

IV.A.1j Catalyzed Nano-Framework Stabilized High Density Reversible Hydrogen Storage Systems

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- Albemarle Corporation, Baton Rouge, LA

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Objectives

Design and synthesize hydride/nano-framework composites with a wider range of doped, functionalized and catalyzed framework chemistries to improve:

- Reversibility
- Desorption temperatures/kinetics - overly stable materials
- Instability at ambient temperature - unstable materials

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
- (E) Charging and Discharging Rates
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project is intended to improve material reversibility and kinetics through nano-confinement and surface chemistry. This approach provides a path to reversible high density H₂ storage systems meeting the DOE 2010 targets:

System Gravimetric Capacity:	1.5 kWh/kg
System Volumetric Capacity:	0.9 kWh/L
Charging/Discharging Rates (system fill time):	1.2 kg/min

Accomplishments

To advance the understanding of how nano-frameworks can enhance the performance of hydrogen storage media, a range of hydride/framework combinations and associated parameters has been investigated in the past year. The accomplishments include:

- Down-selected functionalized C and ZrO₂ as most suitable framework materials for future catalyzed investigations.
- Simulated the atomic mechanism for heterogeneously catalyzed H₂ dissociation and H transfer to kinetically facilitate rehydrogenation of Ca(BH₄)₂ dehydrogenation products.
- Obtained a decrease in H₂ desorption temperature of the stable borohydride Ca(BH₄)₂ incorporated in C aerogels by solution-based incorporation.
- Demonstrated high loading of NaTi(BH₄)₄*ligand in SiO₂ aerogel and improved its stability in the aerogel.



Introduction

Current complex hydrides have yet to meet the 2010 DOE systems targets, presenting a continuing challenge for the discovery of high capacity, reversible hydrides. For example, metal borohydrides [M(BH₄)_n] have the potential to meet the targets, but some materials are unstable (such as those containing Ti, Al, or Sc cations) and decompose within minutes or days. Other metal borohydrides (such as those containing Li, Na, K or Ca cations) decompose at temperatures that are higher than what is desired for proton exchange membrane fuel cell integration and cannot be recharged with gaseous hydrogen at moderate pressures. Thus, there is a need to develop novel techniques that enable high

capacity that is maintained over numerous absorption/desorption cycles. The current project addresses this by incorporating complex metal hydrides, with a focus on borohydrides, into nano-scale frameworks of a low density, high surface area skeleton material to stabilize, catalyze, and control desorption product formation associated with such complex metal hydrides.

Approach

The project at United Technologies Research Center (UTRC) is being conducted in close collaboration with other researchers from the DOE Metal Hydride Center of Excellence. The UTRC, Sandia National Laboratories (SNL), and Albemarle Corporation teamed to develop nano-frameworks compatible with specific advanced hydrogen storage materials.

The team uses an iterative atomistic/thermodynamic modeling and experimental approach to develop hydride/nano-framework composites. The hydride/nano-framework interaction is chemically modified to decrease desorption temperature for highly stable compounds, stabilize unstable high capacity compounds, and influence desorption products to improve reversibility. In addition, nanometer-scale catalytic sites within the nano-framework cells will activate H_2 , and through hydrogen spillover, facilitate reversibility (rehydrogenation). Two high capacity borohydrides, $Ca(BH_4)_2$ and $NaTi(BH_4)_4$ were selected for incorporation into nano-frameworks. $Ca(BH_4)_2$ is a stable hydride that requires high temperature to desorb and reabsorb hydrogen. $NaTi(BH_4)_4$, however, is unstable and requires ligands to stabilize its structure. A variety of framework chemistries were examined to make a relatively broad assessment of the method's potential. These chemistries include functionalized, and catalyzed frameworks. Both melt and solution-based methods were employed for incorporation of hydride into nano-framework materials.

