



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

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Project ID # STP_36_Robertson

Timeline

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

Budget

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

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.

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 $\text{CaB}_6/\text{CaH}_2/\text{Ca}(\text{BH}_4)_2$ 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

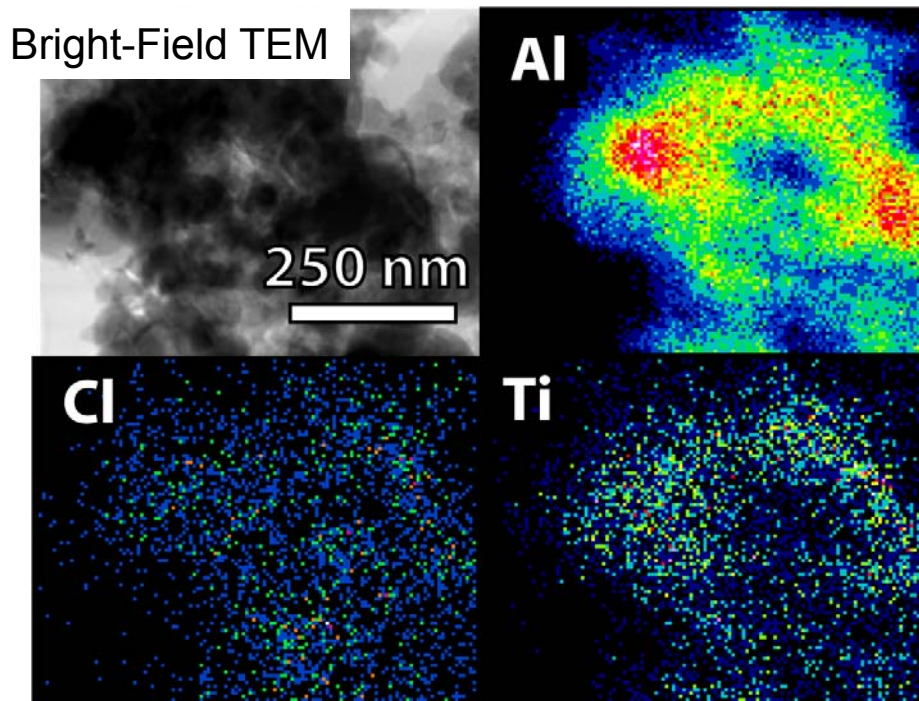
- Task 2: Incorporation and development of new models

- Development of new theoretical models and incorporation into MHCoe work

with Brookhaven National Labs



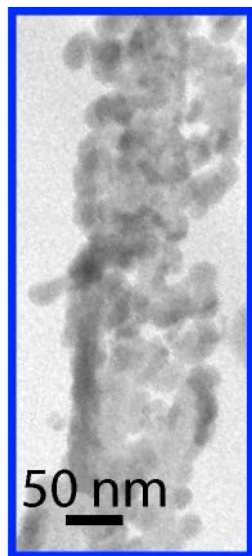
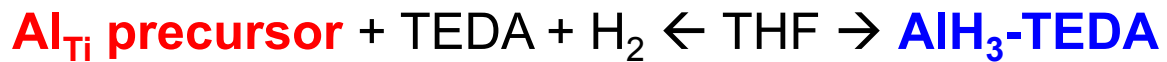
Energy Dispersive Spectroscopy elemental maps of Al_{Ti} precursor doped with 2 mol % TiCl₃ before liquid conversion to a reversible material



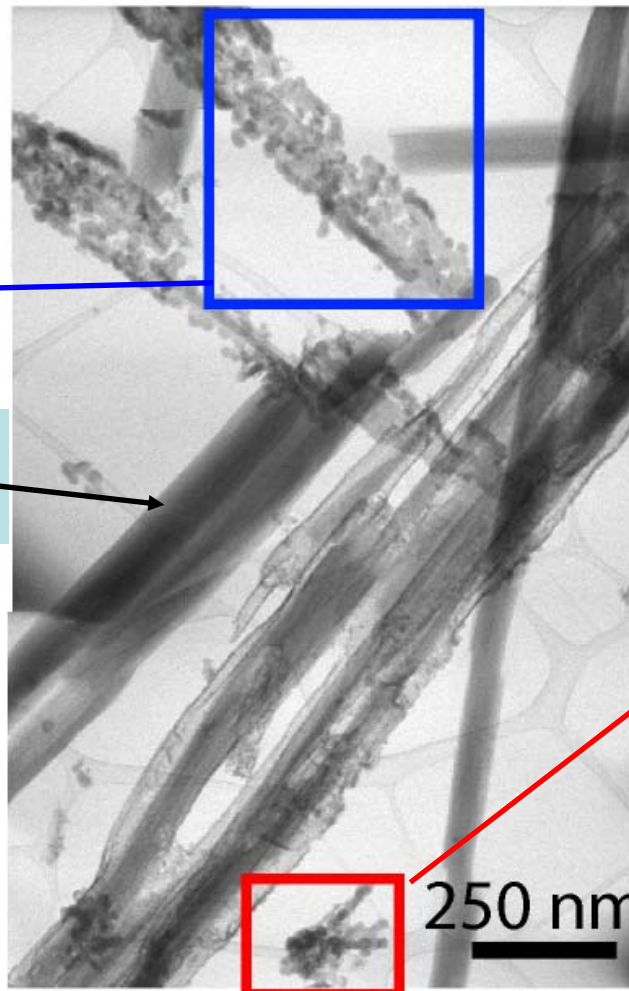
- Extended FY08 analysis to find quantitatively loss of catalyst.
- Quantitative analysis of Ti level (with oxygen excluded) yields 1.2 at% Ti.
- **Data indicates a 50% loss of Ti during precursor steps.**

