



DOE Hydrogen Program

Fundamental Studies of Advanced High-Capacity, Reversible Metal Hydrides

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Member MHCoe

5/13/07

ST19

This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Start date: 3/01/05
- End date: 2/26/10
- Percent complete: 20%

Budget

- Total project funding \$1,041,220
 - DOE share \$823,605
 - Contractor share \$217,615
 - Funding received in FY06 \$270,000
- Funding for FY07 \$300,000

Barriers

1. Lack of understanding of hydrogen chemisorption and physisorption
2. Hydrogen capacity and reversibility
3. Thermal management

Collaborators

- Dr. Etsuo Akiba, Katsu Sakaki - AIST, Tskuba, Japan
- *Dr. Robert Bowman - Jet Propulsion Laboratory*
- Dr. Hendrik Brinks, Prof. Bjorn Hauback - Institute for Energy Technology, Norway
- Prof. Rosario Cantelli - U. Rome
- Dr. Rysuke Kuboto KEK, Tskuba, Japan
- Prof. Sean McGrady, U. New Brunswick
- Prof. Shin-ichi Orimo, Dr. Yuko Nakamori - Tokoku U.
- *Dr. James Reilly, Dr. Jason Graetz - Brookhaven NL*
- *Prof. Ian Robertson - U. Illinois*
- *Dr. Ewa Ronnebro - Sandia National Laboratory*
- Dr. Adriaan Sachtler, Dr. Lisa Knight, Dr. John Low, UOP
- *Dr. Terry Udovic - NIST*
- *Dr. John Vajo - HRL*

Objectives

- I. Develop a new class of “reversible” borohydride complexes with potential to meet the DOE 2010 kinetic and system gravimetric storage capacity targets.

- II. Determine the mechanism of action of dopants for the kinetic enhancement of the dehydrogenation and re-hydrogenation of complex hydrides (FY06 only).

Approach - Materials Discovery

Neutral transition borohydride complexes as hydrogen storage materials

- High, 7-11 H wt%
- Often highly volatile i.e. $\text{Zr}(\text{BH}_4)_4$
- Often decompose at sub-ambient temperatures i.e. $\text{Fe}(\text{BH}_4)_2$, -45°C ; $\text{Cu}(\text{BH}_4)_2$, -12°C
- Diborane eliminated with H_2 i.e. $\text{Zn}(\text{BH}_4)_2$
- Often can only be obtained as Lewis acid adducts
- Irreversible dehydrogenation

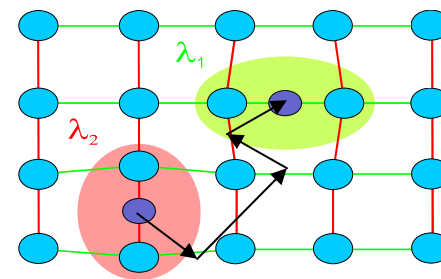
Group I salts of anionic transition borohydride complexes offer several potential improvements

- Higher, 9-13 H wt%
- Ionic character reduces volatility and increases stability
- Different thermodynamic parameters might allow reversibility and eliminate production of diborane during dehydrogenation.

Approach - Catalyst Development

Kinetics limit the practical potential of many borohydrides, amides, and “destabilized metal hydrides”. An “assault on kinetics” is required but there is no guide for an approach. Determination of the mechanism by which dopants enhancement the dehydrogenation and re-hydrogenation of complex hydrides could provide a guide for this effort.

Anelastic spectroscopy has established that Ti promotes the formation of highly mobile, hydrogen containing point defects in NaAlH_4 . However, chemical nature of the point defects could not be determined.



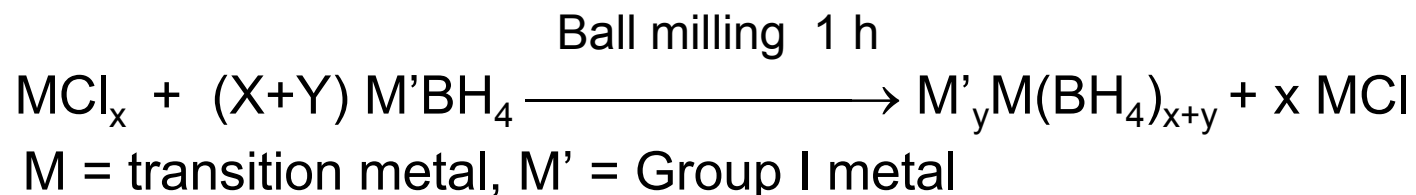
Muon spin resonance is a proven method for determination of the immediate chemical environment of point defects. A collaboration was established with Prof. Kadono of KEK-IMSS, Japan to apply this technique for the elucidation of the chemical nature of the point defects that are responsible for the remarkable hydrogen cyclic kinetics observed for Ti-doped NaAlH_4 .