Results

In Fiscal Year 2009, much effort was devoted to examine chemical interactions of hydrides with a variety of nano-framework chemistries and their impact on the reversibility, hydride stability, and kinetics:

- Atomic Modeling:
 - Evaluated interaction of $Ca(BH_4)_2$ with ZrO_2 framework and its impact on $Ca(BH_4)_2$ dehydrogenation.
 - Investigated the effect of Pt catalyzed ZrO_2 on hydrogen dissociation and $Ca(BH_4)_2$ rehydrogenation.
- Framework and Hydride (Experimental):
 - Conducted evaluation of the reactivity of $Ca(BH_4)_2$ with oxides (Y_2O_3 stabilized ZrO_2

[YSZ], Al_2O_3 and SiO_2) and functionalized carbon aerogels.

- Identified the impact of uncatalyzed framework materials on $Ca(BH_4)_2$ rehydrogenation.
- Incorporated $Ca(BH_4)_2$ and $NaTi(BH_4)_4$ *DME (dimethoxyethane) in aerogels.

Atomic Modeling

1. $Ca(BH_4)_2$ * ZrO_2 Dehydrogenation

Atomic modeling was conducted to evaluate the impact of $Ca(BH_4)_2$ interactions with ZrO_2 frameworks on $Ca(BH_4)_2$ stability and dehydrogenation behavior. The simulations showed strong $Ca(BH_4)_2$ physisorption on the tetragonal $ZrO_2(101)$ surface, locally stabilizing $Ca(BH_4)_2$ at the interface. The simulations evaluated the various possible dehydrogenation reactions with the formation of adsorbed decomposition products. The strongest adsorbed product at the reacting interface was simulated to be CaH_2 . These model configurations are shown in Figure 1. The remaining products were assumed to be desorbed. When interfaced with ZrO_2 , the most accessible $Ca(BH_4)_2$ dehydrogenation reaction to form the CaH_2 , $CaB_{12}H_{12}$ and H_2 products was predicted to have an increased dehydrogenation enthalpy, where the increase was less than +20 kJ/m H_2 . This increase is barely distinguishable from the bulk $Ca(BH_4)_2$ reaction, taking typical calculation error into account. Other competing dehydrogenation reactions showed similar enthalpy increases and followed the same order of relative favorability, compared to bulk $Ca(BH_4)_2$. These simulations showed that the ZrO_2 framework characteristics need to be tuned to enhance $Ca(BH_4)_2$ reversibility.

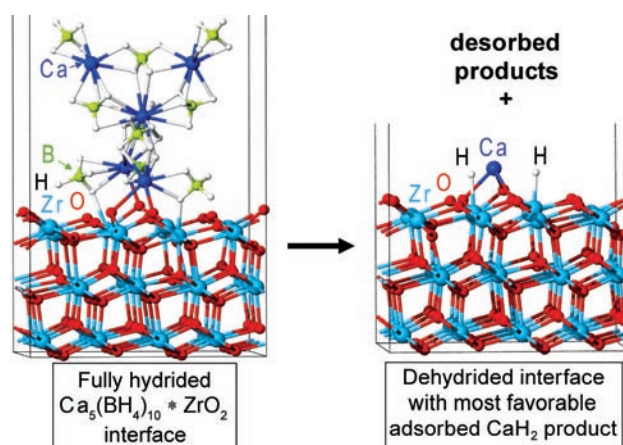


FIGURE 1. Most favorable atomic modeling configurations of $Ca(BH_4)_2$ interface with tetragonal $ZrO_2(101)$ surface, in the fully hydrided (left) and dehydrided (right) states.