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

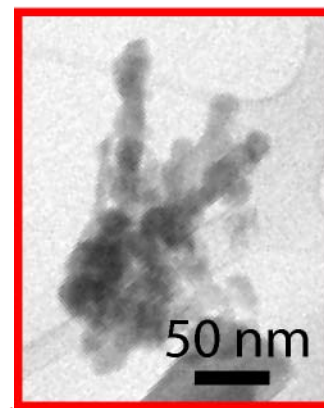
Morphology of Hydrided AlH_3 -TEDA



Al clusters decorating triethyl diamine (TEDA) crystal



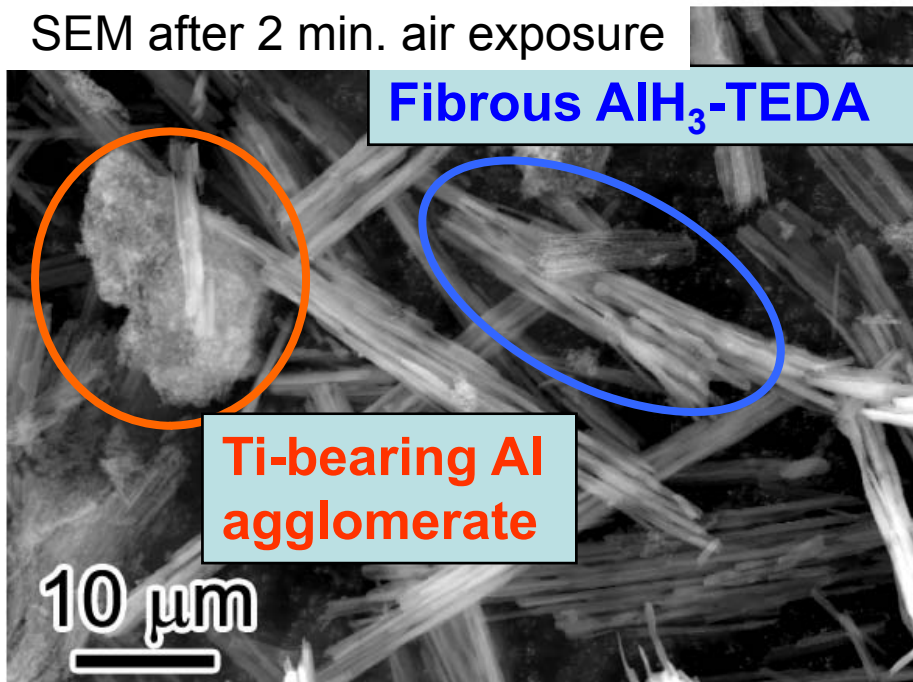
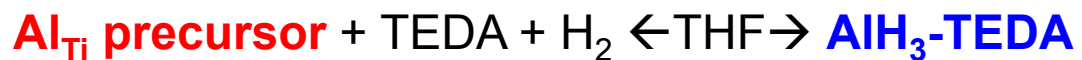
AlH_3 -TEDA, uncoated