Progress/Results

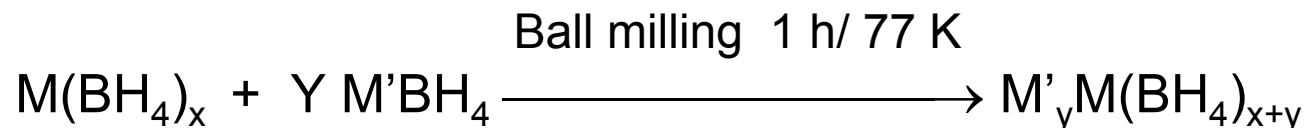
Materials Discovery

Synthesis of Group I salts of anionic transition borohydride complexes

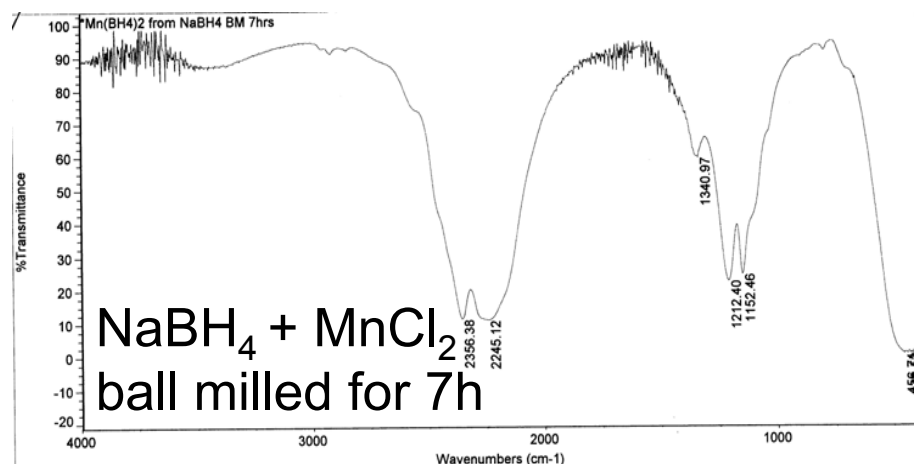
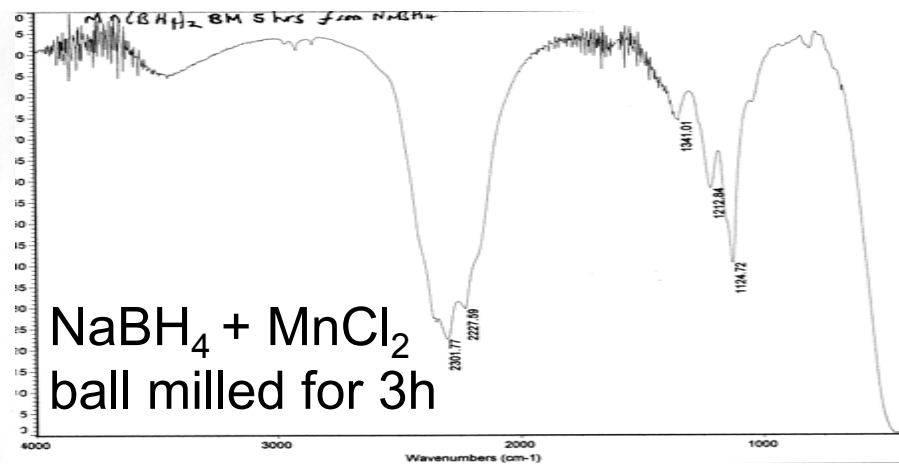
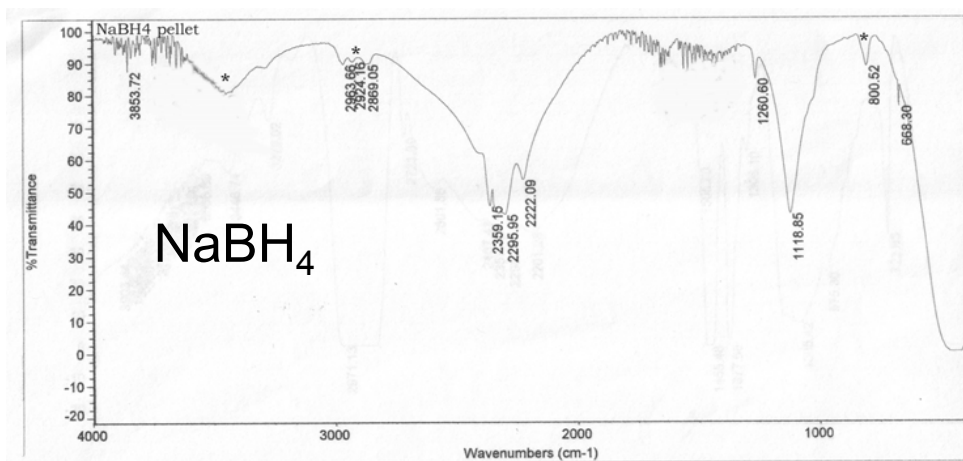
I. Balling of transition metal chlorides with Group I borohydrides



