IV.A.5l Synthesis of Nanophase Materials for Thermodynamically Tuned Reversible Hydrogen Storage

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Objectives

- Determine whether thermodynamically tractable reactions based on hydride destabilization, like $Mg_2Si+2H_2<–>2MgH_2+Si$, that should be reversible but appear not to be, are kinetically limited.
- Investigate short hydrogenation times associated with refueling that will require short solid-state and gas-solid diffusion path lengths.
- Investigate the problems associated with large, light-metal-hydride enthalpies (hydrogen fueling/refueling temperatures) and develop strategies to address thermodynamic issues surrounding the use of these materials through hydride destabilization. Determine systems of interest through "theoretical screening" by Center partner members.
- Investigate issues related to grain growth and surface/interface energies, vital in order to understand the kinetics of hydrogenation/dehydrogenation reactions.
- Follow up on previously studied reactions with phase identification via X-ray diffraction (XRD), nuclear magnetic resonance (NMR), and transmission electron microscopy (TEM).

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume
(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
(Q) Reproducibility of Performance

Technical Targets

Data are typically reported as gravimetric densities on a materials basis only. The contribution to the system weight from the tank walls and tubing is not considered in the values reported herein, whereas the 2010 targets for gravimetric and volumetric capacity of 6% and 0.045 kg/L, respectively, are system values.

The two systems that we have concentrated on are:

- $ScH_2+2LiBH_4 \leftrightarrow ScB_2+2LiH+4H_2$, 8.9 wt% theoretical, 4 wt% observed (400°C); and
- $Ca(AlH_4)_2+2LiBH_4$, 6.6 wt% observed.

Accomplishments

- Worked on synthesis and kinetic evaluation of $ScH_2+2LiBH_4 \leftrightarrow ScB_2+2LiH+4H_2$ (8.9 wt%), which has a 34 kJ/mole reaction enthalpy after zero point correction, with guidance from the Metal Hydride Center of Excellence (MHCoE) theory group.
- Evaluated $Ca(AlH_4)_2+2LiBH_4$ system, which dehydrogenates >6.5 wt% and was not predicted to be reversible but does rehydrogenate under certain conditions.
- Completed electronic structure studies of Mg_2Si system that has not shown rehydrogenation (work on this system has been discontinued).

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Introduction

Candidate hydride destabilization systems of technological interest must generate high gravimetric densities of hydrogen at reaction enthalpy values of between 30 and 40 kJ/mole for tractable thermal management of storage systems. While thermochemical databases have been of use in exploring initial candidate systems, we have relied on the efforts of the MHCoE theory group [1], which has calculated formation and reaction enthalpies of systems that fall within the requisite thermodynamic boundaries.

Reaction kinetics are also a critical gauge of engineering utility; our approach is to work with the most promising candidates as determined by thermodynamics and to study the kinetics of hydrogen release. Kinetics will be dominated by solid-state diffusion rates in hydride destabilization systems and both volumetric and analytical techniques are required in order to understand reaction pathways.

Approach

We have been evaluating the most promising hydride destabilization systems using Sieverts volumetric techniques to determine actual gravimetric hydrogen release and the associated kinetics aided by standard catalysts. We have been working with spectroscopic analyses like NMR in collaboration with the Jet Propulsion Laboratory (JPL) (see report from R. C. Bowman, Jr. of JPL) and the Caltech NMR facility in order to gain insights into these systems, as they oftentimes show no long-range crystallographic order that could otherwise be studied with our typical approach of X-ray diffraction techniques.

Results

The $ScH_2 + 2LiBH_4 \leftrightarrow ScB_2 + 2LiH + 4H_2$ reaction, whose kinetics was calculated recently, has been of particular interest as this system has a potential gravimetric density of 8.9 wt%. While the cost of Sc metal probably makes this system impractical from a commercial standpoint, the importance of validating the role of computational screening and highlighting computational limitations, as noted in our empirical work, offers a valuable feedback mechanism in the search for practical reversible hydrides. Figure 1a shows a temperature ramp to 400°C. We were able to get less than half of the theoretically predicted amount of hydrogen, depending on the source of $LiBH_4$. Our analysis of this system suggests that the high heats of formation of the reactants that are predicted need to be considered, as well as the overall reaction enthalpy. Using NMR and XRD, we were unable to detect the presence of ScB_2 as a reaction product after dehydrogenation, although the presence of elemental B was observed via NMR. Our attempts at rehydrogenating the reaction from right to left, using ScB_2 as a starting material, have as of yet not shown any reaction occurring at temperatures of 350°C.

