Advanced, High-Capacity Reversible Metal Hydrides

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ST 031

Overview

Timeline

- Start Date: March 2005
- End Date: September 2012
- 99% complete

Budget

- Total project funding: $2,945,058
    - DOE share: $2,335,173
    - Contractor share: $609,885
- Funding for FY11: no cost extension only.
- Funding for FY12: no cost extension only.

Barriers

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

Partners

- E. Akiba, K. Sakaki; AIST, Japan
- C. Ahn, S.J. Hwang; California Institute of Technology
- T. Autrey, Pacific Northwest National Lab
- R. Cantelli; University of Rome
- M Conradi, Washington University
- B. Hauback, Institute for Energy Technology, Norway
- H. Hagmann, R. Cerny; University of Geneva
- T. Jensen, Aarhus University, Denmark
- L. Knight, G. Lewis, J. Low, A. Sachtler; UOP, LLC
- R. Kuboto; KEK
- R. Kumar; University of Nevada at Las Vegas
- S. McGrady; University of New Brunswick
- S. Orimo, Y. Nakamori; Tohoku University, Japan
- I. Robertson; University of Illinois
- E. Ronnebro; SNL, PNNL
- T. Udovic; NIST
- J. Vajo, P. Liu; HRL
- A.Zuettel, E. Callinin, EMPA

Objectives and Relevance

Development of a new class of reversible complexes that has the potential to meet the DOE kinetic and system gravimetric storage capacity targets.

Investigations during FY12 focused on:

- Reversible dehydrogenation of $MgBH_4$ (14 wt % theoretical, >12 wt % **demonstrated** reversible capacity)

Approach

Nano-confined Al and Mg Compounds
in Carbon Aerogels (no activity in FY12)
Collaboration with HRL

• Low temperature homogenous organometallic approach to incorporation of Al and Mg based hydrides into carbon aerogels results in unprecedented high loadings without degradation of nano-porous scaffold that occurs with melt intercalation.


Aerogel Scaffold

$\blacksquare$ Heptane

$\bullet$ $MgBu_2$

170 °C, 55 bar H_2

- BuH

MgH_2
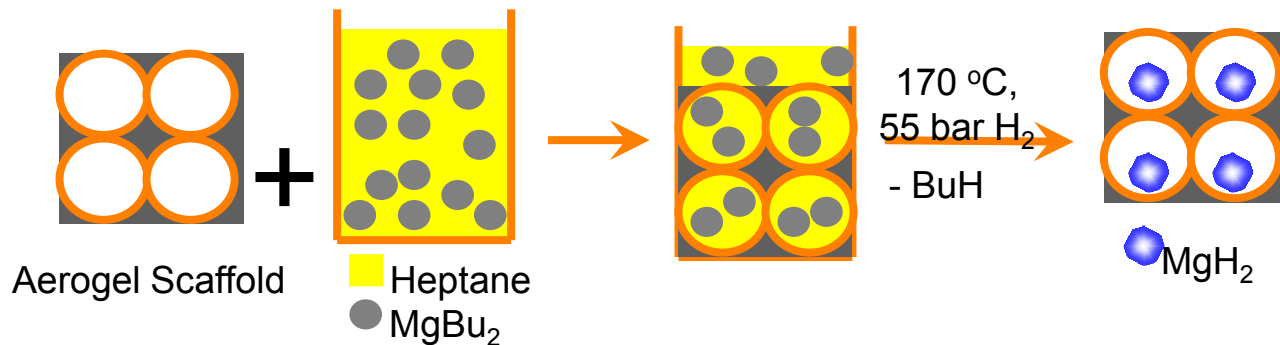
• Determine the effects of nano-confinement on the kinetics and thermodynamics of the dehydrogenation of Al and Mg based hydrides.
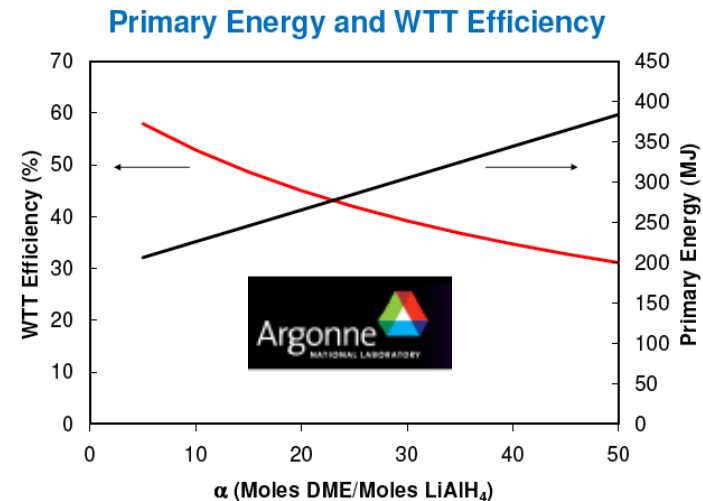
Approach

Re-hydrogenation in Non-conventional Solvents (no activity in FY12)
Collaboration with U. of New Brunswick

➢ Explore hydrogenation of Al to AlH_3; Al/MgH_2 to $Mg(AlH_4)_2$; and LiH/Al to $LiAlH_4$ in supercritical fluids and liquefied gases such as dimethyl ether which can form adducts during synthesis but are easily eliminated due to their high volatility.
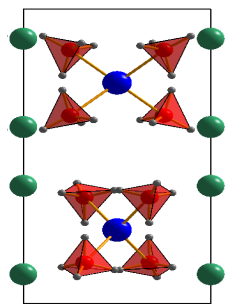
$$LiH + Al[Ti] \xrightarrow[\text{25 }^{\circ}\text{C 24 h}]{Me_2O/H_2 \text{ 100 bar}} LiAlH_4[Ti]$$
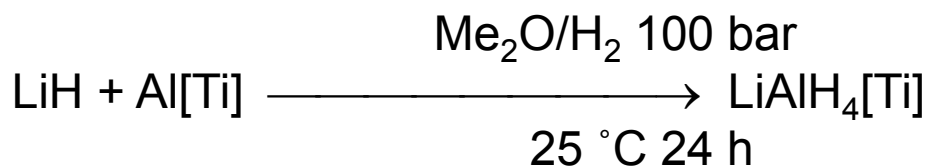
• Solvent vents immediately with excess H_2
• Fully charged Ti-doped $LiAlH_4$ obtained
• Very low levels of Ti can be used (~500 ppm)

