

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

**Gilbert M. Brown PI,
Joachim H. Schneibel, Douglas A. Knight,
Frederick V. Sloop, Jr., and Claudia Rawn**

Oak Ridge National Laboratory
Oak Ridge, Tennessee

May 20, 2009

Project ID #: STP_37_Brown

(This presentation does not contain any proprietary information)

Overview

Timeline

- Start: March 1, 2005
- End: Sept 30, 2010
- 80% complete

Budget

- Total project funding to date - \$2170K (DOE 100%)
- Funding for FY08 - \$670K
- Planned Funding for FY09 - \$700K

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
- JPL and Cal Tech (NMR)
- Brookhaven National Lab

Relevance/Program Objectives

The program objective is to develop the chemistry for a reversible hydrogen storage system based on borohydrides, ammine borohydrides, amides/imides, and alane

- ORNL focuses on high hydrogen content materials (> 10 wt %)
- The ORNL goal is to employ synthetic procedures and other methods appropriate for scale-up to production and practical application.

DOE system goal is 6 wt% hydrogen by 2010, assume 50% containment penalty – 9 wt% needed for H₂ storage material

Materials Investigated by ORNL

Material	Hydrogen wt%
Al(BH ₄) ₃	16.8%
Al(BH ₄) ₃ (NH ₃) ₂	17.2%
Mg(BH ₄) ₂ (NH ₃) ₂	16.0%

Plan and 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

ORNL works with MHCoe partners to investigate the following 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).

Main Milestones for FY09 and Progress

- Investigate ammine metal borohydrides as hydrogen storage materials – good progress, on schedule
- Investigate imidazolium ionic liquid for alane regeneration, material decomposes at low temperature, unsuitable – investigate crown ether stabilized alkali metal alanate salt

Technical Accomplishments and Progress

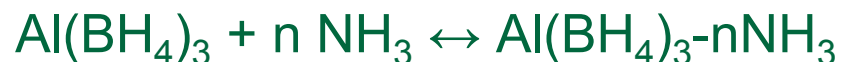
Overview of ORNL current focus for complex anionic materials, MHCoe Project B

- In 2008, initiated a study of ammine metal borohydride (AMBH) complexes: synthesis, structure, and potential as hydrogen storage materials.
- Initially we looked at the Al-AMBH given the readily available, solvent-free $\text{Al}(\text{BH}_4)_3$ used in our group.
- This study advanced to include the Mg- and Ca-AMBH with hopes to develop these materials via a solvent-free synthesis route.
- All materials were thermally desorbed on either a vacuum system with attached mass spec. analysis or on a Sieverts type system to calculate the wt. % H_2 desorbed.
- Structural characterization performed with collaborators

Technical Accomplishments and Progress

Reactions of $\text{Al}(\text{BH}_4)_3$ With NH_3 Formation of Ammine Aluminum Borohydride

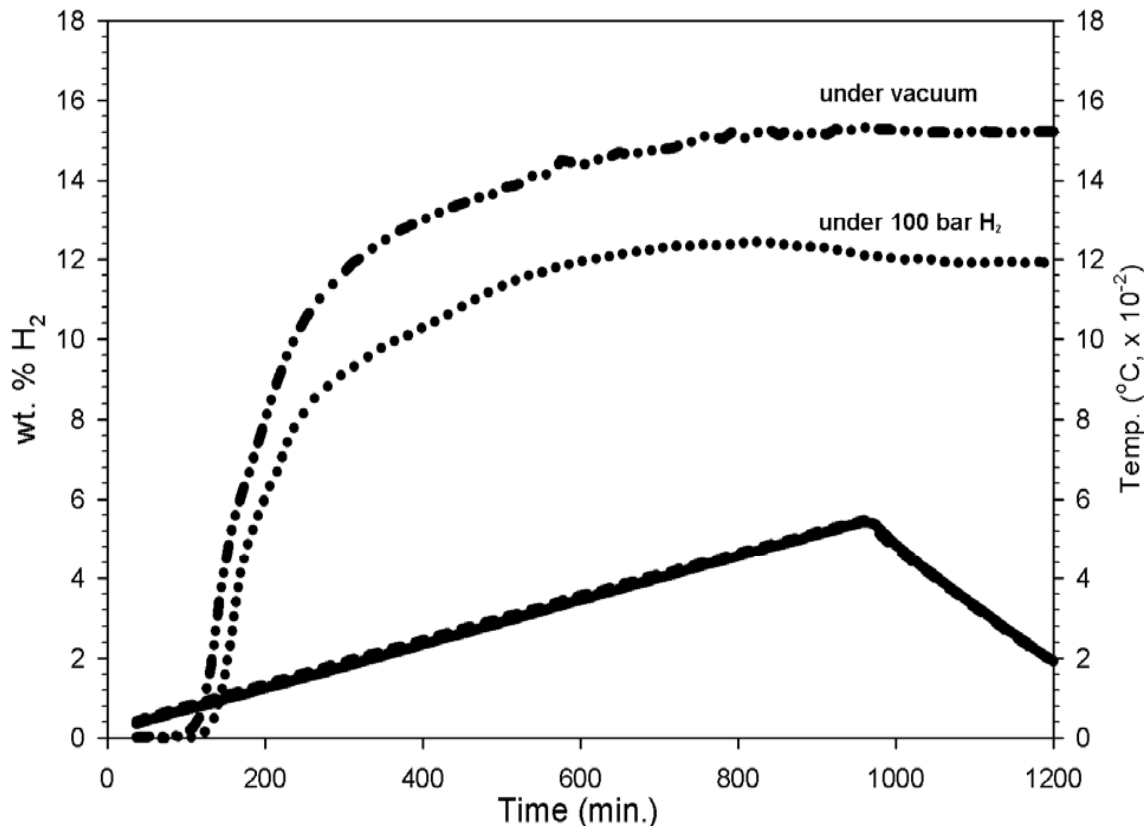
- A rapid, solvent-free reaction occurs between $\text{Al}(\text{BH}_4)_3$ and NH_3 as shown:



- The resulting material is a crystalline, white solid that reacts slowly in air and is also found to be much less reactive with the direct addition of water.
- The exact formula (NH_3 content) is under investigation by means of synchrotron X-ray diffraction and elemental analysis.
- $^{15}\text{NH}_3$ labeled sampled prepared for NMR characterization of products

Technical Accomplishments and Progress

H₂ Desorption of Al(BH₄)₃-nNH₃ With a Desorption Under 100 bar H₂ for Comparison



Addition of NH₃ to Al(BH₄)₃ decreases temperature for significant H₂ desorption by 100 °C