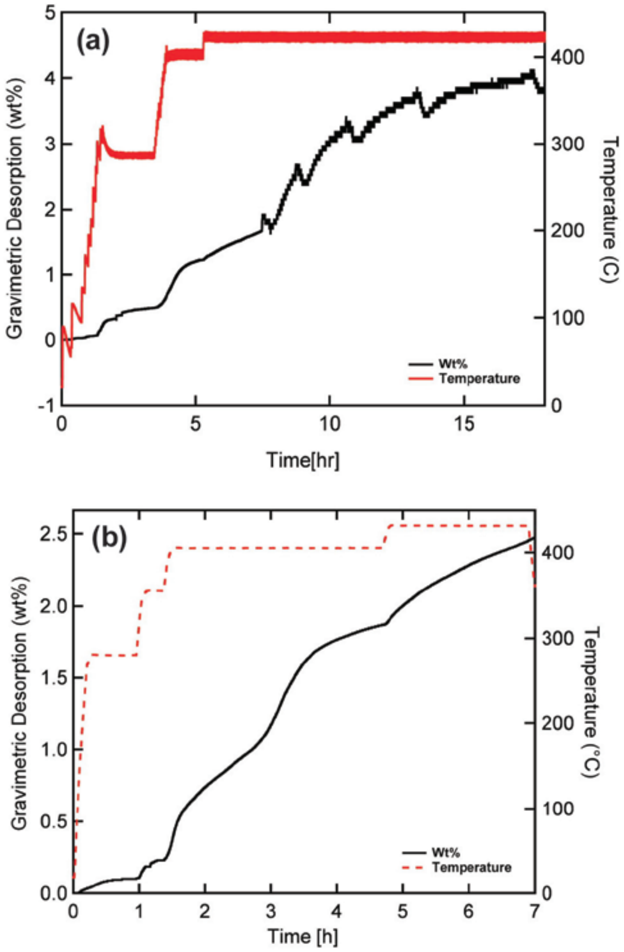


FIGURE 1. (a) top and (b) bottom show kinetic traces of $ScH_2 + 2LiBH_4$ (+2 mol%$TiCl_3$) samples at 400°C. Yields are 3 to 4 wt% using two different $LiBH_4$ materials. Less than 1 wt% H_2 was generated at temperatures below 400°C. The desorbed gas was found to be 99.9% H_2.

Figure 2a shows a comparison of desorption traces with and without a catalyst. Low-temperature kinetic behavior is improved, but the overall amount of desorbed hydrogen begins to converge in both systems after several hours. Figure 2b shows X-ray diffraction patterns of the $ScH_2 + 2LiBH_4 + 2$ mol%$TiCl_3$ system after milling and dehydrogenation. Curves (a) and (b) are the calculated diffraction patterns of ScH_2 and $LiBH_4$, respectively. Curves (c) and (d) are the experimental diffraction patterns after milling and after desorption, respectively.

Figure 3 shows the results of another system of interest to us, the $Ca(AlH_4)_2$:$2LiBH_4$ system, which yields over 6.5% hydrogen. Some reversibility of this system is noted when the reactants are reground after desorption. These results were obtained using $Ca(AlH_4)_2$ synthesized in our lab. The use of a very pure form of $Ca(AlH_4)_2$ has not shown the reversibility we have seen when using our

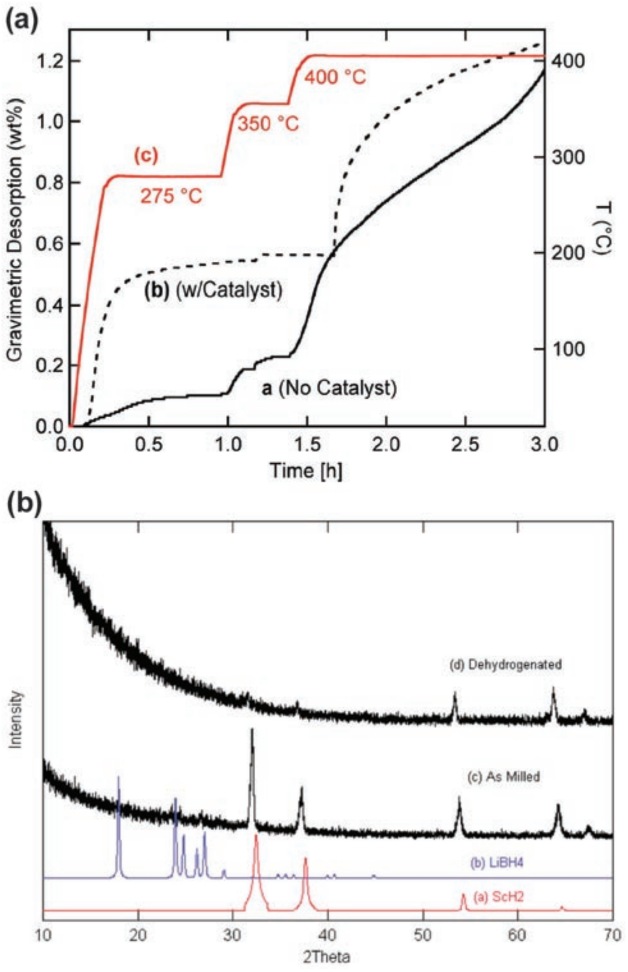
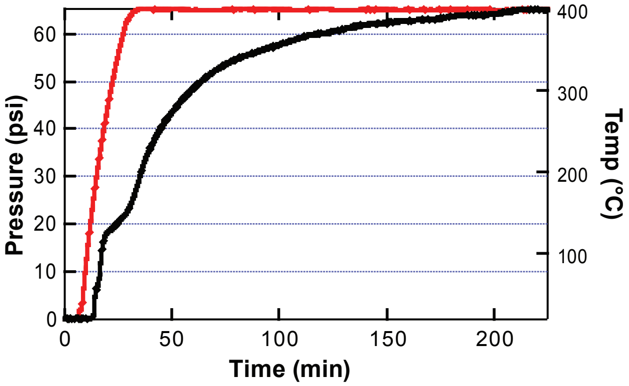


