

## IV.A.1f Reversible Hydrogen Storage Materials – Structure, Chemistry, and Electronic Structure

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### Objectives

- Advance the understanding of the microstructural characteristics of complex light-weight metal hydrides to ascertain controlling mechanisms.
- Develop and apply reliable theoretical methods to assess potential complex metal hydrogen-storage materials, including key issues limiting material performance.

### Technical Barriers

This project addresses the following technical barriers from the Storage section (3.)3 of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (E) Charging/Discharging Rates

### Technical Targets

#### Catalytically Enhanced Hydrogen Storage

**Systems:** This project uses a combined theoretical and experimental approach to gain a fundamental understanding of the role of the catalytic species in several candidate complex hydride storage systems. Insights gained from these studies are applied toward

identifying potential complex metal hydride storage systems as well as optimizing the design and synthesis of systems to meet or exceed the following DOE 2015 hydrogen storage targets:

- System gravimetric capacity in terms of usable, specific-energy from  $H_2$  1.8 kWh/kg.
- System volumetric capacity in terms of usable, specific-energy from  $H_2$  1.3 kWh/L.
- System fill time (for 5 kg  $H_2$ ): 4.2 min (1.2 kg/min).

### Accomplishments

The following accomplishments were made in this fiscal year:

- Improved electron tomography capability and used it to address the question of the dispersion of particles in nanoporous scaffolds.
- Showed in  $MgH_2$  that there is no nanoparticle size effect for dehydrogenation enthalpies, although there is an effect on kinetic barriers with transition metal catalyst.
- Determined universal behavior for core-shell preference in binary nanoparticles.
- Demonstrated that the amount of Ti needed to activate the system is less than introduced initially.
- Established in the  $Ca(BH_4)_2$  system the existence of numerous  $CaB_{12}H_{12}$  polymorphs and the origin for the observed amorphous-structure in dehydrogenated material.



### Introduction

The transition from a petroleum-based to a hydrogen-based fuel for automotive applications depends on finding a viable, reliable and economic means in which to store hydrogen on-board the vehicle. One option is the high-capacity lightweight, metal hydrides that includes aluminum, borohydrides, destabilized metal hydrides, binary hydrides, intermetallic hydrides, and modified lithium amides. This includes exploring the potential of making nanoscale systems and confining them within nanoporous structures to exploit the enhanced properties found in large surface area to volume conditions. However, the challenge was and remains that none of the candidate systems tested to date satisfy the thermodynamic and kinetic constraints imposed by the DOE targets.

