Fundamental Studies of Advanced High-Capacity, Reversible Metal Hydrides

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Members of MHCoE

6/12/08

ST-38

This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Start date: 3/01/05
- End date: 8/31/10
- Percent complete: 55%

Budget

- Total project funding $2,032,936
  - DOE share $1,610,890
  - Contractor share $422,046
  - Funding received in FY07 $400,000
- Funding for FY08 $575,000

Barriers

A. System Weight and Volume
E. Charging/Discharging Rates
F. Thermal management
P. Lack of understanding of hydrogen chemisorption and physisorption

Collaborators

- Dr. Etsuo Akiba, Katsu Sakaki - AIST, Tskuba, Japan
- *Dr. Robert Bowman - Jet Propulsion Laboratory*
- Dr. Mangus Sorby, Prof. Bjorn Hauback - Institute for Energy Technology, Norway
- Prof. Rosario Cantelli - U. Rome
- Prof. Hans Hagmann and Dr. Radovan Cerny - University of Geneva
- Dr. Rysuke Kuboto KEK, Tskuba, Japan
- 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 new materials with potential to meet the DOE 2010 kinetic and system gravimetric storage capacity targets such as novel borohydrides that can be reversibly dehydrogenated at low temperatures and Al and Mg nano-confined in carbon aerogels.

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

III. Develop a method for the hydrogenation of Al to alane, AlH_3 at moderate pressures in hydrogen containing supercritical fluids.

Approach - Materials Discovery

<u>Group I (Li,Na,K) salts of anionic transition metal borohydride complexes</u> Several potential improvements over neutral complexes:

- Higher (9-13 wt %) hydrogen content than neutral TM borohydrides
- Ionic character reduces volatility and increases stability
- For some anionic complexes, the amount of diborane produced during dehydrogenation is very low.

- Altered thermodynamic stability allows reversibility?

<u>Nano-confined Mg in carbon aerogels-collaborarion with HRL</u>

- Test the effects nano-confinement on the kinetics and thermodynamics of the dehydrogenation of MgH_2.
- Novel “neat organometallic” approach to achieve high loadings of carbon aerogels.

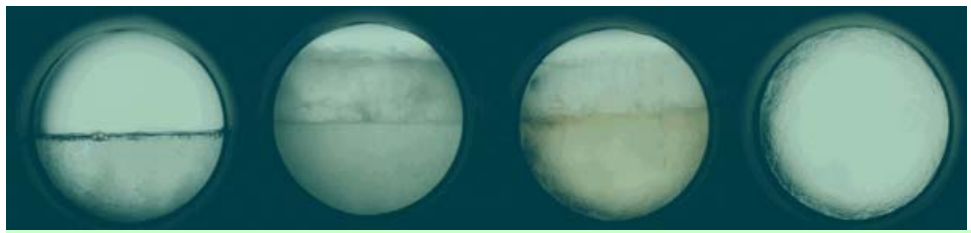
Approach - Hydrogenation of Al in Supercritical Media

- $AlH_3 \rightarrow 3/2\ H_2 + Al \Rightarrow$ 10 wt % available H_2. Controllable dehydrogenation at acceptable rates below 100 ˚C with additives[1] or if ball milled.[2]

1. G. Sandrock, J. Reilly, J. Graetz, W.-M. Zhou, J. Johnson, J. Wegrzy *Appl. Phys. A* **2005**, *80*, 687.

2. S. Orimo, Y. Nakamori, T. Kato, C. Brown, C.M. Jensen *Appl. Phys. A* **2006**, *83*, 5.

- Low (< 10 kJ/mol H_2) $\Delta H_{dehy} \Rightarrow$ very high pressures for charging at ambient or higher temperatures
- Phase boundary between liquid and gas phases disappears in supercritical fluids.
- Supercritical fluids have different physical properties than gases and liquids.



7:1 mixture of liquid CO_2 and H_2 gas converts to a homogenous super critical fluid at 30˚C and 10 atm

- Precedents of hydrogenations at greatly reduced pressures: ubiquidous in organic chemistry and 80% yield of $NaAlH_4$ from NaH/Al at 80 ˚C in supercritical CO_2/H_2- S. McGrady, U. New Brunswick

Milestones

12/07 Go/no-go. Studies of anionic transition metal borohydrides.

