

Fundamental Studies of Advanced, High-Capacity Reversible Metal Hydrides

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of HAWAII®
MĀNOA



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Overview

Timeline

- Start Date: March 2005
- End Date: September 2010
- 73% complete

Budget

- Total project funding:
\$2,945,058
 - DOE share: \$2,235,173
 - Contractor share: \$609,885
- Funding received in FY08:
\$477,587
- Funding for FY09: \$357,587

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
- R. Bowman; Jet Propulsion Laboratory
- R. Cantelli; University of Rome
- B. Hauback, M. Sorby; Institute for Energy Technology
- H. Hagmann, R. Cerny; University of Geneva
- S-J. Hwang, C. Ahn; California Institute of Technology
- 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
- I. Robertson; University of Illinois
- E. Ronnebro; Sandia National Laboratory
- T. Udovic; NIST
- J. Reilly, J. Graetz; Brookhaven National Laboratory
- S. Srinivasan; University of South Florida
- J. Vajo, P. Liu; HRL

Objectives and Relevance

Development of a new class of reversible complexes that have the potential to meet the DOE 2010 kinetic and system gravimetric storage capacity targets.

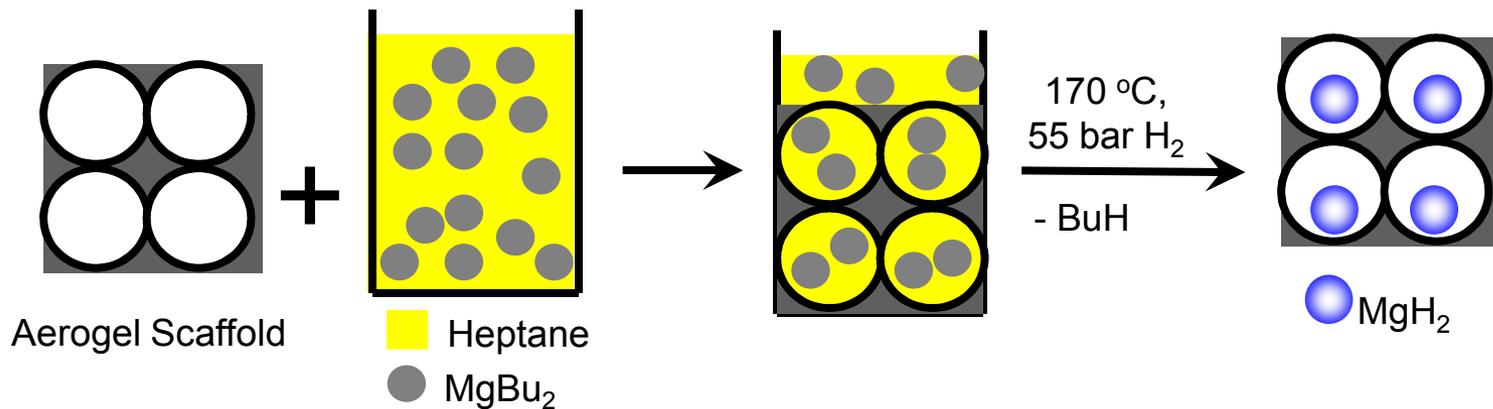
Current investigations include:

- Al and Mg nano-confined carbon aerogels
- Borohydrides that can be reversibly dehydrogenated at low temperatures
- Development of a method for the hydrogenation of Al to alane, AlH_3 and/or LiH/Al to LiAlH_4 at moderate pressures in unconventional solvents.

Approach

Nano-confined Al and Mg in Carbon Aerogels

- Low temperature homogenous organometallic approach to incorporation of Al and Mg into carbon aerogels results in high loadings of clean surface, MgH_2 without degradation of nano-porous scaffold.



- Determine the effects of nano-confinement on the kinetics and thermodynamics of the dehydrogenation of MgH_2 .

Approach

Group I and II 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.
 - Very low levels of diborane are evolved during the dehydrogenation of some ionic complexes such as $\text{Na}_2\text{Zr}(\text{BH}_4)_6$.
- > Altered thermodynamic stability might allow reversibility.

Catalytically Enhanced $\text{Mg}(\text{BH}_4)_2$

- > $\text{Mg}(\text{BH}_4)_2$ evolves **14 wt %** H_2 upon dehydrogenation.
- > Ball-milled mixtures of MgB_2 and the catalytic additive undergoes **full** hydrogenation to $\text{Mg}(\text{BH}_4)_2$ at 400 °C and 900 atm.

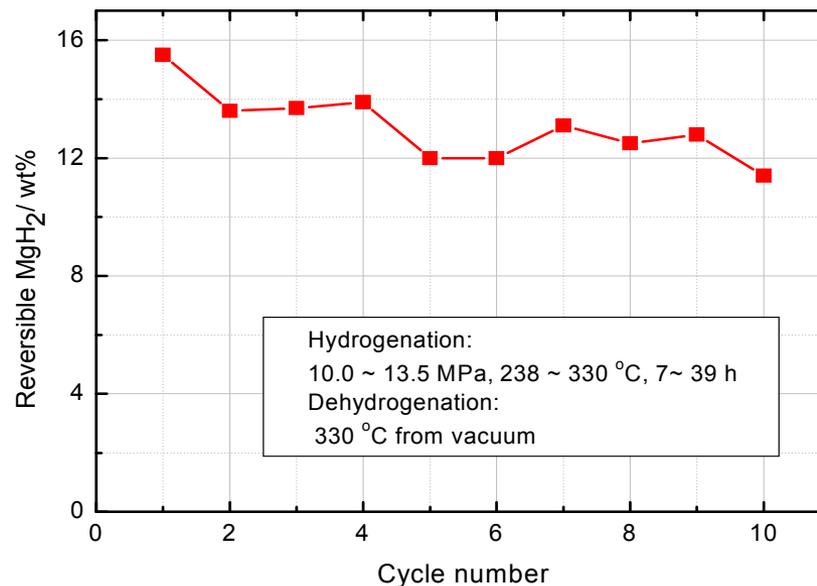
Approach

Hydrogenation of Alane in Non-conventional Solvents

- > Dehydrogenation of AlH_3 to Al gives 10 wt % H_2
- > Controllable dehydrogenation at acceptable rates below 100 °C with additives.
- > Low ($< 10 \text{ kJ/mol H}_2$) ΔH_{dehy} mandates very high pressures for charging at ambient or higher temperatures.
- > Supercritical fluids (SCFs) have different physical properties than gases and liquids and no phase boundary between liquid and gas phases, \Rightarrow reduce the requisite pressures hydrogenations (ie hydrogenations of organic molecules and NaH/Al to NaAlH_4).
- > Explore hydrogenation of Al to AlH_3 ; Al/MgH_2 to $\text{Mg}(\text{AlH}_4)_2$; and LiH/Al to LiAlH_4 in SCFs.
- > Explore hydrogenation of Al to AlH_3 ; Al/MgH_2 to $\text{Mg}(\text{AlH}_4)_2$; and LiH/Al to LiAlH_4 in liquefied gases such as dimethyl ether which can form adducts during synthesis but are easily eliminated due to their high volatility.