Primary Energy and WTT Efficiency

WTT Efficiency (%) / Primary Energy (MJ) vs. α (Moles DME/Moles LiAlH₄)
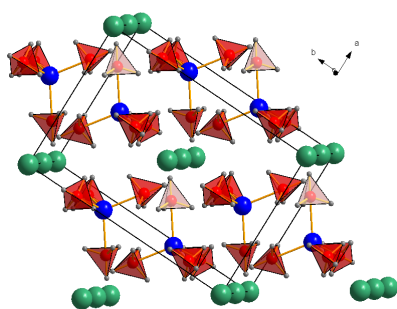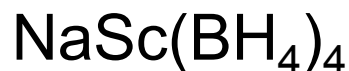
Argonne NATIONAL LABORATORY
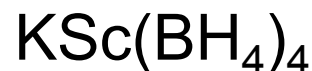
Approach

Mixed Metal Borohydrides

### Collaboration with IFE, Aarhus U., and U. of Geneva

$LiSc(BH_4)_4$

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 J. Phys. Chem B. **2008**, *112*, 7551

$NaSc(BH_4)_4$

R. Černy, G. Severa, D. Ravnsbaek, Y. Filinchuk, V. d'Anna, H. Hagemann, Y. Cerenius, C.M. Jensen, T.R. Jensen *J. Phys. Chem. C* **2010***, 114*, 1357.

$KSc(BH_4)_4$
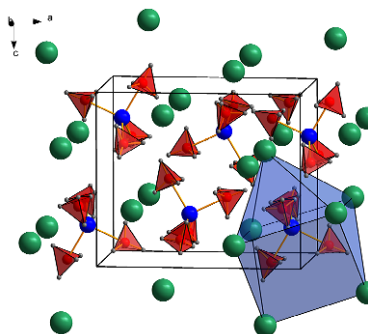
R. Cerny, D.B. Ravnsbaek , G. Severa, Y. Filinchuk, V. d'Anna , H. Hagemann, D. Haase, C.M. Jensen, T.R. Jensen; *J. Phys. Chem. C.* **2010***, , 114*, 19540*.*
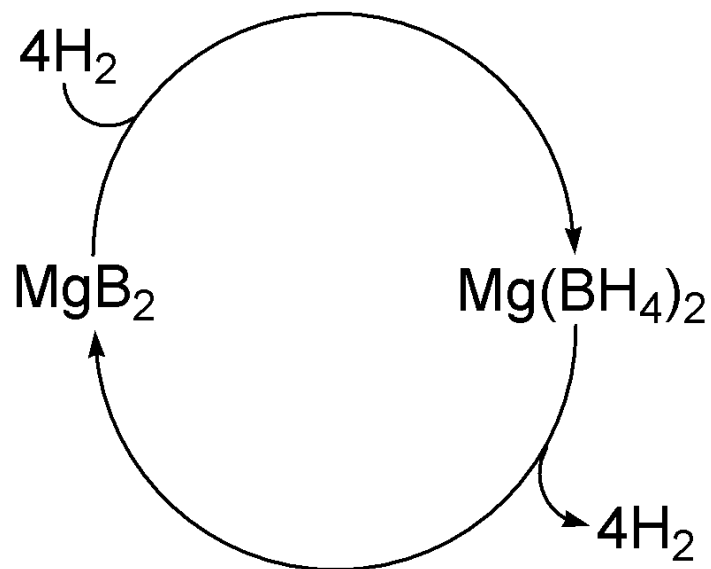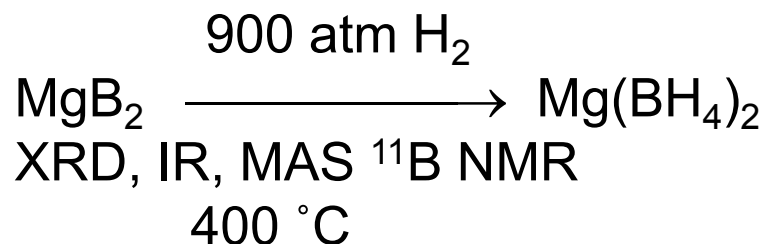
$Na_2Mn(BH_4)_4$
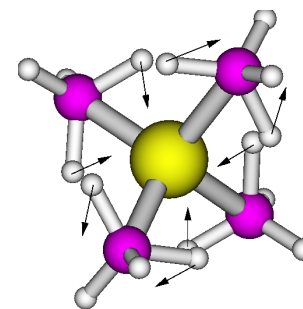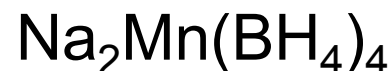
G. Severa, H. Hagemann, M. Longhini, J.W.Kaminski, T.A. Wesolowski, C.M. Jensen; *J. Phys. Chem. C.* **2010**, *114,* 15516.

Approach

Reversible Dehydrogenation of Mg(BH$_4$)$_2$

Collaboration with Sandia and Pacific Northwest National Laboratories

Demonstration of Cycling of
12% wt H

$$MgB_2 \xrightarrow[\text{XRD, IR, MAS }^{11}\text{B NMR}]{900 \text{ atm H}_2} Mg(BH_4)_2$$
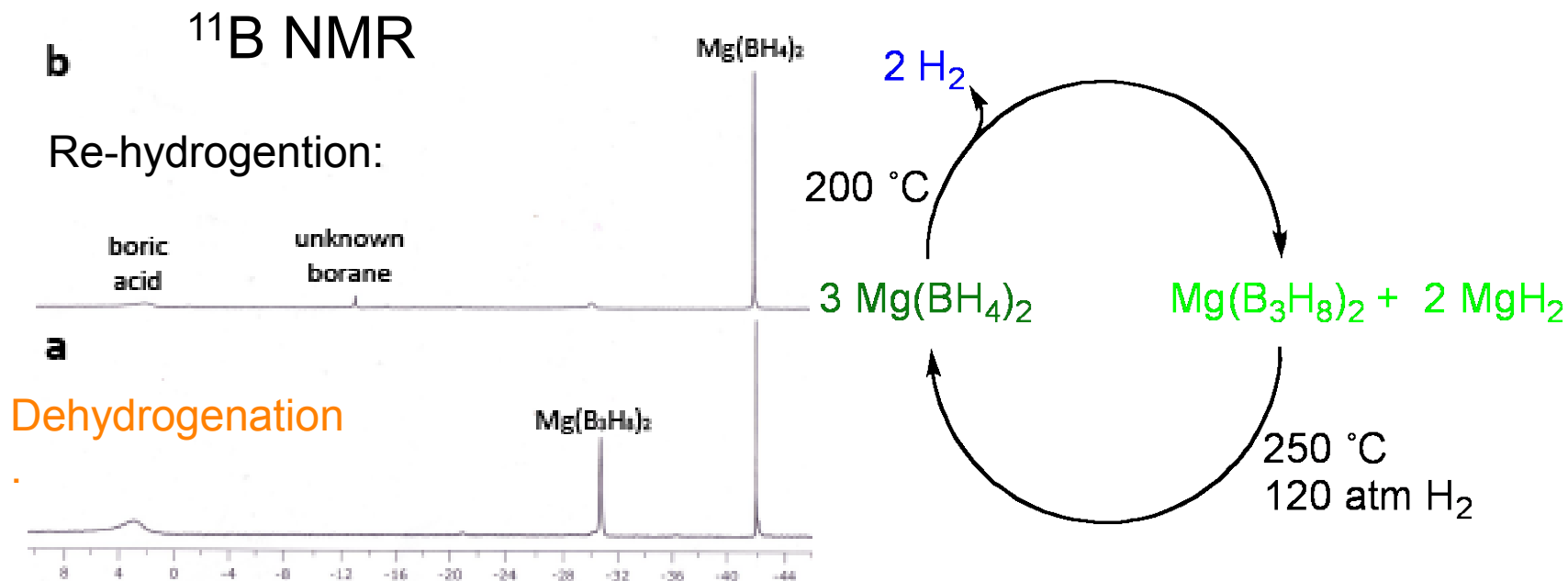
400 ˚C