03/08 Development of an optimized SCF medium for the hydrogenation of Al.

08/08 Development of an optimized SCF medium for the hydrogenation of $MgAl_2$ to $Mg(AlH_4)_2$.

08/08 Obtain sets of mutually consistent analytical data for the products obtained from attempted syntheses of AlH_3 and $Mg(AlH_4)_2$ in SCF media.

Progress/Results
Materials Discovery

Synthesis of Group I salts of anionic transition borohydride complexes

I. Balling of transition metal chlorides with Group I borohydrides

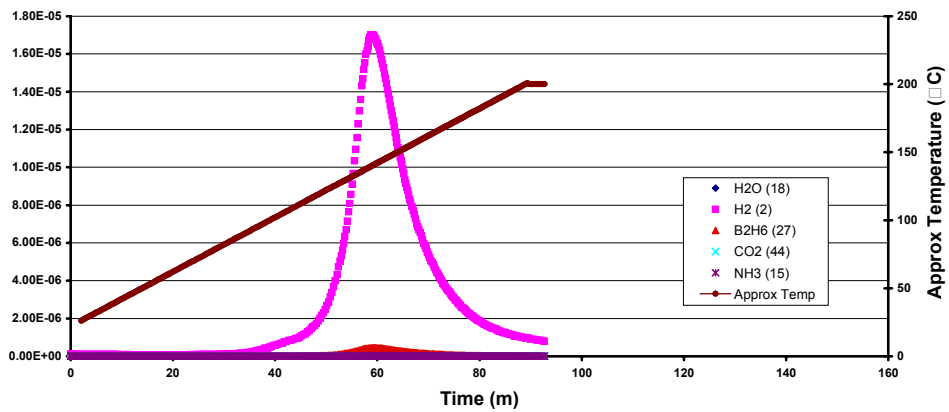
$$MCl_x + (X+Y)\ M'BH_4 \xrightarrow{\text{Ball milling 1 h}} M'_yM(BH_4)_{x+y} + x\ MCl$$

M = transition metal, M' = Group I metal

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

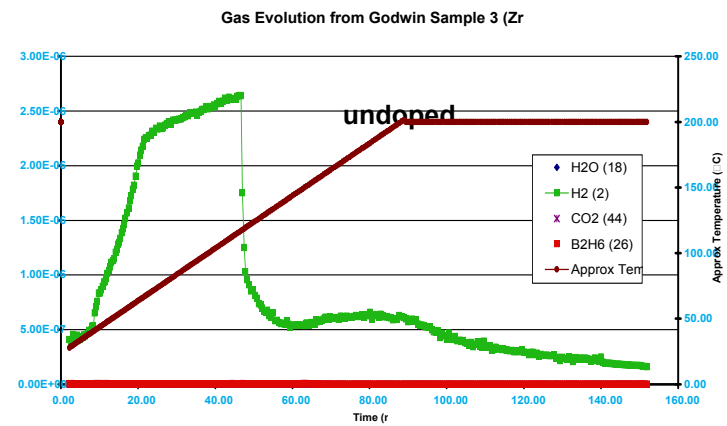
$$M(BH_4)_x + Y\ M'BH_4 \xrightarrow{\text{Ball milling 1 h/ 77 K}} M'_yM(BH_4)_{x+y}$$

Hydrogen is evolved from anionic borohydride complexes at relevant temperatures with low levels of diborane contamination



$NaMn(BH_4)_4$ undergoes rapid dehydrogenation of >3 wt% at 130 ˚C with 50:1 H_2/B_2H_6 molar ratio observed in the eliminated gases.

