



Synthesis of Nanophase Materials for Thermodynamically Tuned Reversible Hydrogen Storage

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California Institute of Technology
with Metal Hydride Center of Excellence
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This presentation does not contain any proprietary or confidential information

Project ID # STP 28

Overview

Timeline

- Project start date:
October 1, 2004
- Project end date:
September 30, 2009

Budget

- Total project funding
 - DOE share \$1M (5 yrs)
 - Contractor share \$250k (5 yrs)
- Funding for FY06
 - DOE share \$250k
 - Contractor share \$62.5k
- Funding for FY07
 - DOE share \$200k
 - Contractor share \$50k

On board hydrogen storage Barriers and Targets

- (B) Weight and volume of on board hydrogen storage systems
- (M) Reversibility of high capacity solid state storage materials
- (N) Kinetics (fueling/refueling times) associated with current solid state storage materials

Partners

Interactions/ collaborations:

HRL Laboratories (John Vajo)
Univ. Illinois (Ian Robertson)
Carnegie Mellon (D. Sholl)
Univ. Pittsburgh (J. Karl Johnson)
Brookhaven Natl Lab (J. Graetz)
NIST (Terry Udovic)

Objectives

- To understand as to whether thermodynamically tractable reactions based on hydride destabilization, like $\text{Mg}_2\text{Si} + 2\text{H}_2 \rightleftharpoons 2\text{MgH}_2 + \text{Si}$ that should be reversible but appear not to be, are kinetically limited.
- To address short hydrogenation times associated with refueling, that will require short solid-state and gas-solid diffusion path lengths.
- To address the problems associated with large, light-metal-hydride enthalpies (hydrogen fueling/refueling temperatures) and develop strategies to address thermodynamic issues surrounding the use of these materials through hydride destabilization. Systems of interest determined through “theoretical screening” by Center partner members.
- To understand issues related to grain growth and surface/interface energies, vital in order to understand the kinetics of hydrogenation/dehydrogenation reactions.
- To follow up on previously studied reactions with phase identification via x-ray diffraction, NMR and transmission electron microscopy.

Current Status

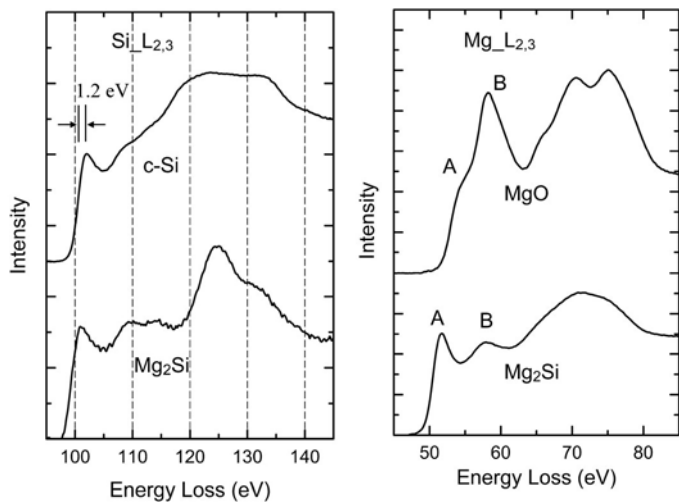
- No Go on Mg_2Si , completion of analysis of MgSi bonding in this system.
- Analysis of $\text{ScH}_2 + 2(\text{LiBH}_4) \leftrightarrow \text{ScB}_2 + \text{LiH} + 4\text{H}_2$ (8.8 wt%), predicted to have ZPE corrected ΔH of ~ 34 kJ/mole but dehydrogenation occurs at temps $> 300^\circ\text{C}$.
- Reverse reaction attempting to hydrogenate ScB_2 as of yet shows no absorption.
- $\text{Ca}(\text{AlH}_4)_2 + 2\text{LiBH}_4$ shows some reversibility on basis of our mechano-synthesis of $\text{Ca}(\text{AlH}_4)_2$ ($\sim 70\%$ yield).
- Recent dehydrogenation using pure $\text{Ca}(\text{AlH}_4)_2$ from Felderhoff shows slightly higher yield (going from ~ 6.6 to $7.3\text{wt}\%$).
- NMR analysis critical in identifying bonding in these systems that have little or no long range order.

