Reversible Hydrogen Storage Materials: Structure, Chemistry, and Electronic Structure

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Project ID # STP_36_Robertson

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Overview

Timeline

- Project start date
  - March 2005
- Project end date
  - February 2010
    - Application to extend project has been made.
- Percent complete 80%

Barriers

- Issues addressed
  - A: Understanding chemical response to hydrogen
  - B: Understanding system weight and particle packing
  - C: Theory support to address critical issues blocking experimental progress.

Budget

- Total project funding
  - $1 600 000 committed
- FY08: $285K ($25k supplement)
- FY09: $100K

Partners

- Project lead: Sandia National Laboratory & MHCoE
- HRL Laboratory, NIST
- Brookhaven National Laboratory
- Pittsburg and Georgia Tech

Objectives/Relevance

- Illinois' main purpose within the MHCoE is
  - Advance the understanding of the microstructural and modeling characteristics of complex hydrides, helping with selection and downselection.
  - Provide feedback and knowledge to partners within MHCoE.
  - Provide more reliable theoretical methods to assess H-storage materials, including key issues affecting materials under study.
  - Help identify downselects, via experimental and theoretical characterization.
  - Help achievement of specific targets and milestones.
  - Provide characterization expertise to other MHCoE and other critical DoE programs, as suggested by Program Officers.
- Some Illinois recent impacts
  - Developed 3-D reconstructions and visualization of system and catalyst locale.
  - In MgH_2 and MOF systems, complete understanding dispersion of materials.
  - Identified new structures that compete in $CaB_6/CaH_2/Ca(BH_4)_2$ systems, showing amorphous intermediate phases are probable in Ca-based systems (*downselected by SNL*).
  - Identified mechanisms for poisoning $LiBH_4$ systems (*downselected by SNL*).
  - Developed quantitative DFT-based theories for complex hydride free energies.
  - Developing new surface capabilities to answer fundamental catalysis questions.

Plan & Approach

80 % complete

- Task 1: Experimental investigation of MHCoE partner materials
  - Investigate and model microstructural and chemical changes in hydrogen storage materials

70 % complete

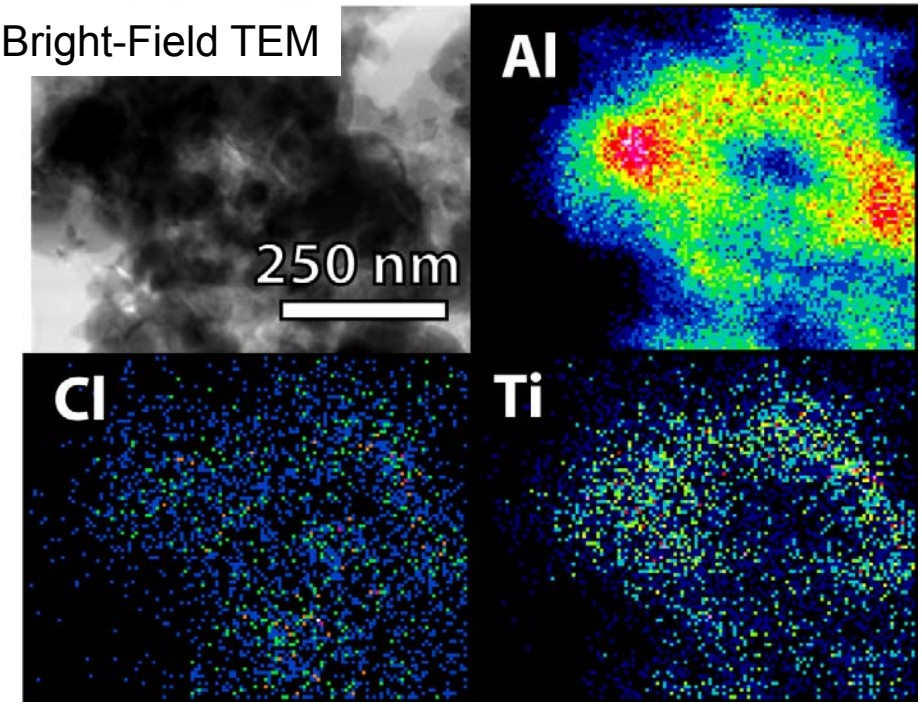
- Task 2: Incorporation and development of new models
  - Development of new theoretical models and incorporation into MHCoE work

Visualizing Location of Ti catalyst in AlH_3 precursor

with Brookhaven National Labs

$AlCl_3$ + 2 mol % $TiCl_3$ + $LiAlH_4$ → $Al_{Ti}H_3$ + heat -> **Al_{Ti} precursor** + H_2

Energy Dispersive Spectroscopy elemental maps of Al_{Ti} precursor doped with 2 mol % $TiCl_3$ before liquid conversion to a reversible material



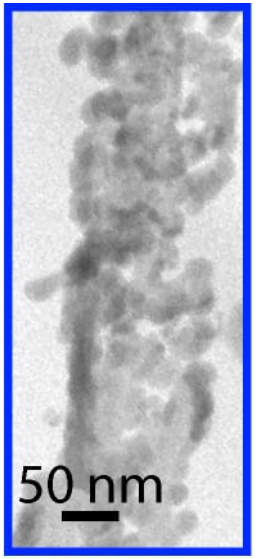
- Extended FY08 analysis to find quantitatively loss of catalyst.
- Quantitative analysis of Ti level (with oxygen excluded) yields 1.2 at% Ti.
- **Data indicates a 50% loss of Ti during precursor steps.**

✓ In alane precursor, the Ti "catalyst" is well mixed, and perhaps dissolved, before TEDA conversion to reversible material, with 50% Ti catalyst loss.