Data obtained at UOP, LLC



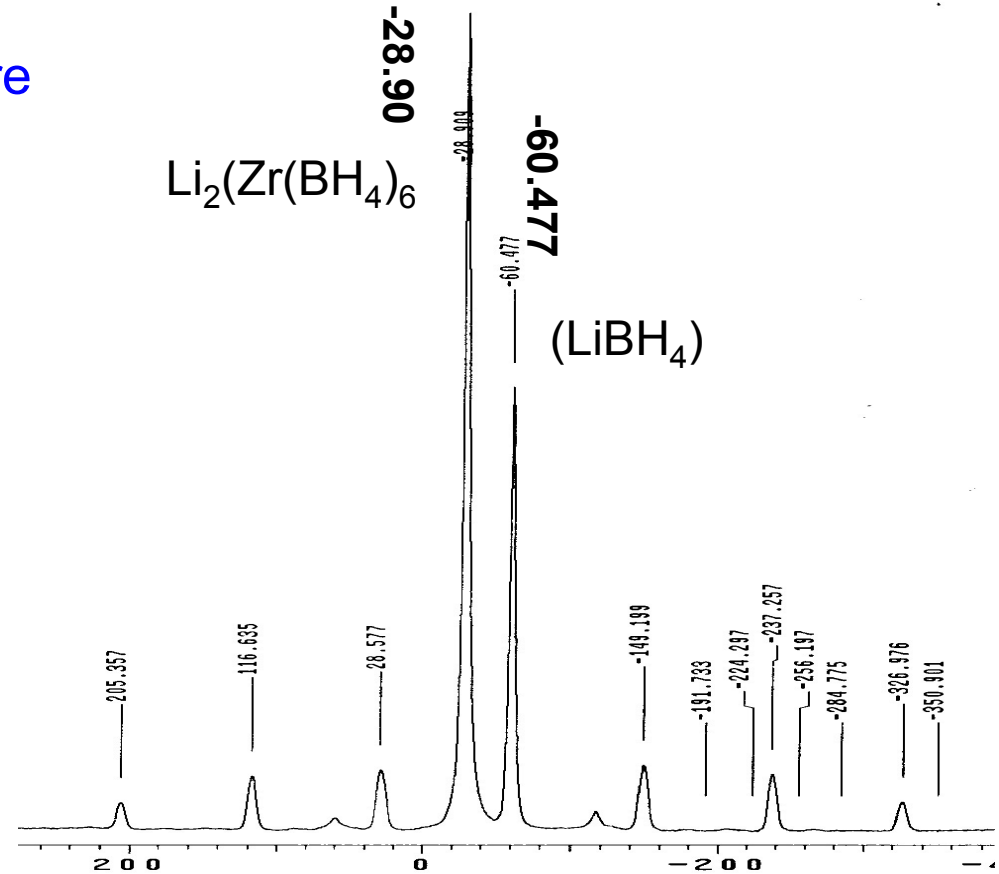
$Na_2Zr(BH_4)_6$, unlike $Zr(BH_4)_4$, is non-volatile undergoes rapid elimination of 2-3 wt % H_2 at 40-110 ˚C with **no** detectable B_2H_6 contamination