Technical Accomplishments and Progress Nano-Confined Mg in Carbon Aerogels

- > Previous Results - High, (9-16 wt %) MgH_2 loadings of carbon aerogel without host degradation are obtained using the organometallic method.
- > TEM imaging, EDS, and XRD confirmed MgH_2 incorporation in aerogel.
- > Higher MgH_2 loadings can be obtained with materials that have larger pore sizes.



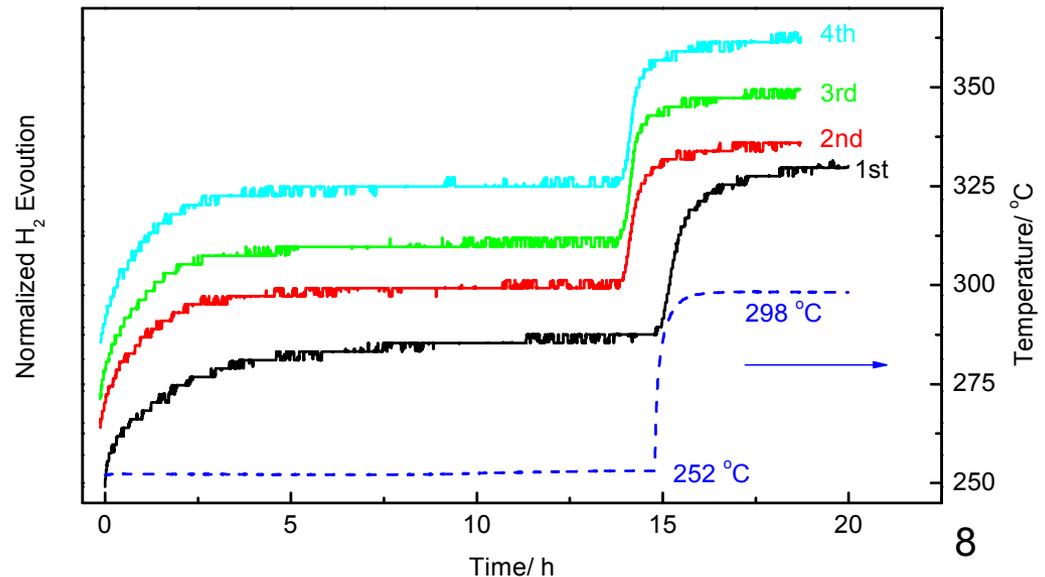
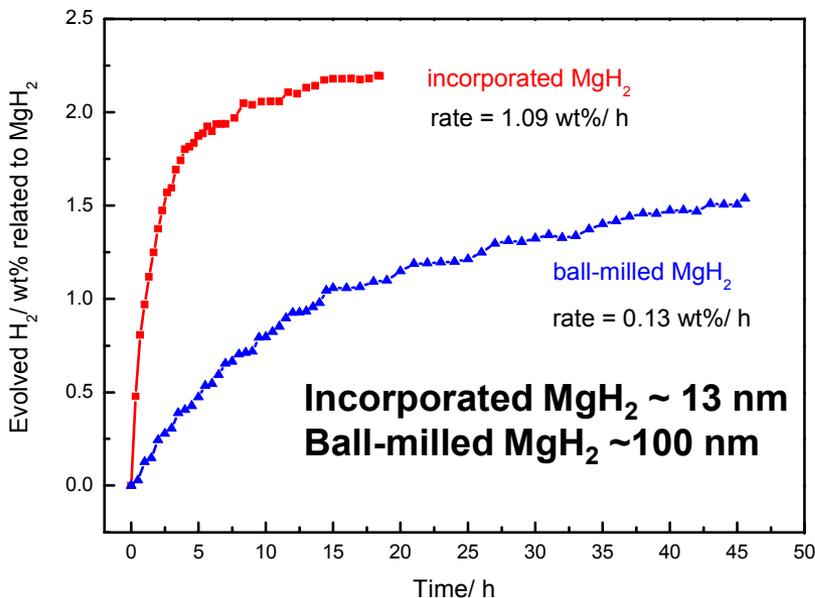
Scaffold	Activated Carbon	13 nm Aerogel	25 nm Aerogel
Average Pore Size (nm)	< 2	13	25
Pore Volume (cm ³ /g)	0.58	0.80	1.38
MgH_2 Loading (wt%)	4.2	17	23