Graetz *et al*, *J Phys Chem C*, 2007

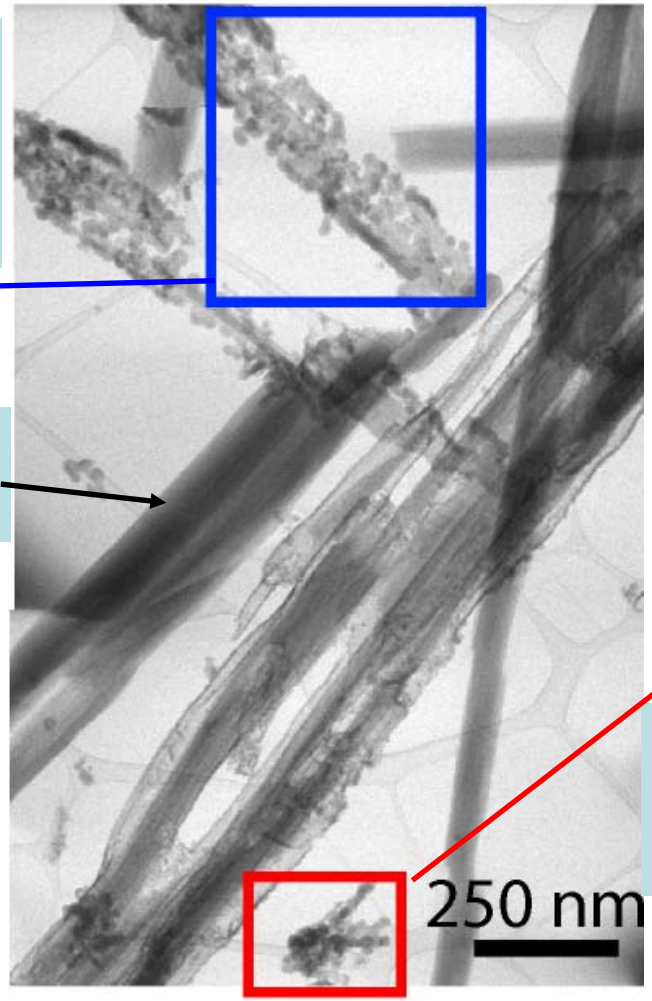
Morphology of Hydrided AlH_3-TEDA

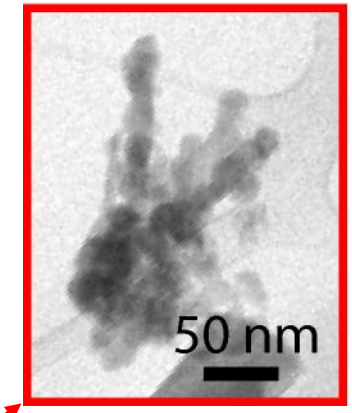
Al_{Ti} precursor + TEDA + H_2 ← THF → **AlH_3-TEDA**



Al clusters decorating triethyl diamine (TEDA) crystal

AlH_3-TEDA, uncoated





Isolated aggregate of ~25 nm Al crystals identified by **EDS**.

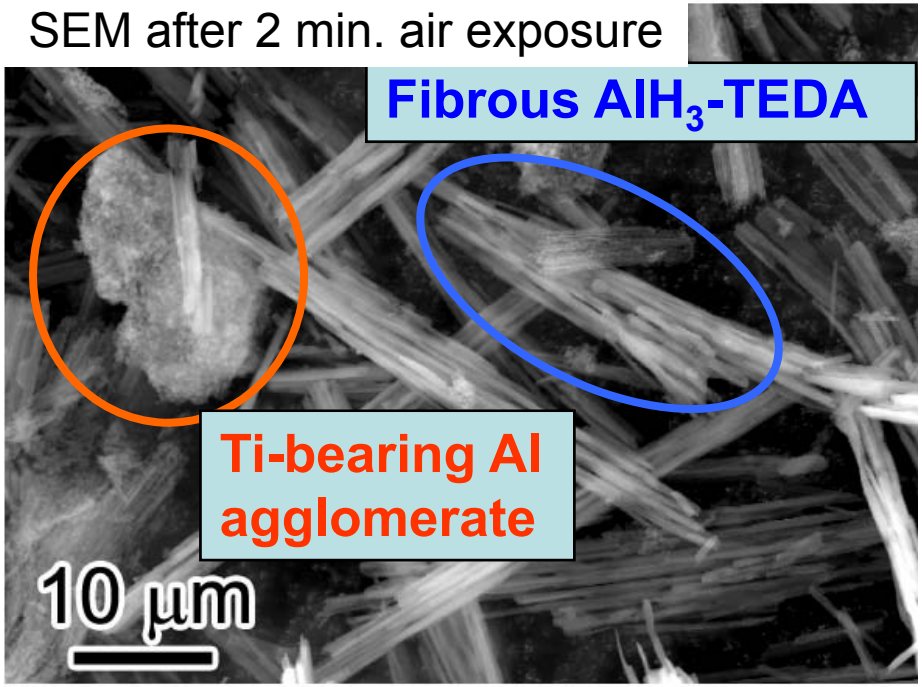
✓ AlH_3-TEDA adduct, showing large AlH_3-TEDA crystals and associated Al clusters.