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

Transition metal borohydrides are generally highly amorphous

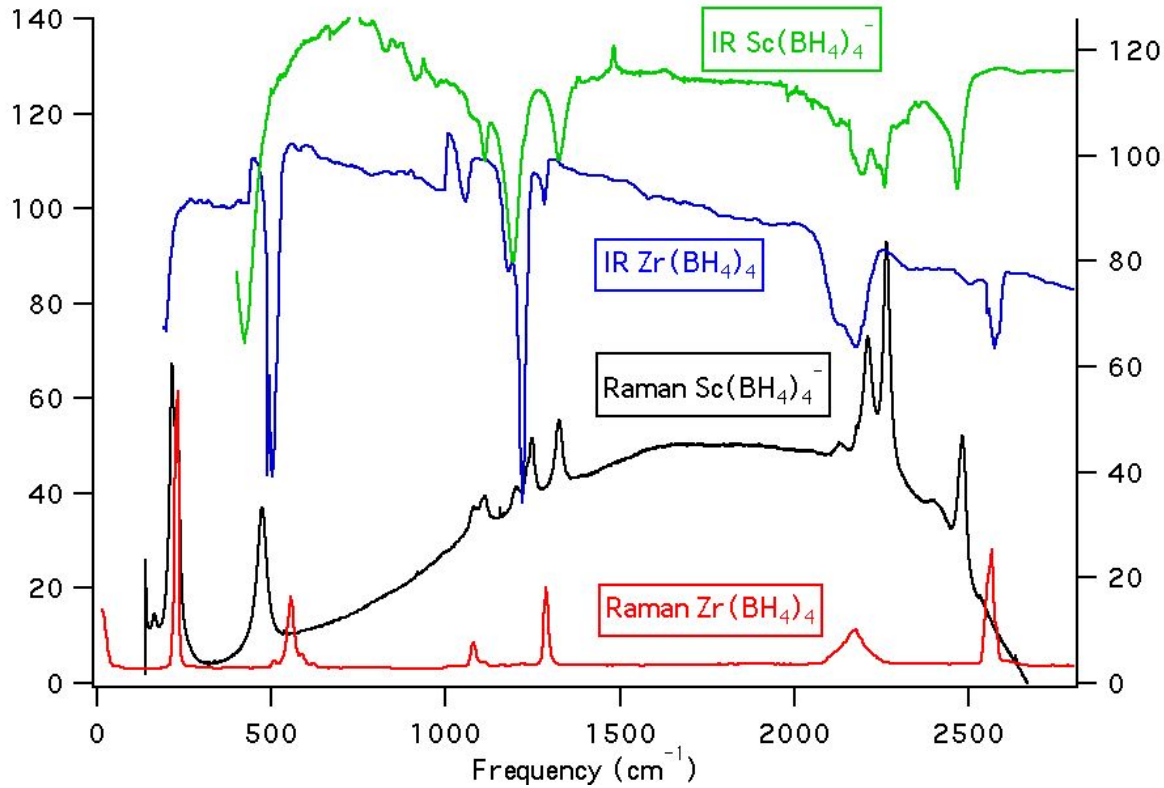
∴ cannot be characterized by XRD.

^{11}B NMR spectroscopy allows detection and differentiation of all the borohydride species that are present.



Characterization of Products by Infra-red and Raman Spectroscopy

Collaboration with University of Geneva



Spectra of $LiSc(BH_4)_4$ and $Zr(BH_4)_4$ provide fingerprints of compounds and reveal details of the coordinative interaction of the BH_4 ligands to the transition metal center.

Synchrotron X-ray Molecular Structure Determination of $LiSc(BH_4)_4$

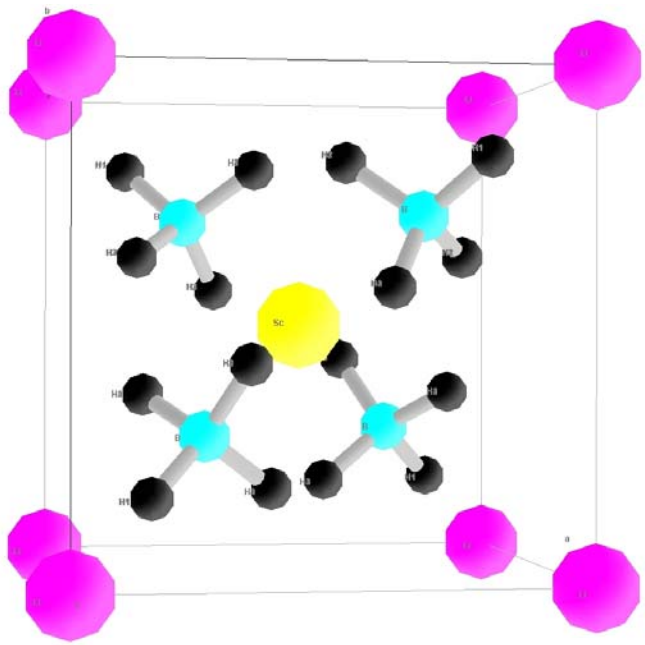
Collaboration with University of Geneva and the Institute for Energy Research, Norway

Confirms:

- $4\ LiBH_4 + ScCl_3 \rightarrow LiSc(BH_4)_4$
- η^3-coordination of the BH_4 ligands to Sc.