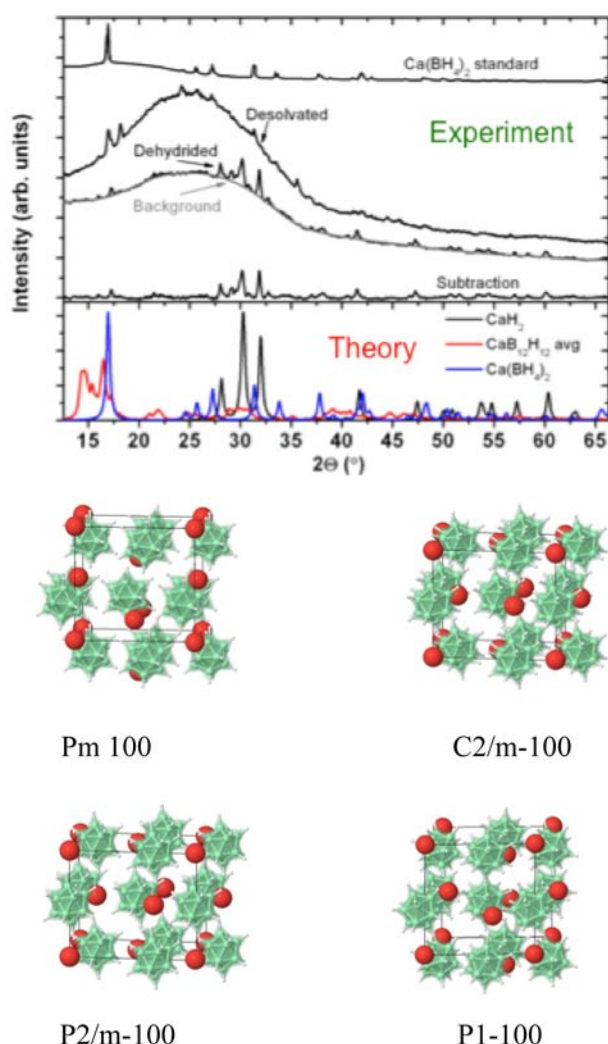
## Approach

State-of-the-art characterization tools, electron microscopy and X-ray diffraction for structural and phase characterization, energy dispersive and electron energy loss spectroscopy for chemical analysis, as well as atomic force microscopy to probe surface interactions, were employed to investigate the microstructural and microcompositional changes that occur in candidate material systems during the uptake and release of hydrogen. The characterization was coupled with first-principles, electronic-structure and thermodynamic theoretical techniques to predict and assess metastable and stable phases, as well as surface effects that can poison or limit kinetics. Electronic-structure and thermodynamic calculations were used to interpret and understand the experimental results on candidate systems. This combined theoretical/characterization effort provides fundamental insight to the processes governing hydrogen uptake and release.

## Results

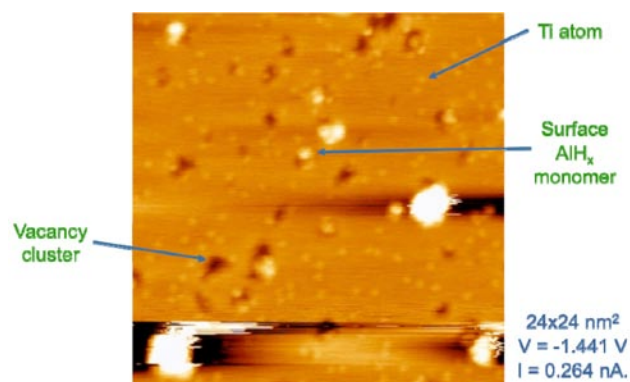
X-ray and electron diffraction of desolvated and dehydrogenated  $\text{Ca}(\text{BH}_4)_2$  showed that after dehydrogenation the  $\text{Ca}(\text{BH}_4)_2$  peaks are replaced with  $\text{CaH}_2$  peaks only, no other crystalline phases were present. Electron diffraction from a single particle showed weak crystalline diffraction spots superimposed on a diffuse background, which is consistent with the particle being amorphous with a low volume fraction of small crystalline regions. Chemical analysis via electron energy loss spectroscopy, confirmed no significant compositional modifications occurred during dehydrogenation.

To interpret these experimental results, theoretical calculations of  $\text{Ca}(\text{BH}_4)_2$  hydride and dehydride reactions that included possible intermediate  $\text{CaB}_{12}\text{H}_{12}$  states were performed. A key finding was the discovery of the existence of numerous polymorphs of  $\text{CaB}_{12}\text{H}_{12}$  that, at low temperatures, would lead to formation of a stable intermediate phase. It was demonstrated via *ab initio* molecular dynamics that these polymorphs arose from the varying bond length of Ca-Ca cations (as opposed to the Ca-B and B-B contained in the stable  $\text{B}_{12}\text{H}_{12}$  unit). Significantly, a mixed state of several polymorphs explained the experimental diffraction pattern; that is, around  $2\theta \sim 22^\circ$  more than two  $\text{CaB}_{12}\text{H}_{12}$  polymorphs were needed to produce the weight at that scattering angle. Consequently, the weighted diffraction signal would produce a pattern that appears amorphous, as observed experimentally. The X-ray diffraction pattern along with the signals from the different polymorphs is shown in Figure 1. Phase segregation as well as complete extraction of all available hydrogen was possible only at higher temperatures.



**FIGURE 1.** Comparison of the X-ray diffraction spectra from the different materials along with those calculated for the different systems. The  $\text{CaB}_{12}\text{H}_{12}$  average is comprised of individual spectra from several of the  $\text{CaB}_{12}\text{H}_{12}$  polymorphs, examples of some of the polymorph structures with different symmetries are shown. See *Journal of Physical Chemistry C*, v 113, n 46, p 20088-20096, 2009 for details.