Graetz *et al*, *J Phys Chem C*, 2007
Graham *et al*, in preparation

Morphology and Composition of Hydrided AlH_3-TEDA with 0.1 at % $TiCl_3$

Al_{Ti} precursor + TEDA + H_2 ←THF→ **AlH_3-TEDA**

SEM after 2 min. air exposure

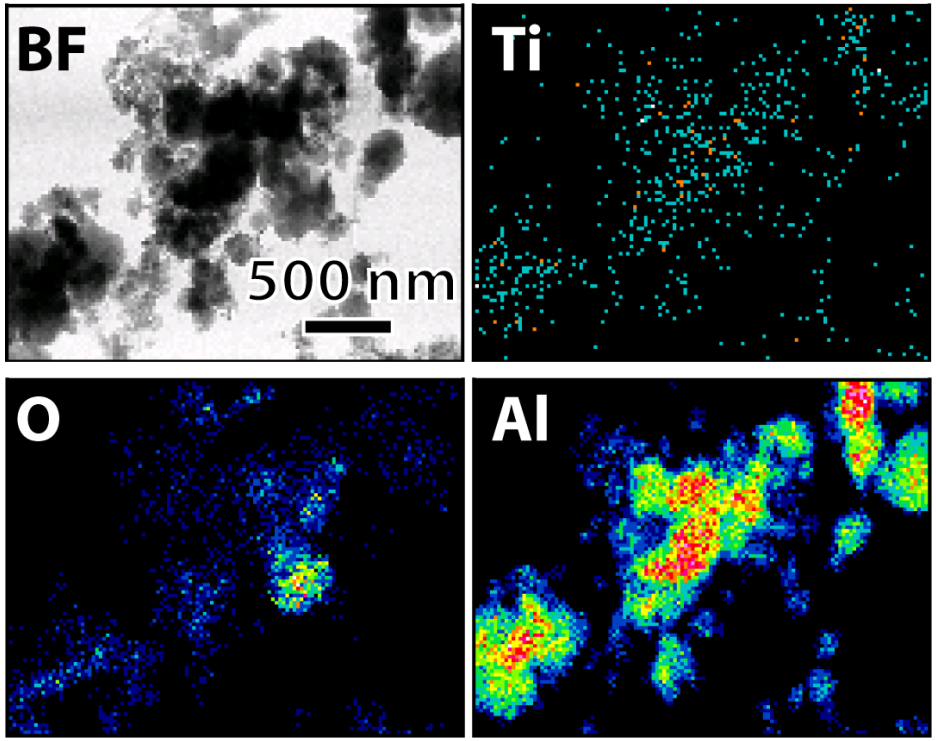


- Fibrous AlH_3-TEDA
  - –Mainly C and N detected.
  - –No Ti, placing an upper bound on the Ti level of ~0.25 at% (the estimated detection limit).
- Al agglomerates
  - – With 0.1 at% added in total, we observe ~0.4 at% Ti (highly localized, concentrated Ti).

- ✓ Demonstrates that TEDA scavenges AlH_3 formed on precursor surface.
- ✓ Ti level in the agglomerates increased from the added level of 0.1 at% to 0.4 at%. Consistent with suggested selectivity of AlH_3 by TEDA.
- ✓ Agglomerates suggest TEDA conversion is incomplete in this reaction.

Graham *et al*, in preparation

Morphology and Composition of Dehydrided AlH_3-TEDA with 2.0 at% $TiCl_3$



- TEM imaging – no air exposure.
- Ti map shows no evidence for local accumulation and redistribution within aggregates of Al crystals.

- Estimated detection limit 0.2 at% Ti – started at 2.0 at%.
- Dehydrided material is lacking appreciable Ti.

✓ Evidence of Ti in precursor-like Al crystals at the *n*m scale is at the detection limit.

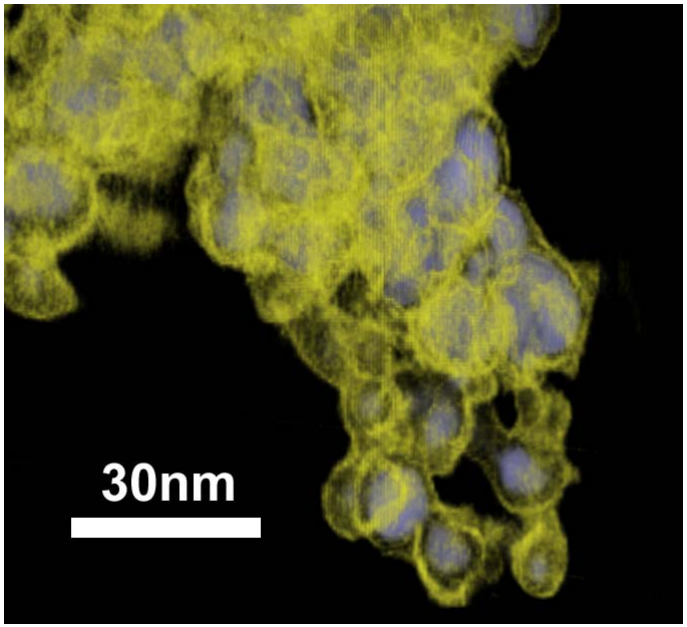
✓ Even at this level, this constitutes a loss of ~90% of the added Ti, suggesting that very low levels of Ti are needed to catalyze the reaction.

Graham *et al*, in preparation

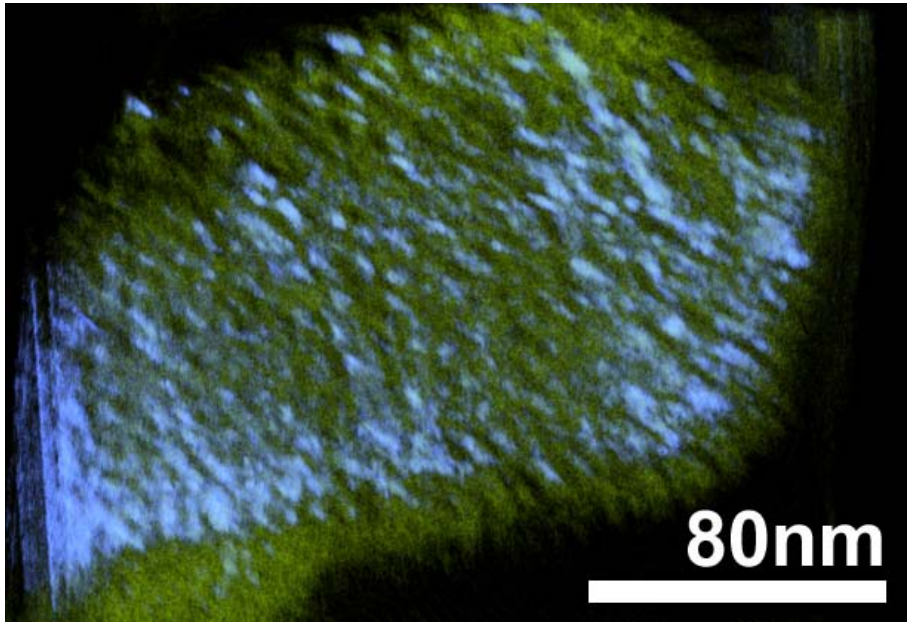
Determining Particle Locations within Frameworks

In collaboration with SNL/Berkeley effort

- Electron Tomography has been used to determine Ag particle locations within a metal organic framework (MOF).
- Using Illinois capabilities to support non-MHCoE DoE activities.