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

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

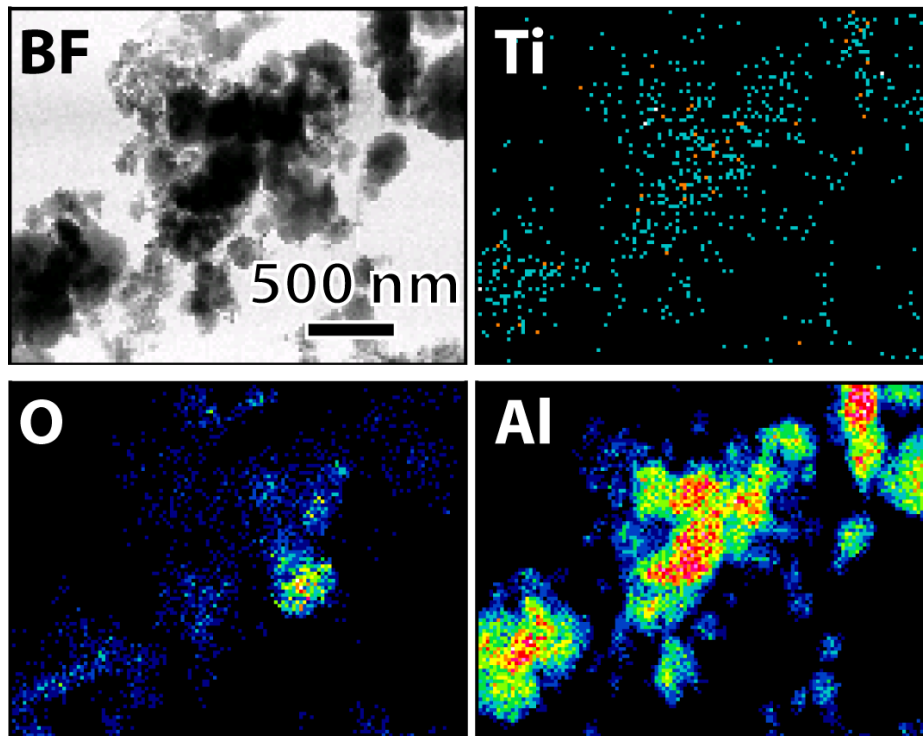
Morphology and Composition of Hydrided AlH_3 -TEDA with 0.1 at % TiCl_3



- 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.

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

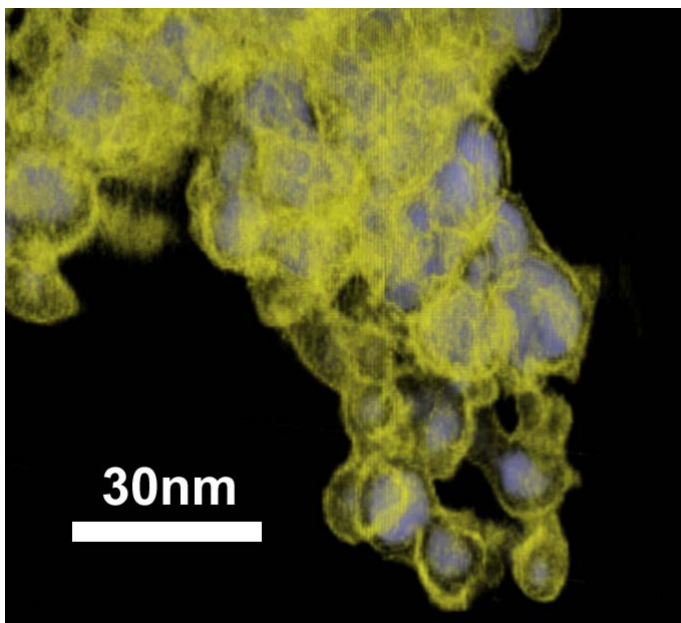


- TEM imaging – no air exposure.
- Ti map shows no evidence for local accumulation and redistribution within aggregates of Al crystals.

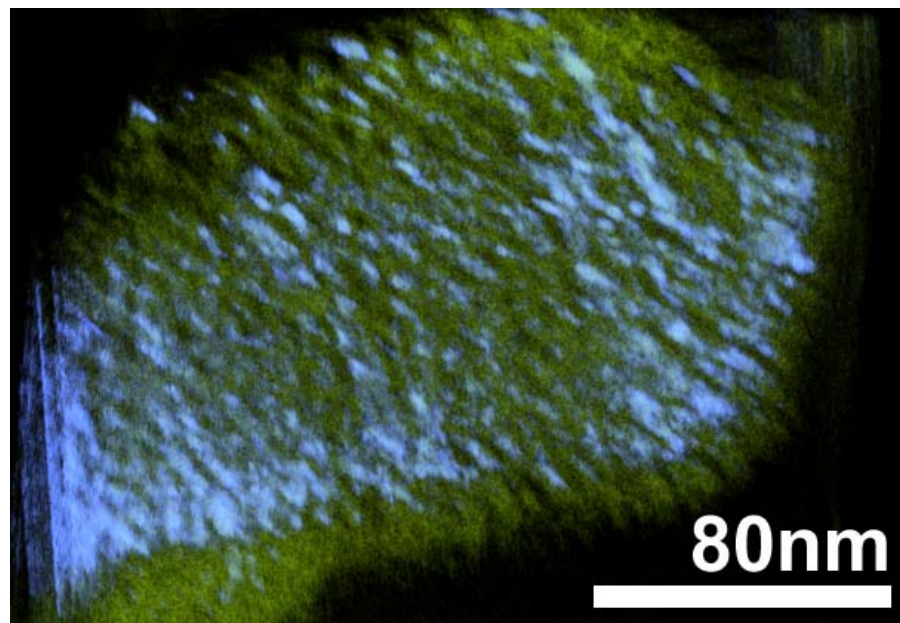
- Estimated detection limit 0.2 at% Ti – started at 2.0 at%.
- Dehydrated material is lacking appreciable Ti.