Challenges

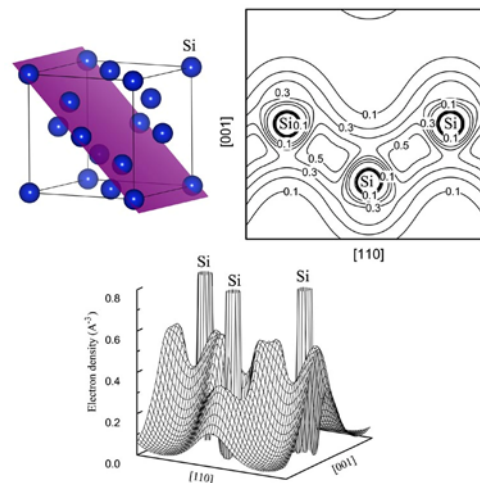
- Reversibility of thermodynamically suitable systems empirically unpredictable on the basis of reaction enthalpies.
- Solid state diffusion of B containing species appears to be a limitation.

Technical Accomplishments: Bonding in Mg₂Si

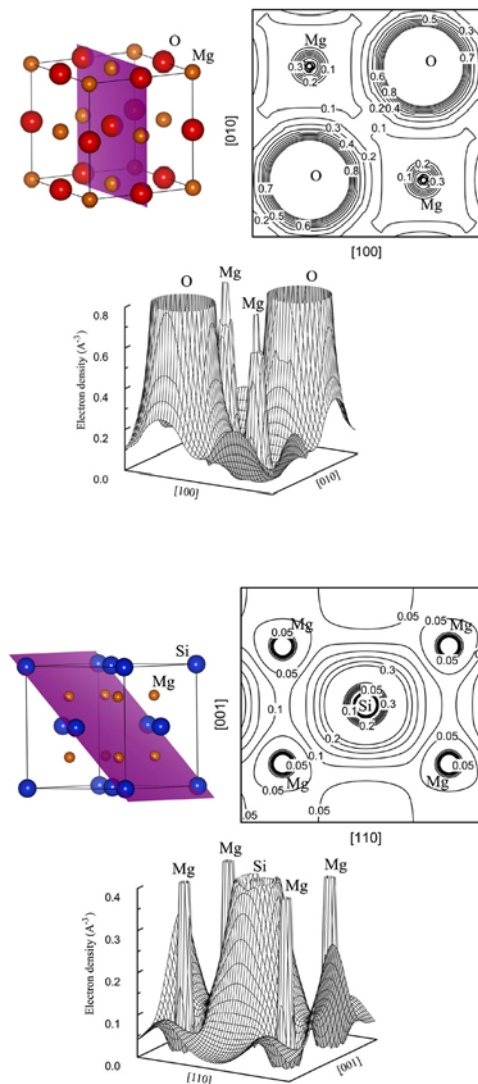
- No Go decision on Mg₂Si given challenges in rehydrogenation.
- Final analysis of this system, spectroscopic and computational approaches in explaining the degree of ionicity and covalency in the bonding between Mg and Si.
- Initial XPS results suggested strong covalency but our electron energy loss and WIEN2k calculations indicate 74% ionic component (generally difficult to dissociate).
- Comparisons with MgO and Si standards for validation. Bader analysis indicates charge transfer of 1.48 electron/Mg atom and Mg L₂₃ edge analysis shows Mg 3s occupancy.



The Si L_{2,3}-edge of c-Si and Mg₂Si, respectively on the left. The spectra were normalized with a 30 eV window 50 eV after the edge threshold. The Mg L_{2,3}-edge of MgO and Mg₂Si, respectively on the right. The spectra were normalized with a window from 80 - 100eV.



The calculated 2-d and 3-d valence electron density of c-Si on {110} type plane shown above, MgO data on {100} shown in upper right and Mg₂Si data on {110} shown at right*.