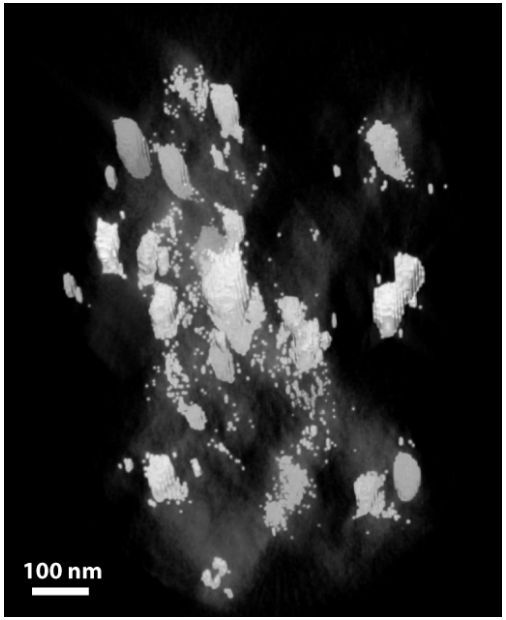
Cured Ag-MOF system
– **Ag particles** (blue)
– inside **framework** (yellow).



Uncured Ag-MOF system
– **Ag particles** (including "**nanowires**" (**blue**)
– inside **framework** (yellow + blue = green).

✓ Electron Tomography enables identification of small particle location in MOFs – see movie of three-dimensional reconstructed images.

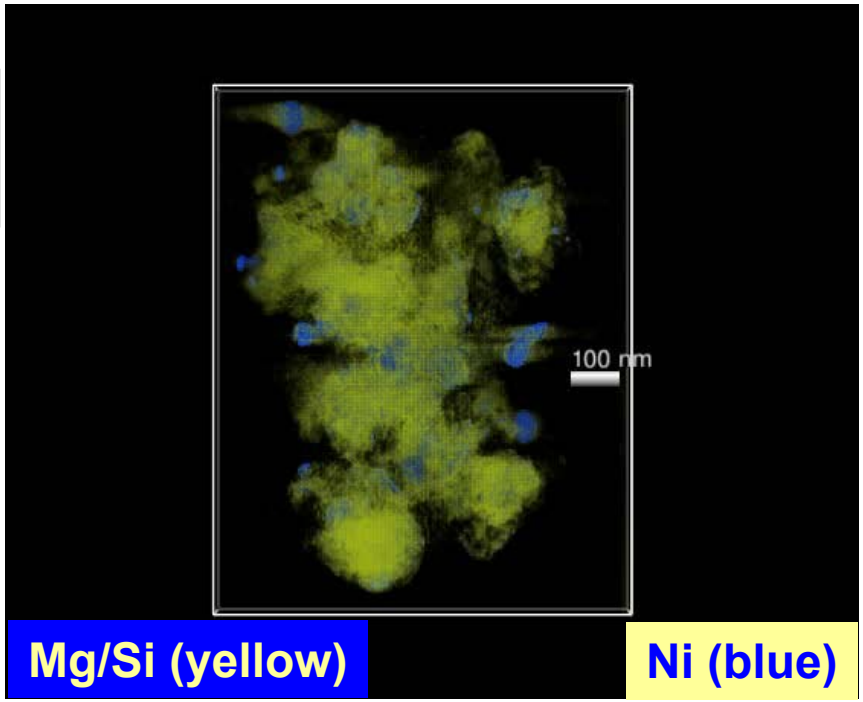
Using electron tomography to visualize catalyst dispersal – Ni in MgH_2/Si



Individual frames used to reconstruct a 3-D image – see movie at poster!

3-D tomographic reconstruction of MgH_2 + Si + 0.05 Ni milled for 5 hrs.

Mg/Si matrix faintly visible.
Elongation of spherical particles artifact of limited microscope tilt.



- ✓ Tomography indicates catalyst dispersal – Ni (blue) not well dispersed and remains chemically distinct from the matrix Mg/Si (yellow).
  Raises important question of how it functions as a catalyst.
- ✓ Dissolution of elements by ball milling not guaranteed:
  - Need fundamental understanding of how H interacts with surface and how this is influenced by the introduction of "catalysts".
  - Effectiveness of ball milling to improve kinetics needs to be answered.