2. Pt Catalyzed Rehydrogenation

Atomic modeling investigations were made to demonstrate the utility of H_2 activation catalysts to facilitate the formation and transfer of atomic H, and enhance the binding and rehydrogenation of $Ca(BH_4)_2$ dehydrogenated phases. The H_2 activation catalysts were represented as 10 atom Pt nano-rafts anchored to the tetragonal $ZrO_2(101)$ surface. The results indicated that H_2 spontaneously dissociated on the Pt nano-raft, consistent with other reported experimental and theoretical findings. The transfer and migration of atomic H to adjacent ZrO_2 support were predicted to be favorable upon H saturation of the Pt nano-raft with increasing H_2 pressure during rehydrogenation. The presence of the Pt nano-raft enhanced the adsorption of $Ca(BH_4)_2$ dehydrogenation products on the surrounding ZrO_2 support. With increasing H_2 pressure, the simulations also showed spontaneous rehydrogenation of the dehydrogenation products adsorbed in the vicinity of the Pt nano-rafts. These predicted atomic configurations are shown in Figure 2. These results confirmed the feasibility and potential benefits for employing H_2 activation catalysts in hydrogen storage nano-frameworks.

Framework and Hydride (Experimental)

1. $Ca(BH_4)_2$ / Nano-Framework Interaction

Experiments were conducted to screen for undesired reactivity of $Ca(BH_4)_2$ with selected nanoscale oxides: SiO_2 , Al_2O_3 , ZrO_2 , and C aerogels: polyimide (PI) and phenolic (PF) derived carbon aerogels, using SPEX milled mixtures. This reactivity study was conducted to ensure the stability of the framework under cycling conditions. The experimental results indicated that ZrO_2 was the most stable oxide framework material under dehydrogenation at $350^\circ C$ and 1 bar hydrogen

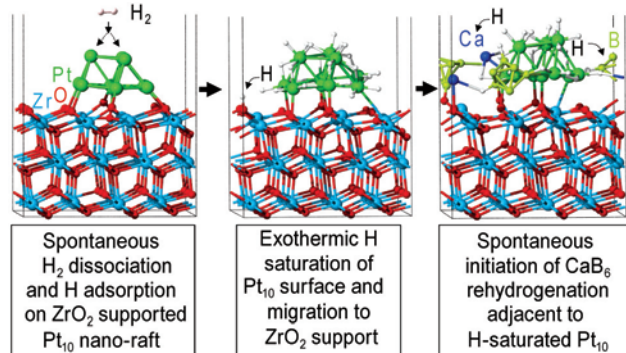


FIGURE 2. Atomic simulations of Pt nano-raft loaded on $ZrO_2(101)$ surface, showing spontaneous H_2 dissociation (left), atom H migration upon saturation (middle), and spontaneous rehydrogenation of co-adsorbed CaB_6 dehydrogenation product (right).

pressure and rehydrogenation at $350^\circ C$ and 190 bar hydrogen pressure cycling conditions. SiO_2 and Al_2O_3 were susceptible to react with $Ca(BH_4)_2$ to form undesirable reaction products. No $Ca(BH_4)_2$ formed after rehydrogenation in the $Ca(BH_4)_2 - ZrO_2$ system, indicating that ZrO_2 inhibited $Ca(BH_4)_2$ formation. In $Ca(BH_4)_2$ - carbon (PI and PF derived) aerogel systems, formation of $Ca(BH_4)_2$ was observed upon rehydrating. No reaction products were observed in the $Ca(BH_4)_2 - C$ (PF) system by X-ray diffraction analysis, while small amounts of $CaNH$ and Ca_3N_2 were detected in the $Ca(BH_4)_2 - C$ (PI) system. Enhanced H_2 desorption was also observed in the SPEX milled $Ca(BH_4)_2 - C$ systems compared with $Ca(BH_4)_2$ only. It was found that surface chemistry of the carbon aerogel affected kinetics of the second H_2 desorption after rehydrating. Based on these results, C aerogel was identified as the best uncatalyzed nano-framework material for $Ca(BH_4)_2$ incorporation. The effect of Pt catalyzed ZrO_2 nano-framework on $Ca(BH_4)_2$ rehydrogenation is currently under examination.