Indicates:

- Material might be an exceptional Li conductor



●=Li ●=Sc ●=B ●=H

H. Hagemann, M. Longhini, J.W. Kaminski, T.A. Wesolowski, R. Černý, N. Penin, M.H. Sørby, B.C. Hauback, G. Severa and C.M. Jensen submitted to J. Phys. Chem B.

Reversibility has been achieved for one compound through high pressure experiments

Collaboration with Eva Ronnebro - Sandia National Lab.

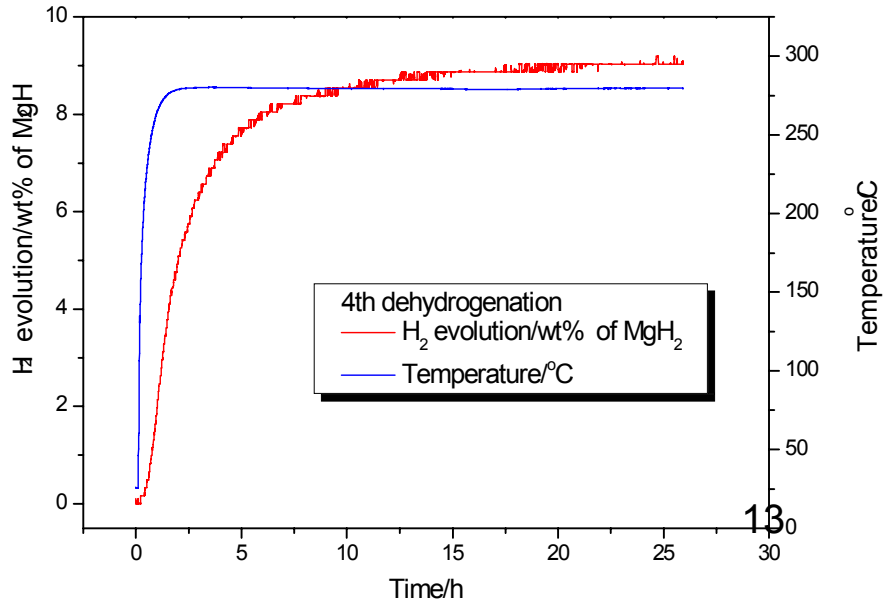
$$MBx \xrightarrow[\text{1000 atm } H_2,\ 230\ ^\circ C]{} M(BH_4)_X$$

High, cyclable Mg loadings of carbon aerogel achieved without host degradation using organometallic approach

Loading procedure:

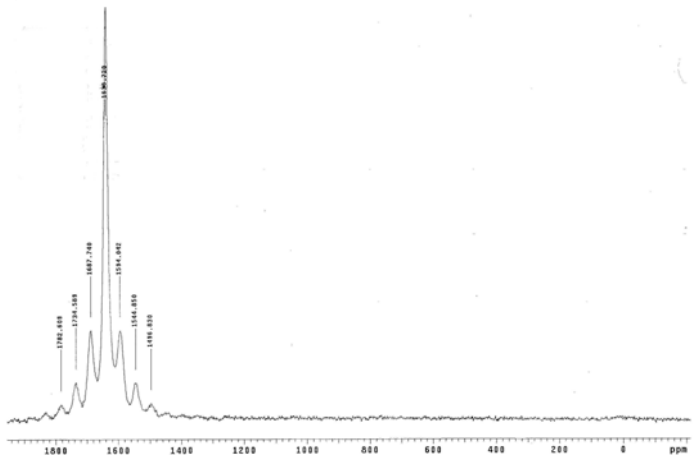
1. Carbon aerogel submerged and stirred in neat liquid organometallic, $Mg(C_4H_9)_2$.
2. Aerogel intercalated with organometallic is filtered from suspension and heated to 200 ˚C to reductively eliminate organic groups.

⇒ High (9-16 wt %) Mg loading achieved without degradation of aerogel. Reversible hydrogenation of material has been demonstrated through 4 cycles.