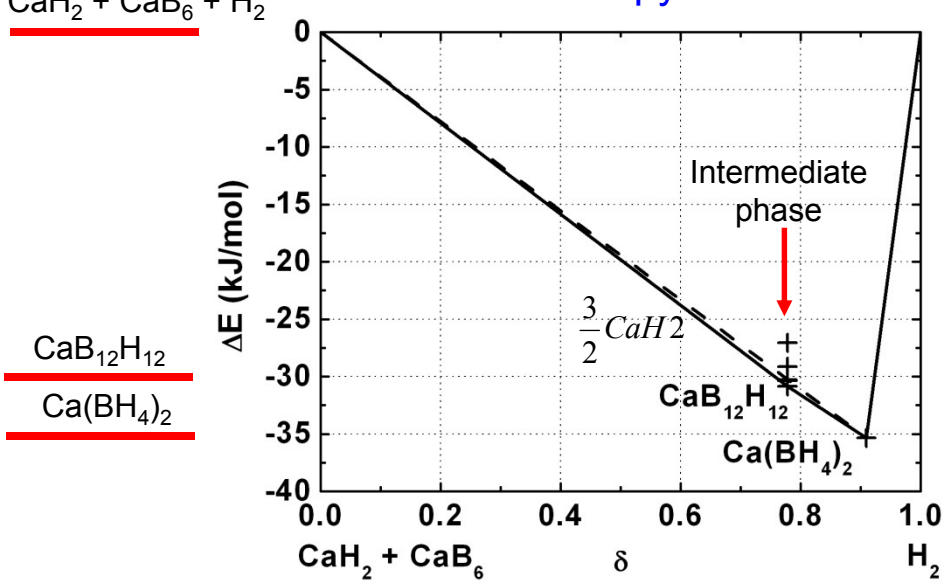
Understanding the lack of reversibility of CaB_6/CaH_2 system: newly predicted competing structures

Sandia proposed reaction

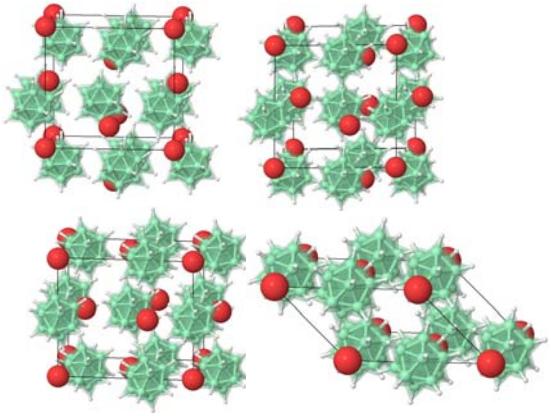
$$\frac{2}{3}CaH_2+\frac{1}{3}CaB_6+\frac{10}{3}H_2 \xleftrightarrow{step-1} Ca(BH_4)_2 \xleftrightarrow{step-2} \frac{5}{6}CaH_2+\frac{1}{6}CaB_{12}H_{12}+\frac{13}{6}H_2$$

(~ 5 wt % H_2)

Formation Enthalpy for Reaction



Some Illinois newly identified $CaB_{12}H_{12}$ structures

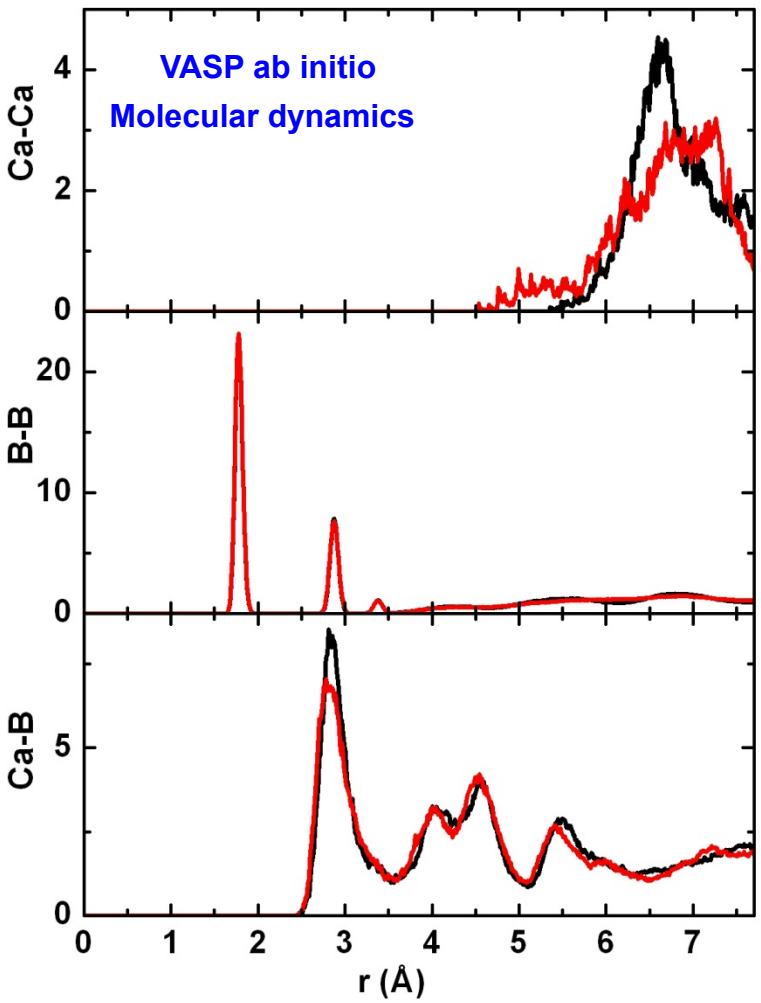


- ✓ Recent NMR results suggest a $B_{12}H_{12}$ environment in Li-based system.
- ✓ Illinois DFT results shows $CaB_{12}H_{12}$ is stable intermediate, but (unlike Li-based systems) with many competing symmetry-distinct phases! Amorphous intermediate phase!
- ✓ Illinois formation energy shows 0.86 (CaH_2 + CaB_6 + H_2) + 0.14 $Ca(BH_4)_2$ = $CaB_{12}H_{12}$.
- ✓ **Irreversible CaB_6/CaH_2 system (except at high T and P) but $Ca(BH_4)_2$ reversible to amorphous $CaB_{12}H_{12}$ (possibly mixed phase) matching observation.**

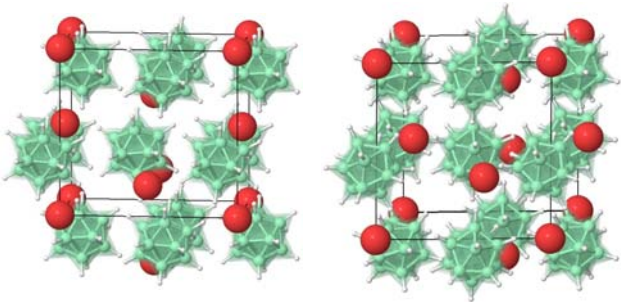
Reported in Illinois paper: Wang, Graham *et al*, submitted
NMR: Hwang *et al.*, J Phys Chem C 112 (2008) 3169

Structural aspects of $CaB_{12}H_{12}$ intermediate phases: Illinois newly identified theoretical structures

g(r) pair correlations at 300 K



- **Example g(r) for two low-E $CaB_{12}H_{12}$ structures** (cells depicted below) identified theoretically by Illinois, with several others also found.