To explore the interaction of molecular hydrogen with an aluminum surface with and without surface Ti atoms, a thin film of Al was deposited on Si(111) substrates both with and without a partial monolayer (0.02 ML) of Ti. Unlike the Al-only films, which exhibited no change when exposed to  $\text{H}_2$ , vacancy islands appeared and increased both in number and size under  $\text{H}_2$  exposure of the Ti-dosed surfaces, Figure 2. The vacancy islands, an indication of hydrogen absorption by the Al, were one atom deep and randomly distributed across the surface. Shortly after the vacancy islands appeared, surface  $\text{AlH}_x$  monomers formed next to a vacancy island. As exposure continued and the number of surface monomers increased, grouping of  $\text{AlH}_x$  complexes formed. Future experiments will



**FIGURE 2.** Scanning tunneling micrograph of an Al surface with 0.2 monolayer of Ti deposited on the surface following dosing with molecular hydrogen.

explore the interactions between Ti, the vacancy islands, and the  $\text{AlH}_x$  complexes. The final series of experiments will explore how the responses differ if the surface is contaminated. In support of these scanning tunneling microscopy experiments, first principles calculations are being conducted to determine the surface projected electronic density of states to make a direct connection to the experimental results.

One possible strategy to improve the thermodynamics of the hydrogenation and dehydrogenation reactions is to reduce the particle size into the nanoscale regime. To explore this possibility, the size effect on desorption enthalpies of nanoparticles vs. bulk were calculated for  $\text{MgH}_2$ -based systems with and without catalyst atoms of Ti and V. The results, reported in Table 1 show there is NO thermodynamic

**TABLE 1.** Dehydrogenation energy ( $\text{kJ/mol-H}_2$ ) from nanoparticle surface site vs. bulk surface site (defined has being bonded to two metal sites).

	$\text{Mg}_{31}\text{H}_{62}$	$\text{Mg}_{30}\text{TiH}_{62}$	$\text{Mg}_{30}\text{VH}_{62}$
<b>Nanoparticle</b>	246	175	190
<b>Bulk (011) Rutile</b>	256	187	205

size effect for hydrogen release (except at very small [ $<10$ ] atom clusters), although there is a catalytic effect with dopant in both bulk and nanoparticle cases.

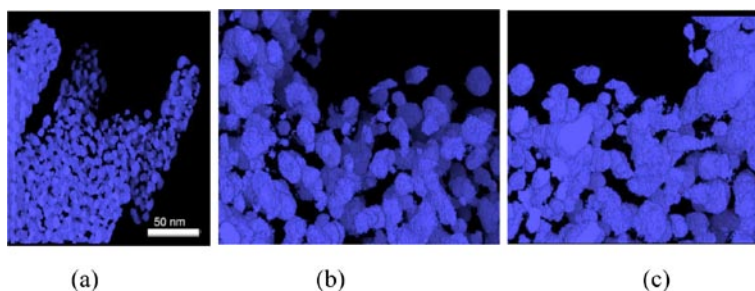
An important aspect of developing nanoparticle hydrogen-storage systems is to employ light-weight scaffolds with nano-sized pores to control particle size and prevent agglomeration. A key question in using such scaffolds is determining if the storage medium actually impregnates the scaffold during the synthesis. To address this issue we have developed and

applied compositional electron tomography to convert conventional two-dimensional compositional images to three-dimensional tomographs of scaffolds containing hydrogen storage materials. These tomographs enable visualization of the impregnated scaffold from any viewing angle. An example of a selection of snapshots from an electron tomogram of silver clusters that had been impregnated in a metalorganic framework are shown in Figure 3; silver is not a candidate system it is used here simply to demonstrate the technique capability.