II. Ball milling of neutral transition metal borohydrides with Group I borohydrides



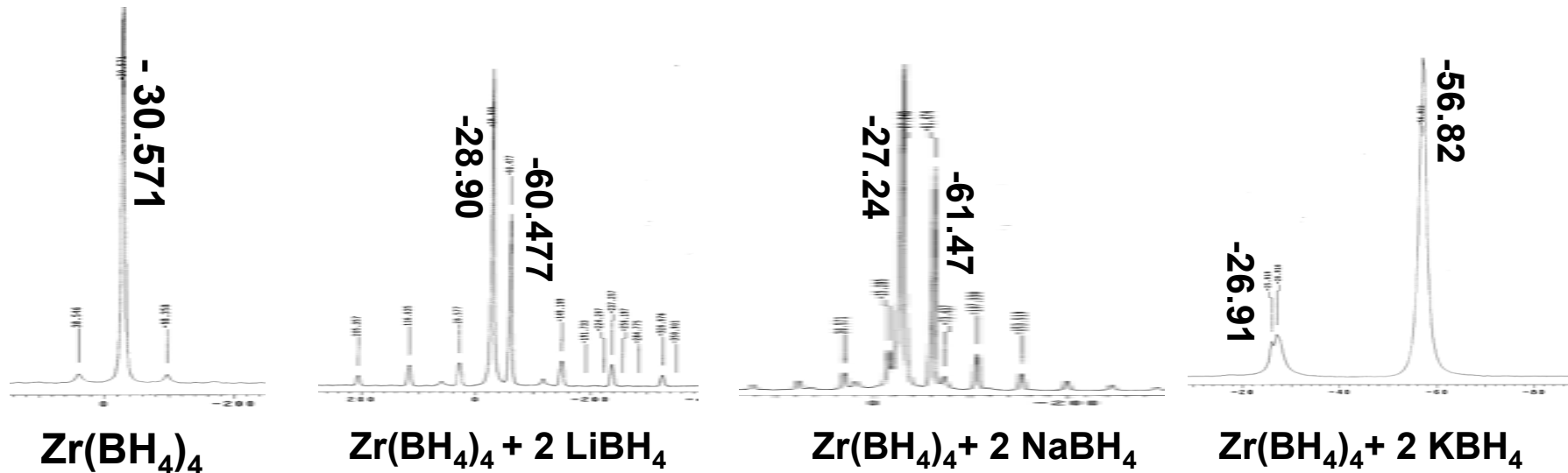
Synthesis reaction can be monitored by infra-red spectroscopy



New peaks appear at 1213 and 1341 cm⁻¹ together with shoulders at 2150 and 2400 cm⁻¹ which increase with ball milling time.