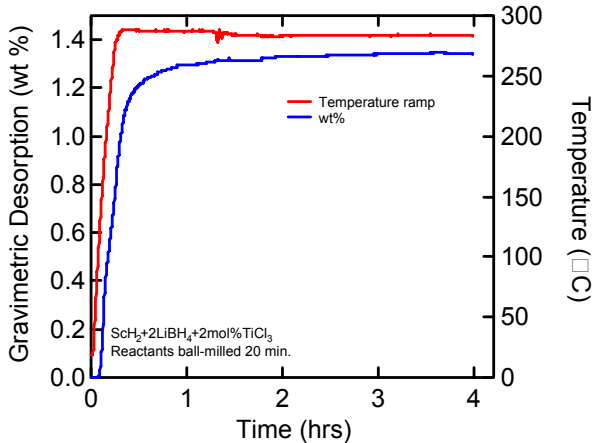
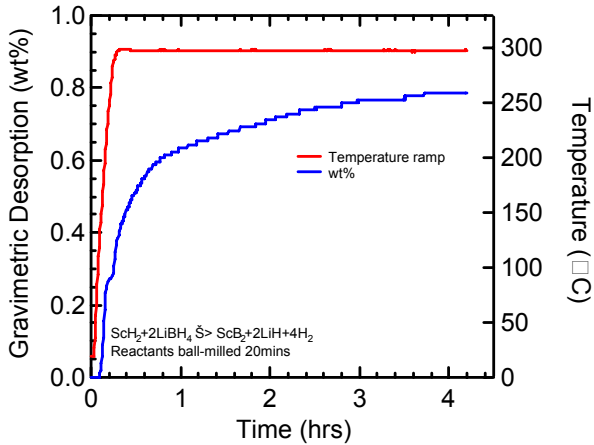


* From S. Miao, PhD, Caltech 2007.

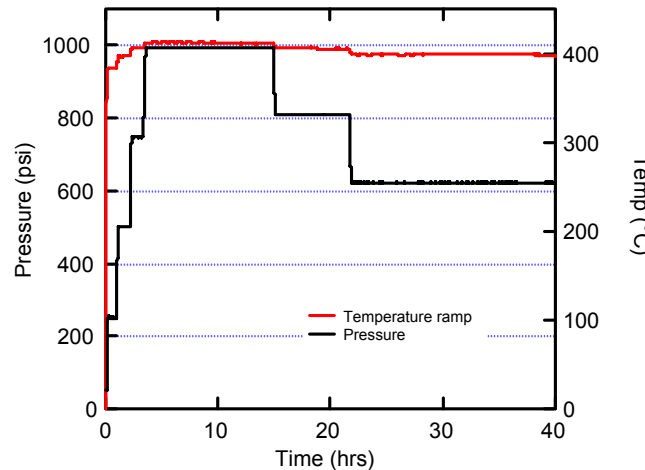
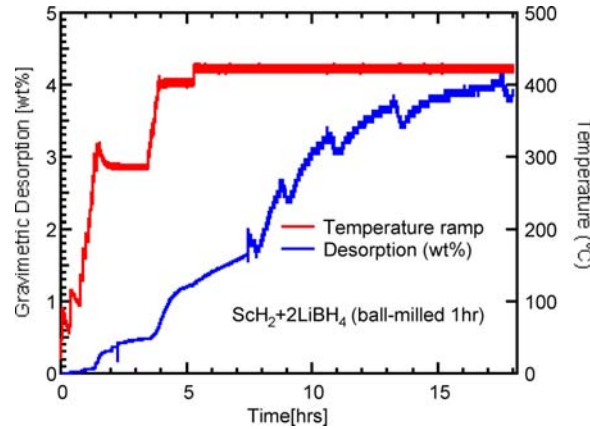
Technical Accomplishments: $\text{ScH}_2+2\text{LiBH}_4$ study, a low reaction enthalpy system

