METAL HYDRIDE CENTER OF EXCELLENCE

Development and Evaluation of Advanced Hydride Systems for Reversible Hydrogen Storage

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JPL
Jet Propulsion Laboratory
California Institute of Technology

Project ID
ST069

This presentation does not contain any proprietary or confidential information

Overview: Project Details

Timeline

- Project start date: April, 2005
- Project end date: Dec., 2010
- 90 % complete

Budget

- Expected total project funding:
  - $1.859M (DOE)
- Funding received in FY09:
  - $500.0K (DOE)
- Funding received for FY10:
  - $200.0K (DOE)

Barriers/System Targets

- A. System Weight and Volume
  - 2010 Targets: 6 wt.% & 45 gH/L
- D. Durability/Operability
  - 2010 Target: Life of 1000 cycles
- E. Charging/Discharging Rates
  - 2010 Target: Fill time of 3 min for 5 kg H_2
- P. Lack of Understanding of Hydrogen Physisorption and Chemisorption

Partners

- Participant in DOE MHCoE – collaborations with partners in all four sub-group Projects, primarily with Caltech, SNL, ORNL, U. Utah, HRL, NIST, Ohio State, U. Nevada (Reno) in FY09-10
- Limited collaboration on inter-Center activities with Hydrogen Storage Engineering Center of Excellence (HSECoE)

Relevance: Objectives

Overall Goal/Primary Objective

Develop and demonstrate light-metal hydride systems that meet or exceed the 2010/2015 DOE goals for on-board hydrogen storage through the validation of storage properties and reversibility in light element hydrides

- Nanophase, destabilized hydrides based upon LiH, MgH_2, & $LiBH_4$
- Complex hydrides (e.g., amides/imides, borohydrides, & AlH_3-based hydrides)
- Samples provided by numerous MHCoE partners, as opportunities are presented

Tasks

1. ***Phase Identification:***
   Perform NMR characterizations of phase relations for Mg-B-H and Al-B-N-H systems, with attention to suitability for cycling, as per:
   - Reversibility
   - Kinetics, towards meeting DOE delivery and refueling targets
   - H_2 storage parameters, with attention to approaching the 2010/2015 goals

2. ***Reaction Pathways:***
   Characterize phases & chemical bonding via MAS-NMR (Caltech) to better understand basic chemisorption processes.
   - Li amides/imides/alanates
   - Borohydrides
   - Other hydrides provided by MHCoE partners

Overview: JPL's Role in MHCoE

DOE

Coordinating Council (2008-2010)

Bruce Clemens (Stanford, POC A), Craig Jensen (UH, POC B), Zak Fang (Utah, POC C), Jim Wegrzyn (BNL, POC D), Don Anton (SRNL), J.-C. Zhao (OSU) Jay Keller (SNL) and Lennie Klebanoff (SNL)

Project Groups

A

Destabilized Hydrides

- **Stanford (POC)**
- Caltech
- **JPL**
- UIUC
- U. Hawaii
- U. Pitt/GT
- HRL
- U. Utah
- NIST

B

Complex Anionic Materials

- **UH (POC)**
- SNL
- OSU
- UIUC
- **JPL**
- ORNL
- NIST
- UNR
- Utah
- UTRC

C

Amides/ Imides (M-N-H)

- **Utah (POC)**
- UNR
- ORNL
- U. Hawaii
- **JPL**
- Caltech
- SRNL
- OSU

D

Alane (AlH_3)

- **BNL(POC)**
- SRNL
- U. Hawaii
- SNL
- UIUC
- UNB
- **JPL**

Approach

- **Multi-disciplinary Analysis and Characterization of Selected Hydrides to Elucidate Fundamental Processes**

- **Thermo-volumetric measurements**
  - Determinations of fundamental hydrogen storage capacities and equilibrium pressures on destabilized nanophase and complex metal hydrides

- **"Magic Angle" Spinning Nuclear Magnetic Resonance (MAS-NMR)**
  - Measurements are performed at Caltech Solid State NMR Facility (CSNF, Dr. Son-Jong Hwang, lead) to assess the phase compositions and chemical bonding parameters
  - NMR analysis is identifying the character of B-H bonding and reaction pathways in the metal-borohydride systems; this technique can distinguish amorphous/nanophase species that are not otherwise sensible via x-ray diffraction or vibrational spectroscopy methods