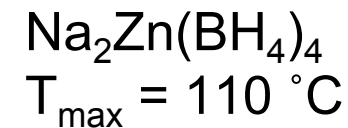
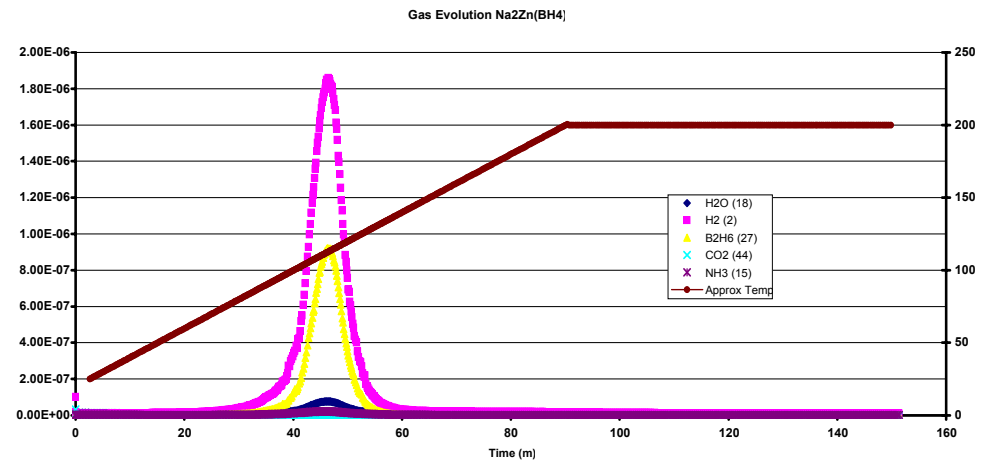
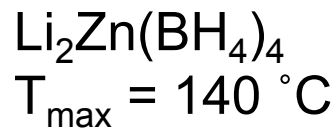
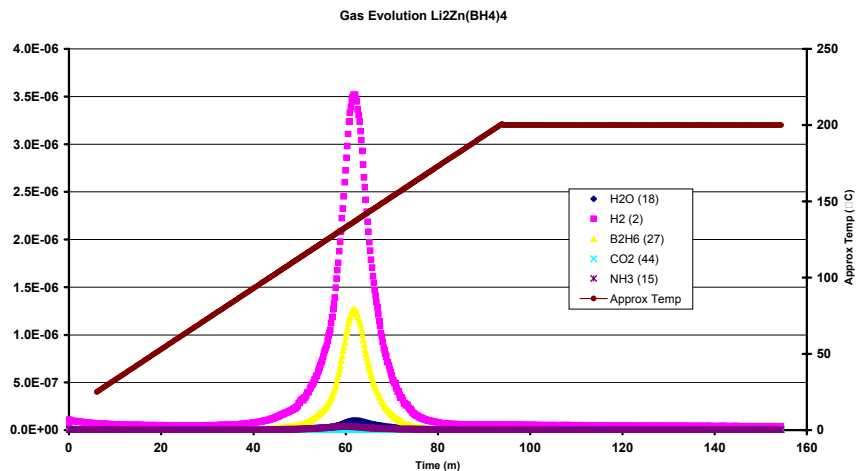
Characterization of products by MAS ^{11}B NMR Spectroscopy

Transition metal borohydrides are generally highly amorphous
 \Rightarrow can not be characterized by XRD.



Chemical shifts (ppm) of Group I borohydrides: LiBH_4 , -60.5 ; NaBH_4 , -61.5 ; KBH_4 , -56.81

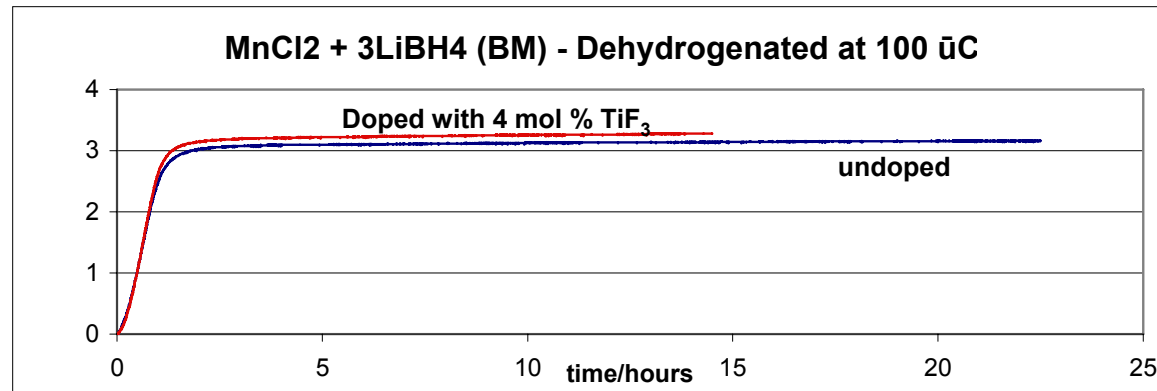
Influence of Cation on Desorption Temperature of $M_2Zn(BH_4)_4$