- Reaction enthalpies of $< 40\text{kJ/mole}$ a priority in order to obviate high exothermic hydrogenation heat.
- While ultimately too costly for engineering applications, $\text{ScH}_2+2\text{LiBH}_4 \rightleftharpoons \text{ScB}_2+2\text{LiH}+4\text{H}_2$ (8.9wt%) identified by Center partners D. Sholl and J.K. Johnson as thermodynamically suitable candidates with ΔH of 34 kJ/mole after zero point energy corrections, an important system to evaluate empirically in order to better address role of computational effort.
- Our kinetic analysis (next slide) shows $< 1\text{wt}\%$ gravimetric H_2 release at 300°C (upper left trace), and $\sim 4\text{wt}\%$ after 17 hrs at 400°C for these reactants (center trace). X-ray analysis of product phase (lower right) shows substantial background, due presumably to large amorphous component and remnant ScH_2 . No formation of ScB_2 discernable during dehydrogenation. Reaction paths for this system of uncertainty and equilibrium not reached.
- Work with catalyst and better initial mixture improves kinetics. However, attempts at hydrogenating an initial ScB_2+2LiH mixture have not as yet been successful.

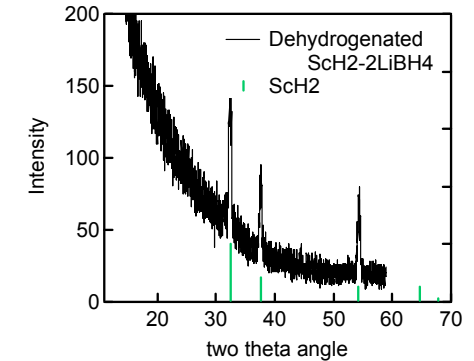
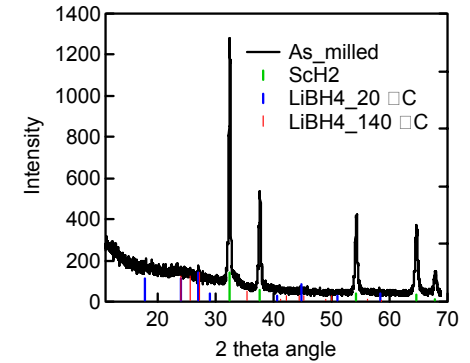
Technical Accomplishments: $\text{ScH}_2+2\text{LiBH}_4$ study, a low reaction enthalpy system cont'd:



Upper figure shows kinetic trace to 300°C. Dehydrogenation < 1wt%. Lower figure shows desorption improvement due to TiCl_3 catalyst incorporation.



