

# Fundamental Studies of Advanced High-Capacity, Reversible Metal Hydrides

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Members of MHCoe

6/12/08

ST-38



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# 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 Haggmann 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,  $\text{AlH}_3$  at moderate pressures in hydrogen containing supercritical fluids.

# Approach - Materials Discovery

## Group I (Li,Na,K) salts of anionic transition metal borohydride complexes

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?

## Nano-confined Mg in carbon aerogels-collaboration with HRL

- Test the effects nano-confinement on the kinetics and thermodynamics of the dehydrogenation of  $\text{MgH}_2$ .
- Novel “neat organometallic” approach to achieve high loadings of carbon aerogels.

# Approach - Hydrogenation of Al in Supercritical Media

- $\text{AlH}_3 \rightarrow 3/2 \text{H}_2 + \text{Al} \Rightarrow 10 \text{ wt } \% \text{ available H}_2$ . Controllable dehydrogenation at acceptable rates below  $100 \text{ }^\circ\text{C}$  with additives<sup>1</sup> or if ball milled.<sup>2</sup>

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

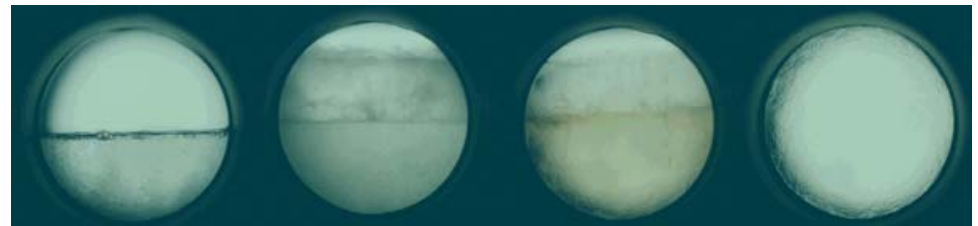
2. S. Orimo, Y. Nakamori, T. Kato, C. Brown, C.M. Jensen *Appl. Phys. A* **2006**, *83*, 5.

- Low ( $< 10 \text{ kJ/mol H}_2$ )  $\Delta H_{\text{dehy}} \Rightarrow$  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.

- Precedents of hydrogenations at greatly reduced pressures: ubiquitous in organic chemistry and 80% yield of  $\text{NaAlH}_4$  from  $\text{NaH/Al}$  at  $80 \text{ }^\circ\text{C}$  in supercritical  $\text{CO}_2/\text{H}_2$ - S. McGrady, U. New Brunswick



7:1 mixture of liquid  $\text{CO}_2$  and  $\text{H}_2$  gas converts to a homogenous super critical fluid at  $30^\circ\text{C}$  and 10 atm

# Milestones

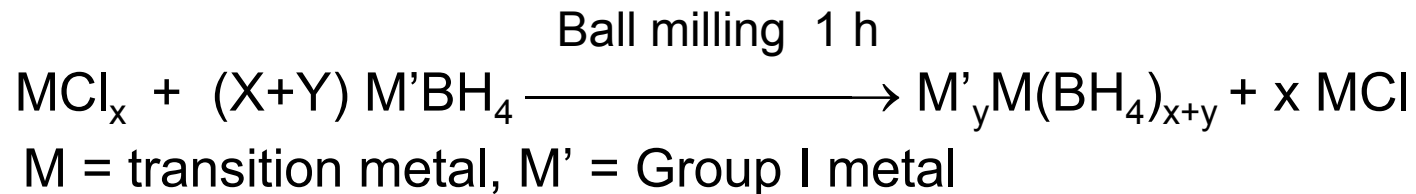
- 12/07 Go/no-go. Studies of anionic transition metal borohydrides.
- 03/08 Development of an optimized SCF medium for the hydrogenation of Al.
- 08/08 Development of an optimized SCF medium for the hydrogenation of  $\text{MgAl}_2$  to  $\text{Mg}(\text{AlH}_4)_2$ .
- 08/08 Obtain sets of mutually consistent analytical data for the products obtained from attempted syntheses of  $\text{AlH}_3$  and  $\text{Mg}(\text{AlH}_4)_2$  in SCF media.