- **Neutron scattering spectroscopy**
  - Examinations of structures by neutron scattering and diffraction, etc. in collaboration with MHCoE partner NIST

- **Raman spectroscopy**
  - Measurements made at Caltech to determine mechanisms of desorption processes

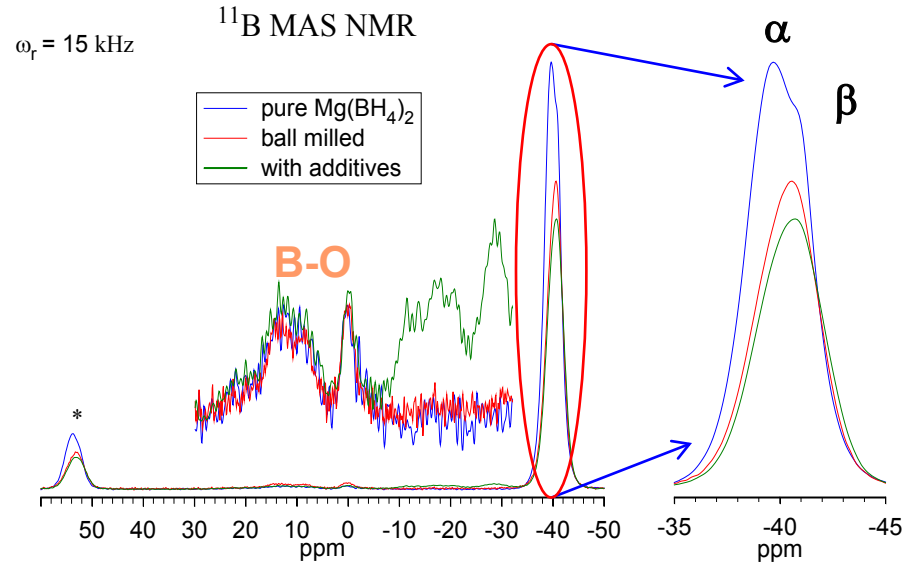
- **Theoretical collaborations**
  - Interactions with MHCoE theory teams on phases and destabilization behavior

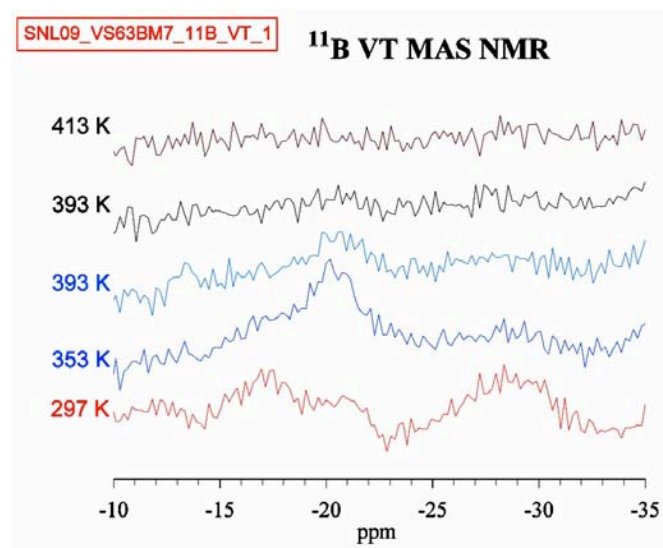
Technical accomplishments:

NMR Investigation of $Mg(BH_4)_2$ + additives Systems (SNL)

- Enhancement in hydrogen release from $Mg(BH_4)_2$ was investigated with use of catalysts ($TiF_3/ScCl_3$) (in collaboration with Dr. V. Stavila at SNL).
- Addition of 5 mol% each TiF_3 and $ScCl_3$ showed remarkable increase in rate of hydrogen desorption compared to the uncatalyzed counterpart.[a]
- Ball milling of $Mg(BH_4)_2$ resulted in partial phase transition at room T, which is relatively well resolved by peak shift in ^{11}B MAS NMR, and the formation of a few transient species (see peaks near -10 ~ - 30 ppm in ^{11}B MAS NMR spectrum) that is nominally due to interaction between the additives and $Mg(BH_4)_2$.
- Use of TiF_3 only did not reveal the formation of the transient species although ^{19}F MAS NMR study showed transformation of TiF_3 as a result of ball milling.
- *In Situ* VT ^{11}B NMR showed the disappearance of the transient species relatively low T, before the decomposition of $Mg(BH_4)_2$.

