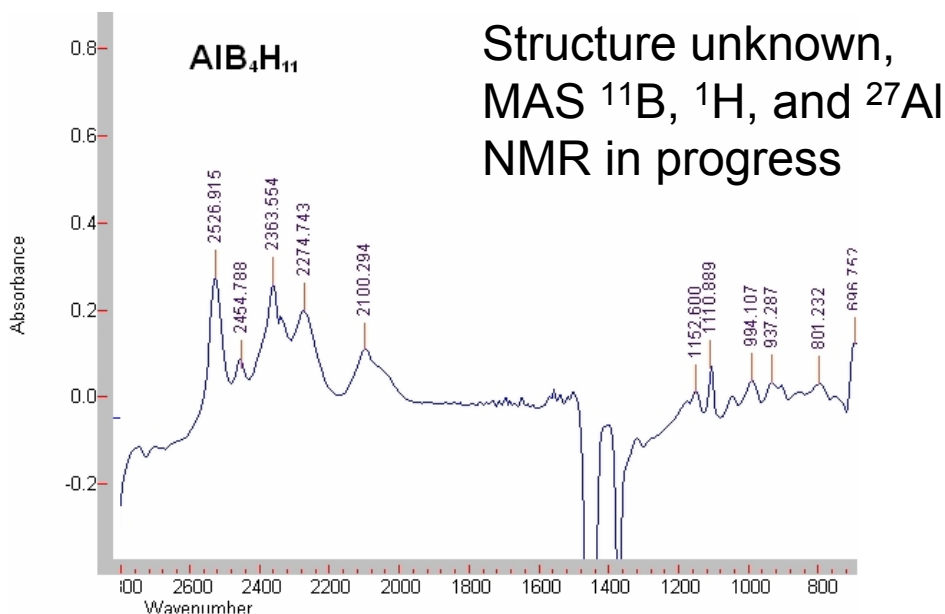
Collaboration with J.-C. Zhao (formally GE, currently Ohio State Univ.), Robert C. Bowman (JPL), Joseph W. Ritter (JPL), Sonjong Hwang (Cal Tech), Chul Kim (Cal Tech)

ORNL worked out the methodology and techniques to safely store, handle, and react diborane on a vacuum line system – 90% H_2 , 10% B_2H_6



benzene solution, 100 °C, 18 hr, product has 13.6% hydrogen

FTIR of product agrees with Himpsl and Bond, *J. Am. Chem. Soc.* **1981**, *103*, 1098-1102



H_2 desorption at low temperature

(D. A. Knight, et al, work in progress)

Is B_2H_6 formation a characteristic of all metal borohydrides?

- Diborane is detected by mass spec. analysis during H_2 desorption of both LiBH_4 and NaBH_4 , both melt before or during H_2 evolution.
- Powder X-ray diffraction (XRD) indicates LiH and NaH around the first step of desorption, Na metal at the end of desorption.
- From this collective evidence we concluded that alkali metal borohydrides evolve diborane as the first step in their desorption process (as did $\text{Al}(\text{BH}_4)_3$):