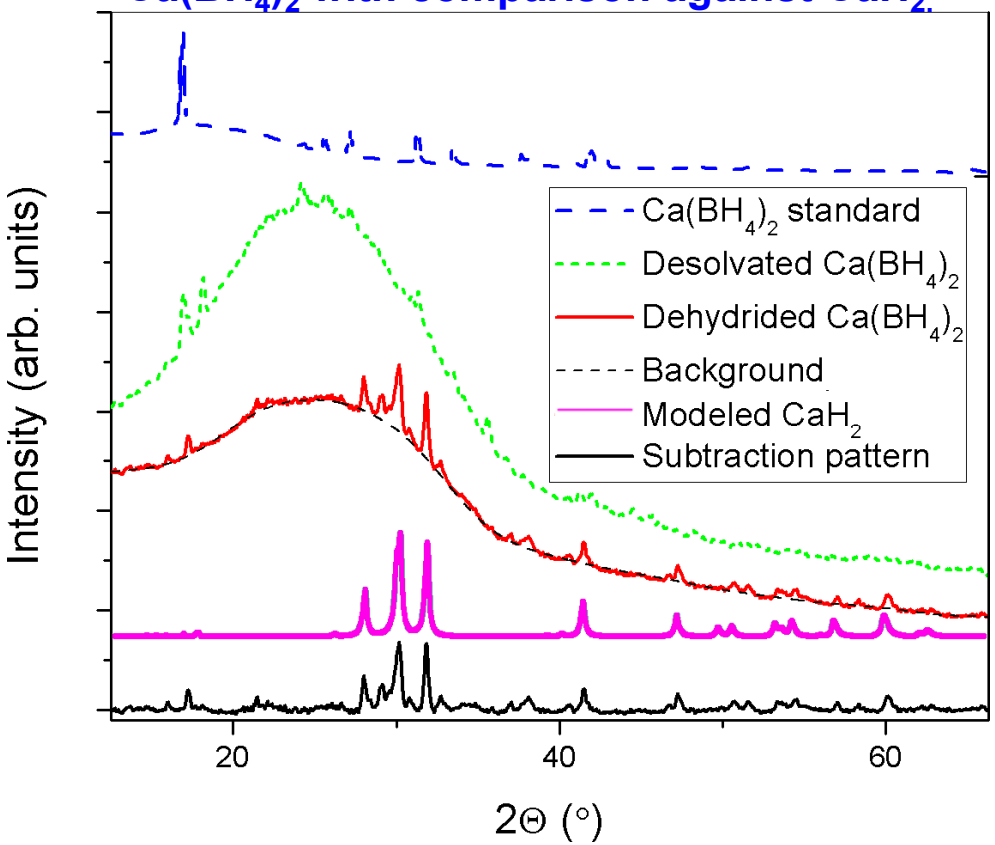


- ✓ DFT g(r)'s shows that several symmetry-distinct $CaB_{12}H_{12}$ phases are (meta)stable!
- ✓ Due to strong binding in *closo*-molecule ($B_{12}H_{12}$) , only Ca-Ca correlation changes with temperature.
- ✓ Even at 300 K the Ca-Ca distribution spans a few Angstroms, possibly leading to broad peak in XRD. (At 1000 K, the Ca move from cell-to-cell, see Karl Johnson *et al*. talk.)

Reported in Illinois paper: Wang, Graham *et al*, submitted

What phases are present in dehydrided $Ca(BH_4)_2$?

Illinois XRD of desolvated and dehydrided $Ca(BH_4)_2$ with comparison against CaH_2.



- CaH_2 seen in dehydrided $Ca(BH_4)_2$; compare modeled pattern with the subtraction pattern.
- No evidence for B-containing crystalline phases.
- Result is inconsistent with other CaB_6-based systems, but is consistent with proposed amorphous intermediate phase of $CaB_{12}H_{12}$.
- Sandia data was not available for comparison.

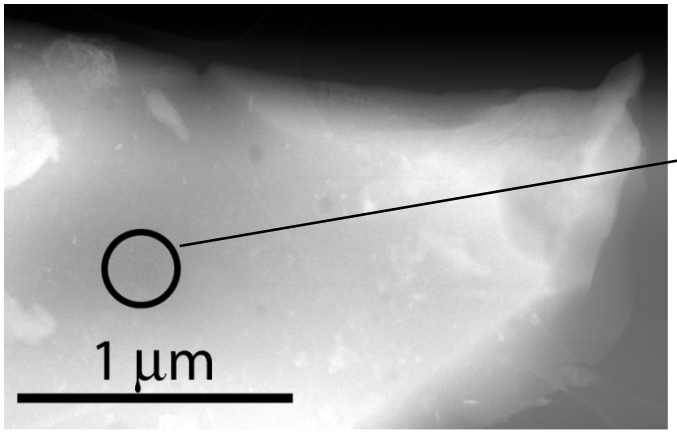
Proposed reaction : $Ca(BH_4)_2 \rightarrow CaB_{12}H_{12} + 5CaH_2 + H_2$ (~ 5 wt % H_2)