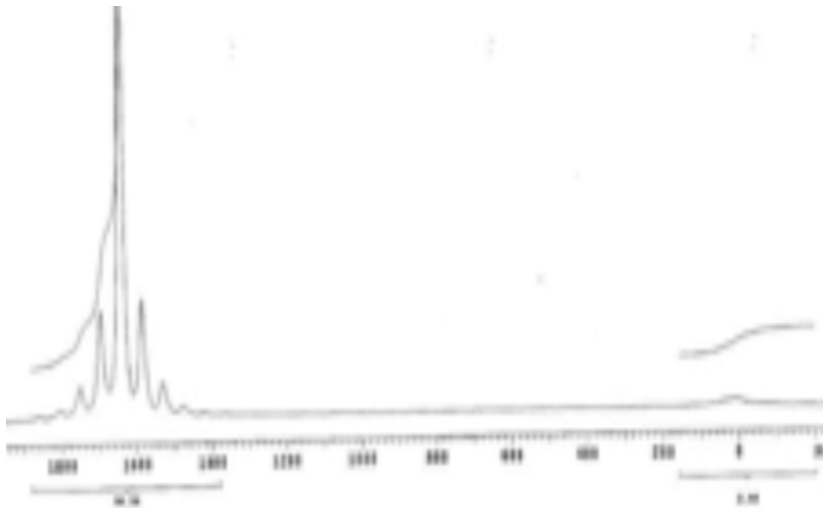


Progress/Results Hydrogenation of Al in Supercritical Fluids

Hydrogenation in 2:1 supercritical CO_2-H_2 confirmed by MAS ^{27}Al NMR.

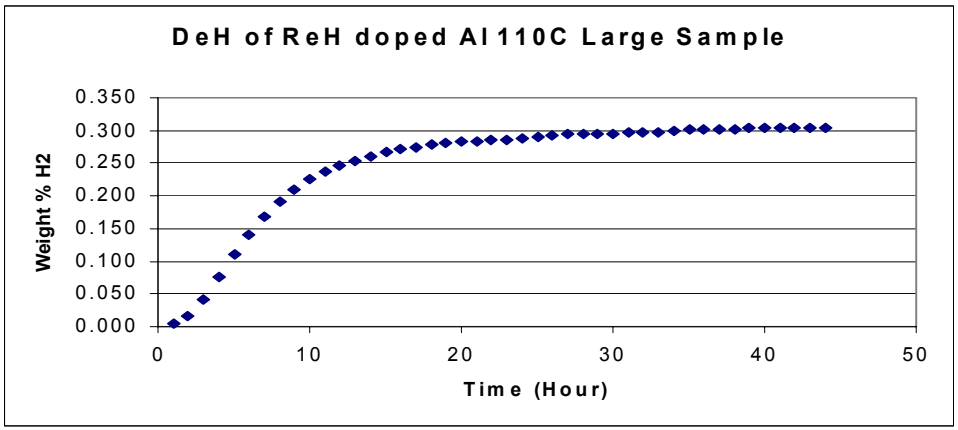


Clean Al before hydrogenation

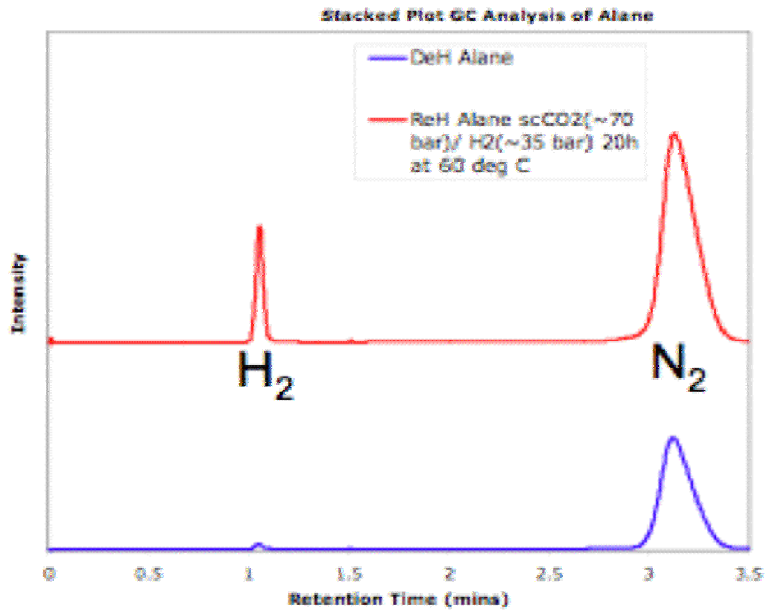


Al after 4 h at 60 °C in supercritical 2:1 CO_2/H_2

Hydrogenation of Al in 2:1 supercritical CO_2-H_2



Isothermal desorption from hydrogenated Al at 110˚C indicates that 3% of was hydrogenated.