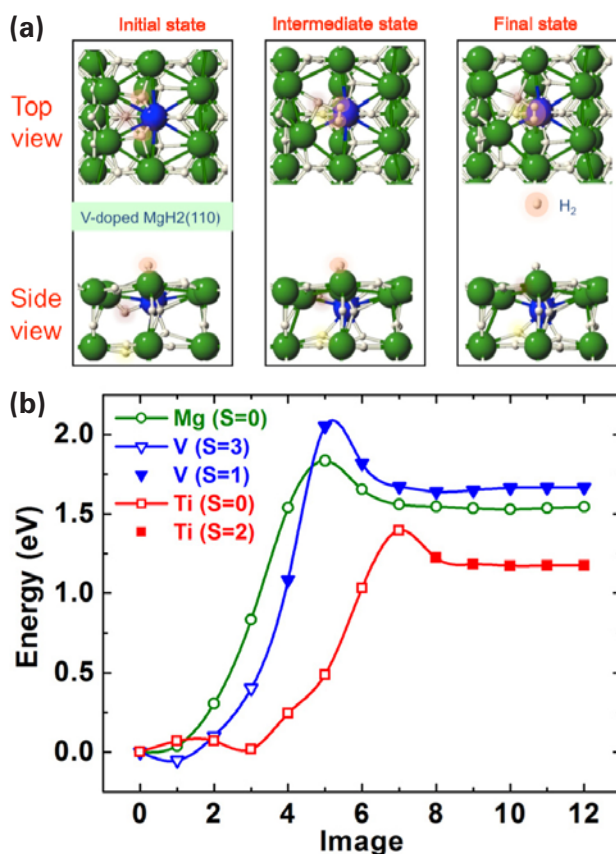
Nudged Elastic Band calculations are being conducted to explore the kinetic barriers of hydrogen desorption from the [110] rutile surface of  $\text{MgH}_2$  with and without catalytic-dopants of Fe, V and Ti. Due to the large size of ball-milled and similar samples, we believe that surface calculations for facets are sufficient to obtain quantitative estimates of kinetic barriers. It is found that for  $\text{H}_2$  desorption, the lowest-energy structures involve dramatic local reconstructions around the catalyst site, with Ti (V) preferring a coordination number of 8 H (7 H) atoms. Thus, as one hydrogen molecule dissociates, hydrogen from the interior is drawn to the surface catalyst atom site so that the process can continue. This can be seen for V in the images shown in Figure 4a. The effects of nanosize and support interactions on H desorption are shown in Figure 4b and this shows the difference between the different catalytic-dopants and the effectiveness of Ti versus V at reducing the kinetic barriers, while no advantage was found by going “nano” with samples for dehydrogenation energies, i.e., no size-effects for thermodynamics.

## Conclusions and Future Directions

- The core-shell behavior in transition-metal nanoparticles is governed by cohesive energy (or surface energy) and size differences, which predicts all observed structures.
- No nanoparticle size effect for dehydrogenation enthalpy exists although there is a reduction in kinetic barrier with catalyst.



**FIGURE 3.** Tomographic snapshots of Ag clusters inside metalorganic framework. (b) and (c) show zoomed images of the nanoparticles.



**FIGURE 4.** (a) Snapshots showing the positions in the release of hydrogen in a V-doped system. (b) VASP calculated kinetic barriers (eV) for H<sub>2</sub> desorption from MgH<sub>2</sub>(110) Rutile bulk surface without and with dopants of V and Ti. Barriers are reduced with Ti dopant but not for V, suggesting what is observed experimentally, namely that Ti is useful catalyst while others are not.

- The role of Ti on clean Al surfaces appears to be to enhance the dissociation of molecular hydrogen to atomic hydrogen.

Our continuing effort will focus on completing the following activities:

- Continue the study of the reaction of H<sub>2</sub> with clean and poisoned Al surfaces with and without catalytic species. We will explore creating small islands of Ti, as opposed to isolated Ti atoms, and, if successful reacting them to form Al<sub>x</sub>Ti<sub>1-x</sub> islands. The interaction of H<sub>2</sub> with these islands will then be investigated. Electronic-structure methods will be used to support these surface-science experiments and to aid the interpretation of the experimental results.
- The electron tomography method will be used to identify the location of MgH<sub>2</sub> in a scaffold (collaboration with University of Hawaii) and LiBH<sub>4</sub>

melt-infiltrated into nanoporous carbon (University of Missouri).