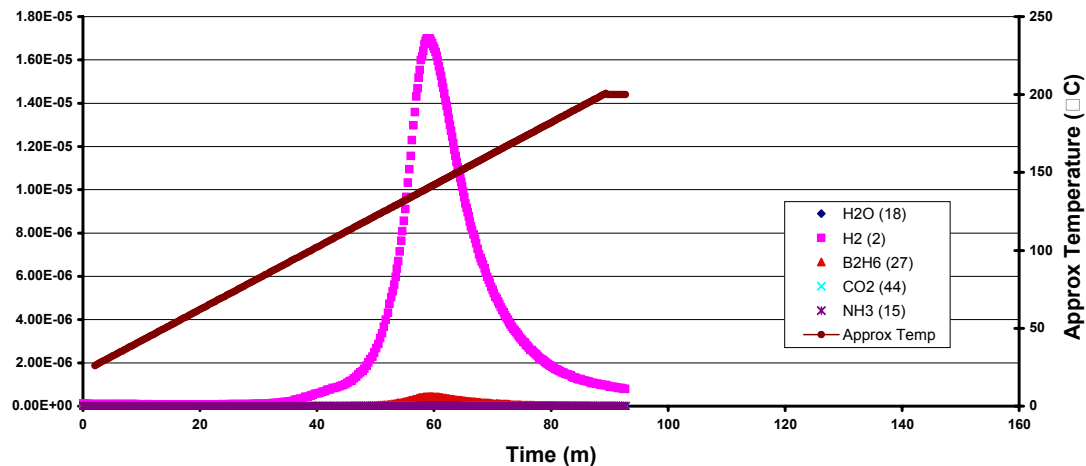
- Exchange of Na for Li lowers desorption temperature by 30°C.
- Tandem diborane elimination is a major issue with both neutral and anionic Zn borohydrides.

Hydrogen is evolved from $M'Mn(BH_4)_3$ at low temperatures without tandem diborane production

$LiMn(BH_4)_3$ undergoes rapid dehydrogenation at 100 °C.



50:1 H₂/B₂H₆ molar ratio observed in gases eliminated from NaMn(BH₄)₃

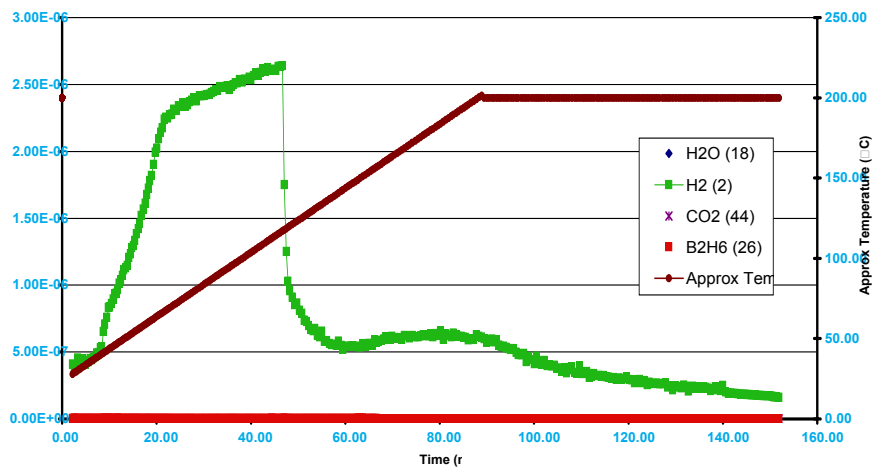


No diborane is observed with hydrogen evolved from anionic Zr borohydrides!

$M_2Zr(BH_4)_6$ compounds are much less volatile than $Zr(BH_4)_4$
 \Rightarrow 2-3 wt % H_2 eliminated at 40-110 °C without complex sublimation

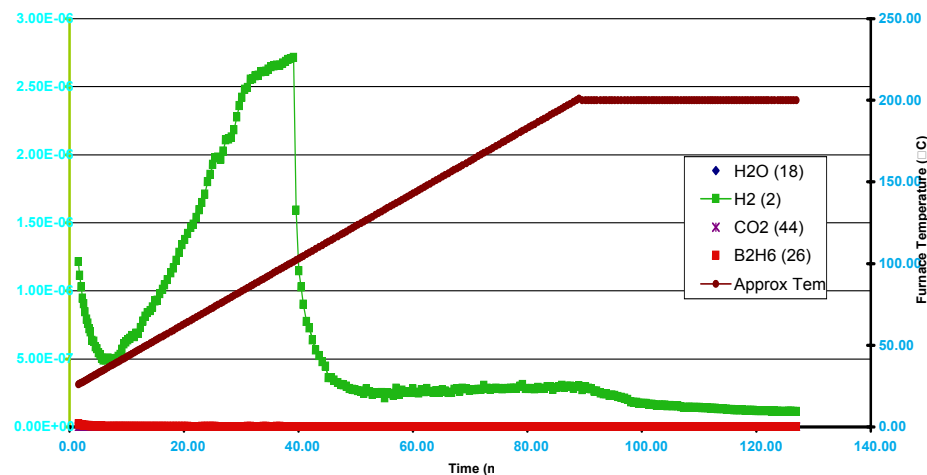
M=Na

Gas Evolution from Godwin Sample 3 (Zr)