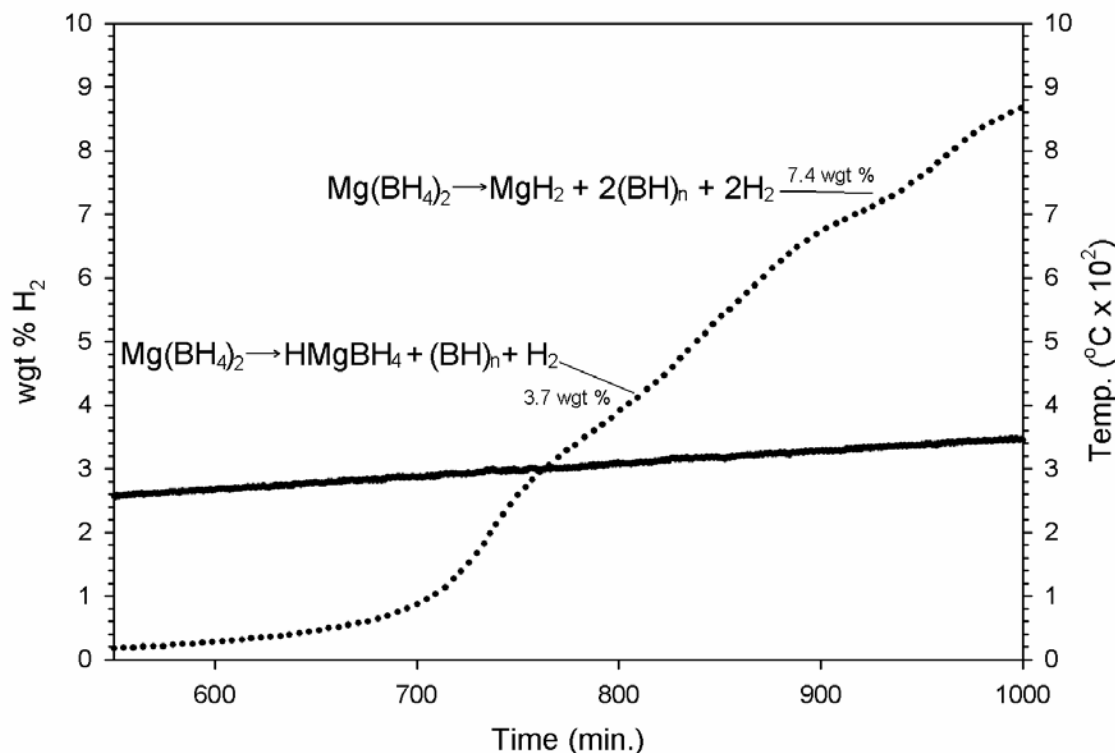
- Mechanism to account for formation of $\text{B}_{12}\text{H}_{12}^{-2}$ anion needed



toluene solution, stir at ambient temperature overnight

[Pierino Zanella, et al, *Inorg. Chem.* **2007**, 46, 9039-9041]