- The electronic structure studies involving the following systems will be continued:
  - Stability of bulk Ca(BH<sub>4</sub>)<sub>2</sub> and clusters of Mg and MgH<sub>2</sub>.
  - Nanocluster structures of MgH<sub>2</sub> and NaAlH<sub>4</sub> with and without interactions to a carbon support (approximating interactions with aerogels).
  - The effects of nanosize and support interactions on H desorption.

## FY 2010 Publications/Presentations

- D.D. Johnson, "Nanoparticle Structure and Properties: universal features, structural instabilities and the effects of size and supports," invited talk to joint Chemistry and Physics Departments, UC Davis, 12 April 2010.
- Lin-Lin Wang, "Surfaces and Interfaces at Nanoscale: from C60 to transition-metal nanoparticles," invited, Oak Ridge National Laboratories, Jan. 2010.
- Lin-Lin Wang, "Surfaces and Interfaces at Nanoscale: from C60 to transition-metal nanoparticles," invited, CNRS MSSMAT, Paris, France, March 2010.
- Jason Reich, Lin-Lin Wang, and D.D. Johnson, "Thermodynamic and kinetic size effects for hydrogen-desorption in catalytically-doped magnesium hydride: nanoparticle versus bulk surface effects" American Physics Society, March 2010, contributed.
- D.D. Johnson, "Structure of Transition-Metal Nanoparticles: Free-standing, Supported and Passivated," invited talk at the Naval Research Laboratory, 26 February 2009.
- Lin-Lin Wang and D.D. Johnson, "Universal Behavior of Core-Shell Preferences in Transition-Metal Nanoparticles," contributed talk at APS March Meeting, Pittsburgh (2009).
- D.D. Johnson, "Quantitative Prediction of Solid-Solid Transformations," invited talk at Lawrence Livermore National Laboratory. 15 April 2009.
- Lin-Lin Wang and D.D. Johnson, "On the reversibility of hydrogen-storage reactions in Ca(BH<sub>4</sub>)<sub>2</sub>: characterization via experiment and theory," contributed talk at MRS Fall Meeting, Boston (2009).
- Presentation at the 2010 March Meeting of the American Physical Society, Portland, OR.
- Lin-Lin Wang, Dennis D. Graham, Ian M. Robertson, Duane D. Johnson On the reversibility of hydrogen-storage reactions in Ca(BH<sub>4</sub>)<sub>2</sub>: Characterization via experiment and theory. *Journal of Physical Chemistry C*, v 113, n 46, p 20088-20096, 2009.
- Predicted Trends of Core-Shell Preferences for 132 Late Transition-Metal Binary Alloyed Nanoparticles L-L. Wang and D.D. Johnson, *J. Amer. Chem. Soc.* 131, 14023-14029 (2009).

- 12.** Ronald J.T. Houk, Benjamin W. Jacobs, Farid El Gabaly, Noel N. Chang, A. Alec Talin, Dennis D. Graham, Stephen D. House, Ian M. Robertson, and Mark D. Allendorf, Silver Cluster Formation, Dynamics, and Chemistry in Metal-Organic Frameworks Nano Letters 9, 3413-3418, 2009.
- 13.** Anant Kulkarni, Lin-Lin Wang, Duane D. Johnson, David Sholl, Karl Johnson, First-Principles Characterization of Amorphous Phases of  $MB_{12}H_{12}$ , M=Mg, Ca. Submitted J. of Phys. Chem. C.
- 14.** D.D. Graham, J. Graetz, J. Reilly, J. Wegrzyn, and I.M. Robertson. Location of Ti catalyst in the reversible  $AlH_3$  adduct of triethylenediamine, Accepted, J. Physical Chemistry
- 15.** J. Reich, L.-L. Wang, and D.D. Johnson, Hydrogen Desorption in  $MgH_2$  Surface and Nanoparticles: Thermodynamic Energetics and Kinetic Barriers in preparation.
- 16.** Benjamin Jacobs, Ronald Houk, Stephen House, Ian Robertson, A. Talin, Mark Allendorf, Ordered Metal Nanostructure Self-Assembly Using Metal-Organic Frameworks as Templates. Submitted. Nano Letters.