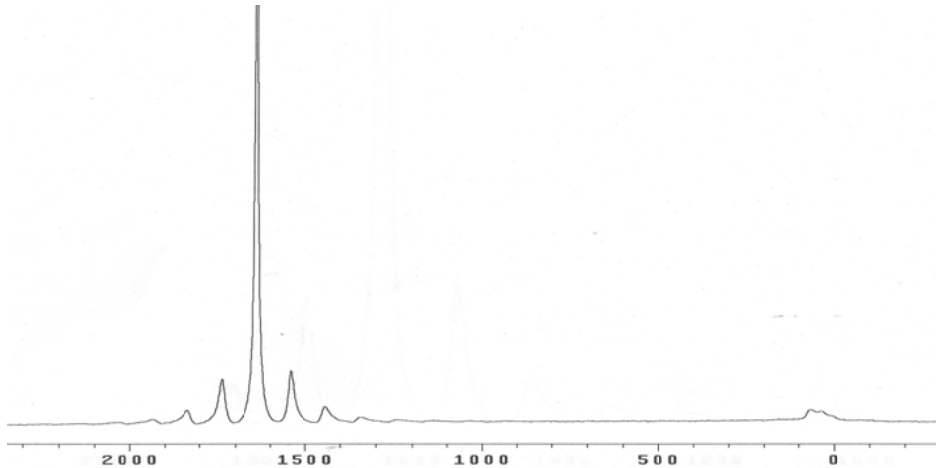
GC analysis show that hydrogen is evolved only from the Al subjected to the supercritical fluid.

New supercritical fluid reaction system has been installed at UNB

Improved AlH_3 Yields in Alternative Supercritical Hydrogen Cocktails

Fluid	T_c/°C	P_c/bar	$/kg
CO_2	31	74	3
C_2H_6	32	49	100
C_3H_8	97	42	10
Me_2O	127	54	15
SF_6	45	38	50
CHF_3	26	48	125

- Complete miscibility with permanent gases like H_2
- Excellent thermal transfer properties
- Option to add co-solvents and solutes (e.g. donors and catalysts)



MAS ^{27}Al NMR Al after 4 h at 60 ˚C in blended supercritical fluid.

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

Summary

- A new borohydride has been found that undergoes **reversible** dehydrogenation to the corresponding boride.
- High Mg loadings of carbon aerogels without host degradation can be achieved using relatively low temperature, “neat organometallic” method.
- Reaction of Ti-doped Al with $scCO_2/H_2$ under relatively mild conditions leads to low-level hydrogenation, presumably on surface of the powder.
- Occurrence of Hydrogenation have been confirmed by MAS ^{27}Al NMR spectroscopy, gas chromatography, and isothermal desorption studies.
- Dedicated SCF reaction station has been constructed.
- Preliminary experiments indicate high levels of hydrogenation can be achieved in an alternative SCF.

Future Work

Borohydrides

- Determine ΔH_{dehyd} through deferential thermal analysis.
- Continue dehydrogenation studies in collaboration with Dr. E. Ronnebro at Sandia National Laboratory. Explore variation in catalysts.

Mg intercalated carbon aerogels

- Determine PCT isotherms to determine if nano-confinment alters ΔH_{dehyd}.
- Conduct isothermal kinetic studies to determine if nano-confinment alters dehydrogenation kinetics.

Alane

- Exploration of improving levels of hydrogenation by conducting reaction in alternative SCFs.
- Hydrogenation of activated Al rather than dehydrogenated alane.
- Screen a variety of initiators/catalysts
- Explore SCF synthesis of $Mg(AlH_4)_2$

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