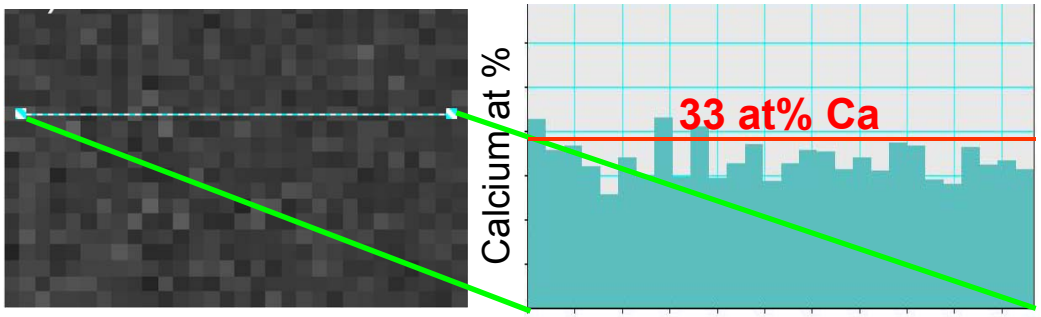
✓ XRD of dehydrided $Ca(BH_4)_2$ supports CaH_2 part of proposed reaction.

Compositional analysis of dehydrided $Ca(BH_4)_2$

Dark-field STEM of dehydrided $Ca(BH_4)_2$ showing the region analyzed with EELS

Proposed reaction:
$Ca(BH_4)_2 \rightarrow CaB_{12}H_{12} + 5CaH_2 + H_2$ (~ 5 wt % H_2)





Ca concentration from EELS spectrum image

Ignoring H (invisible in EELS), expected atomic compositions for proposed phases are:

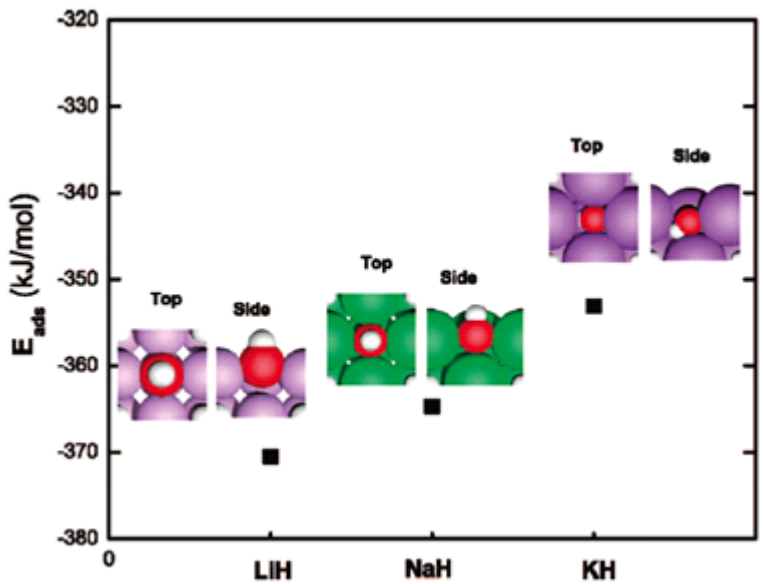
$Ca(BH_4)_2$ = **33 at% Ca**, 66 at% B $CaB_{12}H_{12}$ = 8 at% Ca, 92 at% B CaH_2 = 100% Ca

✓ Composition is the same as parent material $Ca(BH_4)_2$, which means there is no large scale (i.e., > 10 *nm*) elemental redistribution and no compositional evidence for the intermediate $CaB_{12}H_{12}$ phase.

Influences of surface reactions on complex hydride reversibility

Joint theory effort investigated surface reactivities of MH (M= Li, Na, K), products of alkali-metal hexahydride alanates, with H, O, H_2, O_2, and H_2O.

Joint with
Pittsburgh
GaTech
Illinois
Sandia NL



Example:

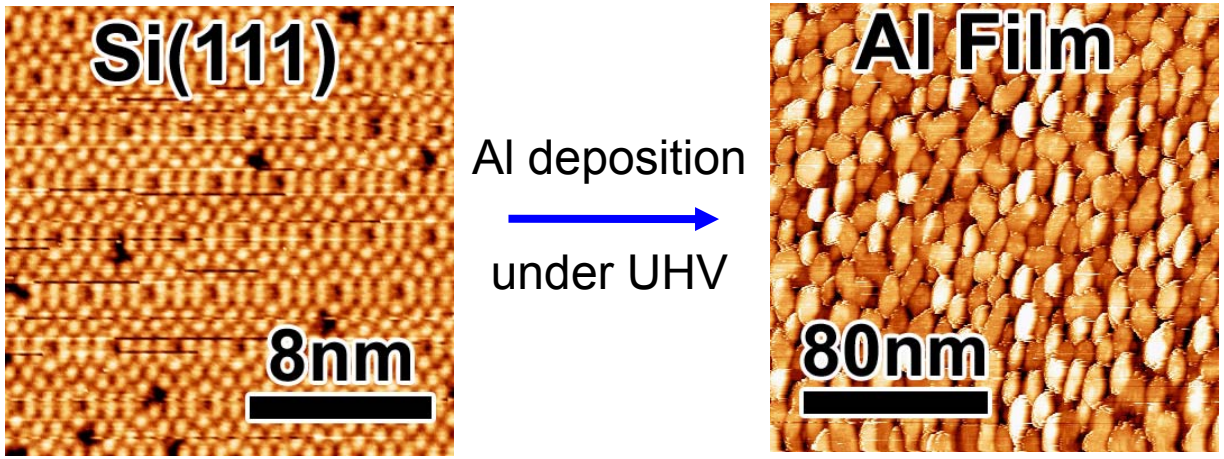
O_2 Adsorption energy for MH

- ✓ DFT results show that LiH has stronger binding to OH, and may contribute to observed differences in rehydriding.
- ✓ But, DFT-based theory also showed that a monolayer of OH forms in less than 10 *ms* for all alkali metals, which does not account for the observed differences in their ability to form M_3AlH_6 phase.
- ✓ We find that there is no substantial differences in MH surface reactivities (i.e., poisoning) that correlate with reversibility to M_3AlH_6 phase.