2. Incorporation of $Ca(BH_4)_2$ using Solution and Melting Methods

$Ca(BH_4)_2$ was incorporated into C aerogels using both solution and melting-based methods. Three solvated $Ca(BH_4)_2$ precursor species (adducts with tetrahydrofuran [THF], pyridine and dimethoxyethane [DME]) were synthesized and evaluated for incorporation via the solution method. The $Ca(BH_4)_2 \cdot THF$ precursor was pursued for incorporation in the C aerogel for its relative ease of desolvation. An estimated 27 wt% of $Ca(BH_4)_2$ was successfully incorporated in C (PI) aerogel. Brunauer-Emmett-Teller (BET) measurements showed that the surface area changed from 580 to 330 m^2/g after incorporation. The pore volume changed from 3.7 to 1.6 cm^3/g and the pore size from 25 to 19 nm. Preliminary testing using a Sievert's apparatus showed the on-set temperature for dehydrogenation decreased at least $50^\circ C$ to $175^\circ C$. Its hydrogen release rate was improved significantly, compared with the SPEX milled $Ca(BH_4)_2 - C$ (PI) system (Figure 3).

Incorporation of $Ca(BH_4)_2$ into carbon aerogel was explored via melting under high H_2 pressure and temperature. When a sample of $Ca(BH_4)_2$ and carbon (PI) aerogel was heated to $560^\circ C$ under 10,000 psi of H_2 , it appeared that $Ca(BH_4)_2$ wetted the surface of the aerogel. However, the change in mass of the carbon aerogel was low, suggesting only minimal incorporation of $Ca(BH_4)_2$ within the pores. BET measurements showed a significant decrease in surface area from 400 to 2 m^2/g . The pore volume decreased from 2.5 to 0.02 cm^3/g . Hydrogen release behavior was measured using SNL's Simultaneous Thermo-gravimetric Modulated-Beam Mass Spectrometer (STMBMS) instrument. It was found that the H_2 release

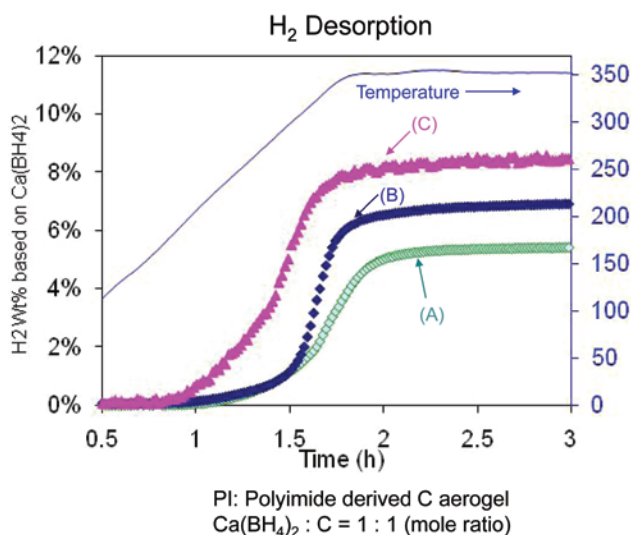


FIGURE 3. H₂ desorption of Ca(BH₄)₂ incorporated in C aerogel, compared with SPEX milled Ca(BH₄)₂ and its mixture with C aerogel. (A) SPEX milled Ca(BH₄)₂, (B) SPEX milled mixture of Ca(BH₄)₂ with C (PI) aerogel, (C) Ca(BH₄)₂ incorporated in C(PI) aerogel at 27 wt% loading level.

temperature for the melt incorporated Ca(BH₄)₂ - C sample was higher than bulk uncatalyzed and catalyzed samples. The inability to achieve high sample loadings and the high H₂ releasing temperature have led to discontinuation of melt based method for incorporating Ca(BH₄)₂ into nano-frameworks.