M=K

Gas Evolution from Godwin Sample 4 (ZrE)



Data obtained at UOP, LLC

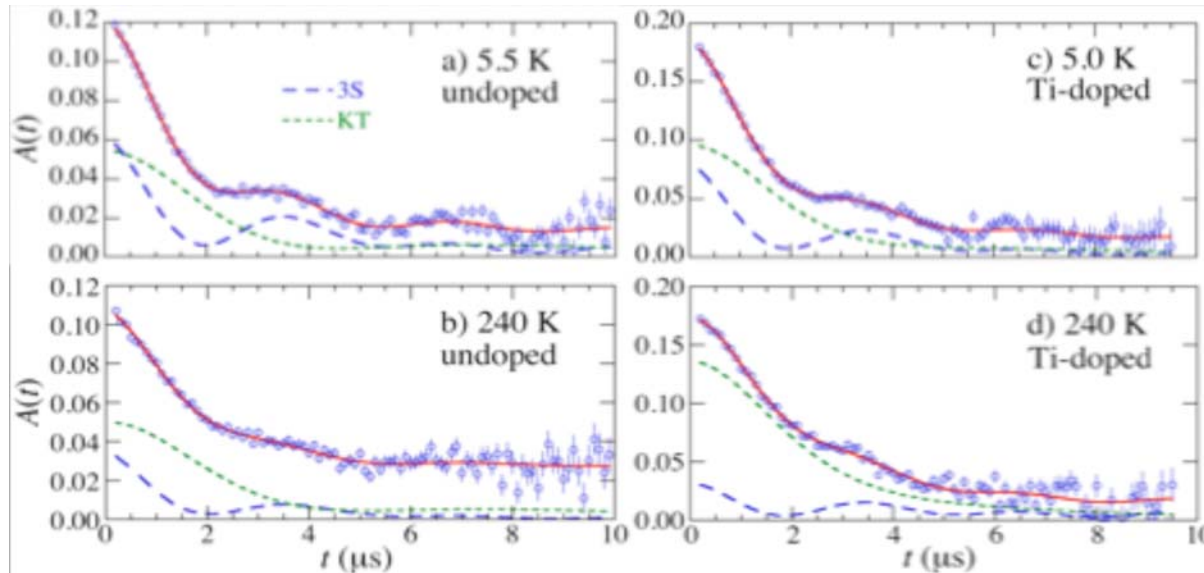
Progress/Results - Catalyst Development

Chemical composition of point defects in NaAlH_4 has been revealed through muon spin resonance spectroscopy (μSR)
Collaboration with R. Kadono - KEK-IMSS, Japan

A fraction of positive muons implanted in NaAlH_4 form a muonium state that selectively substitutes for hydrogen in point defects.

Since muons have a nuclear spin (hyperfine parameter of ~ 420 MHz), information about the immediate chemical environment of the hydrogen in the point defects can be determined from the hyperfine interaction of the muonium state with surrounding spin active nuclei.