Technical Accomplishments and Progress

Nano-Confined Mg in Carbon Aerogels

Kinetic Studies

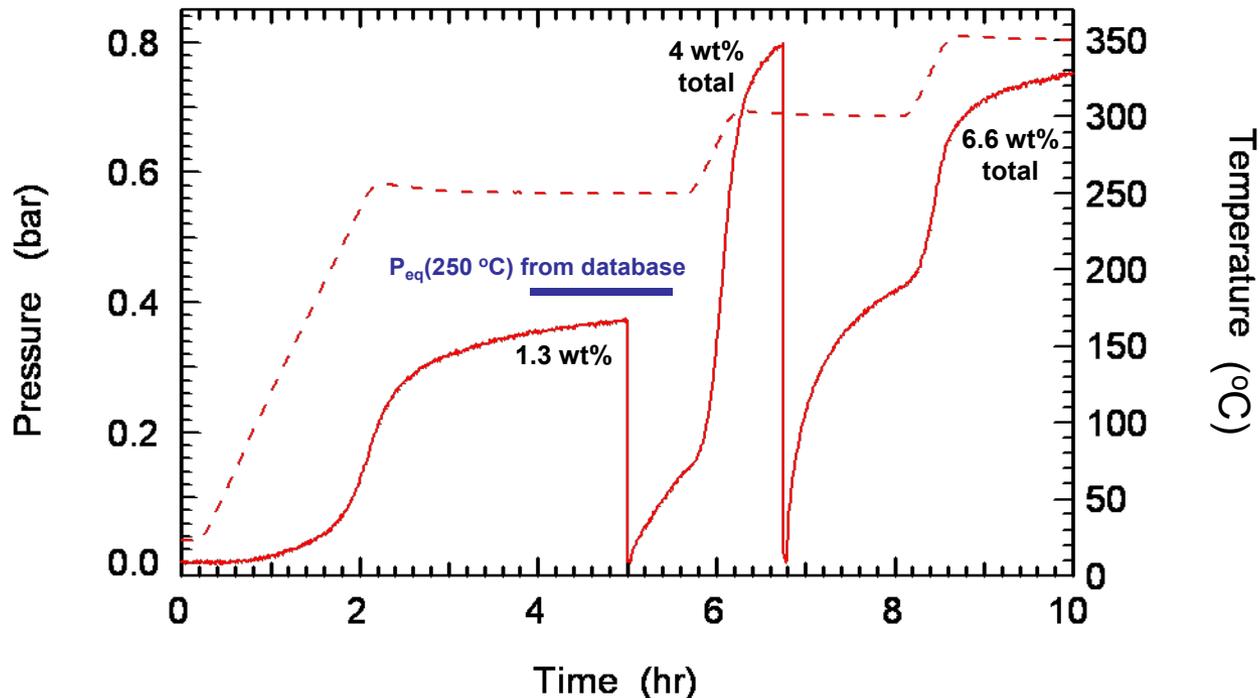
- > The rate of dehydrogenation at 252 °C is >5 times faster than the initial rate found for ball milled MgH_2 and comparable to those found for nano-confined MgH_2 in carbon aerogels by alternative methods at HRL.
- > The rate of dehydrogenation remains approximately the same over 4 cycles of dehydrogenation/rehydrogenation.



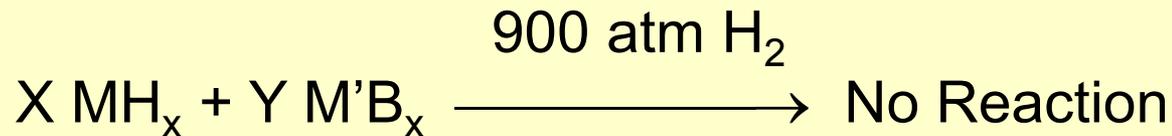
Technical Accomplishments and Progress

Nano-Confined Mg in Carbon Aerogels

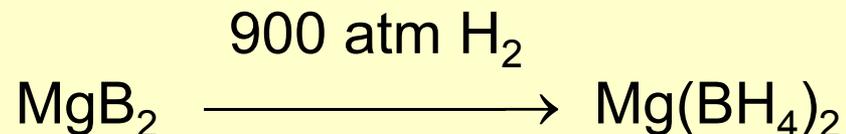
- > Equilibrium pressure of MgH_2 nano-confined in 13 nm aerogel at 250 °C agrees with database value for bulk MgH_2 .
- ⇒ no change in thermodynamics.



Technical Accomplishments and Progress Anionic Borohydrides



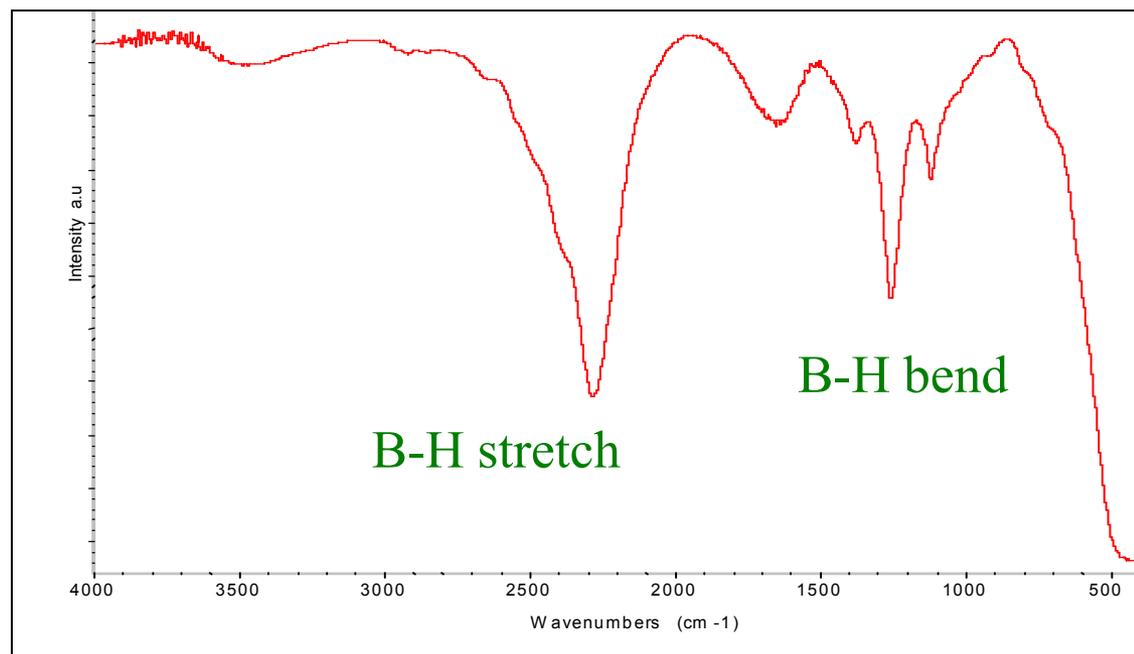
M = Group I or II metal, M' = Transition metal



Rönnebro, Jensen, and Severa US patent application 61/093,937

Technical Accomplishments and Progress Anionic Borohydrides

Infrared spectrum of MgB_2 + 2 mol % additive hydrogenated under 950 bar at 400 °C