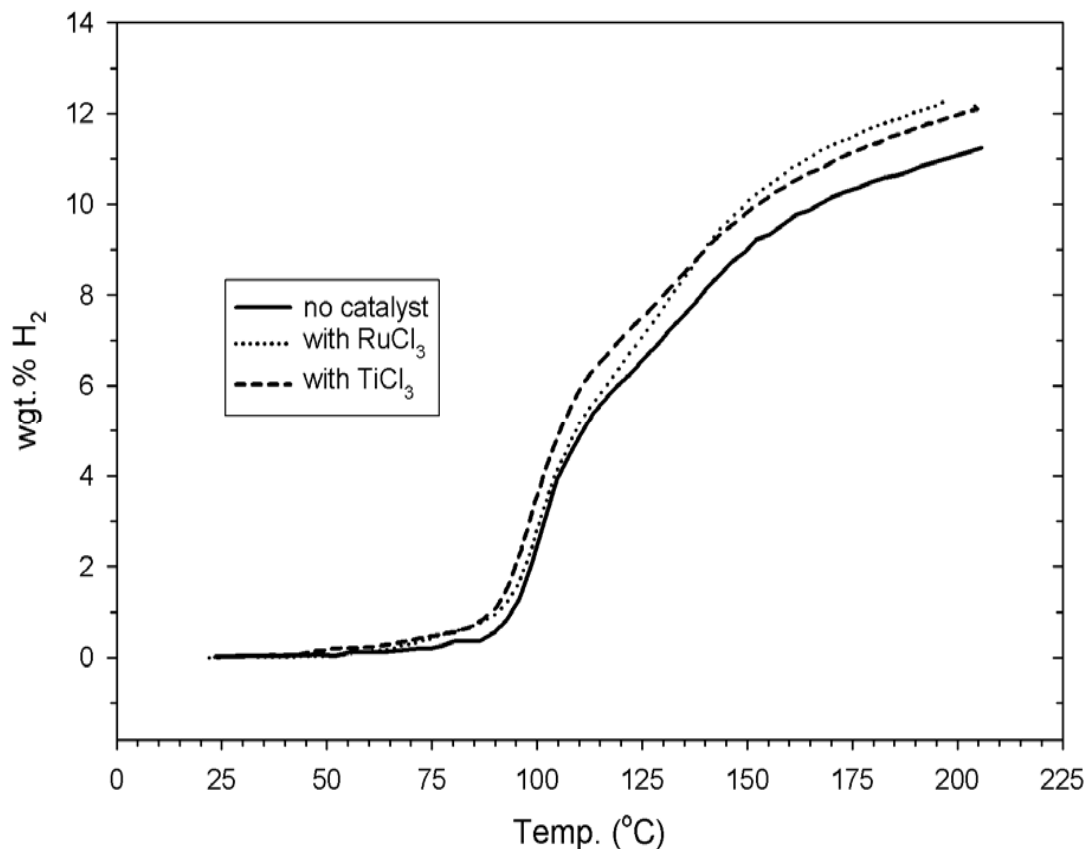
High percentage of H₂ evolved indicates NH₃ groups serve as source of H₂ as well as BH₄⁻ groups

Effect of H₂ pressure gives hope for reversibility

Formation of ammine borohydride increases quantity of hydrogen desorbed from aluminum borohydride at a lower temperature

Technical Accomplishments and Progress

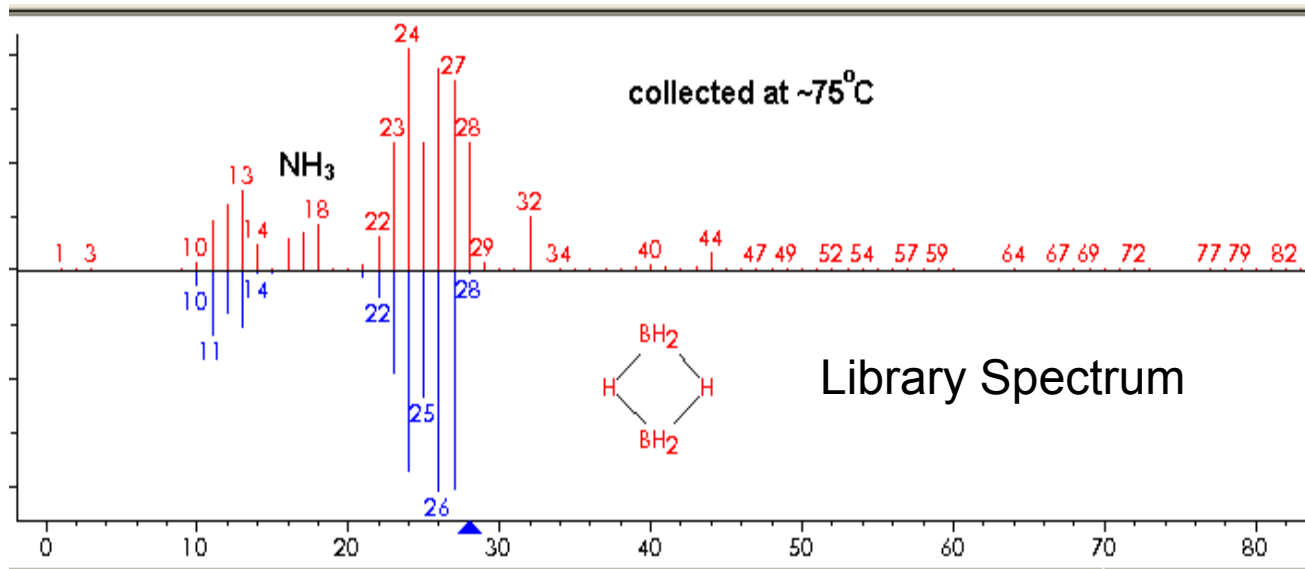
H₂ Desorption of Al(BH₄)₃-nNH₃ Catalyst Comparisons



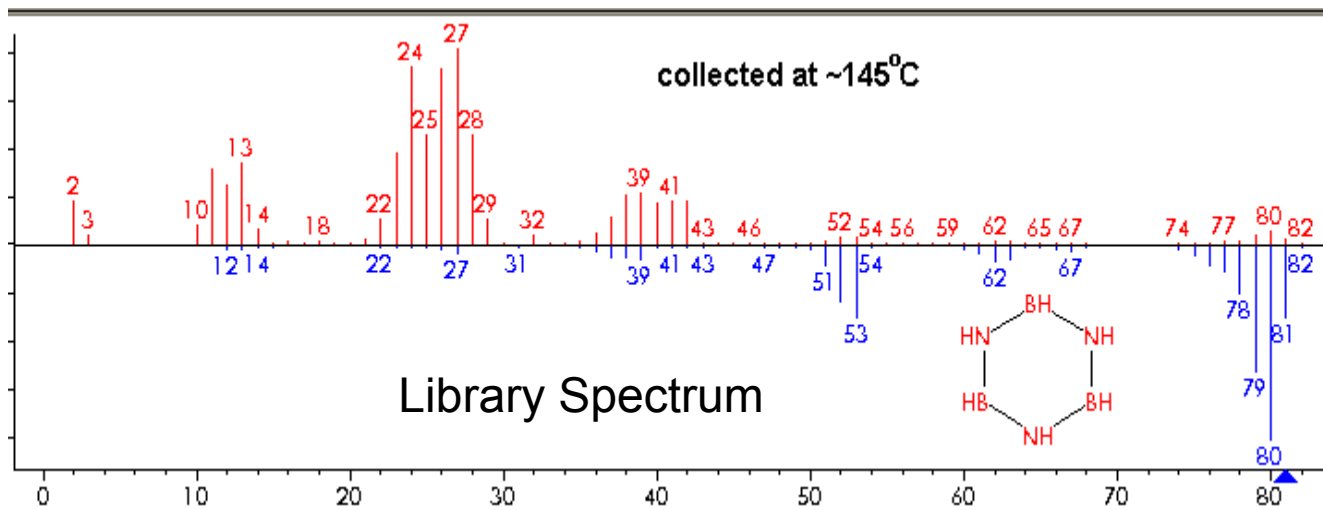
Initial tests shows catalyst has little effect on temperature for H₂ desorption or quantity of H₂ produced

Desorption Gasses Identified

MS Shows Trace Levels of B_2H_6 and NH_3 at $75^\circ C$



Trace borazine is detected at $145^\circ C$



Technical Accomplishments and Progress

Clues to the $\text{Al}(\text{BH}_4)_3\text{-nNH}_3$ Desorption Mechanism

- The appearance of ammonia and borazine as well as diborane and the quantity of hydrogen produced tells us that NH_3 is involved in the hydrogen desorption reaction.
- In comparison, studies of the BH_3NH_3 desorption has also reported the formation of borazine while noting the main process is as follows:



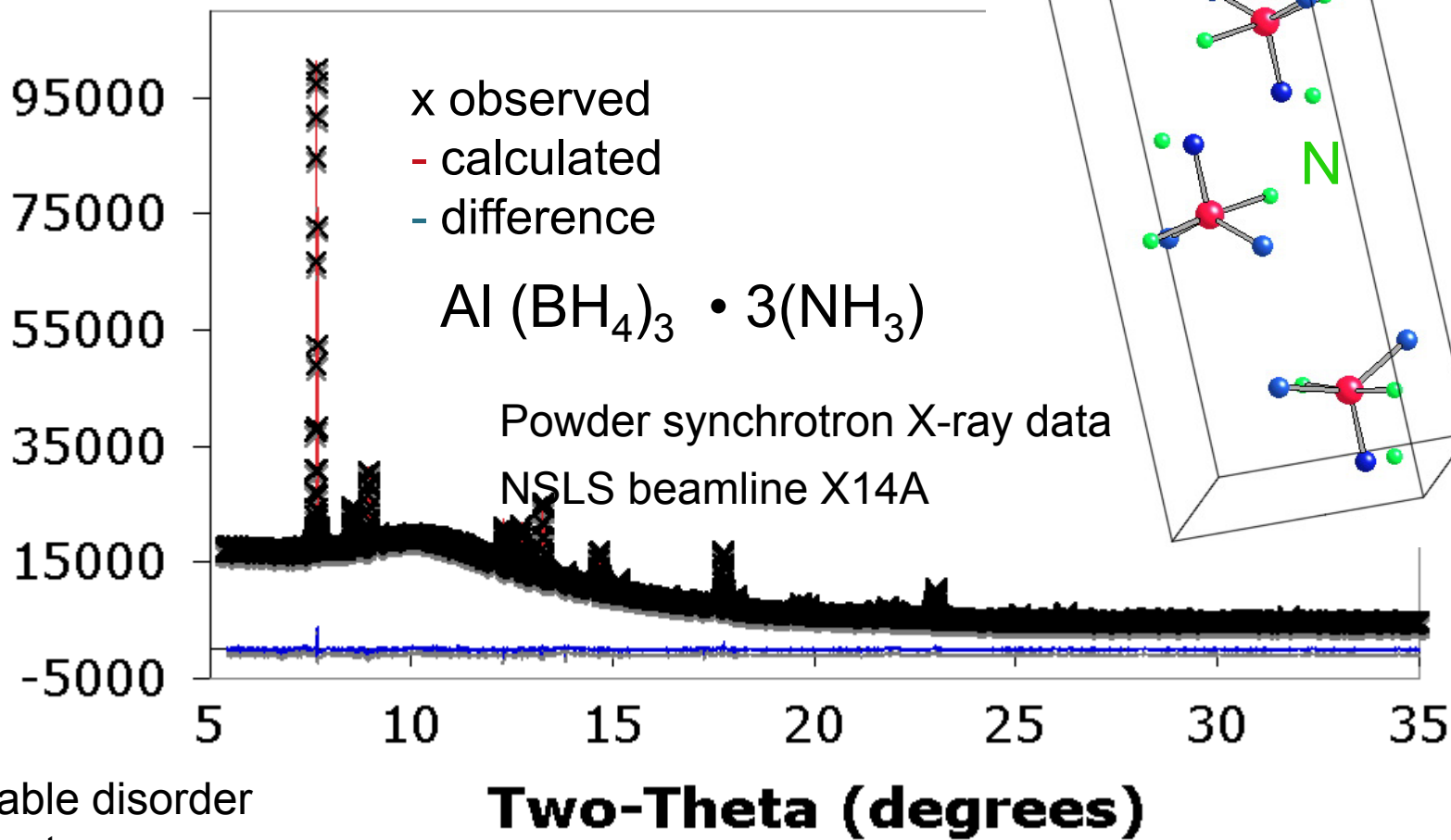
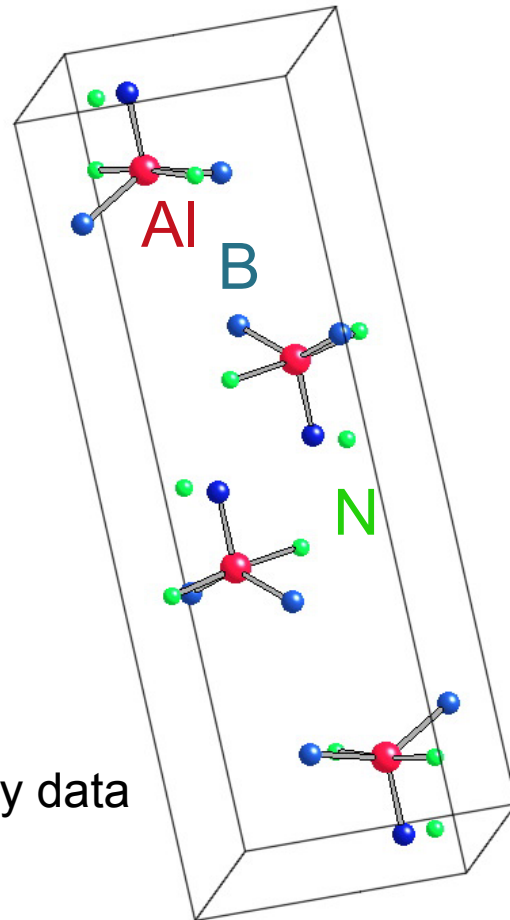
- It is likely that the reaction of $\text{Al}(\text{BH}_4)_3\text{-nNH}_3$ goes through an ammonia borane intermediate which may include a unique interaction with the aluminum coordination site.
- XRD indicates product amorphous after 120 °C
- 98% N-15 NH_3 prepared for solid state MAS-NMR characterization of product
- Analysis of XRD data obtained using synchrotron radiation indicates an aluminum borohydride-ammonia adduct has trigonal bipyramidal geometry; preliminary structure shown on next slide

Space group $P 42/n$

$a = 6.8453(1)$ and $c = 20.2893(9)$

$\chi^2 = 5.111$

wRp = 1.82%



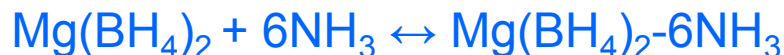
Probable disorder
in structure

In collaboration with C.J. Rawn, A.M. dos Santos, and J. Bai

Technical Accomplishments and Progress

Reactions of NH₃ with Mg and Ca Borohydrides

- J. -C. Zhao (OSU) has presented the synthesis of ammine magnesium borohydride from a diethyl ether solution:



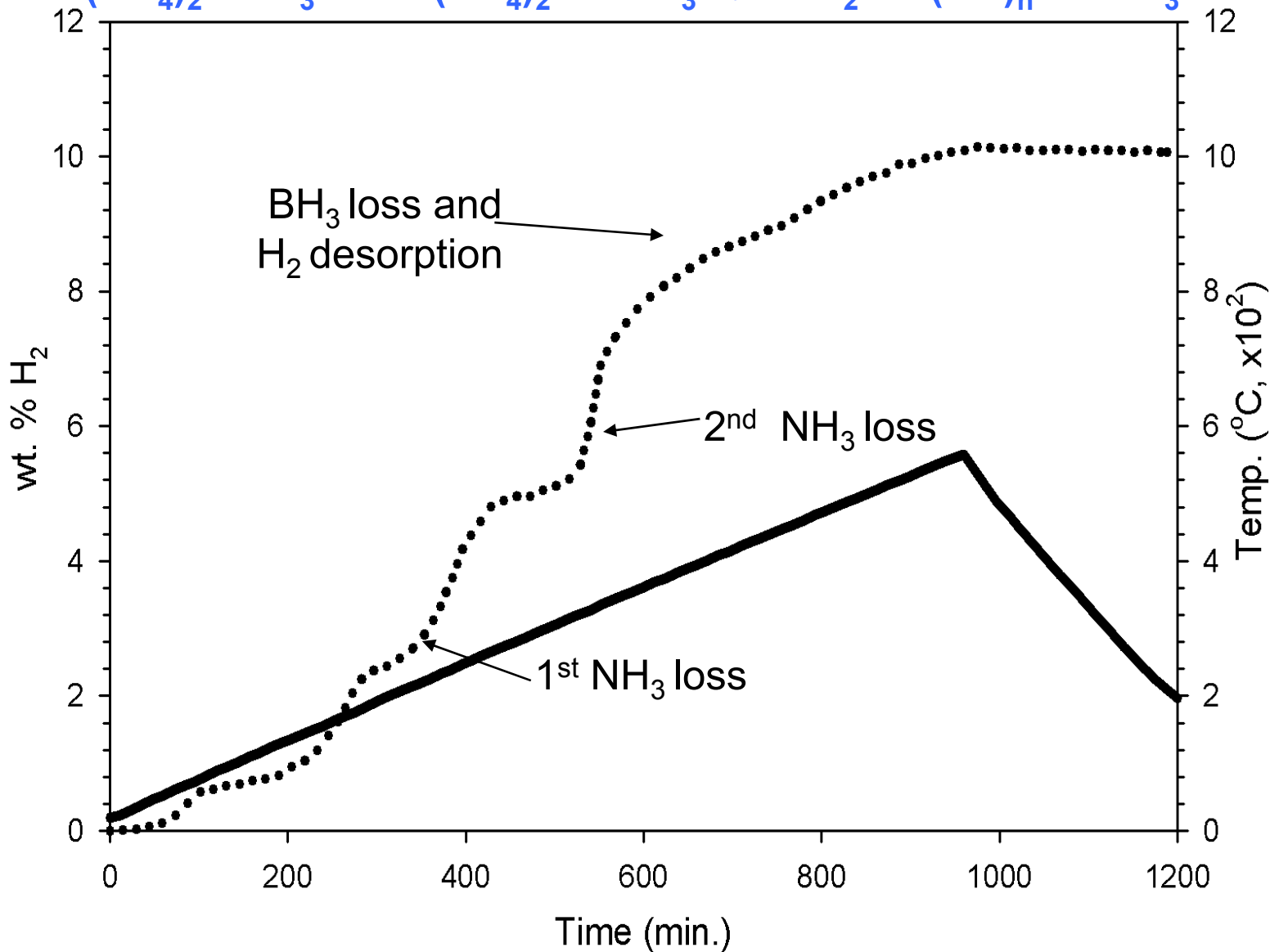
and formed a diammine species by gently heating under vacuum:



[*Inorg. Chem.*, 47(10), 4290, 2008]

- Our experience with Al(BH₄)₃·2NH₃ led us to undertake a **solvent-free** synthesis route to directly synthesize both Mg(BH₄)₂·2NH₃ and Ca(BH₄)₂·2NH₃.
- Recent results indicate that we have successfully synthesized Mg(BH₄)₂·2NH₃, Ca(BH₄)₂·NH₃, and Ca(BH₄)₂·2NH₃ via this solvent-free, one step process.
- N-15 labeled Mg(BH₄)₂·2NH₃ prepared for NMR analysis by collaborators

Sieverts and X-ray diffraction data indicates that $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ first releases the NH_3 followed by the typical desorption of the remaining $\text{Ca}(\text{BH}_4)_2$ as in:



Technical Accomplishments and Progress

Results and Discussion of the $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ Desorption

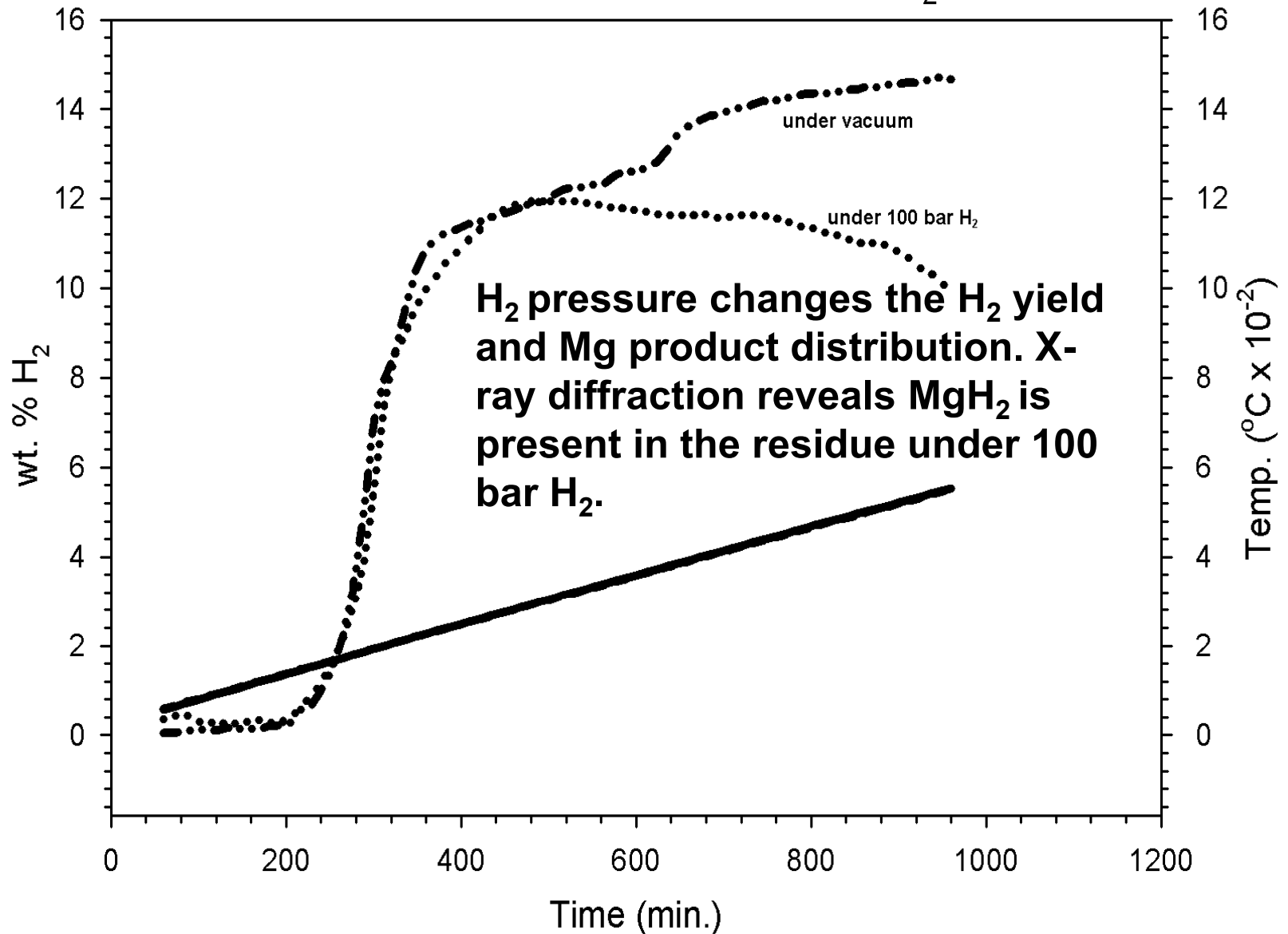
- $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ releases the BH_3 at a much higher temperature than it does the NH_3 , neither of these species can react together during H_2 desorption as did with the $\text{Al}(\text{BH}_4)_3 \cdot 2\text{NH}_3$ material.
- Only the rehydrogenation of Ca is seen when attempting system H_2 recharging.
- Interestingly – $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{THF}$ will form the monoammine, $\text{Ca}(\text{BH}_4)_2 \cdot \text{NH}_3$ upon ammination, then release the NH_3 (at 70°C under vacuum), leaving solvent-free $\text{Ca}(\text{BH}_4)_2$.
- This ammination-desolvation technique could be used to impregnate scaffolds or nanoporous solids with $\text{Ca}(\text{BH}_4)_2$ material.

Technical Accomplishments and Progress

Results and Discussion of the $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ Desorption

- The $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ desorption is currently an ongoing investigation.
- Preliminary observations have shown that this material melts (MP = $\sim 95^\circ\text{C}$) and foams considerably prior to desorption (although Al and Ca borohydride ammines undergo complete solid-state desorption).
- Our study confirms J.-C Zhao's results showing $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ desorbing H_2 some 100° lower than unsolvated $\text{Mg}(\text{BH}_4)_2$.
- The mass spectrometry of the desorbed gasses fails to detect any diborane, ammonia, or borazine.

H₂ Desorption of Mg(BH₄)₂-2NH₃ Under Vacuum vs Under 100 bar H₂



Technical Accomplishments and Progress

Summary of Project B Activities

- The ammine metal borohydrides (AMBH) are easily, and consistently obtained by a solvent-free synthesis.
- The added NH_3 component acts as an additional hydrogen source for the aluminum-AMBH.
- Although the calcium-AMBH loses NH_3 prior to H_2 desorption, the initial amination process can desolvate the commercially available $\text{Ca}(\text{BH}_4)_2\text{-THF}$.
- The behavior of magnesium-AMBH stands apart from the other AMBH's investigated thus far, as it melts prior to desorption and fails to evolve any B_2H_6 , or NH_3 during H_2 desorption.
- The solvent-free synthesis of both the Al and Ca – AMBH's as well as the melting of the Mg-AMBH may be exploited in impregnating nanoporous solids with these type of materials.

Technical Accomplishments and Progress

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

During last quarter of FY09 chemistry of alkali metal salts of cyanamide (NH_2CN) and dicyanamide ($\text{NH}(\text{CN})_2$) will be investigated; attempt hydrogenation (<100 bar)

Fang, et al previously showed LiNH_2 reacted with carbon to make de-protonated lithium cyanamide, Li_2NCN . Complete hydrogenation by one of the reactions below represents significant storage



Catalysts to be investigated include traditional precious metals and nickel

Nontraditional catalysts to be investigated include (a) BNL developed Ti activated Al and (b) Nevada-Reno version of $\text{LiNH}_2/\text{Li}_2\text{NH}/\text{Li}_3\text{N}$ system

React $\text{LiN}(\text{CN})_2$ with AlCl_3 (with and without TiCl_3 catalyst) to form $\text{Al}[\text{N}(\text{CN})_2]_3$ and attempt hydrogenation

Technical Accomplishments and Progress

Ionic Liquids for Regeneration of Alane MHCoe Project D

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

Theory suggests Al_2H_7^- important intermediate in H_2 desorption/adsorption from AlH_3 and $\text{AlH}_4^- / \text{Al}$ metal (*Proc Nat Acad Sci*, **2008**, 105, 3673)

Tetraalkylammonium tetrahydroaluminate ($\text{R}_4\text{N}^+ \text{AlH}_4^-$) salts known; formation of Al_2H_7^- established; dehydrogenation to Al metal demonstrated; mass too high

Plan: Investigate sterically hindered trialkylamines in ionic liquid to assess ability of hindered pair to split hydrogen



AlH_4^- to react with Al metal to form AlH_3

Can ionic liquid promote H-H bond breaking to regenerate alane?

Technical Accomplishments and Progress

Alane and Alanate Studies

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

NMR spectroscopy indicates the AlH_4^- anion is reacting with the imidazolium cation as material melts – need alternative plan

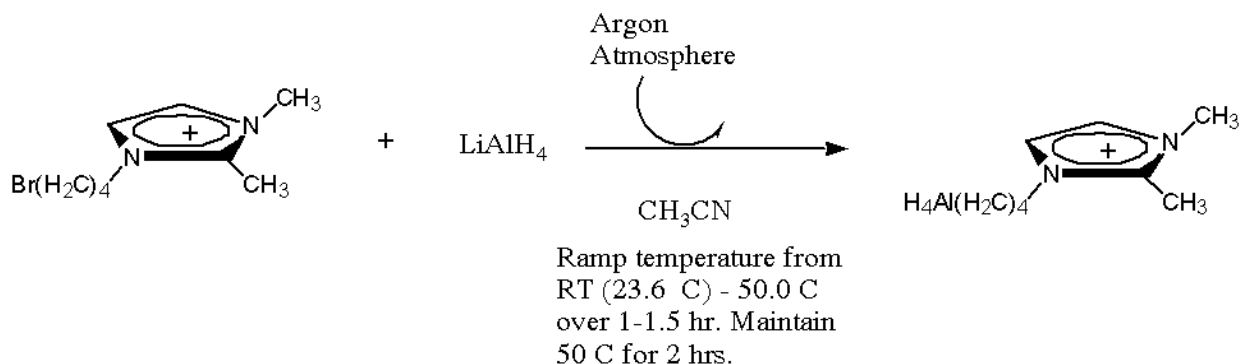
Future Work – Project D

Tetraalkylammonium tetrahydroaluminate synthesis to be repeated

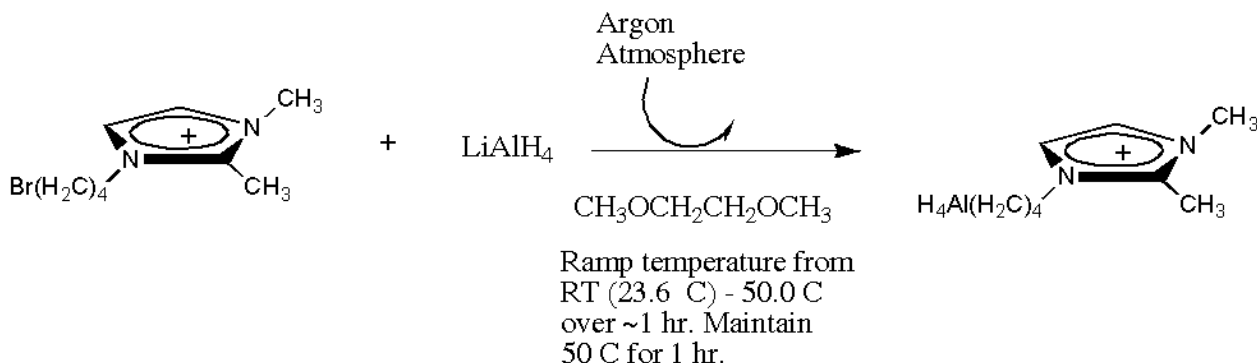
Lithium 14-crown-4 complex with tetrahydroaluminate salt to be prepared, AlH_3 reacts to make Al_2H_7^- anion reported in literature

Synthesis of 1,2-Dimethyl-3-*n*-Butylimidazolium Tetrahydroaluminate on a Small Scale

Acetonitrile Solvent



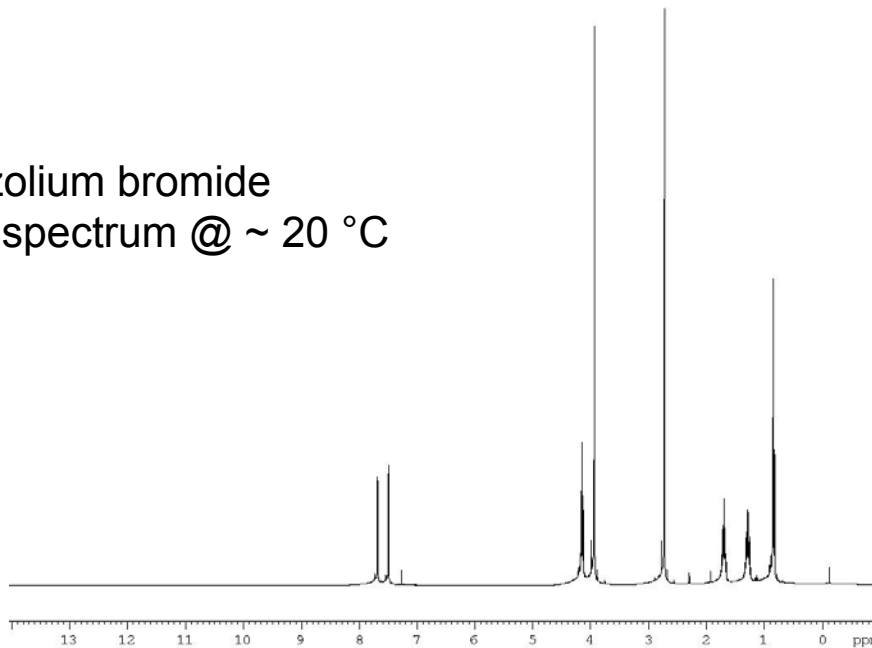
1,2-dimethoxyethane solvent



Gas evolution by 100 °C, decomposition evident

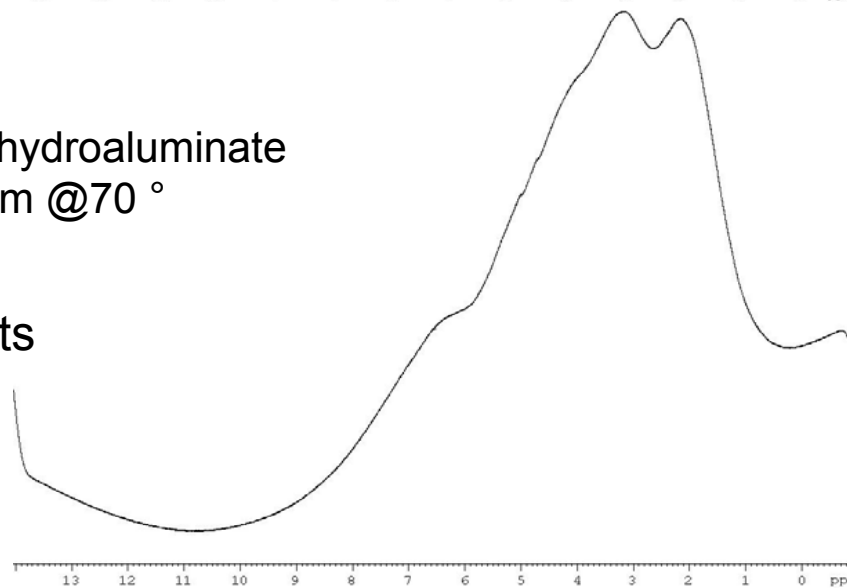
^1H NMR of AlH_4 -imidazolium salt as T increases, Br^- salt in solution for comparison and reference

2,3-dimethyl-N-butylimidazolium bromide
36 mgs in 600 μL CDCl_3 , proton spectrum @ $\sim 20^\circ\text{C}$



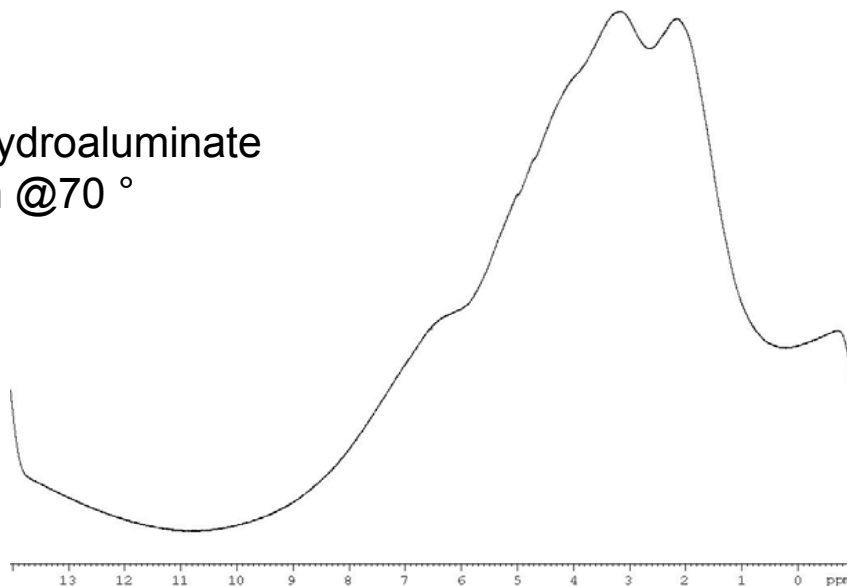
2,3-dimethyl-N-butylimidazolium tetrahydroaluminate
 ~ 30 mgs solid, proton spectrum @ 70°

Broad signals because salt reacts
with melting to precipitate

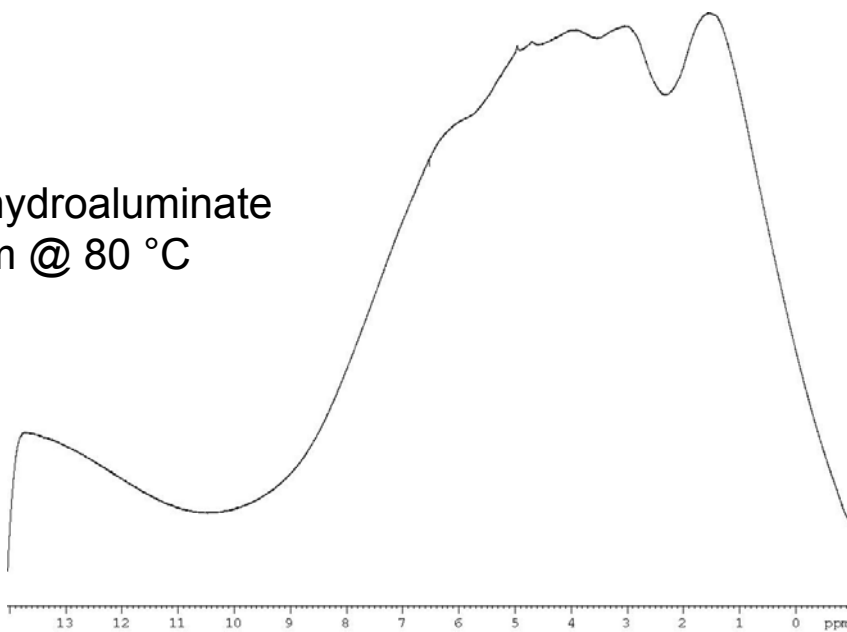


^1H NMR of material as temperature increases

2,3-dimethyl-N-butylimidazolium tetrahydroaluminate
~ 30 mgs solid, proton spectrum @70 °



2,3-dimethyl-N-butylimidazolium tetrahydroaluminate
~ 30 mgs solid, proton spectrum @ 80 °C

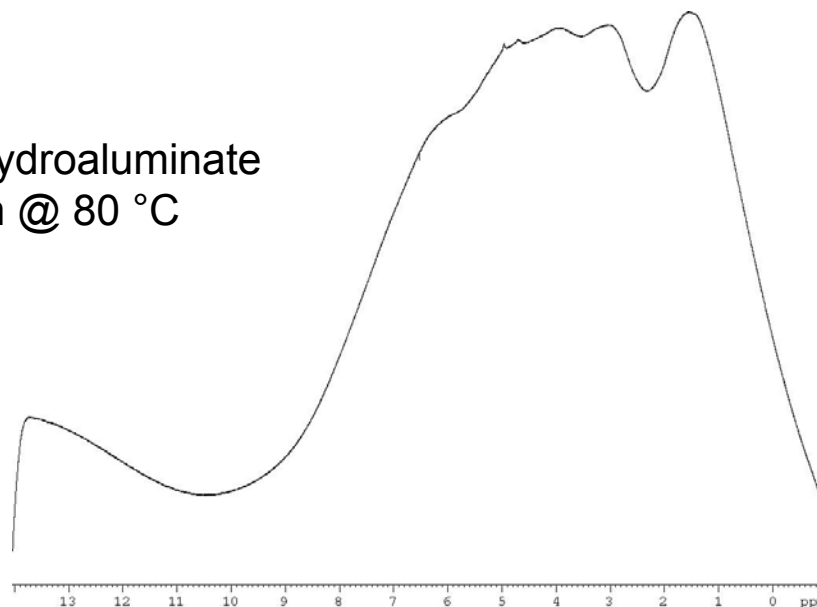


Imidazolium salt is probably
getting hydrogenated

^1H NMR of material with further increase in temperature

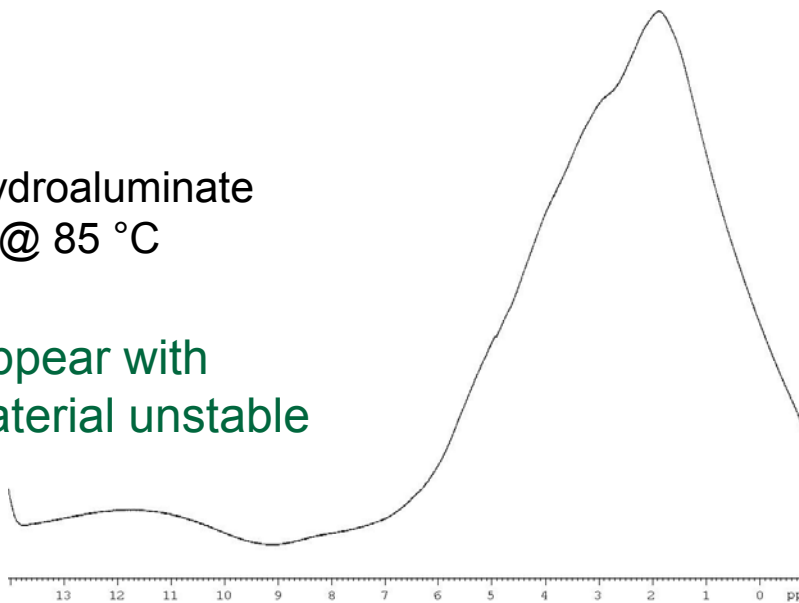
2,3-dimethyl-N-butylimidazolium tetrahydroaluminate
~ 30 mgs solid, proton spectrum @ 80 °C

Signals broad due to
presence of solids



2, 3-dimethyl-N-butylimidazolium tetrahydroaluminate
~ 30 mgs solid, proton spectrum @ 85 °C

Hydridic and aromatic protons disappear with
appearance of aliphatic protons, material unstable



Collaborations

MHCoE Partners

- J.-C. Zhao, Ohio State University – Development of aluminoboranes such as $\text{AlB}_4\text{H}_{11}$ 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 Rawn, MSTD, ORNL – Synchrotron based X-ray diffraction for structural determination

Future Plans

- Determine the yield of the $B_{12}H_{12}^{-2}$ species in desorption of $Mg(BH_4)_2$ in borohydride eutectic melt – continuation of work reported in FY08
- Refine the elemental analysis of the Al-AMBH's and further refine the structural data obtained from recently obtained high definition X-ray diffraction obtained at the Brookhaven National Laboratory National Synchrotron Light Source. Multinuclear solid MAS-NMR of AMBH's and desorption products to identify primary products.
- Continue study of aluminoboranes in collaboration with J.-C. Zhao, Ohio State Univ.
- Continue our study of the AMBH's, looking at how mixtures and catalysts might affect the desorption/absorption processes.
- Develop synthesis of titanium borohydride and titanium ammine borohydride and investigate stability and desorption characteristics of the latter.
- Investigate chemistry of alane amines ($AlH_3 \cdot nNH_3$)
- Utilize the chemistry of Ti catalyzed Al/ AlH_3 with an amine in cycle to hydrogenate and regenerate higher H-content materials (cyanamides, etc)

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:

- The ammine metal borohydrides (AMBH) of Al, Mg, and Ca are readily obtained by a solvent-free synthesis route. The added NH_3 component acts as an additional hydrogen source for the aluminum-AMBH. These AMBH's in liquid NH_3 are suggested as a way of impregnating nanoporous supports with these materials.
- Investigated ionic liquids as a reaction medium for regenerating alane. The AlH_4^- appears to react with the imidazolium cation of the ionic liquid. The work will be repeated with a tetraalkylammonium cation with a September 30, 2009 go/no-go.

Collaborations: ORNL has developed strong collaborations with Ohio State Univ, in AMBH and related materials, with CalTech/JPL in materials characterization, and with BNL in AlH_3 chemistry

Proposed Future Research: We will continue AMBH studies with an emphasis on identifying BN product, aluminoborane research will continue, and chemistry of AlH_3 with ammonia will be initiated