- ✓ Evidence of Ti in precursor-like Al crystals at the *nm* 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.

- **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.



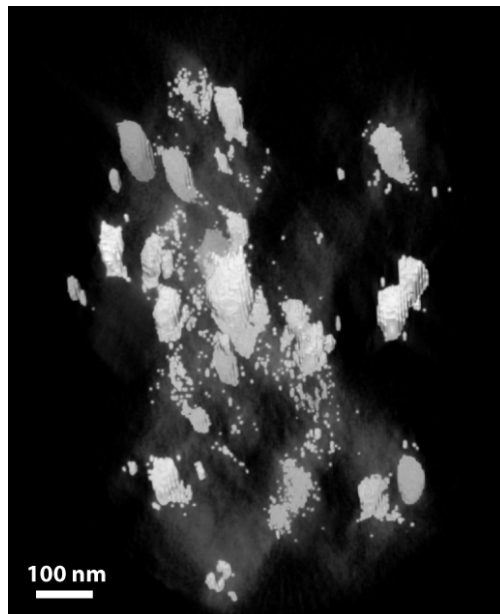
Cured Ag-MOF system
 – Ag particles (blue)
 – inside framework (yellow).



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 MgH₂/Si

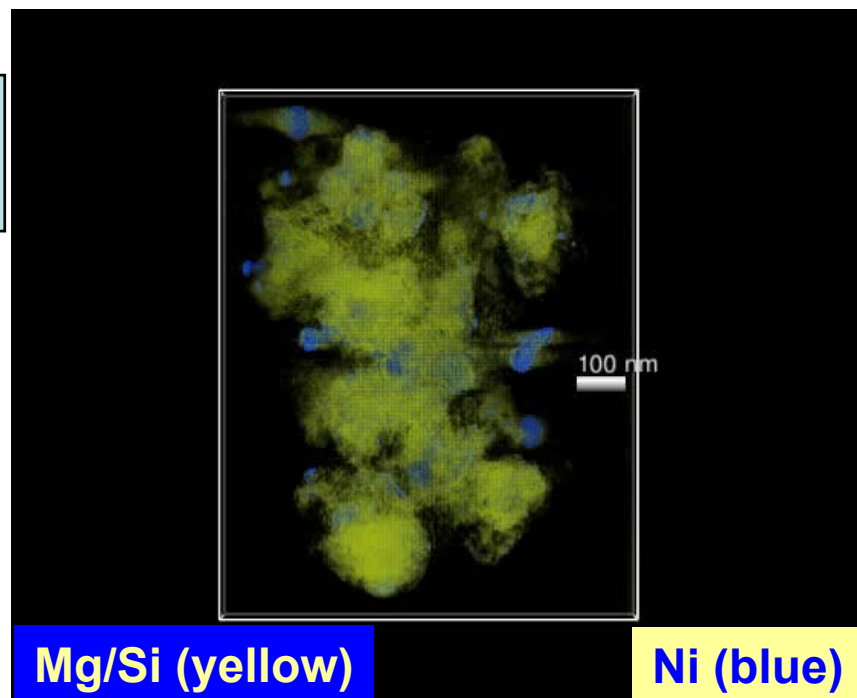


Individual frames used to reconstruct a 3-D image – see movie at poster!



3-D tomographic reconstruction of MgH₂ + Si + 0.05 Ni milled for 5 hrs.

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



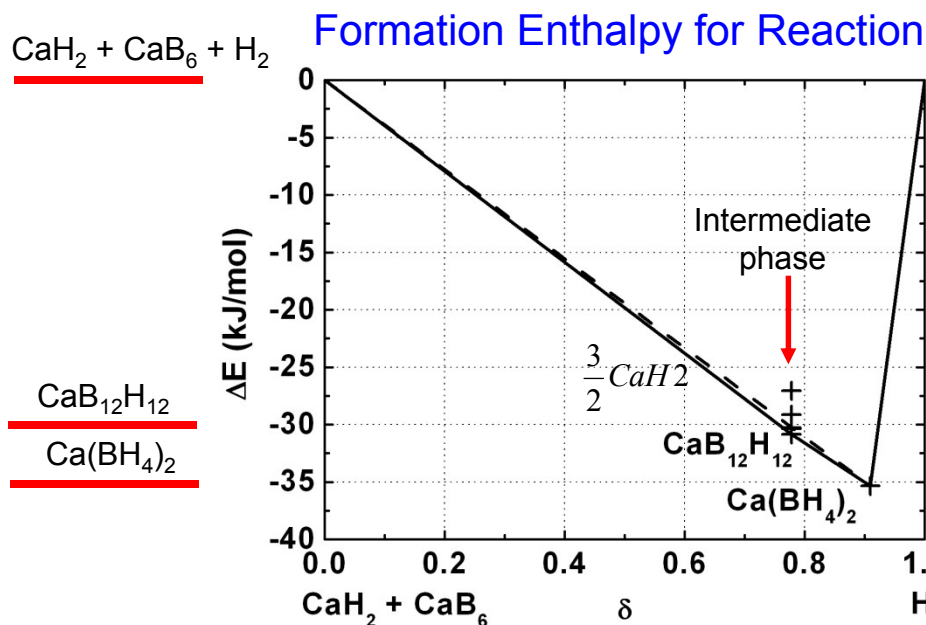
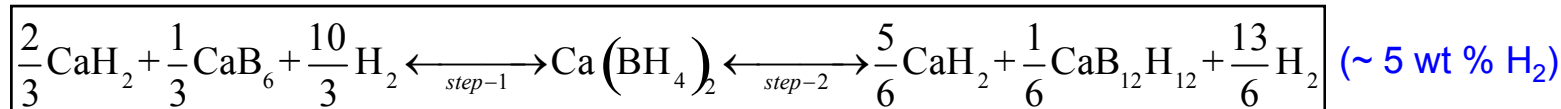
Mg/Si (yellow)