# Progress/Results

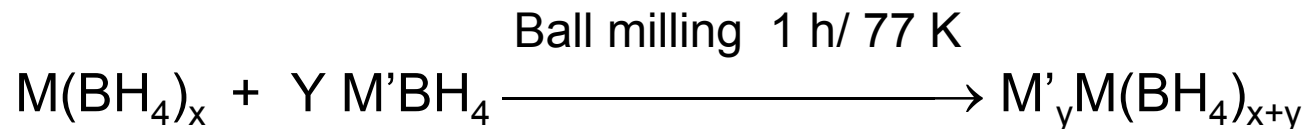
## Materials Discovery

Synthesis of Group I salts of anionic transition borohydride complexes

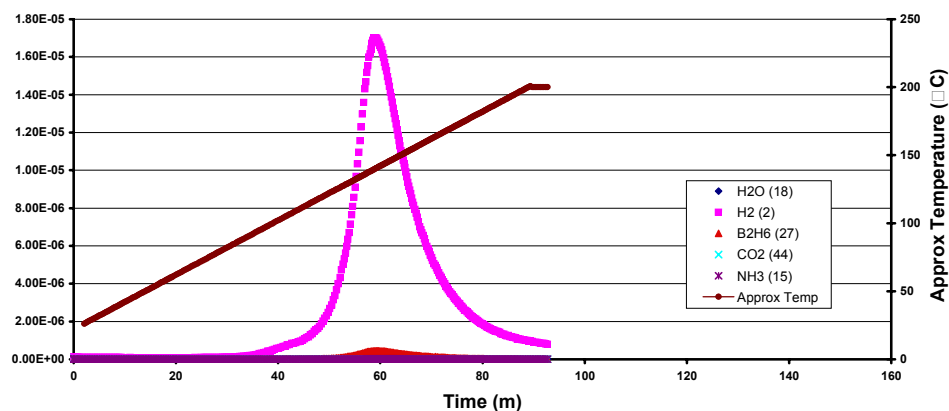
I. Balling of transition metal chlorides with Group I borohydrides



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

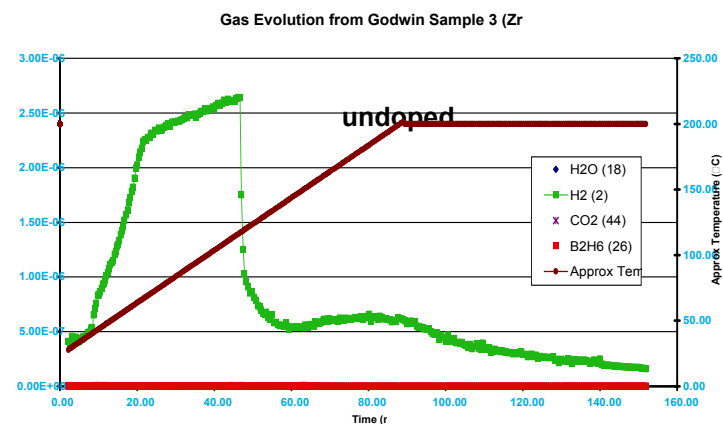


# Hydrogen is evolved from anionic borohydride complexes at relevant temperatures with low levels of diborane contamination



NaMn(BH<sub>4</sub>)<sub>4</sub> undergoes rapid dehydrogenation of >3 wt% at 130 °C with 50:1 H<sub>2</sub>/B<sub>2</sub>H<sub>6</sub> molar ratio observed in the eliminated gases.