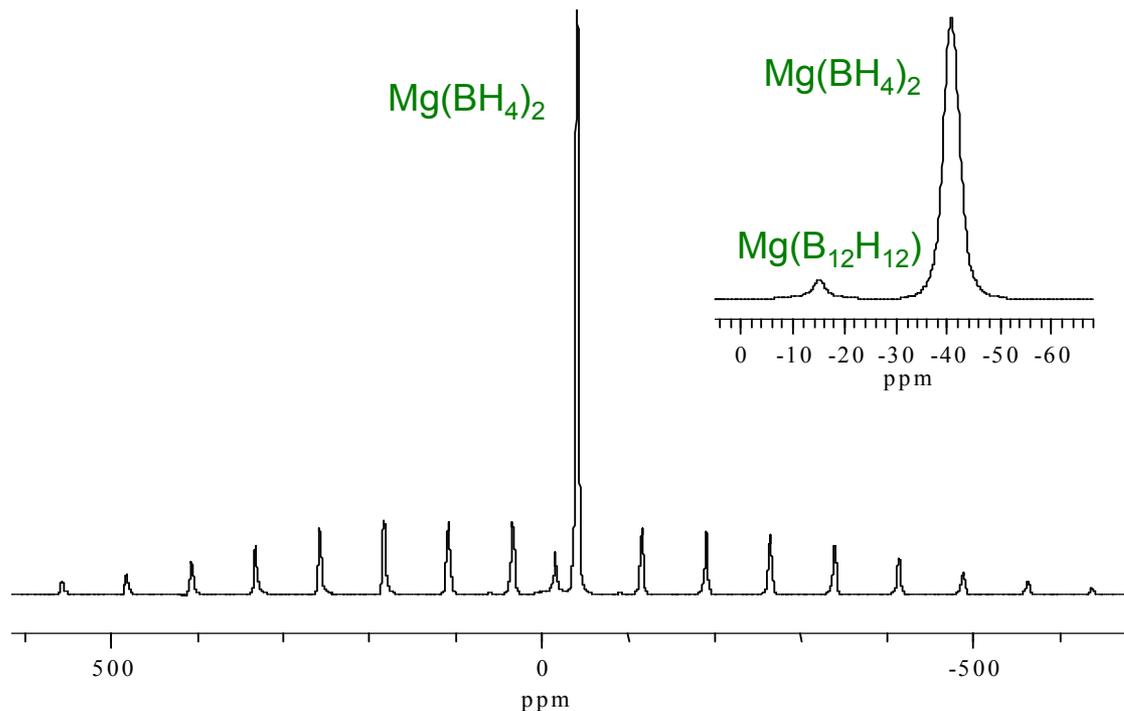


Absorptions for B-H stretching and bending modes at characteristic frequencies indicate formation of $\text{Mg}(\text{BH}_4)_2$

Technical Accomplishments and Progress Anionic Borohydrides

MAS ^{11}B NMR

- > XRD not generally used due to the highly amorphous nature of boranes and borohydrides.
- > MAS ^{11}B NMR spectroscopy allows detection and differentiation of all the boron containing species that are present.

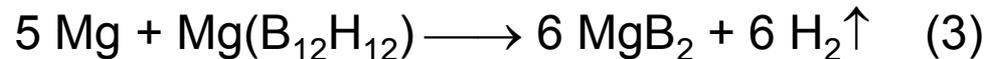
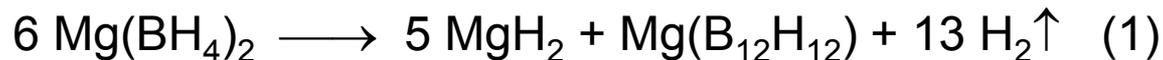


MAS ^{11}B NMR MgB_2 + 2 mol % additive hydrogenated under 950 bar at 400 °C

- > Full Hydrogenation of MgB_2 beyond $\text{MgB}_{12}\text{H}_{12}$ to $\text{Mg}(\text{BH}_4)_2$
- > One major boron containing product is observed.
- > Chemical shift of -41 ppm: $\text{Mg}(\text{BH}_4)_2$.
- > Minor signal observed for $\text{MgB}_{12}\text{H}_{12}$, at -24 ppm, represents < 5% of product mixture.
- > Not clear if the catalyzed reaction pathway is the same as the uncatalyzed pathway.

Technical Accomplishments and Progress Anionic Borohydrides

- > Previous studies headed by researchers at GE within the MHCoe showed $\text{Mg}(\text{BH}_4)_2$ undergoes stepwise dehydrogenation to give MgB_2 while releasing 14.8 wt% H_2 .



- > The ΔH_{dehyd} of 42 kJ/mole suggests that it should be possible to hydrogenate MgB_2 to $\text{Mg}(\text{BH}_4)_2$ at moderate temperatures and pressures.
- > Experimentally it has not proven possible to reverse the processes in equations 2 and 3 at temperatures lower than 500 °C.
- > It has been suggested that this is due to the high kinetic stabilization of $\text{MgB}_{12}\text{H}_{12}$.

Does the catalytic pathway circumvent the $\text{MgB}_{12}\text{H}_{12}$ “sink”?

Technical Accomplishments and Progress Hydrogenation in Non-conventional Solvents

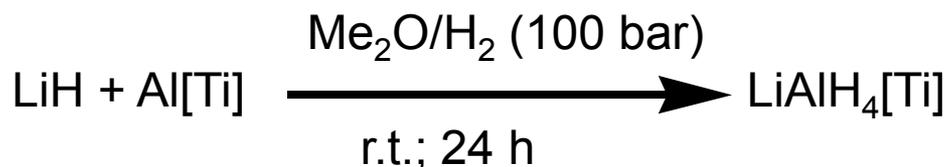
- > Hydrogenation in alternative SCFs, catalysts, and/or activation of Al have yet to produce higher yields of alane than the ~5% obtained in Me₂O/H₂ that was reported last year.
- > Focus turned to LiAlH₄