[a]Newhouse, R. J et al. J. *Phys. Chem. C, 2010,114, 5224.*

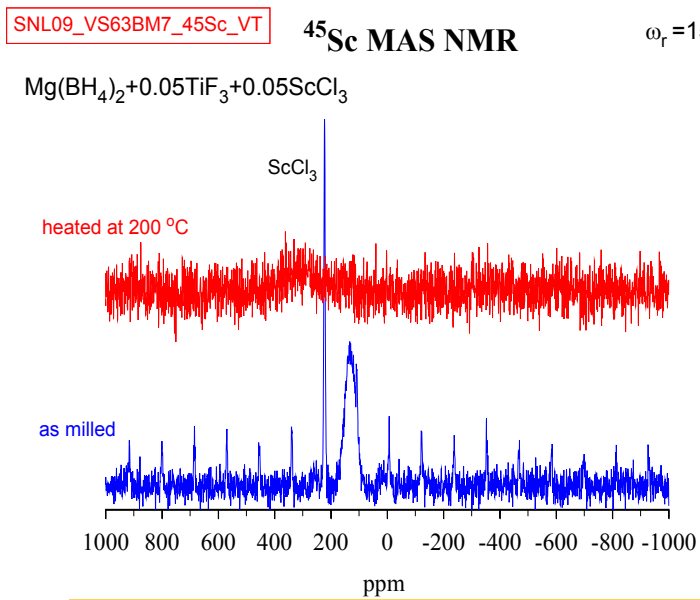


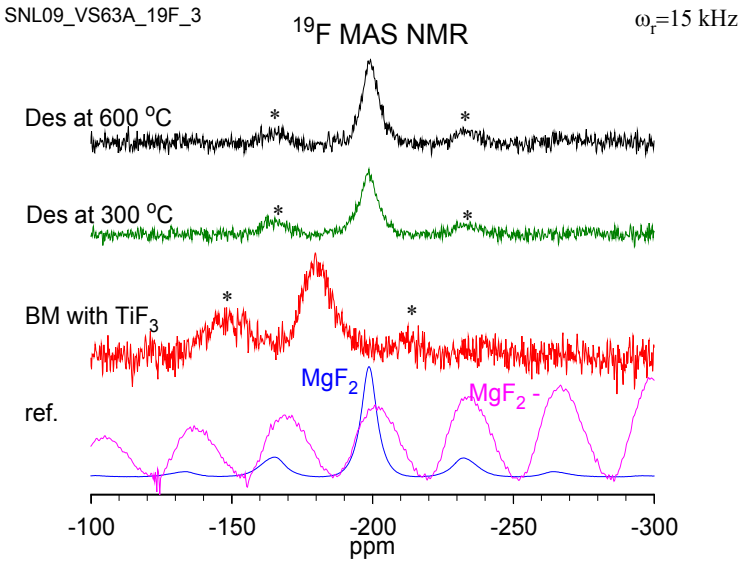


Technical accomplishments:

NMR Investigation of Desorption/Absorption of $Mg(BH_4)_2$ + additives

- More than 60% of $ScCl_3$ transforms to render a broad signal (133.2 ppm) in ^{45}Sc MAS NMR and its structure is yet to be identified. In conjunction with ^{11}B NMR, the formation of $ScCl_x(BH_4)_y$ type of species can be speculated.