Data obtained at UOP, LLC



Na<sub>2</sub>Zr(BH<sub>4</sub>)<sub>6</sub>, unlike Zr(BH<sub>4</sub>)<sub>4</sub>, is non-volatile undergoes rapid elimination of 2-3 wt % H<sub>2</sub> at 40-110 °C with **no** detectable B<sub>2</sub>H<sub>6</sub> contamination

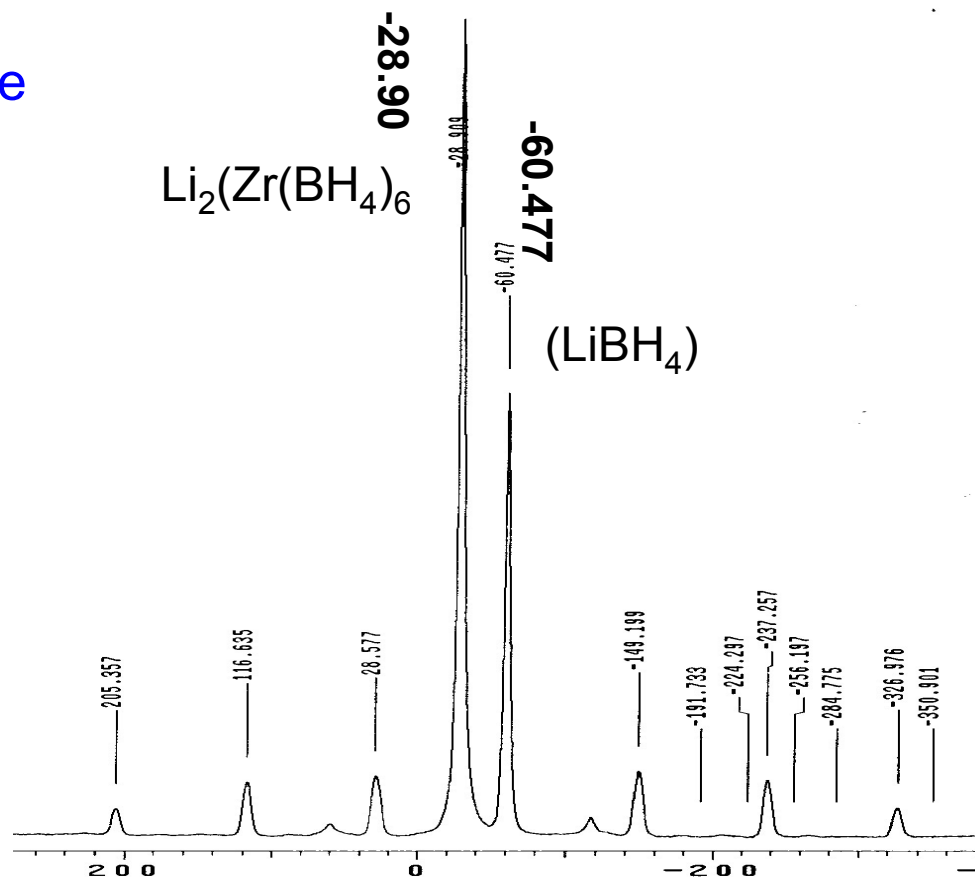


# Characterization of Products by MAS $^{11}\text{B}$ NMR Spectroscopy

Transition metal borohydrides are generally highly amorphous

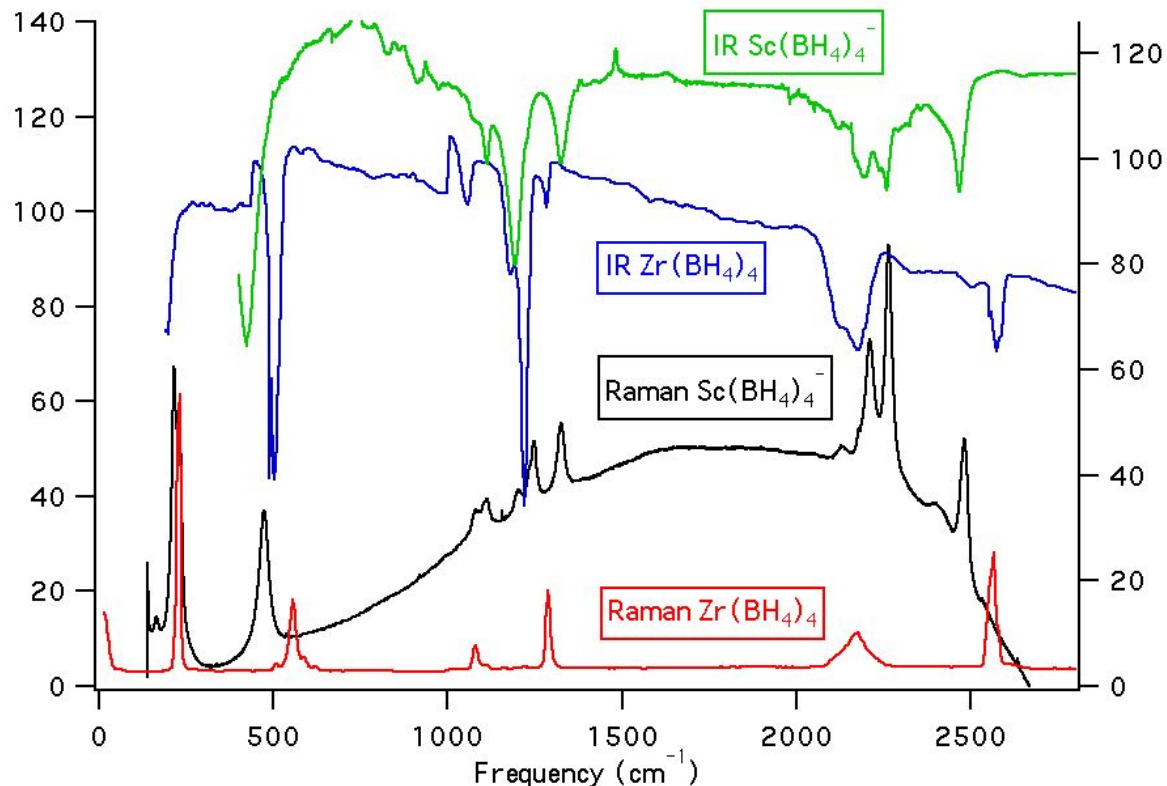
$\therefore$  cannot be characterized by XRD.