Reported in: Bing Dai, *et al*. J. Phys. Chem. C 112, 18270 (2008).

How hydrogen interacts with the surface?

- Existing work strongly suggests that how hydrogen interacts with pure and contaminated surfaces is crucial to understanding the fundamental processes of hydrogen uptake and release and impact of catalyst species.
  - Thin film of Al grown epitaxially on Si(111) substrate at Illinois.

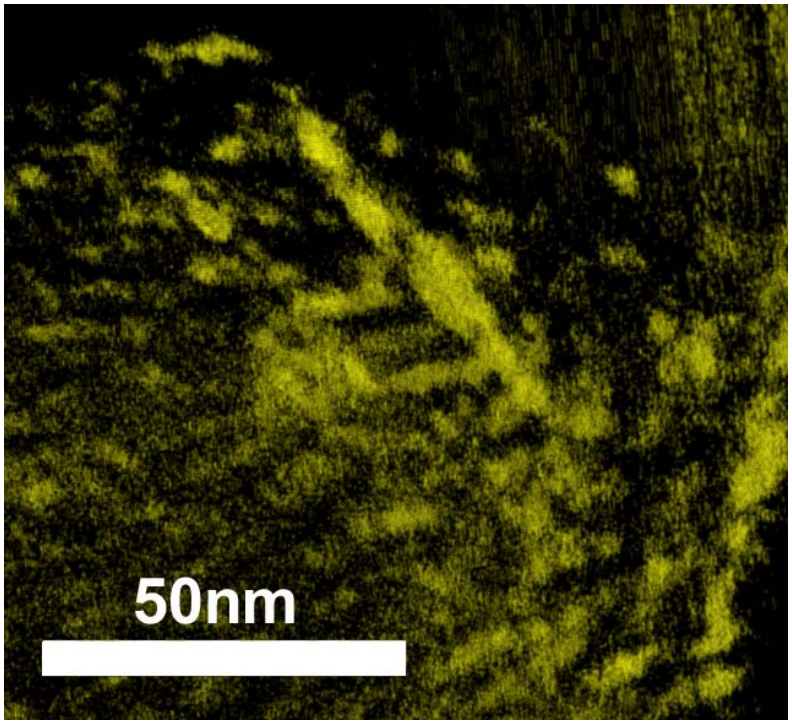


Si(111) with Al epitaxial layer chosen due to know growth conditions and similarity to other hydrogen-storage materials. (See, e.g., Hasan, et al. Vacuum 41 (1990) 1121.)

✓ Initial work: Made and characterized Al systems for use in examining effects of Ti and surface poisoning on the interaction with hydrogen

Collaborations in Center

- **Sandia NL**
  - Answered fundamental questions regarding $Ca(BH_4)_2$ systems.
  - Provided SNL/Berkley effort with some DFT MgH_2-cluster/C data.
  - Looking at size effects on melting of borohydrides, e.g. in aerogels.
- **HRL Laboratories**
  - Catalytic particles & tomography.
- **Brookhaven NL**
  - Introductory work on catalyzed AlH_3 systems.
- **Pittsburgh/GaTech/U. Miss. St. Louis**
  - From theory, addressed surface reactions on complex hydride reversibility.
  - Understanding nature of intermediate M-$CaB_{12}H_{12}$ phases (M= Mg, Ca, …).



Close-up of nanowire structure in Ag-MOF – submitted to *Nanoletters.*

Highlighting Illinois support of DoE partners external to MHCoE efforts.

Future Work - For FY09-10

- **Analysis of systems using spectrographic, surface, and tomographic capabilities of which we are an integral part**
  - Continue work on MOF systems (with SNL)
  - Complete thermodynamic work on $Ca(BH_4)_2$ but, due to downselect of materials, we will not pursue finding the most effective catalyst.
  - May explore theoretically the effect of catalyst on barriers and uptake.
  - Continue work with BNL on alane systems.
  - Complete Al/Ti surface study (with BNL).
  - Extend collaborations to Physisorption Center.

- **Modeling complex hydride systems –**
  - With SNL Identify materials not downselected to help improve properties.
  - Quantify size and confinement effects on Mg/MgH_2 supported nanoparticles and their adsorption properties (w/ SNL, HRL).
  - Apply reaction enthalpy prediction to systems of interest, and use these accurate predictions for van't Hoff plots (w/ GaTech).
  - Help understand intermediate phase and reversibility (w/ SNL)
  - Complete joint experiment and theory analysis on T-dependent XRD in $LiBH_4$. (w/ SNL, UMSL)

Project Summary

Relevance: We have demonstrated and used a framework for the microstructural analysis of complex hydrides

Approach: Characterization and theoretical tools are general and can be used with many materials above and beyond complex hydride materials.

Technical Accomplishments and Progress:

- Demonstrated ability to quantify efficacy of ball-milling and mixing for dispersion of catalyst.
- Addition of powerful tomographic technique.
- Answered questions regarding use of dopants in Ca-based materials, with theory showing limitations of this system and explaining expt.
- Theory provided reliable means to predict quantitatively the reaction enthalpies and structures in various hydrogen-storage materials, including intermediate phases and reversibility (w/ SNL) as planned in 2008-09.
- Surface reactions will be quantified in future.

Technology Transfer/Collaborations: Active interfacing with MHCoE partners, presentations, publications.

- We address critical issues in H-storage materials synthesis and characterization brought to us by MHCoE partners.