3. Stabilization of NaTi(BH₄)₄*DME in SiO₂ Aerogel

NaTi(BH₄)₄*DME is a mixed alkali transition metal borohydride that was developed in a previous DOE contract (Complex Hydride Compounds with Enhanced Hydrogen Storage Capacity, DE-FC36-04GO14012) involving UTRC and the Albemarle Corporation. The complex is unstable at ambient temperature and decomposes within 1-2 days. In this project, NaTi(BH₄)₄*DME was incorporated into an oxide nano-framework to improve its stability. High surface area SiO₂ has been used as the nano-framework for the initial experiments. NaTi(BH₄)₄*3DME was used as the precursor for its high solubility in DME. Two levels of incorporation, 40 and 50 wt%, were achieved. After removing two portions of DME ligands, the loading levels became 26 and 34 wt% of NaTi(BH₄)₄*DME respectively. The stability of the incorporated material was improved from 1-2 days to >10 days at ambient temperature, as shown in diffuse reflectance infrared Fourier transform spectra (DRIFTS) of freshly made and aged NaTi(BH₄)₄*DME - SiO₂ composite (Figure 4). The improvement of stability was found to be more significant at the 26 wt% loading level than at 34 wt%.

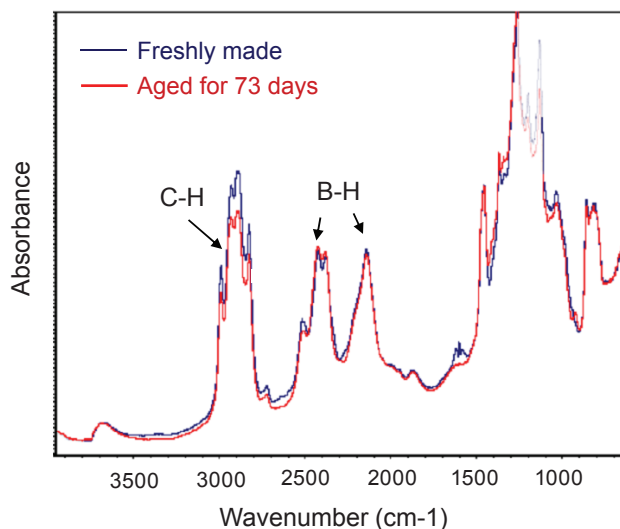


FIGURE 4. DRIFTS of NaTi(BH₄)₄*3DME complexes incorporated in silica.

These results indicate that the hydride/nano-framework surface interaction helps to stabilize such unstable hydrides.

Conclusions and Future Directions

We have down-selected functionalized C and ZrO₂ as the most suitable framework materials. Atomic modeling indicated that Pt catalyzed zirconia aerogel can kinetically facilitate rehydrogenation of Ca(BH₄)₂. Ca(BH₄)₂ was successfully incorporated in C aerogels by solution method and its desorption kinetics were improved significantly. It was also demonstrated that SiO₂ aerogel can improve hydride stability of the unstable NaTi(BH₄)₄*DME.

Future Work

Atomic Modeling

- Design doped-ZrO₂ to balance interfacial interactions of hydrided and dehydrided storage material candidates.
- Survey influence of nano-framework surface functionalization on hydride/nano-framework interactions.

Framework and Hydride

- Evaluate the impact of Pt catalyzed ZrO₂ (YSZ) nano-frameworks.
- Examine stabilization effect of YSZ and C aerogels on the stability of NaTi(BH₄)₄*DME and removal of ligand.

- Consideration of alternate hydride candidates, such as $\text{Mg}(\text{BH}_4)_2$.

Publications/Presentations

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2. S.M. Opalka, X. Tang, T.H. Vanderspurt, D.A. Mosher, and B.L. Laube, "Complex borohydride and hydrogen interactions with Pt-loaded ZrO_2 frameworks," American Chemical Society Spring 2009 Meeting, Symposium on H_2 storage in nanoporous materials, Salt Lake City, UT, March 22–26, 2009.
3. D.A. Mosher, S.M. Opalka, X. Tang, S. Arsenault, T.H. Vanderspurt, B.L. Laube, R.J. Brown, "Catalyzed Nano-Framework Stabilized High Density Reversible Hydrogen Storage Systems," IEA Task 22 Meeting, Rome, Italy, October 6–10, 2008.
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