BACKGROUND

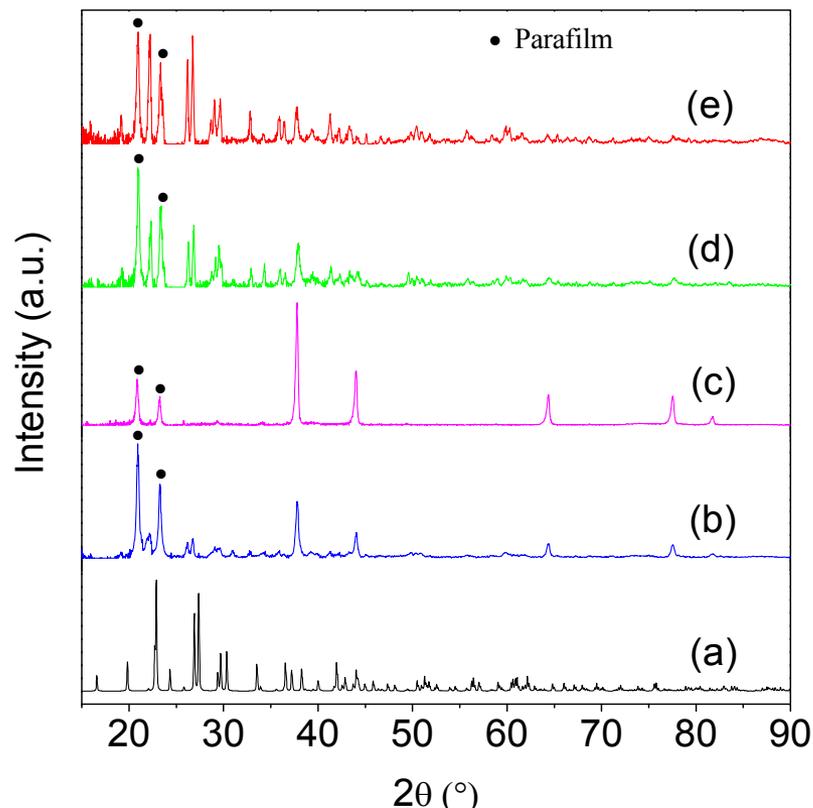
- Like sodium alanate, stepwise dehydrogenation, BUT first step is **exo**thermic
 - Step 1:** $3\text{LiAlH}_4 \rightarrow \text{Li}_3\text{AlH}_6 + 2\text{Al} + 3\text{H}_2 \quad \Delta H = -30 \text{ kJ}$
 - Step 2:** $\text{Li}_3\text{AlH}_6 \rightarrow 3\text{LiH} + \text{Al} + 1.5\text{H}_2 \quad \Delta H = 38 \text{ kJ}$
- 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 °C for 6 h. Incompatible with Ti catalyst since dehydrogenation occurs at the temperature required for removal of THF.

Technical Accomplishments and Progress Hydrogenation in Non-conventional Solvents

Using liquid dimethyl ether as solvent eliminates adduct removal issues



- Solvent vents immediately with H₂
- Fully charged Ti-doped LiAlH₄ obtained
- Very low levels of Ti can be used (~500 ppm)



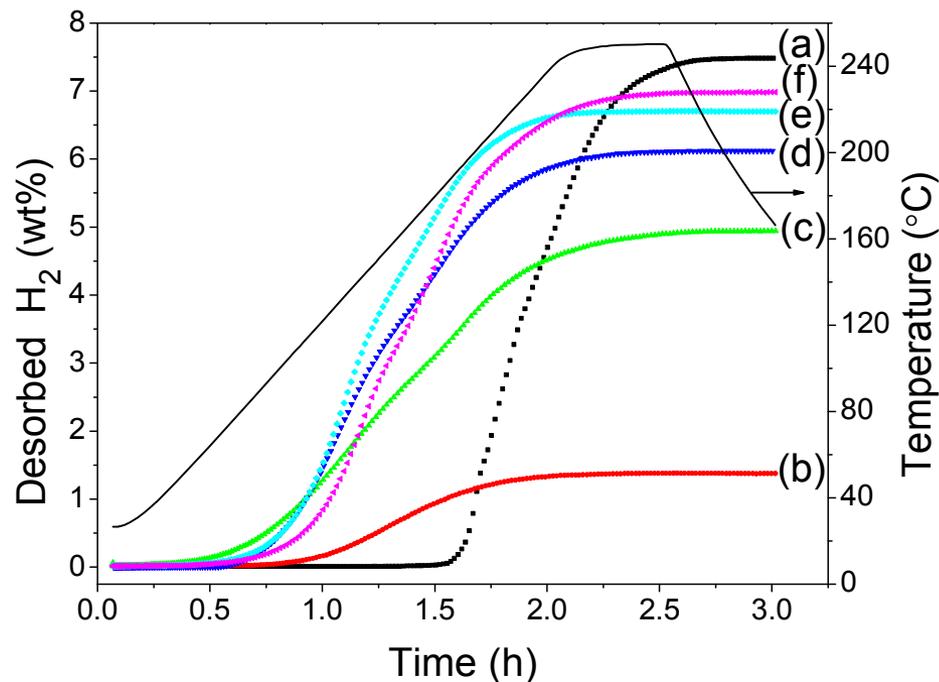
XRD patterns of LiAlH₄ samples: (a) ICDD ref; (b) ball milled (2.0 mol% TiCl₃); (c) fully de-H (0.2 mol% TiCl₃); (d) re-H (2.0 mol% TiCl₃); (e) re-H (0.2 mol% TiCl₃).

Technical Accomplishments and Progress Hydrogenation in Non-conventional Solvents

H₂ Desorption from Ti-Doped LiAlH₄

- 0.5-0.2 mol% Ti optimal
- ~7 wt% H at 80-180 °C
- Excellent kinetics

Xi. Liu, G.S. McGrady, H. W. Langmi, C.M. Jensen; *J. Am. Chem. Soc.* **2009**, in press.



TPD plots for LiAlH₄ samples: (a) as-received; (b) milled with 2.0 mol% TiCl₃; (c) re-H (2.0 mol% TiCl₃); (d) re-H (1.0 mol% TiCl₃); (e) re-H (0.5 mol% TiCl₃); and (f) re-H (0.2 mol% TiCl₃).

Technical Accomplishments and Progress Hydrogenation in Non-conventional Solvents

Why does dimethyl ether work so well?