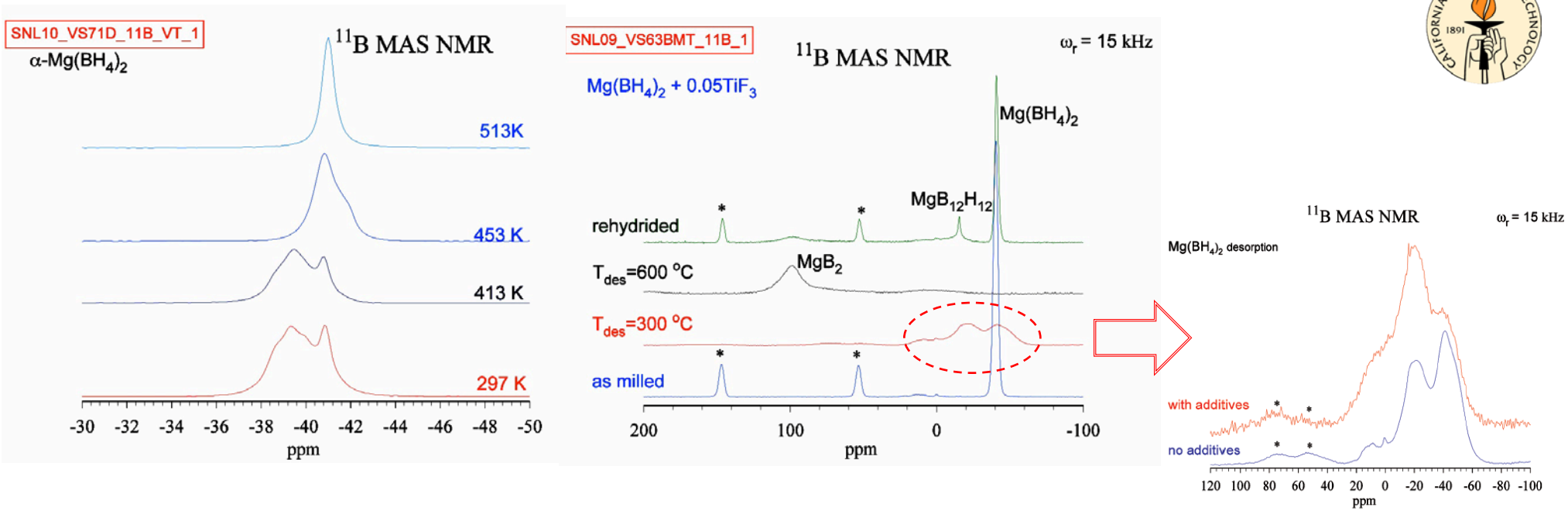
Phase changes associated with the additives (TiF_3 and $ScCl_3$) were monitored by ^{19}F and ^{45}Sc MAS NMR Exp as the desorption proceeds. Reference spectra (TiF_3-Aldrich, $ScCl_3$-Alfa) for ^{19}F NMR are provided. Note that TiF_3 shows a number of spinning sidebands with its center band peak at ~ -234 ppm.

- Variable T NMR experiments revealed that disappearance of ^{45}Sc signal after heating, indicating formation of species with invisible broad signal (only 5 mol%) or paramagnetic.
- ^{45}Sc NMR confirmed no formation of ScF_3 (-52ppm)[a], ScB_2 (~ 760 ppm) or ScH_2 (> 600 ppm).

[a]Lo, A. Y. H. et al. *J. Am. Chem. Soc. 2007, 129, 4687.*

Technical accomplishments:

NMR Investigation of Desorption/Absorption of $Mg(BH_4)_2$ + additives



^{11}B MAS NMR spectra acquired for $Mg(BH_4)_2$ after reactions showed

- phase transition (α to β) takes place near at 413 K with additives, which is about 40 degree below that without additives: Improved kinetics.
- Partition of numerous intermediates (analyzed from peak decomposition, see Table I) were found to be different depending on the presence of additives.
- Mostly MgB_2 were formed when heated up to 600 ºC.
- Rehydrogenation (90 Mpa H_2 at 392 ºC for 72 h) from the decomposition product to $Mg(BH_4)_2$ as well as intermediates such as $MgB_{12}H_{12}$.

TABLE 1: Proposed Boron Species from the Deconvolution Analysis of ^{11}B MAS NMR Spectra of $Mg(BH_4)_2$ with Additives and without after Desorption at 300 °C

	chemical shift (ppm)	relative quantity	
		no additives	with additives
B_2O_3 or B−OH type oxide contaminant	20−0	0.03	0.04
amorphous	2.2	0.06	0.23
$MgB_{12}H_{12}$	−16.8	0.01	<0.002
early stage intermediates	−21.8	0.43	0.5
$Mg(BH_4)_2$-I	−39.4	0.06	0.03
$Mg(BH_4)_2$-II	−45.4	0.41	0.2

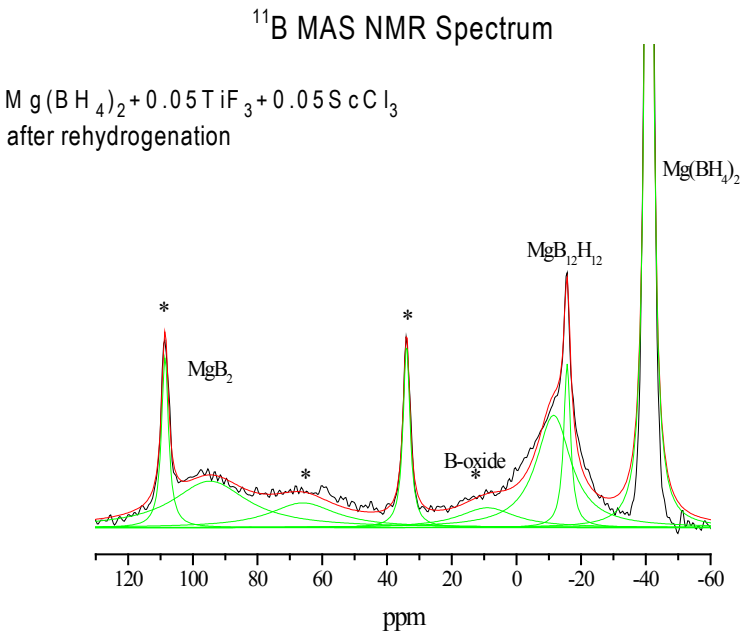
Technical accomplishments:

NMR Investigation of Desorption/Absorption of $Mg(BH_4)_2$ + additives

Table II. Proposed boron species based on deconvolutions of ^{11}B MAS NMR spectra of samples after the rehydrogenation reaction.

	Chemical shift (ppm)	Relative quantity	
		no additives	with additives
MgB_2	97.3	0.25	0.21
Amorphous*	-11	0.04	0.23
$MgB_{12}H_{12}$	-15.5	0.05	0.07
$Mg(BH_4)_2$	-40.95	0.66	0.49

***Amorphous phase in this system means nearly $[B_{12}H_{12}]^{2-}$ related species.**

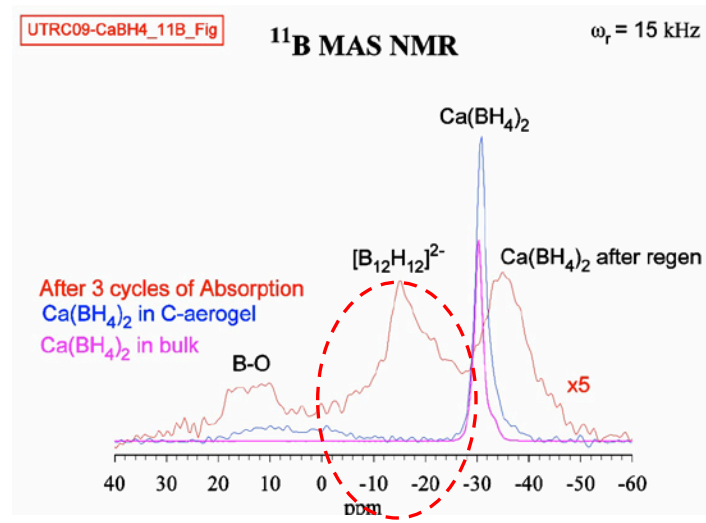


Technical accomplishments:

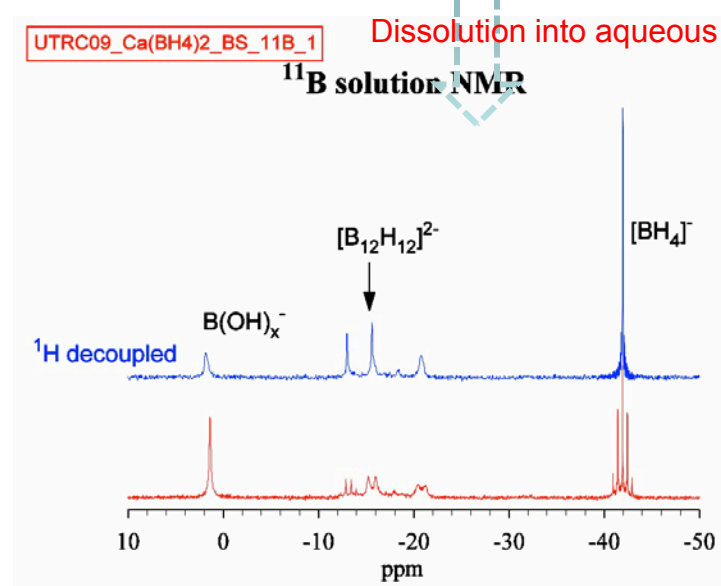
NMR Analysis of $Ca(BH_4)_2$ in C-aerogel system (UTRC)

Table III. Phase distribution after cycles of Des/Absorption for a system of $Ca(BH_4)_2$ incorporated into C-aerogel

Sample	Description	[H] (a.u)	$Ca(BH_4)_2$	Intermediate (-6 ~ -26 ppm)	B-O (> 0 ppm)
UTRC-09-06	$Ca(BH_4)_2$ in C-aerogel	100	100		27.4
UTRC-09-06-1	After 3 cycled of hydrogenation	42.9	40.2	44.8	20.0