$^{11}\text{B}$  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  $\text{LiSc}(\text{BH}_4)_4$  and  $\text{Zr}(\text{BH}_4)_4$  provide fingerprints of compounds and reveal details of the coordinative interaction of the  $\text{BH}_4$  ligands to the transition metal center.

# Synchrotron X-ray Molecular Structure Determination of $\text{LiSc}(\text{BH}_4)_4$

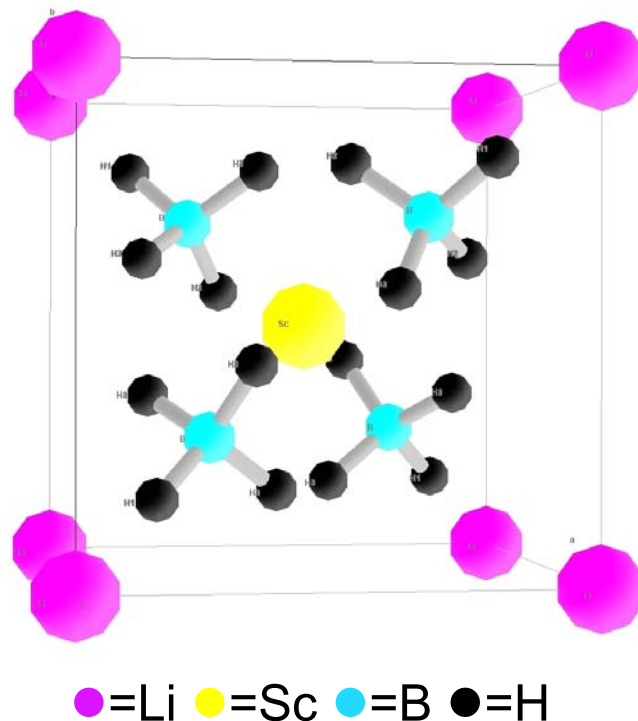
Collaboration with University of Geneva and the Institute for Energy  
Research, Norway

Confirms:

- $4 \text{LiBH}_4 + \text{ScCl}_3 \rightarrow \text{LiSc}(\text{BH}_4)_4$
- $\eta^3$ -coordination of the  $\text{BH}_4$  ligands to Sc.