H_2 Desorption of $\text{Mg}(\text{BH}_4)_2$

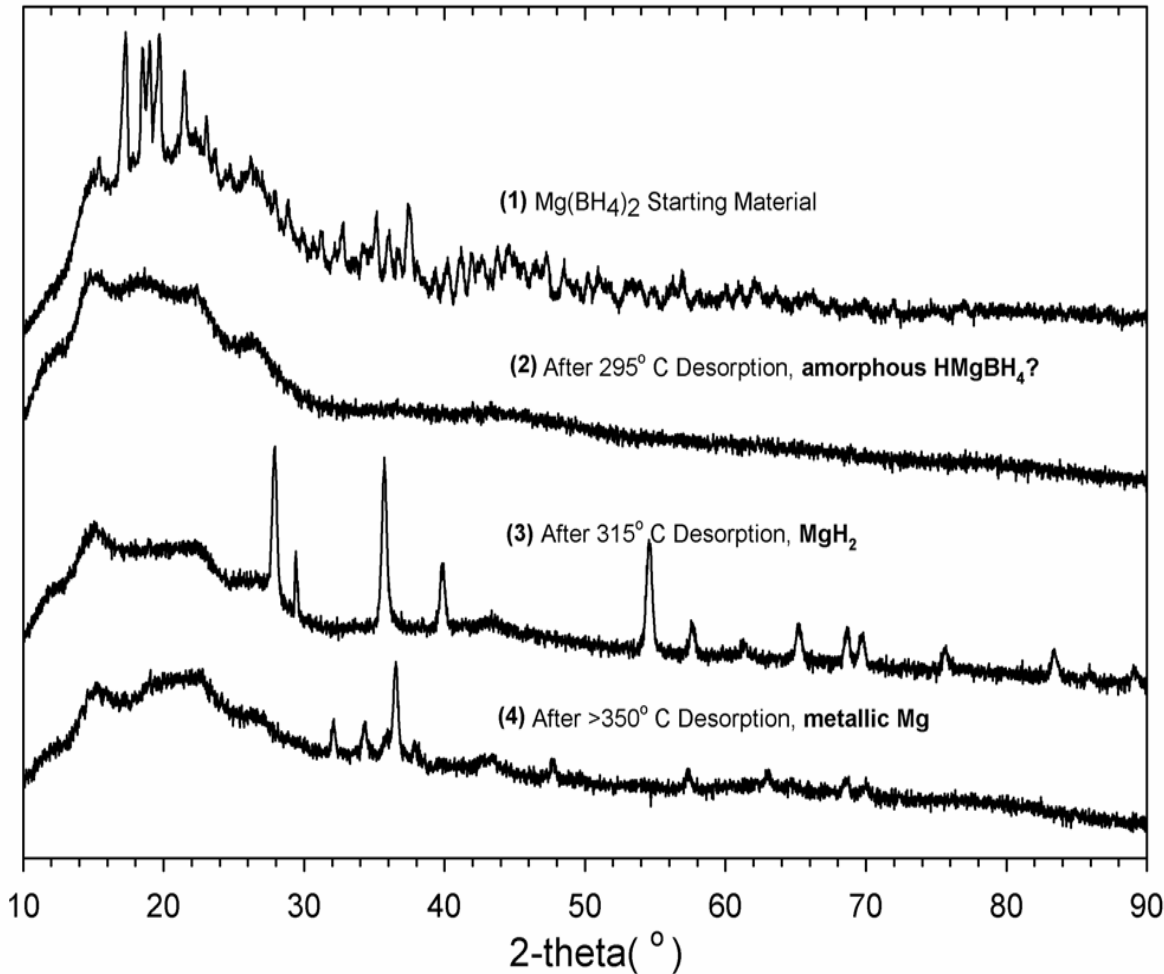


Where's the Diborane?

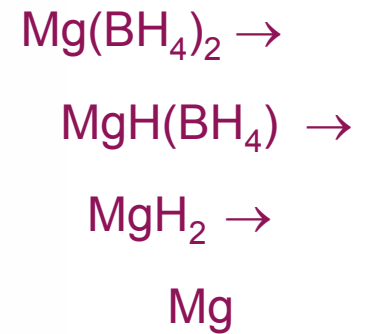
TPD-MS shows no evidence for volatile boron hydride products

Hwang, et al show formation of $\text{B}_{12}\text{H}_{12}^{-2}$ during reaction by NMR

How does the $\text{B}_{12}\text{H}_{12}^{-2}$ cluster form?



Recovered samples for XRD at various stages of H₂ desorption process – no evidence for MgB₂ at 350° C