Dissolution into aqueous phase

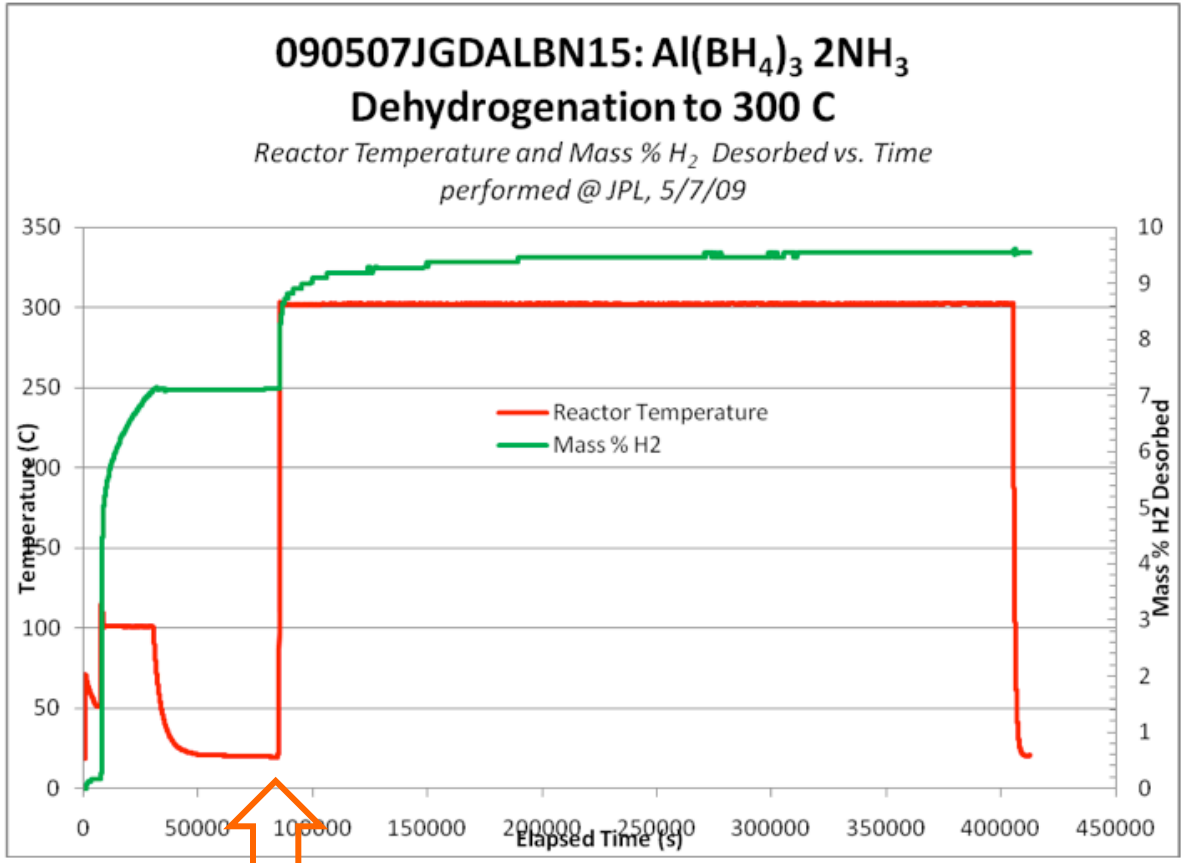


- As made: 38 wt% of $Ca(BH_4)_2$ was loaded into C-aerogel.
- ^{11}B MAS NMR showed no noticeable broadening of $Ca(BH_4)_2$, indicating no particular interaction of the borohydride with the surface of C-aerogel.
- The rehydrogenated $Ca(BH_4)_2$ reveals significant peak shift (from -30 ppm to -35 ppm) and broadening, and this result is noticeably different from that of bulk reaction case.
- Accumulation of the intermediate (mostly CaB12H12) was also observed for this system like the case of bulk samples.
- Dissolution of the reaction intermediate into aqueous phase again confirmed the formation of $[B_{12}H_{12}]^{2-}$ via ^{11}B solution NMR.

Technical Accomplishments:

$Al(BH_4)_3 \bullet 2(^{15}NH_3)$ Intermediate Study

- $Al(BH_4)_3$ was enriched with 15N-labeled NH3 for the purpose of enhancing NMR activity
- Desorption occurred @JPL in two steps, with samples removed at 7% mass loss for NMR screening
- Total desorption shows net ~7% @ 250°C, >9% @ 330°C



Partial sample removed from reactor; desorption continues (mass% results adjusted accordingly)

- NMR investigations of the products of these reactions are still underway!

For additional detail, see Brown et. al., poster ST068

Proposed Future Work

- **All Projects**
  - [FY10] Complete active project investigations and archive extant data for transmission to MHCoE Leadership; provide feedback as required to support upselect of promising storage materials for use in the ongoing Engineering Center effort.
    - Prepare to close-out MHCoE effort, Oct-Dec 2010

Summary

- **Approach**
  - Systematic characterizations of phase formation and hydride reversibility using solid state NMR and volumetric measurements (Projects A, B, C, & D)

- **Technical Accomplishments**
  - Phase characterization, kinetics (i.e., diffusion behavior), & reversibility assessments via MAS NMR in numerous systems, including C60 scaffolded architectures
  - NMR analysis is identifying the character of B-H bonding and reaction pathways in the metal-borohydride systems; this technique can distinguish amorphous/nanophase species that are not otherwise sensible via x-ray diffraction or vibrational spectroscopy methods

- **Collaborations**
  - Caltech, U. Utah, SNL, Ohio State, ORNL, NIST, SRNL, & UTRC

- **Future directions**
  - Continue aggressive investigations of destabilization routes in the Al-B-N-H system
  - Utilize NMR methods within ^{15}N-enriched systems

Back-up Slides (Not Presented)

Caltech Solid-State NMR Facility

- Equipped with three solid sample NMR spectrometers.
- A number of solution and solid sample NMR probes available.
- Capability of in-situ variable temperatures (-100 ^{o}C ~ +150 ^{o}C)
- Dr. Son-Jong Hwang is CSNF manager and lead NMR spectroscopist.

Bruker DSX 500 spectrometer (11.7 T)

Used for majority of MHCoE samples, including both those direct from JPL and those acquired in collaborative work with partners

Bruker AM 300 spectrometer (7.0 T)

Also in use; spectrometer console was updated in 2008 via DOE/EERE support for doing more routine MAS-NMR measurements (i.e., variable temperatures, etc.)