FIGURE 2. (a) Results of catalyst addition on the ScH_2+$2LiBH_4$ mixture with Ti, by means of dry-milling with 2 mol% $TiCl_3$. Dramatic improvement in the kinetics and yield at 275°C, just below the melting-point of $LiBH_4$, can be seen. Above 400°C, there is little difference between desorption profiles of the Ti-doped and undoped samples. (b) ScH_2+$2LiBH_4$+2 mol%$TiCl_3$ X-ray diffraction patterns of starting materials and as-milled and as dehydrogenated material.

materials, and we are presently exploring the reaction paths that are responsible for this behavior.

Conclusions and Future Directions

- ScH_2:$2LiBH_4$ is of particular interest as a 34 kJ/mole system when zero point energy correction is taken into account. Dehydrogenation temperatures of up to 400°C are still not high enough to completely extract the theoretical value of hydrogenation. Predicted reaction products are not discernable via X-ray or NMR. Reverse reaction (hydrogenation) does not appear to occur.
- The $Ca(AlH_4)_2$:$2LiBH_4$ system is of interest in dehydrogenation/hydrogenation reactions, but reaction pathways are not well understood.



Cycle	1	2	3
Desorption (mass loss, wt%)	6.64	2.65	2.74
Reabsorption (mass gain, wt%)	1.65	4.56	3.06

FIGURE 3. Kinetic Trace from the $Ca(AlH_4)_2$:$2LiBH_4$ System with Yields as Noted in the Table beneath the Plot (Highlighted data are those that underwent mechanical grinding after reaction.)

- NMR analysis is of value at this point in identifying near neighbor species that are not distinguishable via X-ray diffraction.
- We will coordinate with T. Baumann (Lawrence Livermore National Laboratory) in synthesis of aerogels with pore size range down to 1 to 2 nm. Surface/interface effects will play a dominant role in reaction enthalpy behavior at these size dimensions, where we plan to use aerogels as scaffolds to maintain short diffusion distances and perhaps highlight the role of hydride size/stability.
- We will conduct a wetting behavior analysis of $NaAlH_4$ (as an already thermodynamically well-understood model system) and Mg to determine contact angle dependence on carbon surface treatment, necessary to understand minimum size constraints in aerogel pores.
- We will examine use of surface treatments/additives to enhance wetting of hydrides in aerogel pores. We will also confirm lowered enthalpies and diffusion paths in $NaAlH_4$ and Mg encapsulated within aerogel pores.

FY 2007 Publications/Presentations

1. Shu Miao, "Bonding in Mg_2Si," Chapter 5 (PhD Thesis, Caltech Jan. 2007).

2. H. Kabbour, C. C. Ahn, S.-J. Hwang, R. C. Bowman, Jr., and J. Graetz, "Direct Synthesis and NMR Characterization of Calcium Alanate", *J. Alloys Compounds* (in press 2006).

3. R. C. Bowman, Jr., S-J. Hwang, C. C. Ahn, M. R. Hartman, T. J. Udovic, J. J. Rush, and J. J. Vajo, "Destabilization Behavior and Phase Compositions for LiH-Ge", poster presentation at MH2006, Maui, HI, October 1–5, 2006.

4. J. Purewal, M. Winterrose, H. Kabbour, B. Fultz, S. Hwang, C. Ahn, J. Reiter, and R. C. Bowman, Jr., "Hydrogen Sorption Behavior in Destabilized Scandium Hydride," Hydrogen in Metals, Gordon Conf. poster presentation, Colby College, Waterville, ME 2007.

References

1. S. Alapati, J. Johnson, and D. Sholl, *Phys. Chem. Chem. Phys*., 2007, 9, 1438-1452.