Indicates:

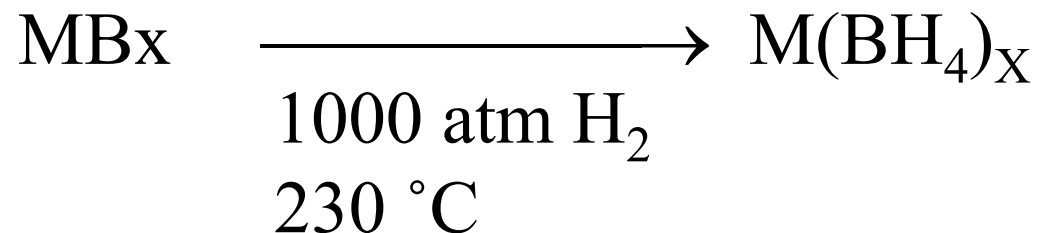
- Material might be an exceptional Li conductor



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.



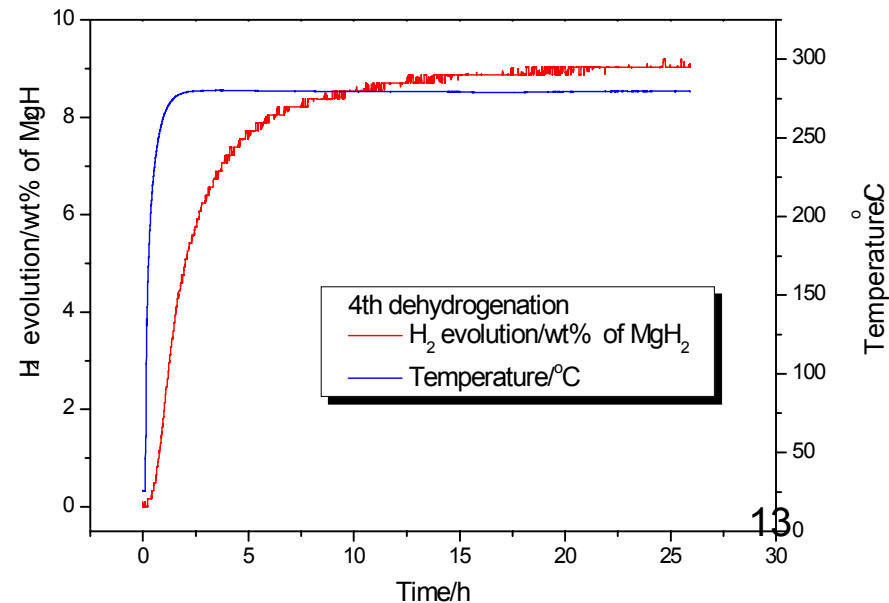
# High, cyclable Mg loadings of carbon aerogel achieved without host degradation using organometallic approach

Loading procedure:

1. Carbon aerogel submerged and stirred in neat liquid organometallic,  $\text{Mg}(\text{C}_4\text{H}_9)_2$ .
2. Aerogel intercalated with organometallic is filtered from suspension and heated to  $200\text{ }^\circ\text{C}$  to reductively eliminate organic groups.

⇒ High (9-16 wt %) Mg loading achieved without degradation of aerogel.

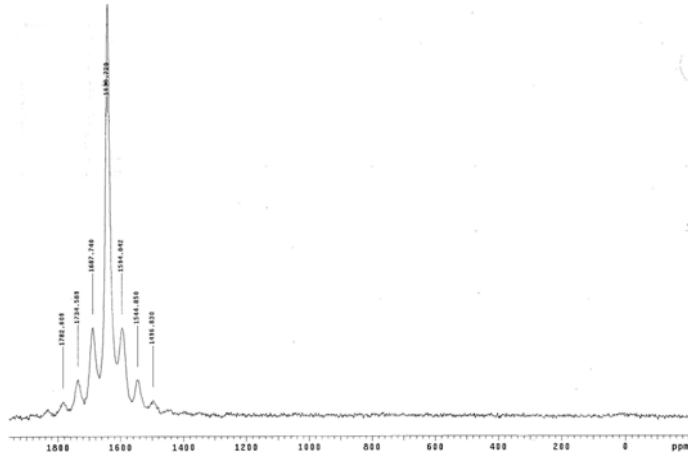
Reversible hydrogenation of material has been demonstrated through 4 cycles.