Rönnebro, Jensen, and Severa US patent application U.S. Patent 12/553,633.
G. Severa, E. Rönnebro, C.M.Jensen; *Chemical Commun.* **2010**, *46,* 421.

Accomplishments (FY11)

Hydrogen Cycling of $Mg(BH_4)_2$ Under Mild Conditions

First example of the **reversible**, solid state dehydrogenation of a borohydride at temperatures below 350 °C.

^{11}B NMR

b

Re-hydrogention:

boric acid

unknown borane

$Mg(BH_4)_2$

a

Dehydrogenation

.

$Mg(B_3H_8)_2$

$2 H_2$

200 °C

$3 Mg(BH_4)_2$ → $Mg(B_3H_8)_2 + 2 MgH_2$

250 °C
120 atm H_2

M. Chong, A. Karkamkar, T. Autrey. S. Jalisatgi, S. Orimo, C.M. Jensen; *Chem. Commun.* **2011**, *37*, 1330.

FY12 Accomplishments

Independent Synthesis $Mg(B_3H_8)_2$

$$BH_3THF + MgHg\ amalgam \xrightarrow{\ 25\ ^\circ C\ } Mg(B_3H_8)_2 \quad 95\%\ yield$$
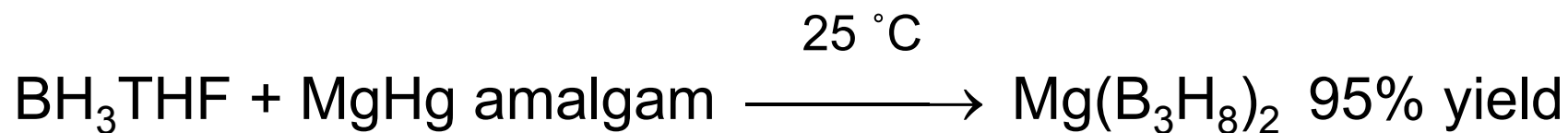
FY12 Accomplishments

Hydrogenation Reaction

$$2\ MgH_2 + Mg(B_3H_8)_2 \xrightarrow[\text{100 °C, 3 h}]{\text{5 atm } H_2} 3\ Mg(BH_4)_2$$
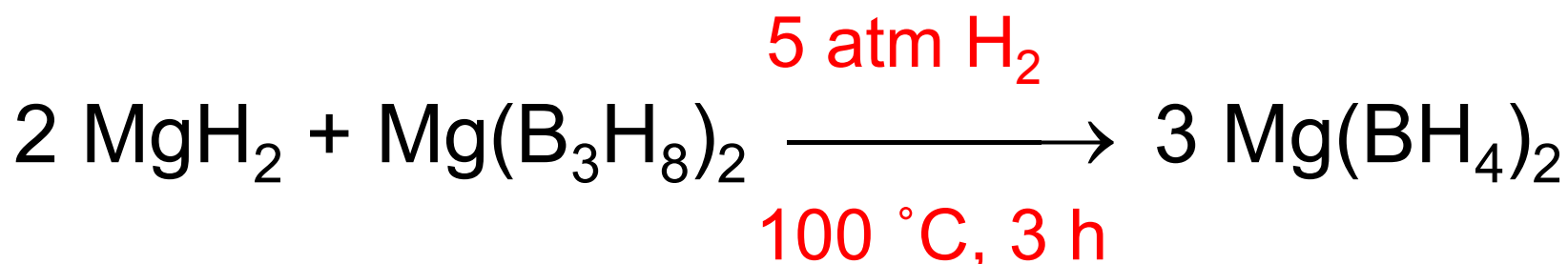
- MgH_2 must be activated by ball milling
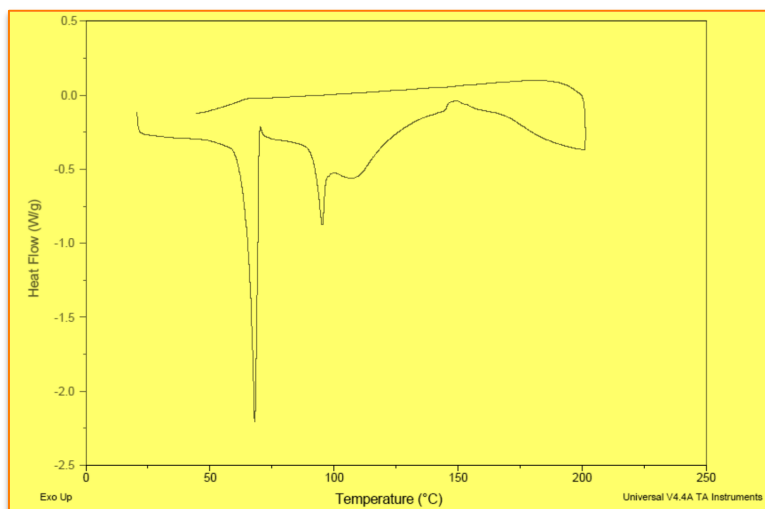- $MgB_{12}H_{12}$ is formed if reaction mixture contains <2 equivalents of MgH_2. → Condensation to higher boranes **does not require** metal hydride.
- MAS ^{11}B NMR shows that hydrogenation of $Mg(B_3H_8)_2$ with 4 equivalents of LiH or NaH also gives $[BH_4]^-$.