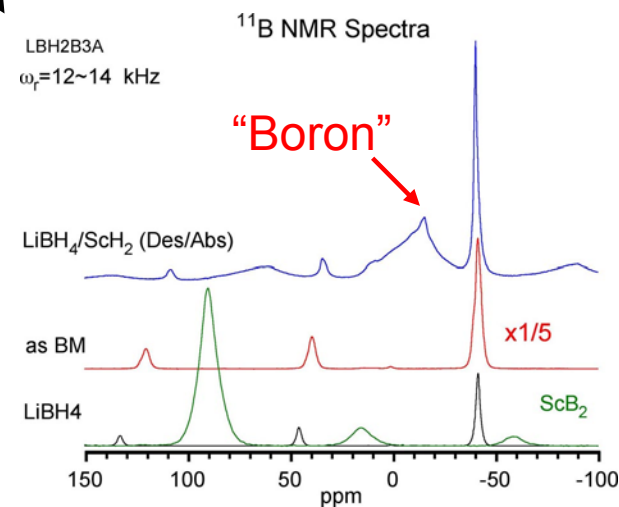
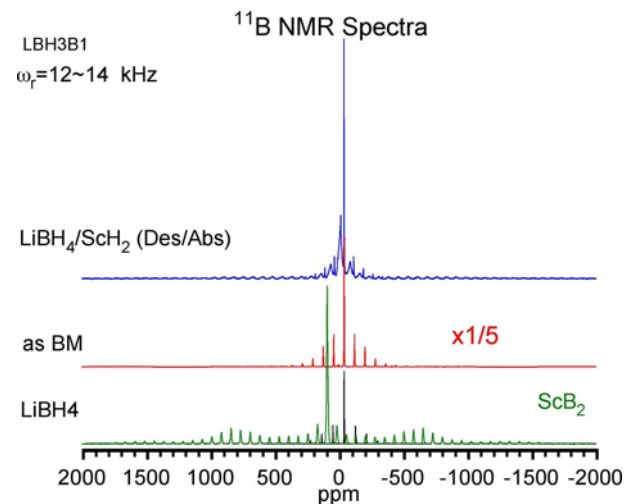
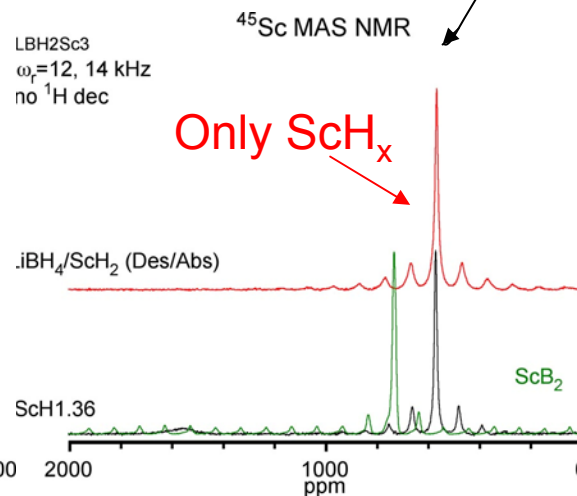
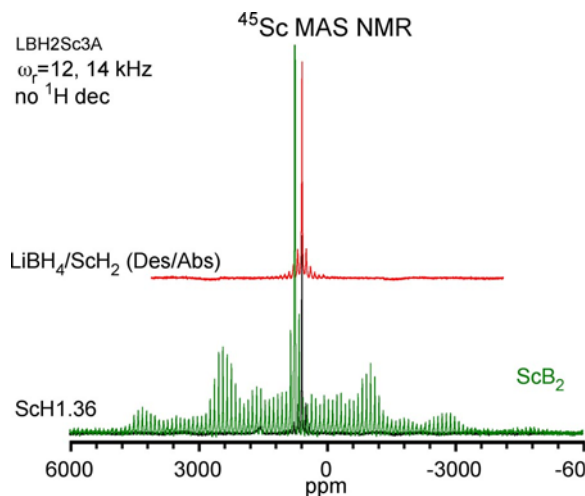
Desorption limits ~4 wt% at 400°C shown in upper plot. Theoretical limit for gravimetric desorption is 8.9 wt%. Lower plot shows absorption attempt with initial ScB_2+2LiH starting mixture. No absorption seen. Pressure behavior indicates gas law dependence only.



X-ray data of reaction product from 400°C desorption in lower plot shows remnant ScH_2 . Kinetics in this system are either slow or the reaction pathways to equilibrium are more complex than assumed.

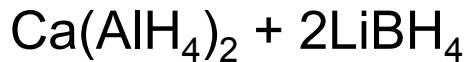
Technical Accomplishments: NMR of $\text{ScH}_2+2\text{LiBH}_4$ System

- Lack of crystallographic data from x-ray diffraction => spectroscopic analysis via NMR virtually the only way to identify bonding in product phases from previous kinetic reactions.
- Upper plot in lower right spectra show presence of elemental Boron. Boron in diboride structures in hexagonal layered form between metal but non-hexagonal formation usually irreversible.
- Upper plot of lower center spectra indicate presence of ScH_x verifying ScH_2 presence as noted in x-ray diffraction data.
- Identification of reactants that cannot be rehydrogenated of value in ultimately determining reaction pathways not predicted from thermodynamics.

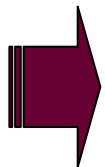


Technical Accomplishments: $\text{Ca}(\text{AlH}_4)_2 + 2\text{LiBH}_4$

- $\text{Ca}(\text{AlH}_4)_2$ not viable as stand-alone hydride:
 $\Delta H = +12.5 \text{ kJ/mol}^*$ so no reversibility expected**.
- But possible destabilization reaction with LiBH_4 as noted by Center partner J.K. Johnson.