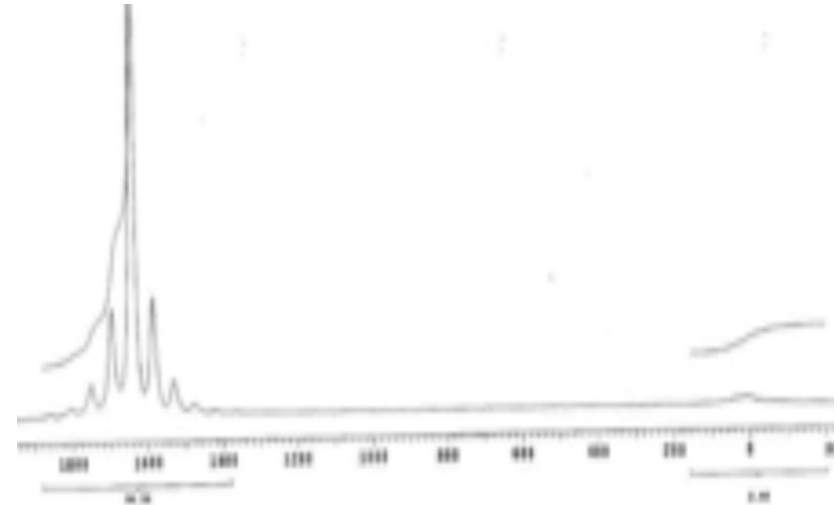
# Progress/Results

## Hydrogenation of Al in Supercritical Fluids

Hydrogenation in 2:1 supercritical CO<sub>2</sub>-H<sub>2</sub> confirmed by MAS <sup>27</sup>Al NMR.



Clean Al before hydrogenation



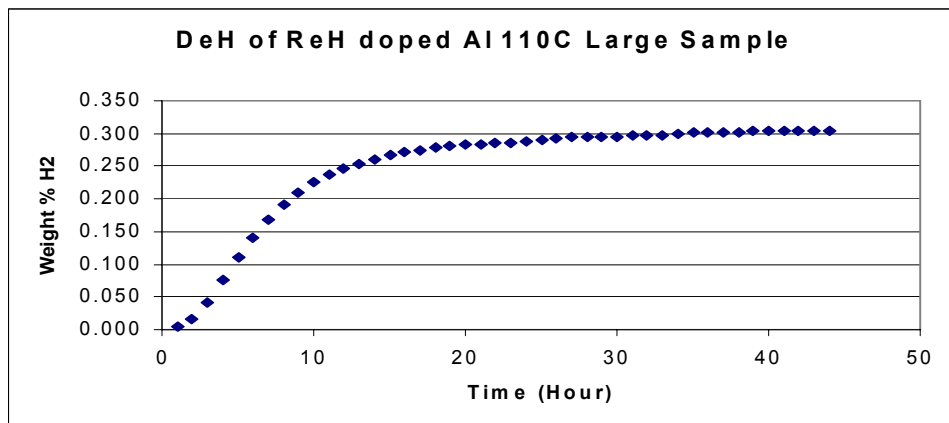
Al after 4 h at 60 °C in supercritical 2:1 CO<sub>2</sub>/H<sub>2</sub>



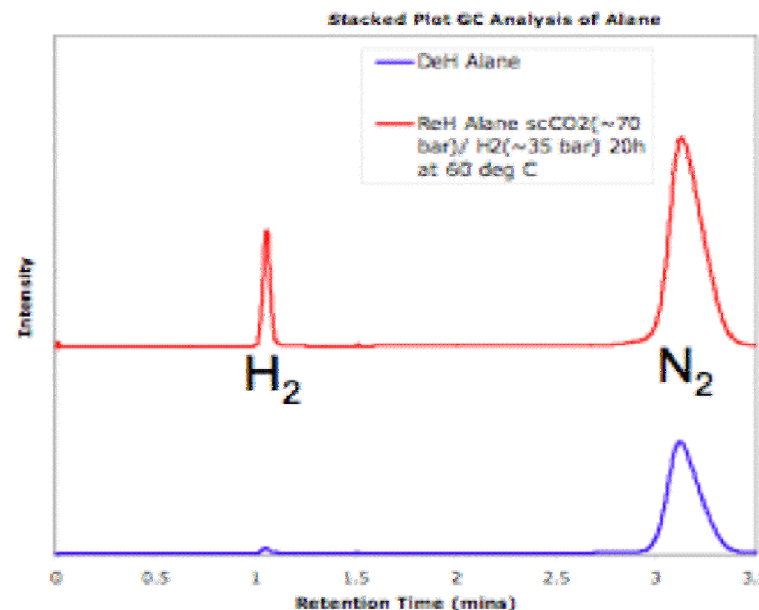
# Hydrogenation of Al in 2:1 supercritical CO<sub>2</sub>-H<sub>2</sub>



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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







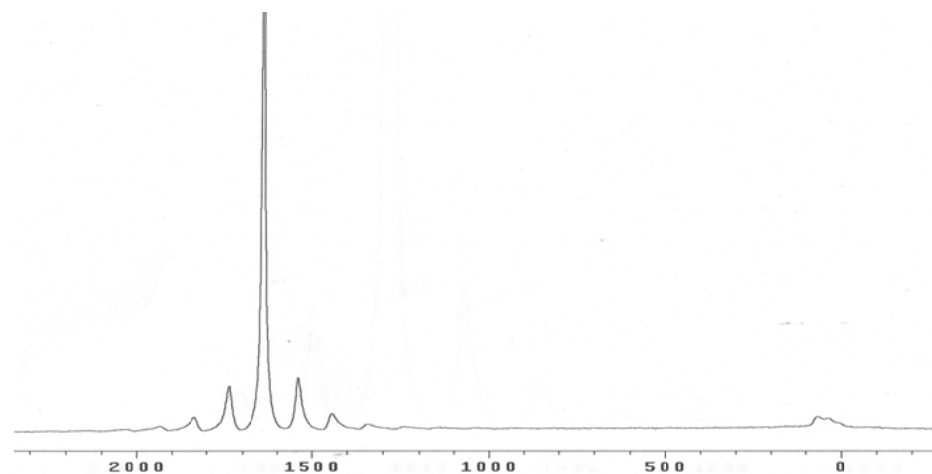
# Improved $\text{AlH}_3$ Yields in Alternative Supercritical Hydrogen Cocktails



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Fluid	$T_c/^\circ\text{C}$	$P_c/\text{bar}$	\$/kg
$\text{CO}_2$	31	74	3
$\text{C}_2\text{H}_6$	32	49	100
$\text{C}_3\text{H}_8$	97	42	10
$\text{Me}_2\text{O}$	127	54	15
$\text{SF}_6$	45	38	50
$\text{CHF}_3$	26	48	125

- Complete miscibility with permanent gases like  $\text{H}_2$
- Excellent thermal transfer properties
- Option to add co-solvents and solutes (e.g. donors and catalysts)



MAS  $^{27}\text{Al}$  NMR Al after 4 h at  $60^\circ\text{C}$  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 ( $\sim 100$  °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<sub>2</sub>/H<sub>2</sub> under relatively mild conditions leads to low-level hydrogenation, presumably on surface of the powder.
- Occurrence of Hydrogenation have been confirmed by MAS <sup>27</sup>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  $\Delta H_{\text{dehyd}}$  through differential 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-confinement alters  $\Delta H_{\text{dehyd}}$ .
- Conduct isothermal kinetic studies to determine if nano-confinement 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  $\text{Mg}(\text{AlH}_4)_2$   
Supercritical hydrogenation to be carried out at UNB. Product characterization (XRD, MAS  $^{27}\text{Al}$  NMR) and analysis/quantification of desorbed hydrogen to be carried out at UH.