The chemical environment of point defects is revealed from decay asymmetry

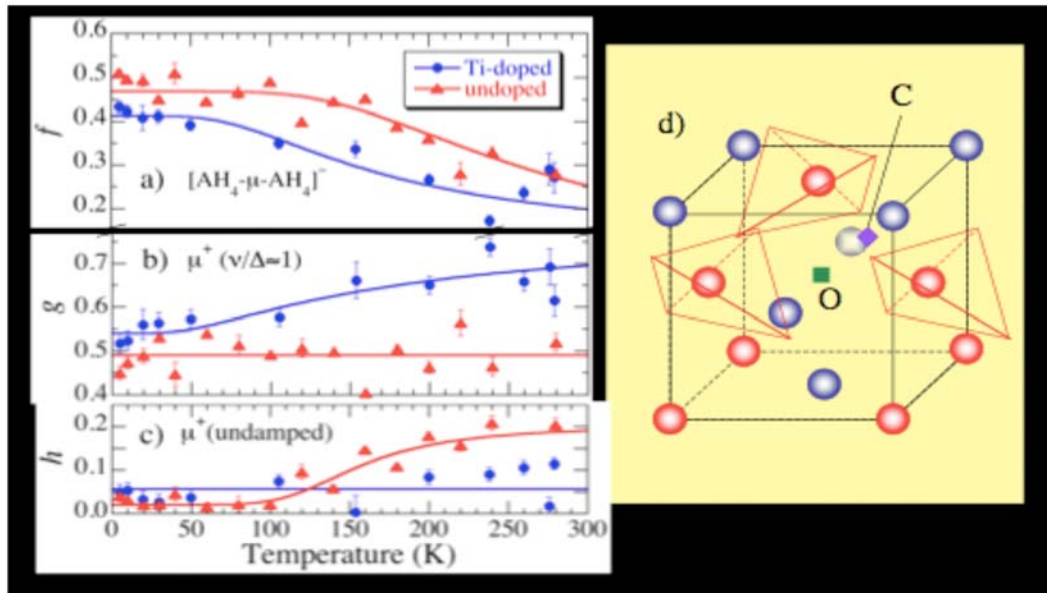


Positron decay (muon polarization) is asymmetric because of overlap of the Gaussian damping with a sinusoidal oscillation.

NaAlH_4 is a non-magnetic, insulator \Rightarrow origin of the oscillation is the formation of local atomic cluster consisting of ^+u and small number of atoms.

R. Kadono, K. Shimomura, K.H. Satoh, S. Takeshita, A. Koda, K. Nishiyama, E. Akiba, R.M. Ayabe, M. Kuba, C.M. Jensen *Phys. Rev.* **2007** in press

Point Defect's composition is $\text{AlH}_4^- - \mu^+ - \text{AlH}_4^-$
 \Rightarrow proton transfer catalyzes the
 intake/release of hydrogen



χ^2 -minimization fits of temperature dependent muon spin resonance data indicates the point defect is $\text{AlH}_4^- - \mu^+ - \text{AlH}_4^-$. Ti reduces the activation energy required to form the point defect.

The composition of the point defect suggests that proton transfer catalyzes the intake/release of hydrogen in NaAlH₄. This effect might be common to other complex hydrides.

R. Kadono, K. Shimomura, K.H. Satoh, S. Takeshita, A. Koda, K. Nishiyama, E. Akiba, R.M. Ayabe, M. Kuba, C.M. Jensen *Phys. Rev.* **2007** in press

Future Work

Materials Discovery

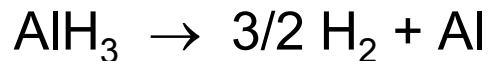
Reversibility of anionic transition metal borohydrides must be addressed. Re-hydrogenation has not as not been achieved for any of member of this class of materials under pressures of up to 100 atm of H₂.

- Determine ΔH_{dehyd} through deferential thermal analysis.
- Attempt rehydrogenation at high pressures in collaboration with Dr. Ronnebro at Sandia National Laboratory.

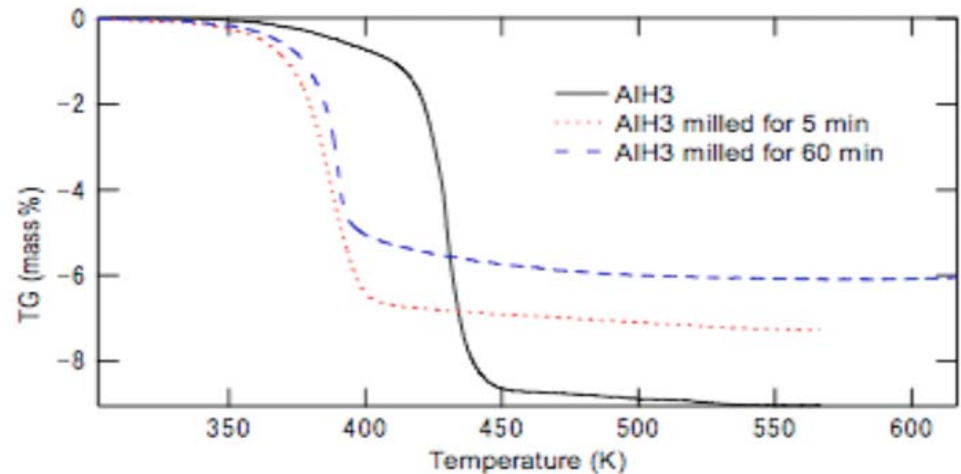
Future Work - New Award

“Recharging of Light Metal Hydrides through Supercritical Fluid Hydrogenation”
-S. McGrady, U. New Brunswick, co-PI

Background



- 10 wt % available H_2
- Controllable dehydrogenation at acceptable rates below 100 °C.