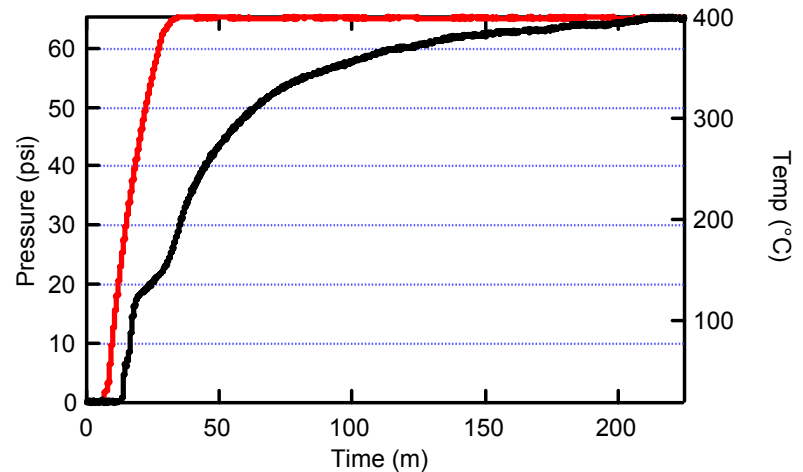


Activated using ball-milling, 1 hour at 400 rpm



Desorption up to 400°C
6.6–7.3 wt%

Reabsorption up to ~65 bar



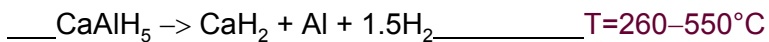
Cycle	1	2	3
Desorption (mass loss, wt.%)	6.64	2.65	2.74
Reabsorption (mass gain, wt.%)	1.65	4.56	3.06

As milled

Sample reground

**but as a stand-alone hydride, hydrogen would be released via following 3 decomposition steps:

(from Mal'tseva et al, Russ. J. Inorg. Chem., 46, 1793 (2001))



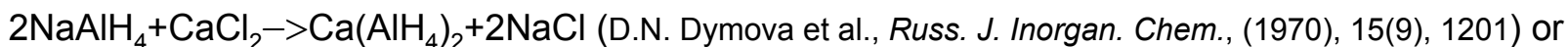
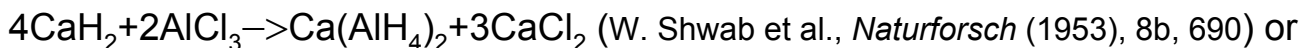
2 first steps would yield ~ 5.9 wt. % H_2

While endothermic heat and stable end-products were determined for this system theoretically, kinetic pathways are not always predictable and the ability to rehydrogenate this system suggests that further study and phase identification warranted.

Technical Accomplishments: $\text{Ca}(\text{AlH}_4)_2 + 2\text{LiBH}_4$ cont'd

Initial work on this system required $\text{Ca}(\text{AlH}_4)_2$ initial product.

Ball milling or THF processing with salt by-product typical as with:



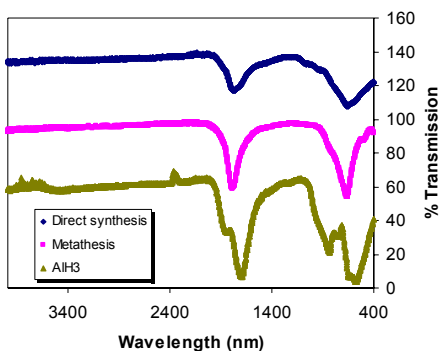
but salt by-products require further processing to remove.

Our approach used for 1st time is direct mechano-synthesis using ball mill



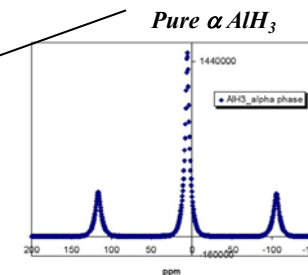
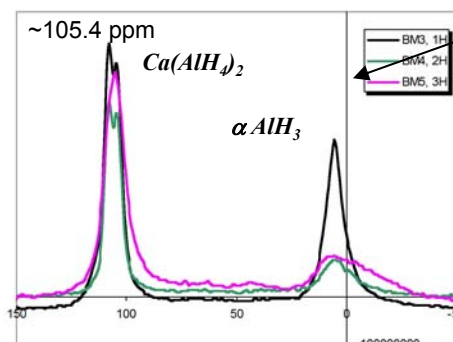
Sample preparation conditions as noted in Table below. >70% yield as determined by Al NMR.