Ni (blue)

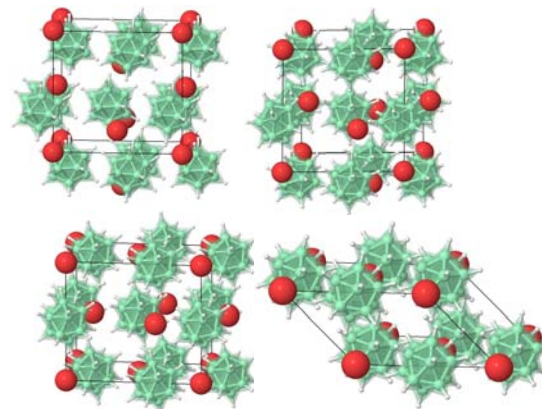
- ✓ Tomography indicates catalyst dispersal – Ni (blue) not well dispersed and remains chemically distinct from the matrix Mg/Si (yellow).
Raises important question of how it functions as a catalyst.
- ✓ Dissolution of elements by ball milling not guaranteed:
 - Need fundamental understanding of how 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 CaB₆/CaH₂ system: newly predicted competing structures

Sandia proposed reaction



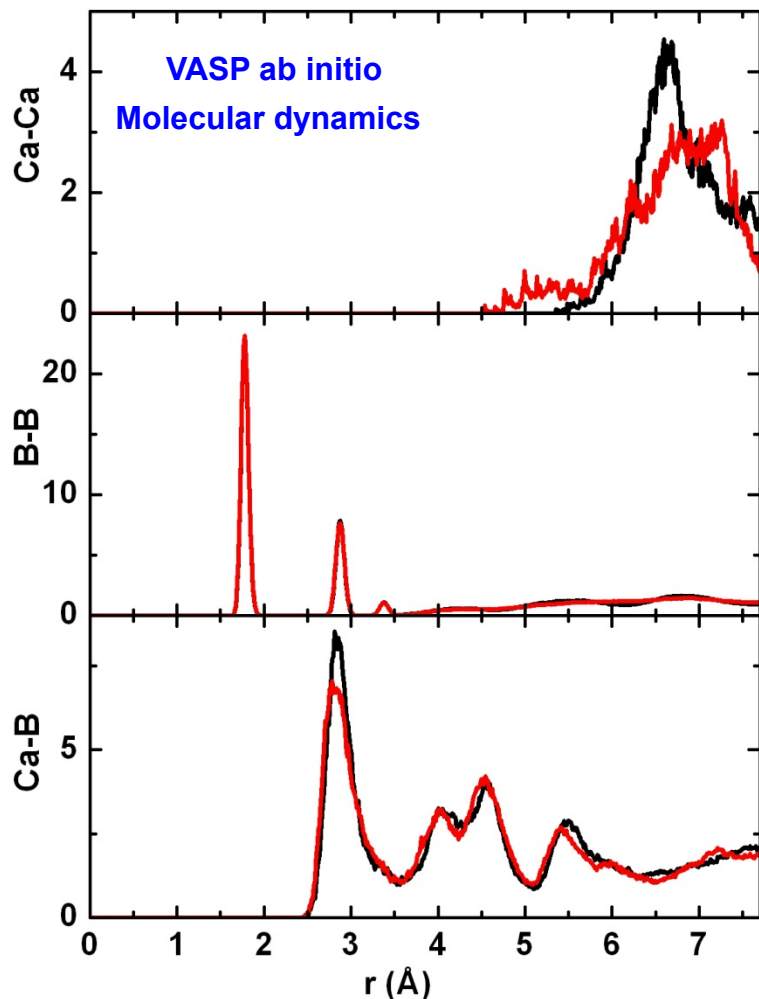
Some Illinois newly identified CaB₁₂H₁₂ structures



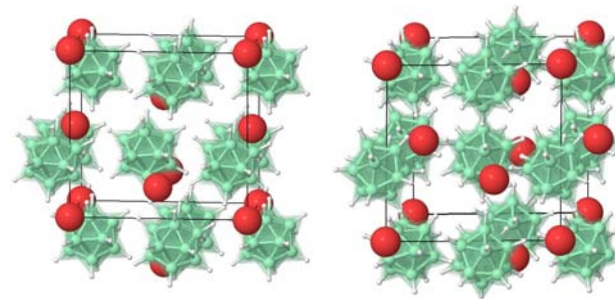
- ✓ Recent NMR results suggest a B₁₂H₁₂ environment in Li-based system.
- ✓ Illinois DFT results shows CaB₁₂H₁₂ is stable intermediate, but (unlike Li-based systems) with many competing symmetry-distinct phases! **Amorphous intermediate phase!**
- ✓ Illinois formation energy shows $0.86 (\text{CaH}_2 + \text{CaB}_6 + \text{H}_2) + 0.14 \text{Ca}(\text{BH}_4)_2 = \text{CaB}_{12}\text{H}_{12}$.
- ✓ **Irreversible CaB₆/CaH₂ system (except at high T and P) but Ca(BH₄)₂ reversible to amorphous CaB₁₂H₁₂ (possibly mixed phase) matching observation.**

Structural aspects of $\text{CaB}_{12}\text{H}_{12}$ intermediate phases: Illinois newly identified theoretical structures

$g(r)$ pair correlations at 300 K

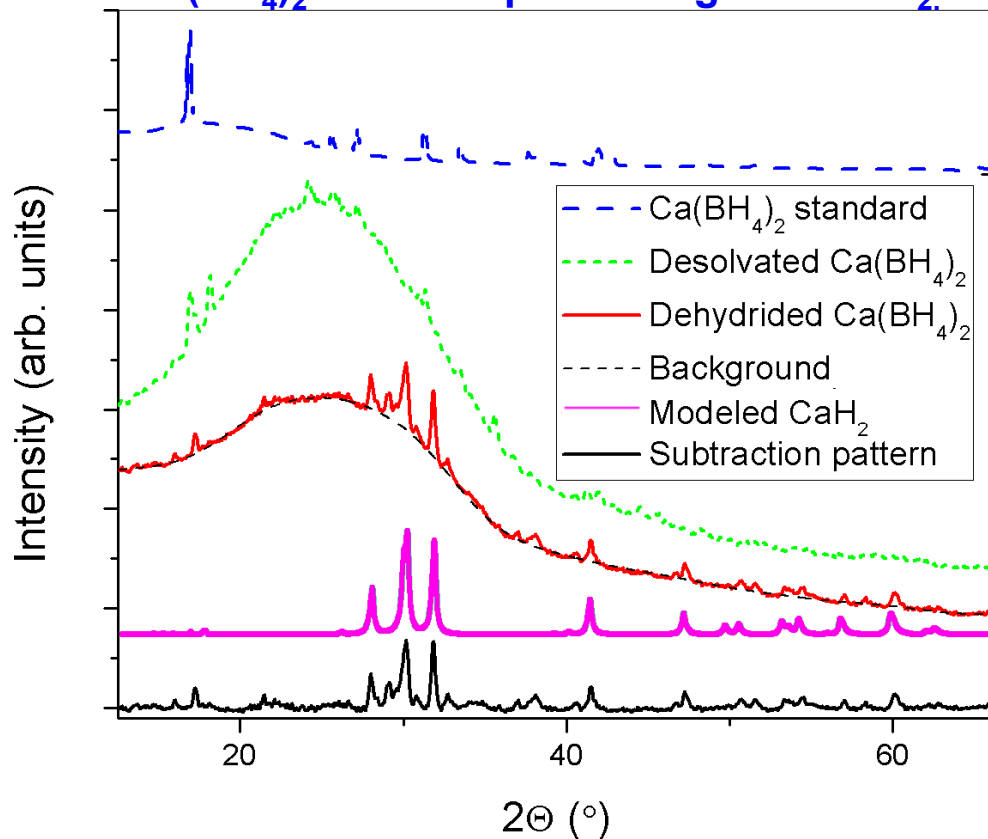


- **Example $g(r)$ for two low-E $\text{CaB}_{12}\text{H}_{12}$ structures** (cells depicted below) identified theoretically by Illinois, with several others also found.



- ✓ DFT $g(r)$'s shows that several symmetry-distinct $\text{CaB}_{12}\text{H}_{12}$ phases are (meta)stable!
- ✓ Due to strong binding in *c/oso*-molecule ($\text{B}_{12}\text{H}_{12}$), 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.)

Illinois XRD of desolvated and dehydrated $\text{Ca}(\text{BH}_4)_2$ with comparison against CaH_2 .



- CaH_2 seen in dehydrated $\text{Ca}(\text{BH}_4)_2$; 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 $\text{CaB}_{12}\text{H}_{12}$.
- Sandia data was not available for comparison.

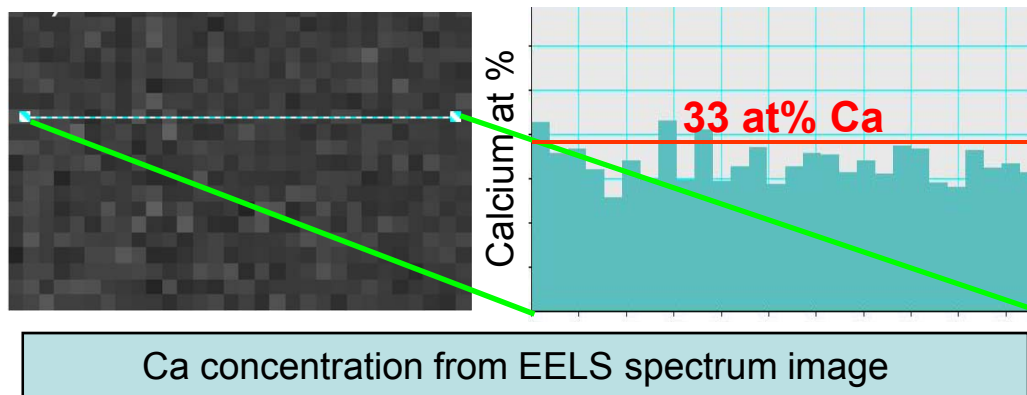
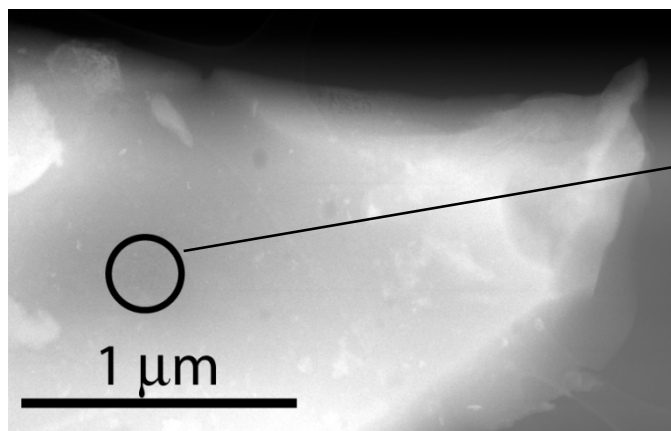
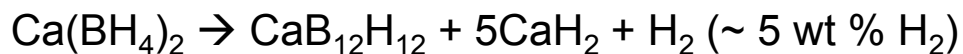


✓ XRD of dehydrated $\text{Ca}(\text{BH}_4)_2$ supports CaH_2 part of proposed reaction.

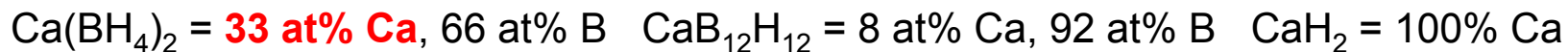
Compositional analysis of dehydrated $\text{Ca}(\text{BH}_4)_2$

Dark-field STEM of dehydrated $\text{Ca}(\text{BH}_4)_2$ showing the region analyzed with EELS

Proposed reaction:



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

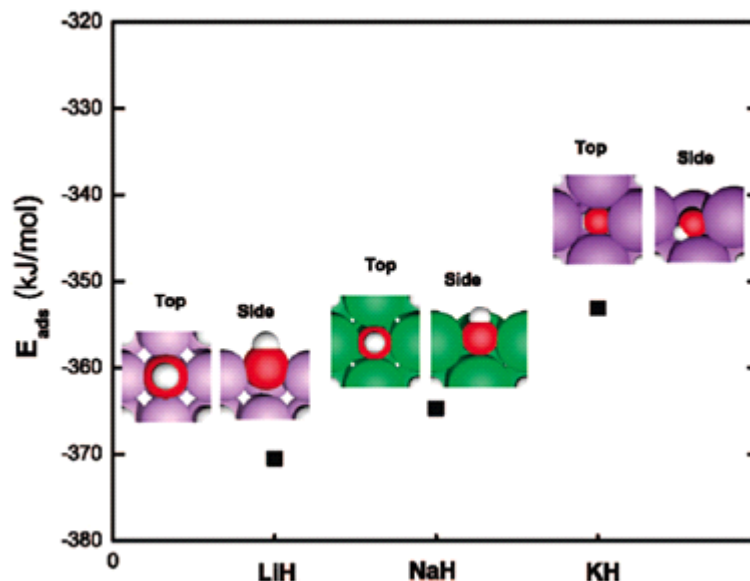


✓ Composition is the same as parent material $\text{Ca}(\text{BH}_4)_2$, which means there is no large scale (i.e., $> 10 \text{ nm}$) elemental redistribution and no compositional evidence for the intermediate $\text{CaB}_{12}\text{H}_{12}$ phase.