Mg[B₁₂H₁₂] must be amorphous

Mixture of 45% LiBH_4 , 10% NaBH_4 , and 45% KBH_4 melts at 96 °C

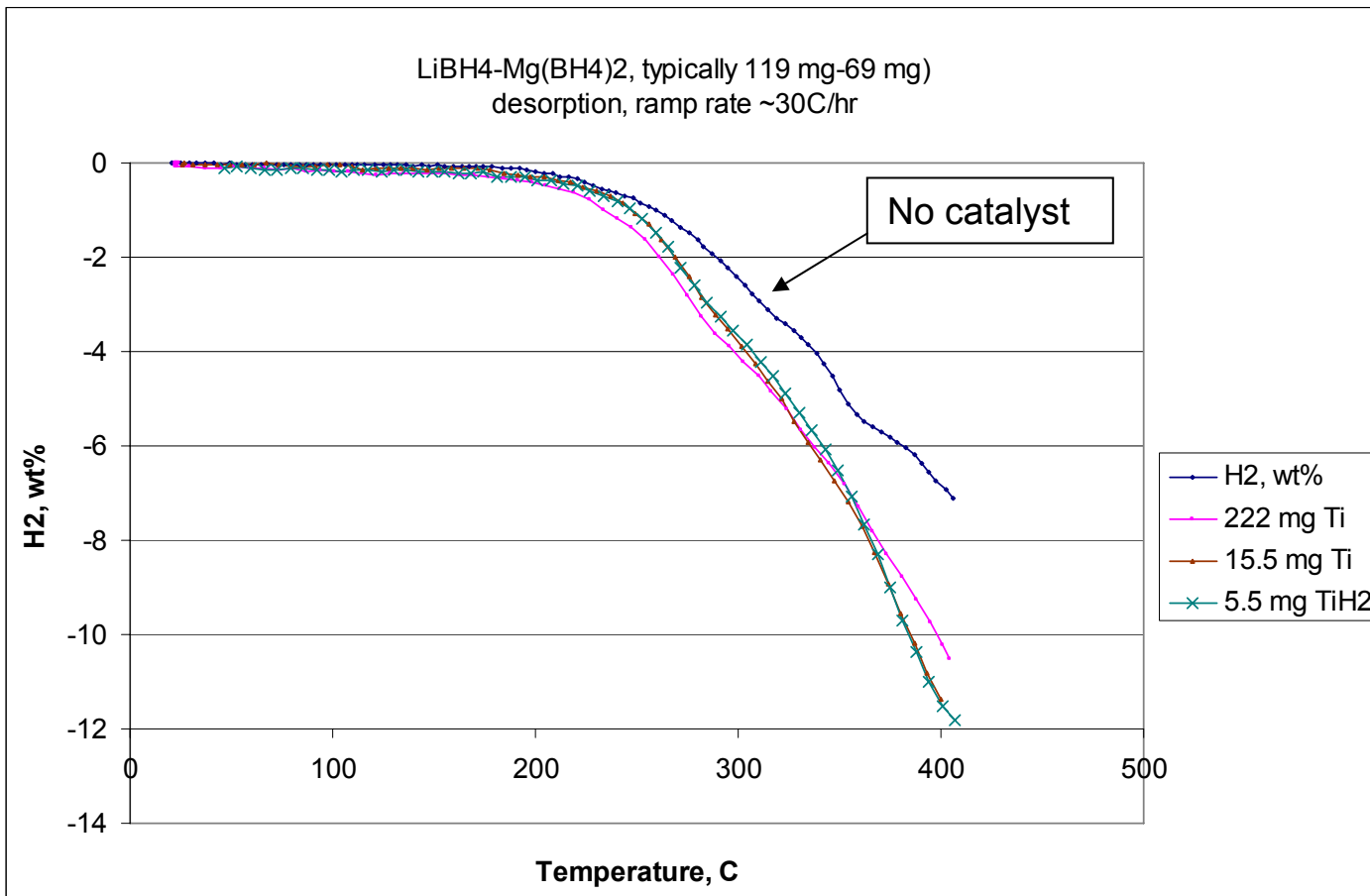
[G. F. Huff, US Patent 2,935,428, May 3, 1960]

We have discovered a low melting $\text{Mg}(\text{BH}_4)_2 - \text{LiBH}_4$ eutectic, melts at ~190 °C

H_2 desorption at lower T than $\text{Mg}(\text{BH}_4)_2$ alone

Catalysis: TiCl_3 catalyzes B_2H_6 formation (via formation of $\text{Ti}(\text{BH}_4)_3$?)

Ti metal or TiH_2 , H_2 evolution partially reversible



(D. A. Knight and J.H. Schneibel, unpublished results)

Understanding the Mechanism of H₂ Desorption-Sorption in Borohydrides is a Critical Need

Our observation of B₂H₆ as product in Al(BH₄)₃ and alkali metal MBH₄ indicates reaction pathway is



Diborane reacts with borohydride to form B₃H₈⁻ and H₂; borane adds to boron hydride anions to form higher B anions and eliminate H₂



Metal hydrides abstract a proton from neutral boron hydride clusters to form anions and eliminate H₂ – MH reacts with B₅H₉ to form H₂ and B₅H₈⁻

Beall and Gaines, *Inorg. Chim. Acta*, **1999**, 289, 1-10

Observation of B₁₂H₁₂⁻² as product is very important and supports borane formation as a first step

Hwang, et al, *J Phys Chem C*, **2008**, 112, 3164-3169.; Zuttel, et al, *Script Met*, **2007**, 56, 823-828

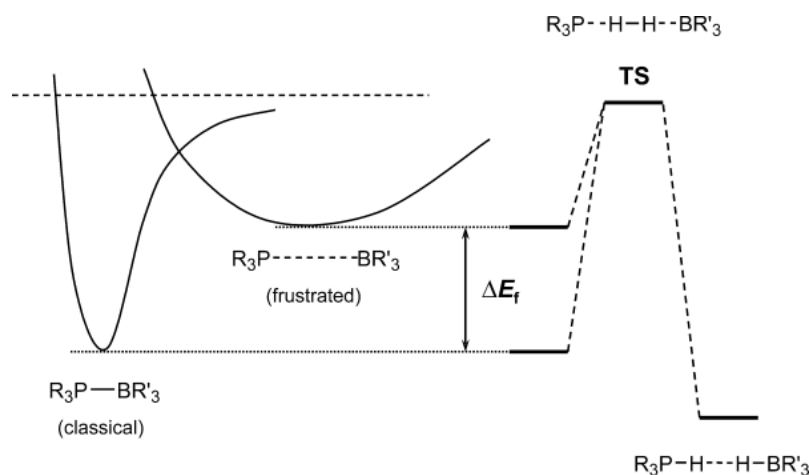
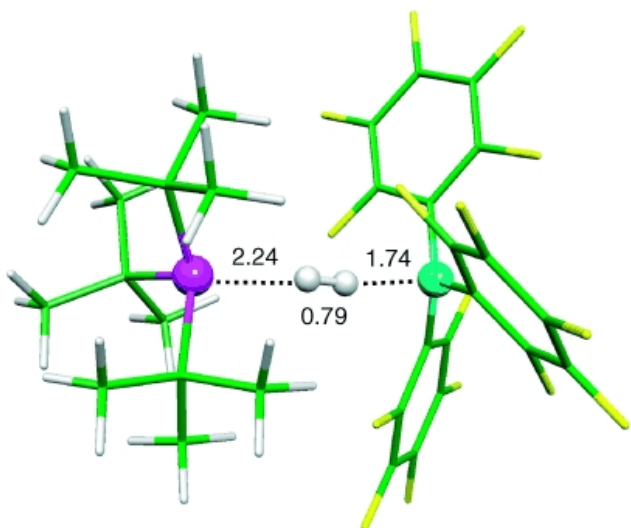
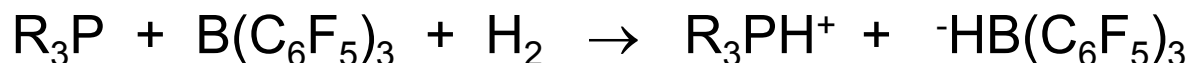
Decomposition of diborane to form higher borohydrides and H₂ is reversible up to B₆ species, reactions slow at low pressure of H₂ [Greenwood, *Chem Soc Rev*, **1992**, 21, 49-57]

Dehydrogenation reaction under H₂ pressure to prevent cluster formation

ORNL has prepared Mg(B₃H₈)₂ and investigations of reactions in progress

- Ionic liquids as a reaction medium for alane regeneration – imidazolium and quaternary ammonium tetrahydroaluminates
- Hindered amines to stabilize alane formation
- Alternative transition metal catalysts

“Frustrated Lewis Pair” activates H_2 in solution at room temperature and atmospheric pressure - D. W. Stephan, et al, U of Windsor, Ontario

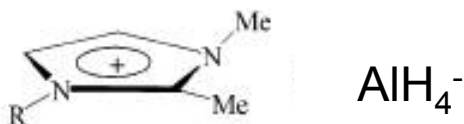


Ionic Liquids for Regeneration of Alane

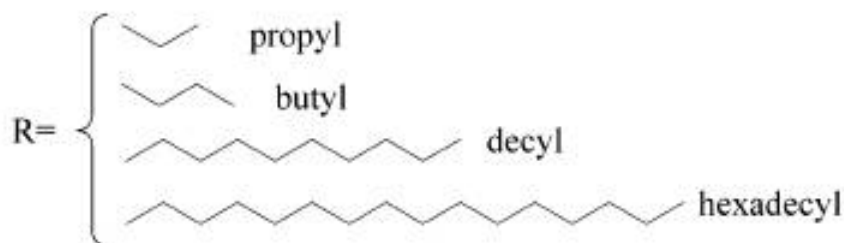
Ionic liquids as a reaction medium favors polar intermediates and transition states

Tetraalkylammonium tetrahydroaluminate ($R_4N^+ AlH_4^-$) salts known; formation of $Al_2H_7^-$ established; dehydrogenation to Al metal demonstrated; mass too high

We prepared imidazolium tetrahydroaluminate salt by reacting imidazolium bromide with $LiAlH_4$ in acetonitrile – $LiBr$ precipitate removed by filtration



Dimethyl alkyl imidazolium salts



Investigating to have the shortest alkyl chain that allows material to be a liquid at $< 100\text{ }^\circ\text{C}$

2-position of imidazolium (between N groups) protected with methyl group to prevent abstraction of hydrogen by tetrahydroaluminate

Use solution NMR (^{27}Al and ^1H) to study $Al_2H_7^-$ formation, higher oligomer to maximize AlH_3 loading

Determine temperature and reaction pathway for dehydrogenation/hydrogenation 16

Sterically Hindered Amines

Investigate sterically hindered trialkylamines to assess ability of hindered pair to split hydrogen



AlH_4^- to react with Al metal to form AlH_3

New Transition Metal Catalysts

Addition of $TiCl_3$ to alane results in formation of Al_3Ti alloy as the active catalyst – too active, dehydrogenation at ambient temperature

Investigate organometallic compounds of Ti, V that will retain auxillary ligands to reduce activity – dialkylamide, alkyl, aryl, cyclopentadienyl as auxillary ligand – provide materials to BNL

Complex anionic materials (MHCoE Project B)

- Investigate $\text{Li}[\text{M}(\text{BH}_4)_4]$ and $\text{Mg}[\text{M}(\text{BH}_4)_4]_2$ where $\text{M} = \text{Al}, \text{Ti}$
- Continue characterization of $\text{AlB}_4\text{H}_{11}$ and dehydrogenation products
- Continue characterization of low melting eutectic of borohydrides; useful test-bed for catalysis
- Reactions of $\text{Mg}(\text{B}_3\text{H}_8)_2$ and $\text{M} - \text{B}_5\text{H}_8^-$ compounds
- Dehydrogenation and re-hydrogenation of $\text{Al}(\text{BH}_4)_3 \cdot 2(\text{NH}_3)$

Amide/imide (M-N-H) systems (MHCoE Project C)

- Hydrogenation of cyanamide NH_2CN and dicyanamide $\text{NH}(\text{CN})_2$

Regeneration of alane (MHCoE Project D)

- Ionic liquids as a reaction medium for alane regeneration
- Hindered amines to stabilize alane
- Alternative transition metal catalysts
- Utilize the chemistry of Al/AlH_3 in cycle to regenerate higher H-content

Re-hydrogenation of $\text{Al}(\text{BH}_4)_3$ decomposition product is not possible in absence of catalyst.

$\text{Al}(\text{BH}_4)_3$ useful synthon for other materials. $\text{AlB}_4\text{H}_{11}$ needs further characterization but is promising material. $\text{Al}(\text{BH}_4)_3 \cdot 2\text{NH}_3$ is promising

Low melting eutectic mixtures of alkali and alkali earth metal borohydrides are promising system for further study; Li-Mg system partially reversible with catalyst

Key to reversibility of borohydrides is to prevent formation of large B-H clusters such as $\text{B}_{12}\text{H}_{12}^{-2}$ anion. Hydrogen back pressure during dehydrogenation process may be important consideration

“Frustrated Lewis Pair” concept of Stephan, et al good model for design of reversible hydrogenation-dehydrogenation reactions

We need to pay close attention to reaction pathways for the design of reversible hydrogen storage materials

Acknowledgements

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