Speed (rpm)	500	500	500	200	500
Time (hours)	1	2	3	10	6
Ratio via Al NMR	57.5/42/0.5	72.2/26.7/1.1	71.6/26.3/2.1	No reaction	decomposes



FTIR results at left show overlap of AlH_3 and $(\text{CaAlH}_4)_2$ bonds but NMR data at right show reaction products clearly identified.

^{27}Al NMR measurements

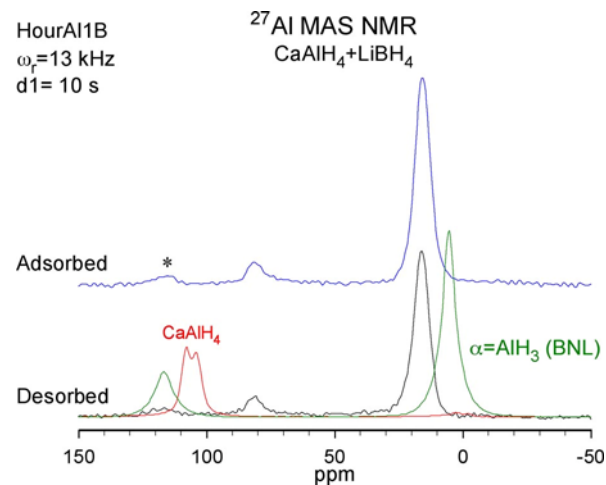
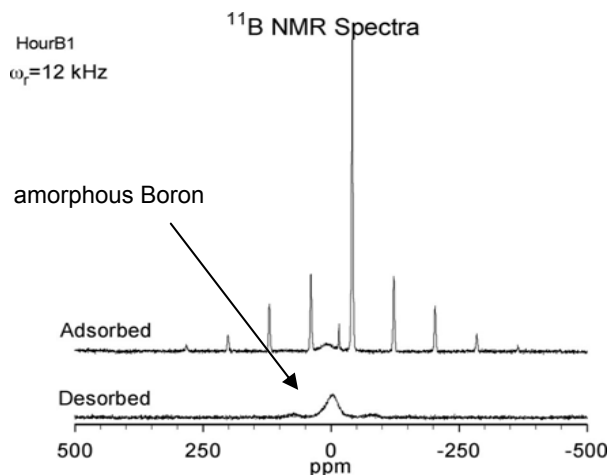
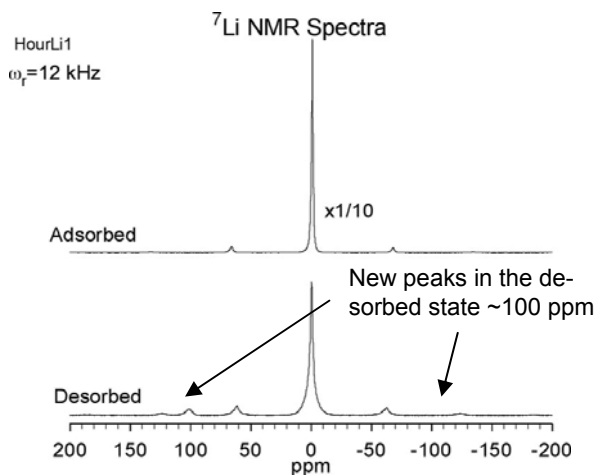
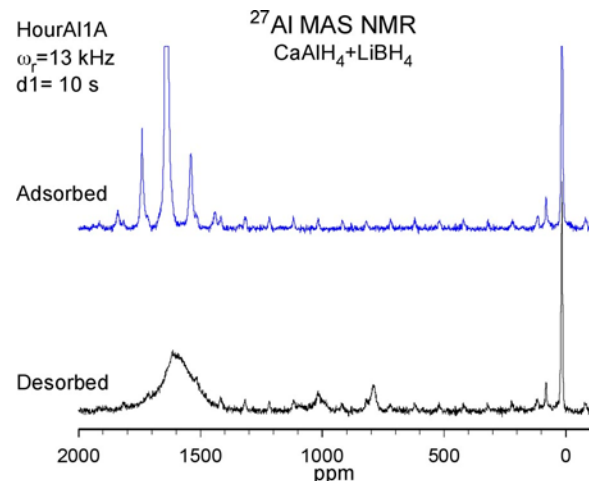


Technical Accomplishments: NMR of $\text{Ca}(\text{AlH}_4)_2 + 2\text{LiBH}_4$

Absorption/Desorption of a $\text{Ca}(\text{AlH}_4)_2 + 2\text{LiBH}_4$ ball milled mixture

As with ScH-LiBH_4 system, no discernable x-ray crystalline peaks after 1st desorption, reliance on NMR data necessary to understand bonding over short spatial scales.