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, H₂, O₂, and H₂O.

Joint with
Pittsburgh
GaTech
Illinois
Sandia NL

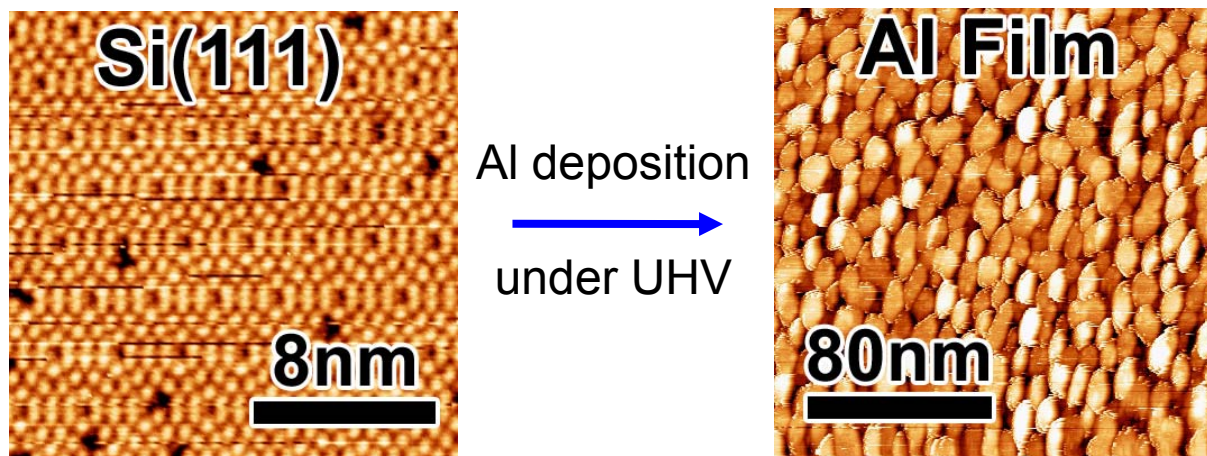


Example:
O₂ Adsorption
energy for MH

- ✓ 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 M₃AlH₆ phase.
- ✓ We find that there is no substantial differences in MH surface reactivities (i.e., poisoning) that correlate with reversibility to M₃AlH₆ phase.

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

- **Sandia NL**

- Answered fundamental questions regarding $\text{Ca}(\text{BH}_4)_2$ 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**

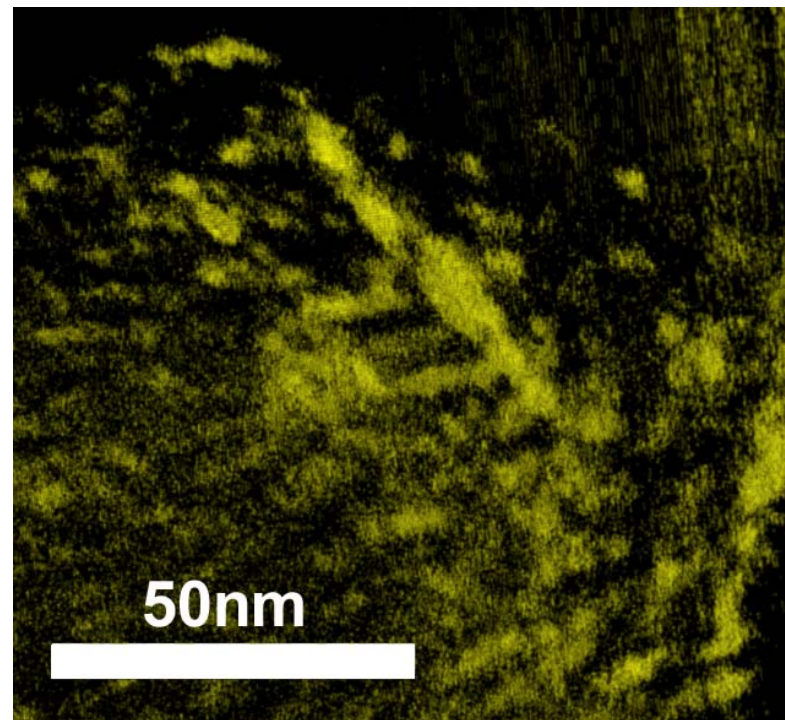
- Catalytic particles & tomography.

- **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 $\text{M-CaB}_{12}\text{H}_{12}$ 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 $\text{Ca}(\text{BH}_4)_2$ 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/MgH₂ 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 LiBH₄. (w/ SNL, UMSL)

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.