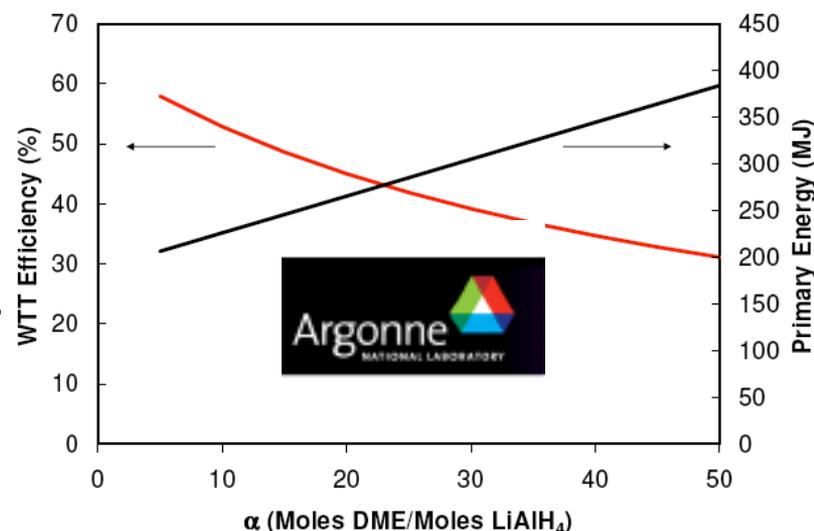
- Me₂O is both more polar and more volatile than Et₂O
- Forms strong complex with Li⁺
- Evaporates quickly at r.t.

What is Wells-to-Wheels efficiency of a hydrogen storage system based on re-hydrogenation in liquid Me₂O?

- Energy for compression of Me₂O and H₂ is ~ 1/5 that of H₂ production.
- High ~ 5M solubility of LiAlH₄ in Me₂O pushes the WWT to 60%.

Solvent	b.p./°C	D/debye
Me ₂ O	-24	1.30
Et ₂ O	+35	1.15
THF	+66	1.63

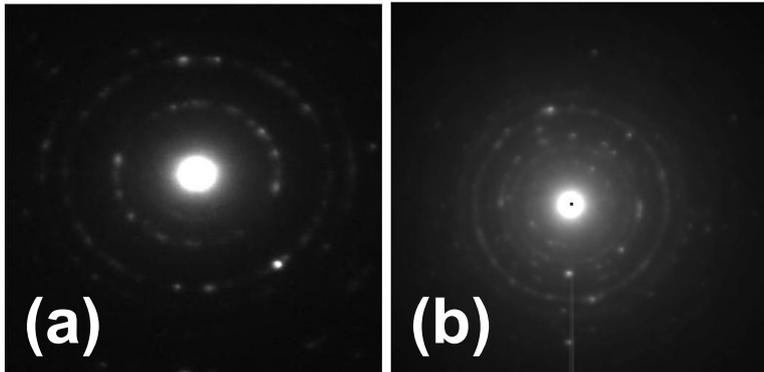
Primary Energy and WTT Efficiency



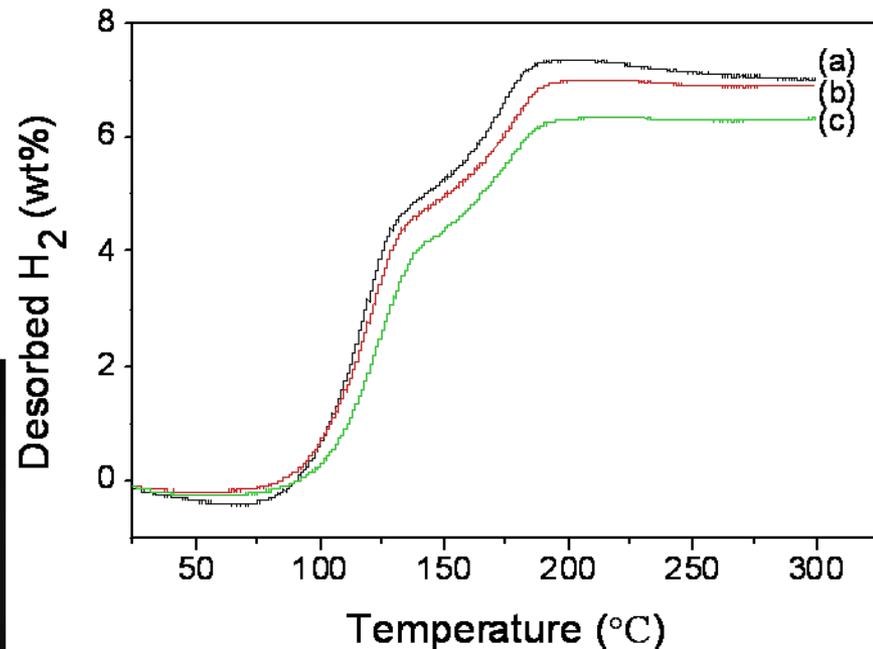
Technical Accomplishments and Progress Hydrogenation in Non-conventional Solvents

Cycling Studies

Material shows a drop in capacity over several cycles due to formation of Ti_xAl_{1-x} phase.



TEM-EDAX patterns of $LiAlH_4/0.5$ mol% Ti: (a) after first de-H; (b) after second de-H indicates Ti clustering and formation of Ti_xAl_{1-x} phases.



Cycle performance of hydrogenated $LiH/Al/TiCl_3$ (1:1:0.005). (a) Cycle-1; (b) Cycle-2; (c) Cycle-3.

Future Work

Nano-confined Mg in Carbon Aerogels

- Determine dehydrogenation and re-hydrogenation kinetics of aerogels loaded with both MgH_2 and Ti-catalyst.
- Preparation of nano-confined MgH_2 from the hydrogenation of dimethyl magnesium intercalated aerogels to increase loadings.
- Determine PCT isotherms to determine effect of nano-confinement on the ΔH_{dehyd} of MgH_2 .

Anionic Borohydrides

- Explore variations in reactions conditions to improve yield of lower pressure hydrogenation of MgB_2 to $\text{Mg}(\text{BH}_4)_2$.
- Continue the studies of the catalyzed and un-catalyzed hydrogenation of MgB_2 utilizing MAS ^{11}B NMR to determine mechanism in order to improve kinetics.