^7Li & ^{27}Al NMR spectra indicate other phases in addition to LiBH_4 and LiH as reaction products – we are presently trying to identify these (eg., CaAlH_5 , etc.)



FY 2007-2008 plans

FY 07 plans:

- Milling time and catalyst dependent studies of $\text{ScH}_2 : 2\text{LiBH}_4$ system.
- Reaction path investigation in $\text{Ca}(\text{AlH}_4)_2 : 2\text{LiBH}_4$ system to understand reversibility mechanism.
- NaAlH_4 wetting and aerogel pore size enthalpy dependent studies.
- Continued NMR studies to identify reaction species that lack definitive crystallographic features
- Enthalpy studies in micropore sized aerogels.
 - Our initial work on nanoparticle synthesis had difficulties in addressing subsequent grain/particle growth under hydrogenation/dehydrogenation conditions. These are obviated to extent by the use of scaffolds that “contain” hydrides and limit diffusion during cycling.
 - Recent studies indicate that surface oxidized carbon substrates upon which nanoscaled NaAlH_4 is deposited has cyclable properties w/out need for catalyst¹.
 - Moreover, improvements in encapsulated (aerogel) vs bulk behavior shows improvements in capacity for NaAlH_4 .²
 - Recent reports that 1-2 nm sized Mg incorporated into aerogels have reaction enthalpy to 45 kJ/mole (down from 76 kJ/mole in bulk)³

FY 2007-2008 plans cont'd

- Coordination with T. Baumann (LLNL) in synthesis of aerogels with pore size range down to 1 to 2 nm. Surface/interface effects will play a dominant role in reaction enthalpy behavior at these size dimensions.
- Wetting behavior analysis of NaAlH_4 (as an already thermodynamically well-understood model system) and Mg to determine contact angle dependence on carbon surface treatment, necessary to understand minimum size constraints in aerogel pores.
- Use of surface treatments/additives to enhance wetting of hydrides in aerogel pores.
- Confirmation of lowered enthalpies and diffusion paths in NaAlH_4 and Mg encapsulated within aerogel pores.

- 1 C.P. Bald, B.P.C. Hereijgers, J.H. Bitter, and K.P. de Jong, "Facilitated Hydrogen Storage in NaAlH_4 Supported on Carbon Nanofibers" *Angew. Chem. Int. Ed.* 2006, 45, 3501–3503.
- 2 International Patent Application WO 2005/014469 A1, F. Schuth, B. Bogdanovic, A. Taguchi. "Materials encapsulated in porous matrices for the reversible storage of hydrogen"
- 3 R. W. Wagemans, T. M. Eggenhuisen, K. P. de Jong, P. E. de Jongh, "Magnesium-Carbon Nanocomposites for Hydrogen Storage?," at MH2006 International Symposium on Metal-Hydrogen Systems, Maui, Oct 2006.

Summary:

- Approach: Synthesis of destabilized hydride systems and kinetic analysis of dehydrogenation/hydrogenation reactions in “theoretically screened” systems of interest.
- Technical accomplishments and progress:
 - $\text{ScH}_2:2\text{LiBH}_4$ of particular interest as a 34kJ/mole system. Dehydrogenation temperature of up to 400°C still not high enough to completely extract theoretical value of hydrogenation. Predicted reaction products not discernable via x-ray or NMR. Reverse reaction does not appear to hydrogenate.
 - $\text{Ca}(\text{AlH}_4)_2:2\text{LiBH}_4$ system of interest in dehydrogenation/hydrogenation reactions but reaction pathways also not well understood.
- NMR analysis of value at this point in identifying near neighbor species that are not distinguishable via x-ray diffraction.
- Collaborations: HRL, JPL, U. ILL, Carnegie Mellon, U. Pittsburgh, NIST