- Low (< 10 kJ/mol) $\Delta H_{\text{dehy}} \Rightarrow$ very high pressures for charging at ambient or higher temperatures

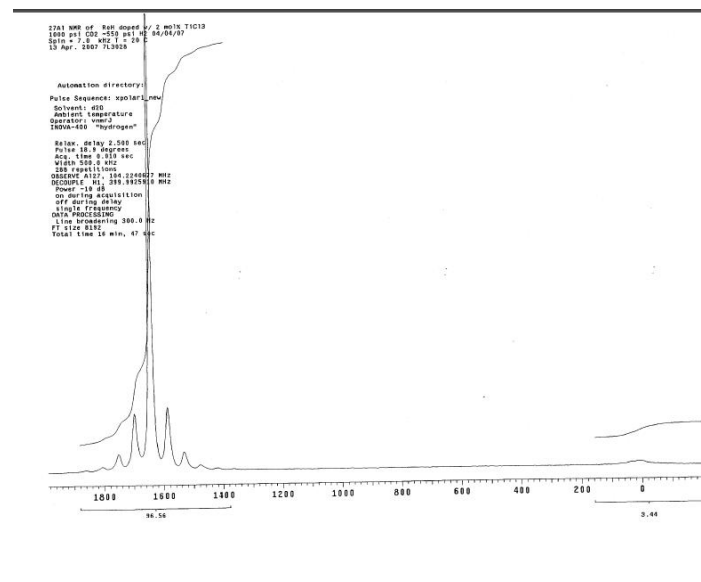
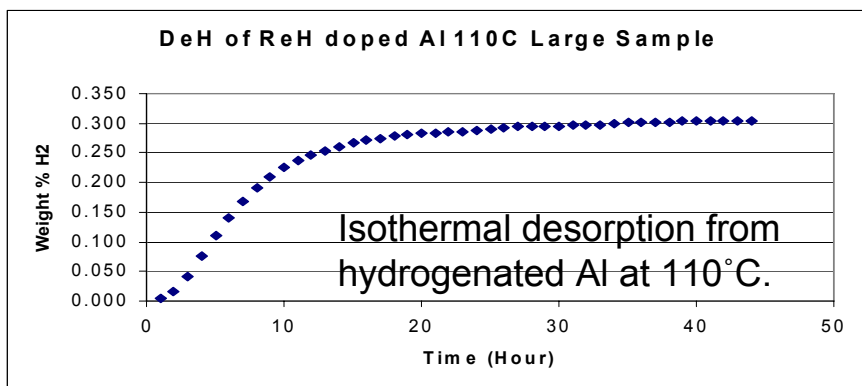
High solubility of hydrogen in supercritical fluids reduces requisite high pressure for Al hydrogenation

Alanate

- S. McGrady, U. New Brunswick
- Hydrogenation of NaH/Al to NaAlH₄ at 80 °C and 15 atm of H₂.
- Yields improved from <1 to >80 % upon fine tuning of conditions.

Alane

- UNB/UH collaboration
- Hydrogenation to AlH₃ at 60 °C and 40 atm H₂
- Yields have been improved in first iteration refinement of conditions from <1 to 3 %.



MAS ²⁷Al NMR spectrum of Al hydrogenated in supercritical CO₂

Plans for FY08

Variations to be explored

- Temperature - Lowering temperature improves the thermodynamics of hydrogenation but reduces the rate. Temperature dependence studies will be carried out to determine best balance of rate and yield.
- Other supercritical fluids - Explore supercritical fluids in which H₂ is more soluble.
- Hydrogenation of activated Al rather than dehydrogenated alane.
- Screen a variety of initiators/catalysts
- Synthesis of Mg(AlH₄)₂

Supercritical hydrogenation to be carried out at UNB.

Product characterization (XRD, MAS ²⁷Al NMR) and analysis/quantification of desorbed hydrogen to be carried out at UH.

Summary

- Anionic transition metal borohydride complexes can be conveniently prepared from balling milling of alkali metal borohydrides with transition metal chlorides or transition metal borohydrides.
- Anionic transition metal borohydride complexes, unlike most neutral transition metal borohydride complexes, are non-volatile and highly stable at ambient temperatures.
- Anionic transition borohydride complexes have been found which undergo rapid elimination of 2-7 wt % H at relevant (~ 100 °C) temperatures.
- Anionic Mn and Zr borohydride complexes have been found to undergo elimination of hydrogen at low temperatures with little or tandem elimination of diborane.
- Muon spin resonance has detected the presence of an $\text{AlH}_4^- - \mu^+ - \text{AlH}_4^-$ complex. Ti reduces the activation energy required to form the muon-bialanate state. The identification of this species suggests that proton transfer catalyzes the intake/release of hydrogen in sodium alanate and this effect might be common to other complex hydrides..
- Supercritical fluids may provide a means to effect the low pressure hydrogenation of Al.