Hydrogenation in Nonconventional Solvents

- Maximize the extended cycling capacity of Ti-doped LiAlH_4 through variation of the dopant concentration and recharging conditions in liquid Me_2O .
- Continue exploration of improving levels of hydrogenation of alane using alternative SCFs and variety of initiators/catalysts.
- Explore SCF synthesis of $\text{Mg}(\text{AlH}_4)_2$.
- Further evaluation of WTT efficiency of the $\text{DME}/\text{LiAlH}_4$ system to be examined in collaboration with Argonne National Lab.

Summary

Nano-confined Mg in Carbon Aerogels

- High, (9-16 wt %) MgH_2 loadings of carbon aerogel without host degradation are obtained using the organometallic method.
- Higher MgH_2 loadings obtained with materials that have larger pore sizes.
- Nano-confinement of MgH_2 improves kinetics but does not appear to effect ΔH_{dehyd} .

Anionic Borohydrides

- Full hydrogenation of MgB_2 to $\text{Mg}(\text{BH}_4)_2$ can be achieved in the presence of a catalyst at pressures as low as 120 atm.
- MAS ^{11}B NMR spectroscopy confirms that the product of the hydrogenation is $\text{Mg}(\text{BH}_4)_2$ and provides tool to probe the whether $\text{MgB}_{12}\text{H}_{12}$ is an intermediate in the catalyzed and uncatalyzed hydrogenation pathways.

...

Hydrogenation in Non-conventional Solvents

- Fully charged, Ti-doped LiAlH_4 can be obtained in major yields from the direct hydrogenation of Ti-doped LiH/Al in liquefied dimethyl ether at room temperature in 100 bar of $\text{Me}_2\text{O}/\text{H}_2$.
- WTT efficiency of a LiAlH_4 based hydrogen system utilizing liquid DME as a re-hydrogenation medium approaches the 60% target.

Collaborations

Nano-confined Mg in Carbon Aerogels

C. Ahn; California Institute of Technology (Academic): Characterization by TEM imaging.

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

Anionic Borohydrides and Complex Hydrides

E. Akiba, K. Sakaki; AIST, Tsukuba (Government): Characterization by positron annihilation.

T. Autrey; PNNL (Government): Synthesis.

R. Cantelli; University of Rome (Academic): Characterization by anelastic spectroscopy.

H. Haggmann, 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 NMR spectroscopy.

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

Collaborations

Anionic Borohydrides and Complex Hydrides

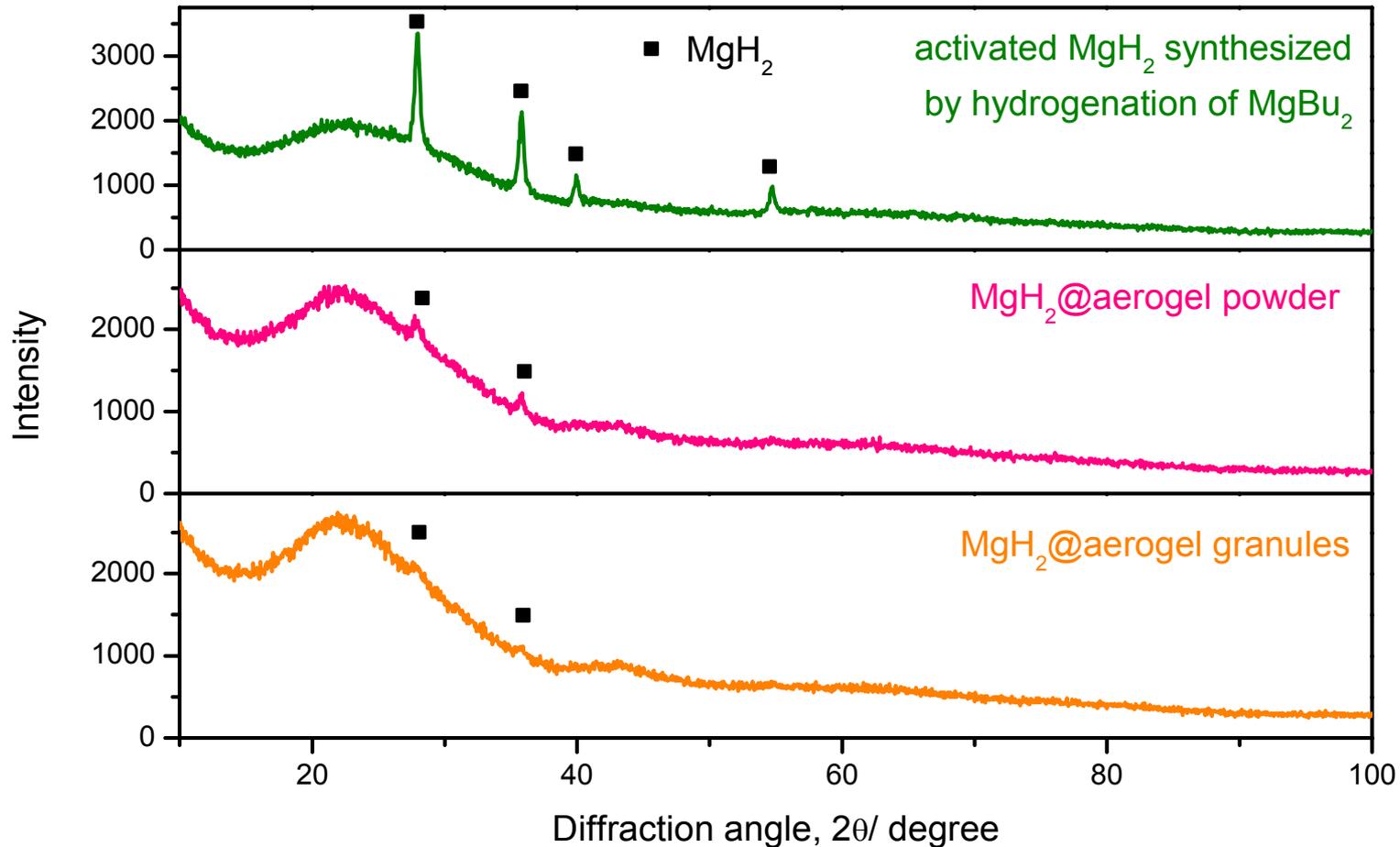
- R. Kuboto; KEK, Tsukuba (Government): characterization by muon spin resonance.
- S. Orimo; Tohoku University (Academic): Characterization by DSC and XRD. Synthesis.
- I. Robertson; University of Illinois (Academic): Characterization by TEM.
- E. Ronnebro; SNL (now with PNNL), Government: High pressure studies.
- S. Srinivasan; University of South Florida (Academic): Characterization by DSC.
- T. Udovic; NIST (Government) Characterization by Inelastic Neutron Scattering.