FY12 Accomplishments

DSC Studies Mg(B$_3$H$_8$)$_2$ and Mg(B$_3$H$_8$)$_2$ /MgH$_2$ Collaboration with Tohoku U.

Mg(B$_3$H$_8$)$_2$ alone shows a strong exotherm due to melting at 60 ˚C. MAS ^{11}B NMR confirms [B$_3$H$_8$]$^-$ still intact.
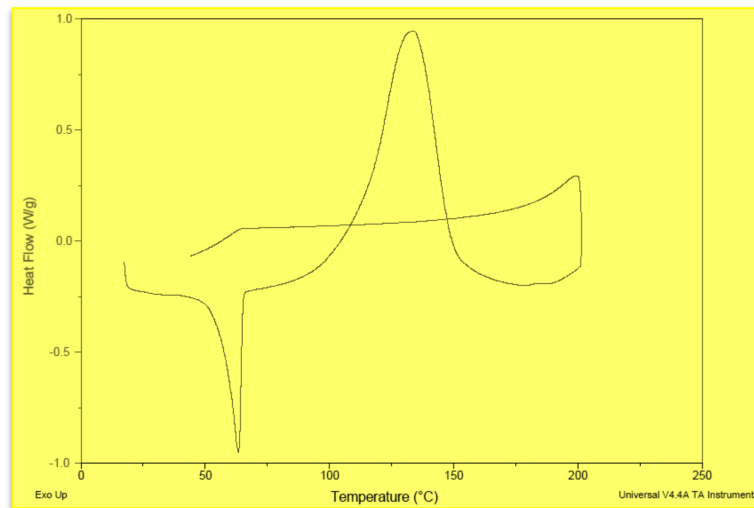
Mg(B$_3$H$_8$)$_2$/ 2 MgH$_2$ under 50 atm H$_2$ shows that after melting a strong endothermic peak occurs at ~130°C. ^{11}B NMR a shows at this point B is predominantly BH$_4$^{11}

FY12 Accomplishments

Diborane emission from $MSc(BH_4)_4$ (M = Li,Na,K) – collaboration with Callini and Zuettel EMPA

- Discrepancies in the literature regarding diborane resulting from thermal decomposition of $MSc(BH_4)_4$ (M = Li,Na,K).

- EMPA equipment for IR detection and quantification of diborane emission from borohydrides.

- Results indicate thermal decomposition proceeds via:

$$MSc(BH_4)_4 \longrightarrow MBH_4 + Sc(BH_4)_3$$

$$Sc(BH_4)_3 \longrightarrow x\ B_2H_6 + y\ H_2 + Sc(?)$$
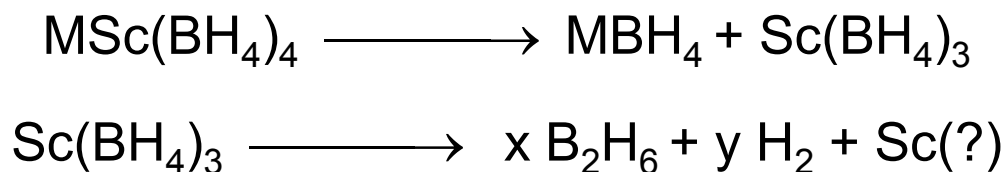
Collaborations

FY12

T. Autrey; PNNL (Government): Character by solution NMR analysis
S. Orimo; Tohuku University (Academic): Characterization by DSC and XRD.
A. Zuettel, E. Callini, EMPA (Academic), Detection and Quantification of diborane by IR

Project

C. Ahn; California Institute of Technology (Academic): Characterization by TEM imaging
E. Akiba, K. Sakaki; AIST, Tsukuba (Government): Characterization by positron annihilation.
R. Cantelli; University of Rome (Academic): Characterization by anelastic spectroscopy.
H. Hagmann, R. Cerny; University of Geneva (Academic): Characterization by IR and Raman Spectroscopy and XRD.
B. Hauback, M. Sorby; Institute for Energy Technology (Government, Norway): Characterization by Synchrotron X-ray and Neutron Diffraction.
S-J. Hwang; R. Bowman California Institute of Technology, JPL (Academic, Government): Characterization by solid state NMR spectroscopy.
T. Jensen, Aahus University, Denmark (Academic); Characterization by XRD.[13]

Collaborations

Project (continued)

L. Knight, G. Lewis, J. Low, A. Sachtler; UOP, LLC (Industrial): Characterization by XRD and mass spectroscopy.

R. Kuboto; KEK, Tsukbua (Government): characterization by muon spin resonance.

R. Kumar; University of Nevada at Las Vegas (Academic) high pressure neutron diffraction studies.

I. Robertson; University of Illinois (Academic): Characterization by TEM.

E. Ronnebro; SNL (now with PNNL), Government: High pressure studies.

S. Srinivasan; University of South Florida (Academic): Characterization by DSC.

V, Stavila; Sanida National Laboratory (Government); high pressure hydrogenation.

X. Tang: UTRC (Industrial); Confinement in alternative scafolds.

T. Udovic; NIST (Government) Characterization by Inelastic neutron scattering.

J. Vajo, P. Liu; HRL (Industrial): Characterization by PCT.

Future Work

Borohydrides

- Adjustment of conditions to maximize trade off between cycling capacity and temperature/pressures required for reversible dehydrogenation of $Mg(BH_4)_2$.

Hydrogenation in Non-conventional Solvents

- Further evaluation of WTT efficiency of the $DME/LiAlH_4$ system to be examined in collaboration with Argonne National Lab.

FY12 Summary

- $Mg(B_3H_8)_2/2\ MgH_2$ undergoes rapid hydrogenation to $Mg(BH_4)_2$ at **100 ˚C** under **50 atm** of H_2. The rapid kinetics are at least in part due to the fact that $Mg(B_3H_8)_2$ is in the liquid state above 60 ˚C. This finding points to the possibility of finding mild, PEM fuel relevant conditions for the reversible dehydrogenation of borohydrides that avoid the thermodynamic sinks such as $[B_{12}H_{12}\}^{2-}$.

- The thermal decompostion of $MSc(BH_4)_4$ (M= Li, Na, and K) gives rise to MBH_4 and $Sc(BH_4)_3$. The neutral Sc borohydride is unstable and decomposes to produce diborane. Thus $MSc(BH_4)_4$ will not undergo reversible dehydrogenation. ˎ   …

Supplemental Slides

Back-up Technical Slide 1

Previous Results

- High, (9-16 wt % confirmed by TEM, EDS, and XRD) MgH_2 loadings of carbon aerogel without host degradation are obtained using the organometallic method.

- The rate of dehydrogenation at 252 ˚C is >5 times faster than the initial rate found for ball milled MgH_2 and comparable to those found for nano-confined MgH_2 in carbon aerogels by alternative methods at HRL. The rate remains the same over 4 cycles of dehyrogenation-rehydrogenation.

Back-up Technical Slide 2

Improved kinetics observed for nano-confined $Mg(BH_4)_2$
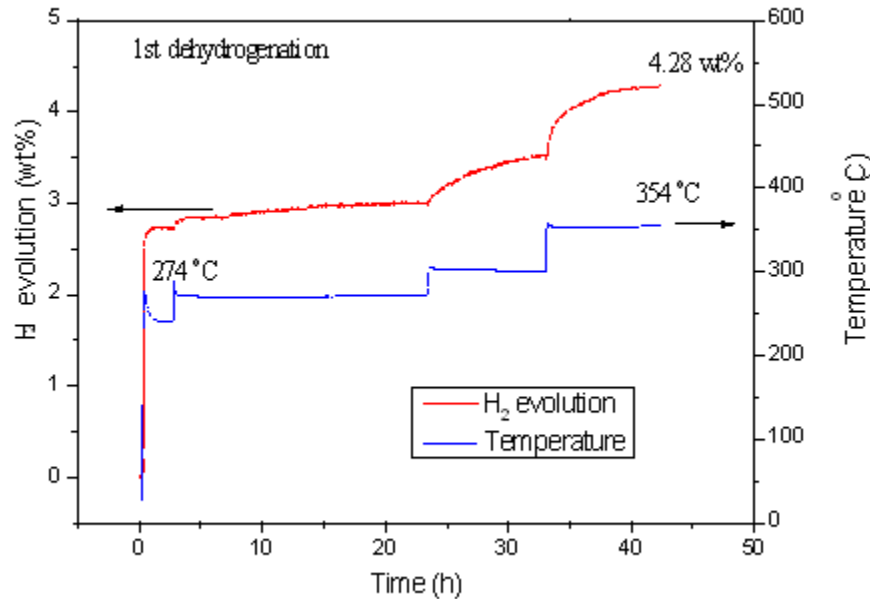
Hydrogen is evolved at the rate of 0.1 wt%/min at 270 °C during the elimination of the first 4.0 H wt%. However, re-hydrogenation of the resulting MgB_2 under 120 atm at 220 °C gives rise to $Mg(B_{12}H_{12})_2$ as occurs with bulk $Mg(BH_4)_2$.

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Back-up Technical Slide 3

Synthesis of nano-confined $Mg(BH_4)_2$

- Hydride incorporated into carbon aerogel through immersion in molten $Mg(BH_4)_2 \cdot O(C_2H_5)_2$. Diethyl ether adduct removed at 220 °C en vacuo.
- 60 wt% of $Mg(BH_4)_2$ is incorporated into aerogel.

Broaden of XRD peaks indicates incorporation into aerogel.
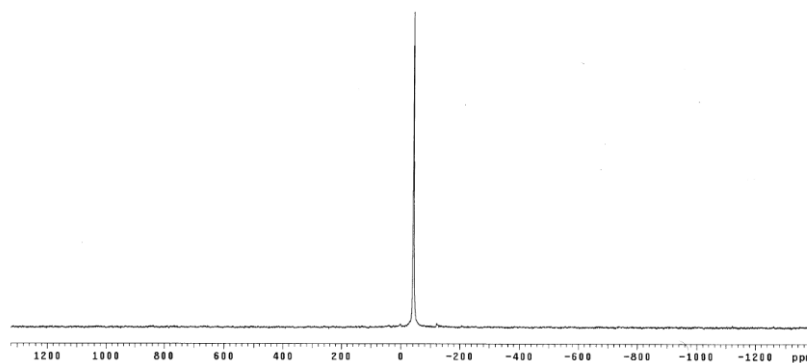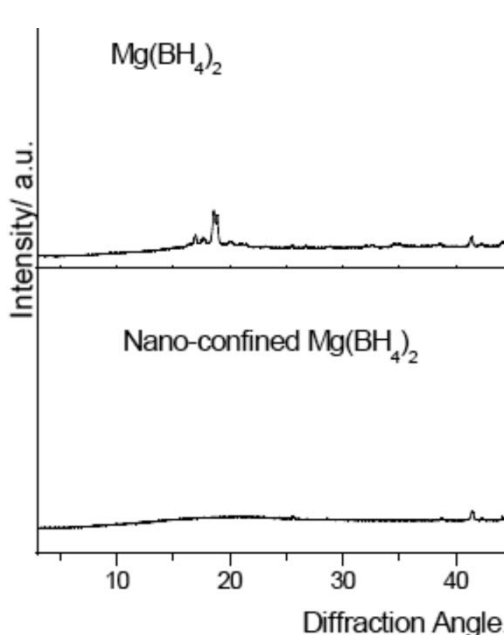
MAS 11B NMR spectrum of the hydride incorporated aerogel verifies that $Mg(BH_4)_2$ is the only boron containing species present in the aerogel.

Back-up Technical Slide 4

BACKGROUND

- Like sodium alanate, stepwise dehydrogenation, BUT first step is exothermic.

  Step 1: $3LiAlH_4 \rightarrow Li_3AlH_6 + 2Al + 3H_2$ $\triangle H = -30$ kJ

  Step 2: $Li_3AlH_6 \rightarrow 3LiH + Al + 1.5H_2$ $\triangle H = 38$ kJ

- Together steps 1 and 2 provide ~7.9 wt %H.

- Ashby (1963) – thermodynamics altered by adduct formation, reversible in THF (high T and P).

- Ritter (2007) – reversible in THF (high energy milling) with Ti catalyst. Requires material to be ball milled prior to each hydrogenation half-cycle.

- Graetz (2008) – reversible in THF (low T and P) with Ti catalyst.

- THF removal requires heating to 60 ºC for 6 h.Incompatible with Ti catalyst since dehydrogenation occurs at the temperature required for removal of THF.

Back-up Technical Slide 5

Using liquid dimethyl ether as solvent eliminates adduct removal issues

$$\text{LiH} + \text{Al[Ti]} \xrightarrow[\text{r.t.; 24 h}]{\text{Me}_2\text{O/H}_2 \text{ (100 bar)}} \text{LiAlH}_4\text{[Ti]}$$
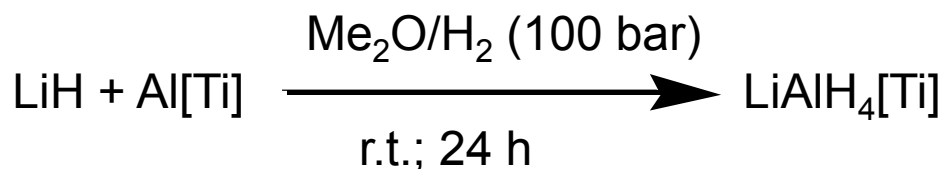
- Solvent vents immediately with H_2
- Fully charged Ti-doped $LiAlH_4$ obtained
- Very low levels of Ti can be used (~500 ppm)
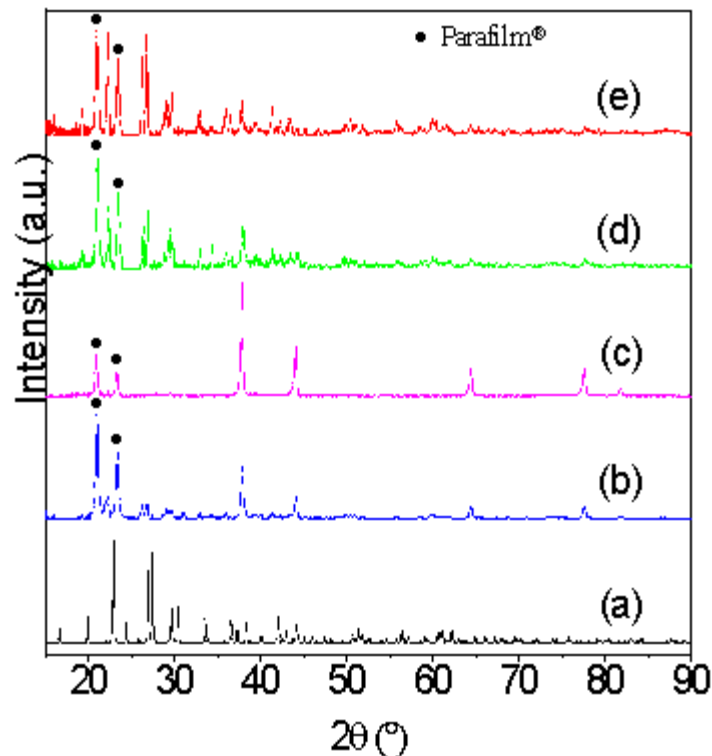
XRD patterns of LiAlH₄ samples: (a) ICDD ref; (b) ball milled (2.0 mol% TiCl₃); (c) fully de-H (0.2 mol% TiCl₃); (d) re-H (2.0 mol% TiCl₃); (e) re-H (0.2 mol% TiCl₃).

G.S. McGrady and C.M. Jensen U.S. Patent Application 60/945,650.

Back-up Technical Slide 6

H$_2$ Desorption from Ti-Doped LiAlH$_4$

- 0.5-0.2 mol% Ti optimal
- ~7 wt% H at 80-180 ^{o}C
- Excellent kinetics

Xi. Liu, G.S. McGrady, H. W. Langmi, C.M. Jensen; *J. Am. Chem. Soc*. **2009**, 131, 5032.
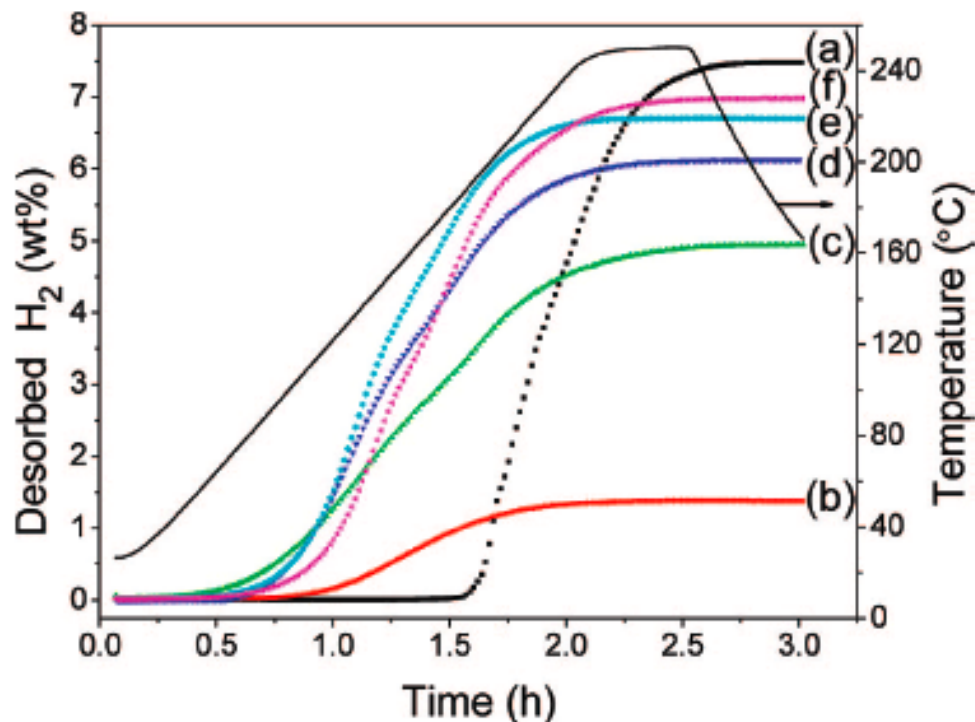
TPD plots for LiAlH$_4$ samples: (a) as-received; (b) milled with 2.0 mol% TiCl$_3$; (c) re-H (2.0 mol% TiCl$_3$); (d) re-H (1.0 mol% TiCl$_3$); (e) re-H(0.5 mol% TiCl$_3$); and (f) re-H (0.2 mol% TiCl$_3$).
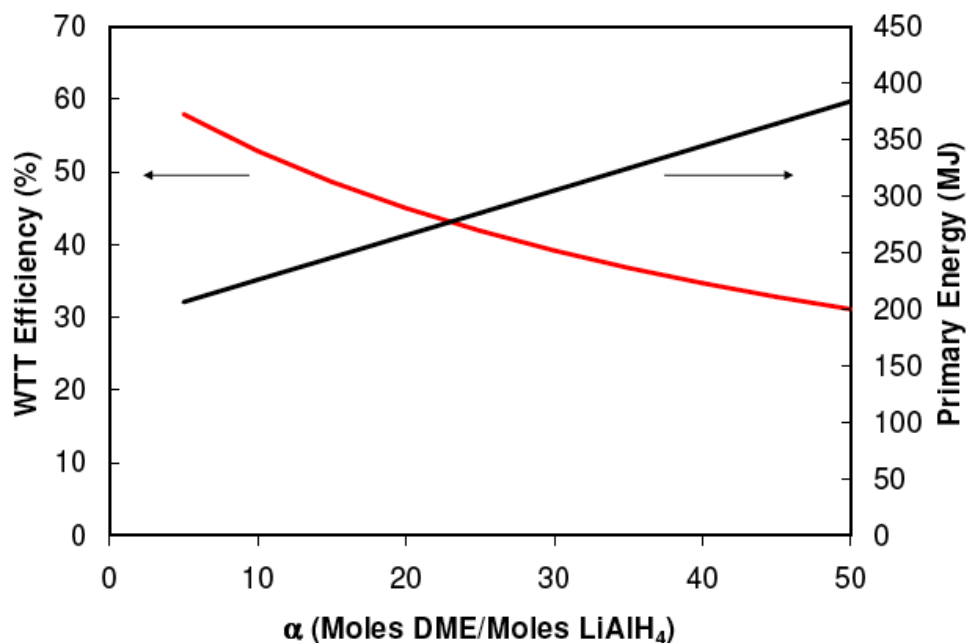
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Back-up Technical Slide 7

WTT energy efficiency approach 70% US DOE target for off-board recharging!

- Energy for compression of Me_2O and H_2 is ~ 1/5 that of H_2 production.
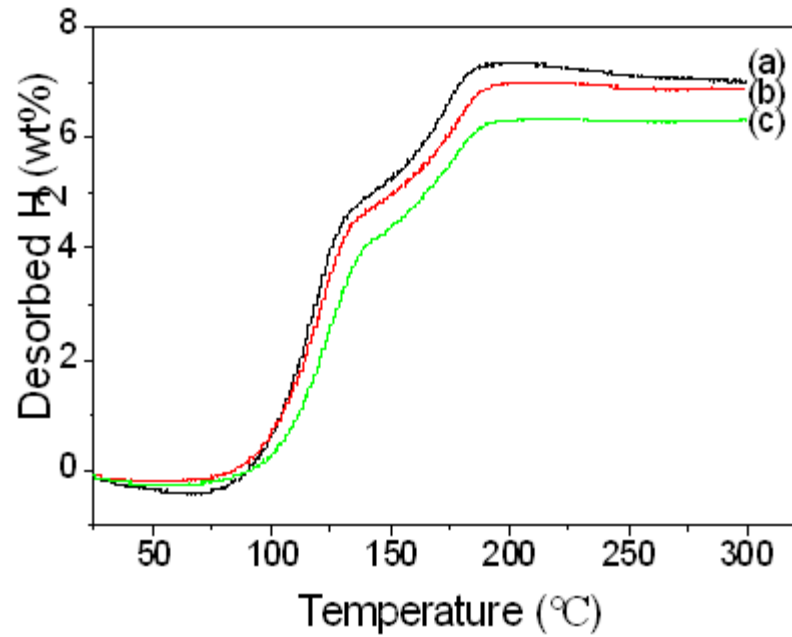- High ~ 5M solubility of $LiAlH_4$ in Me_2O is the key in high efficiency.

Primary Energy and WTT Efficiency

Left axis: WTT Efficiency (%), 0 to 70
Right axis: Primary Energy (MJ), 0 to 450
X-axis: α (Moles DME/Moles $LiAlH_4$), 0 to 50

Back-up Technical Slide 8

Ti-doped LiAlH$_4$ shows a drop in capacity over several cycles due to formation of Ti$_x$Al$_{1-x}$ phase.

Cycle performance of hydrogenatedLiH/Al/TiCl$_3$ (1:1:0.005). (a) Cycle 1; (b) Cycle 2; (c) Cycle-3.

Back-up Technical Slide 9

MAS ^{11}B NMR

> XRD not generally used due the highly amorphous nature of boranes and bororhydrides.

> MAS ^{11}B NMR spectroscopy allows detection and differentiation of all the boron containing species that are present.

MAS ^{11}B NMR MgB_2 + 2 mol % additive hydrogenated under 950 bar at 400 °C
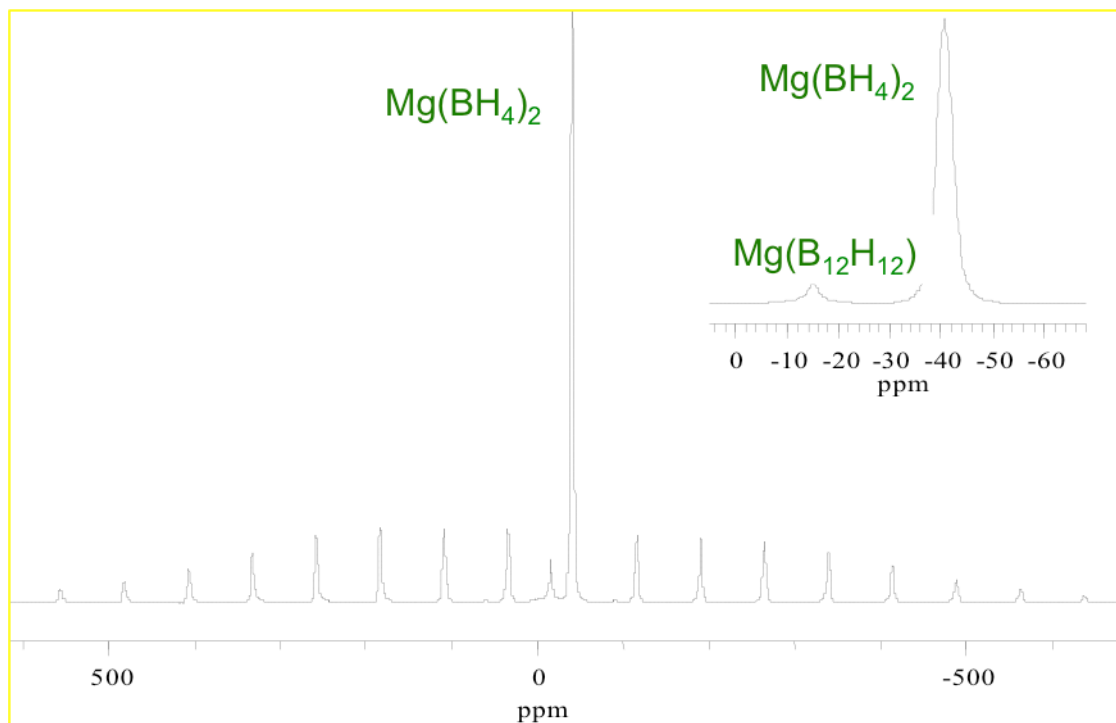
> Full Hydrogenation of MgB_2 beyond $MgB_{12}H_{12}$ to $Mg(BH_4)_2$
> One major boron containing product is observed.
> Chemical shift of -41 ppm: $Mg(BH_4)_2$.
> Minor signal observed for $MgB_{12}H_{12}$, at -24 ppm, represents < 5% of product mixture.
> Not clear if the catalyzed reaction pathway is the same as the uncatalyzed pathway.

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Back-up Technical Slide 10

Major products (mol %) formed in decomposition of $Mg(BH_4)_2$ determined from ^{11}B NMR

d/ppm	Species	300 1C	350 1C	400 1C
5	$B(OH)_4^-$	86	87	83
−15.2	$(B_{12}H_{12})^{2-}$	0.4	1.5	4.5
−29.2	$(B_{10}H_{10})^{2-}$	0.8	0.2	0.0
−30.3	$(B_3H_8)^-$	12.6	9.0	6.5

• Boric is acid is major species observed in the ^{11}B NMR.
  $\Rightarrow$ the major products are arachno- and nido- boranes.
• Concentration of the triborane increases lower temperatures.
  $\Rightarrow$ First step in the decomposition of $Mg(BH_4)_2$ involves the formation of $Mg(B_3H_8)_2$.

M. Chong, A. Karkamkar, T. Autrey. S. Jalisatgi, S. Orimo, C.M. Jensen; *Chem. Commun.* **2011**, *37*, 1330.

Mechanism of the Build-up of the Increasing Higher B_nH_{n+x} Species

Metal ion assisted BH condensation pathway
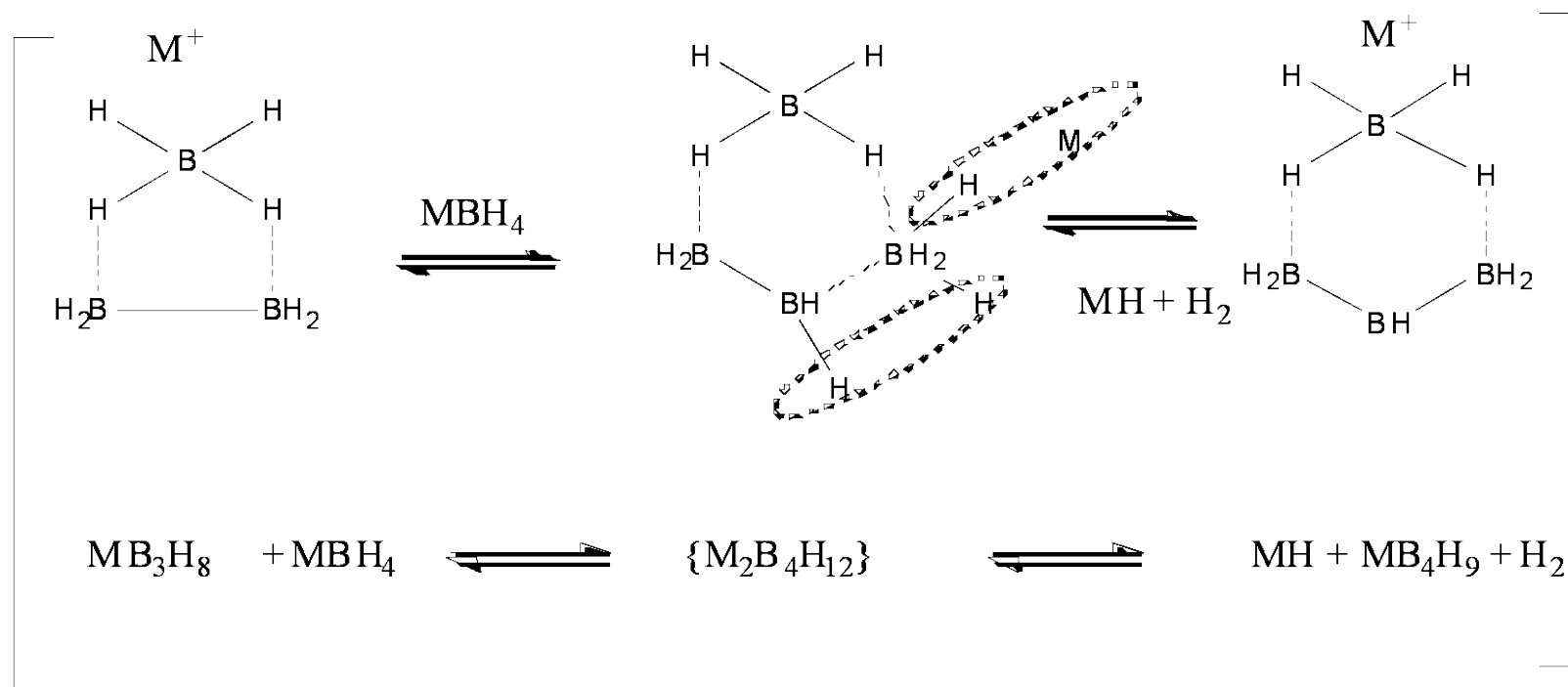
$$MB_3H_8 + MBH_4 \rightleftharpoons \{M_2B_4H_{12}\} \rightleftharpoons MH + MB_4H_9 + H_2$$

M. Chong, A. Karkamkar, T. Autrey. S. Jalisatgi, S. Orimo, C.M. Jensen; *Chem. Commun.* **2011**, *37*, 1330.

Back-up Technical Slide 12

	wt% H theory	wt% H exp	T_D (°C)	level of diborane
$LiSc(BH_4)_4$	14.6	3.5	175, 260	ppm
$NaSc(BH_4)_4$	12.8	1.0	170, 225	ppm
$KSc(BH_4)_4$	11.3	1.0	190, 240	ppm
$Na_2[Mn(BH_4)_4]$	6.9	2.9	120	50:1 H_2:B_2H_6 due to
$Mn(BH_4)_2$				contamination