Hydrogenation in Non-conventional Solvents

- S. McGrady; University of New Brunswick (Academic): SCF reaction system.

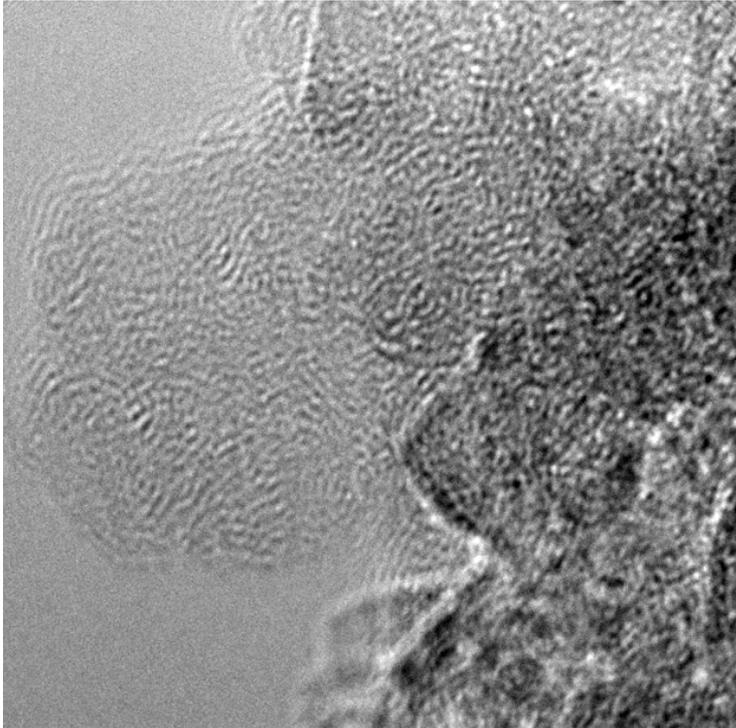
Supplemental Slides

Characterization: XRD

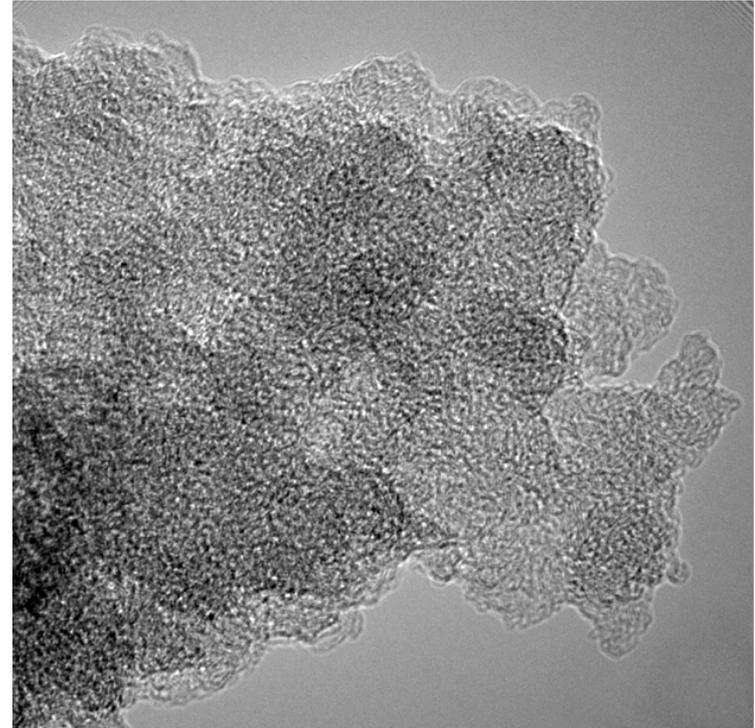


Weak MgH_2 X-ray diffraction peaks indicate nanosized MgH_2 was incorporated in the 13 nm aerogel scaffold without contamination or graphite.

Characterization: TEM



5nm

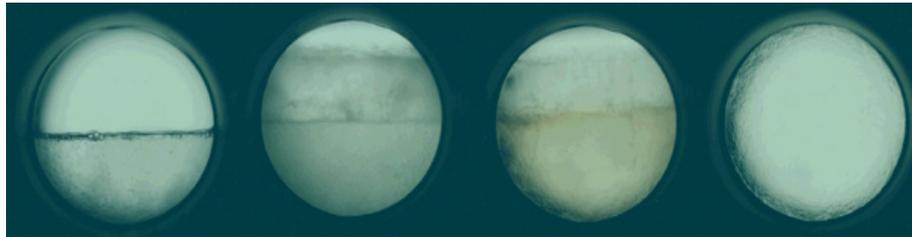


10 nm

Carbon appears to have remained as 13 nm aerogel clusters. No Mg particles were observed, indicative of nanosized MgH_2 incorporation. EDS shows that the Mg concentration varied from 1.4 to 4.5 wt%, indicative of nanosized MgH_2 incorporation.

Hydrogenation of Al in Supercritical Media

Phase boundary between liquid and gas phases disappears in supercritical fluids (SCFs)....



7:1 mixture of liquid CO₂ and H₂ gas converts to a homogenous super critical fluid at 30°C and 10 atm

SCFs have different physical properties than gases and liquids.... as a result, the thermodynamics and kinetics of chemical processes can be modified when run in SCF solutions.

Hydrogenation of Al in Supercritical Fluids

TITANIUM DOPED AL IN 2:1 SUPERCRITICAL CO₂-H₂

- > Hydrogenation of titanium-doped aluminum in 2:1 supercritical CO₂-H₂.
 - Higher levels of hydrogenation.
 - Isothermal desorption at 110 °C indicates 3% of the Al was hydrogenated.
 - GC analysis: Hydrogen evolved only from the Al subjected to the SCF.
 - Low-level hydrogenation occurs on the surface of the powder.
- > Confirmed by MAS ²⁷Al NMR:

