Catalyzed Nano-Framework Stabilized High Density Reversible Hydrogen Storage Systems

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METAL HYDRIDE CENTER OF EXCELLENCE

DOE Hydrogen Program
Annual Merit Review
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Project ID: ST_10_Tang

Overview

- **Timeline**
  - Start : 7/1/07
  - Finish: 7/1/10
  - 65% Complete
- **Budget**
  - $1.26M Total Program
  - DOE: $1.01M
    - SNL: $360k
    - Albemarle: $90k
    - Cost share: 20% (31% UTRC $)
  - FY07: $80k
  - FY08: $470k
  - FY09: $460k (planned)
- **Barriers Addressed**
  - A. System Weight and Volume
  - E. Charging/Discharging Rates
  - P. Lack of Understanding of Hydrogen Physisorption and Chemisorption

  www.eere.energy.gov/hydrogenandfuelcells/mypp
- **Partner Participation**
  - United Technologies Research Center (Project Lead)
  - Sandia National Laboratories
  - Albemarle Corporation
  - Aspen Aerogels

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aspen aerogels

Challenges & Objectives

Challenges:

- A wide range of high-capacity on-board rechargeable material candidates have exhibited non-ideal behavior related to:
  - Reversibility
  - High desorption temperatures
  - Instability at ambient temperature
- While different material compositions are continuing to be developed in the world-wide research community, the scope of novel, high-potential storage materials has its limits.

Objectives:

The use of nano-frameworks offers a distinct material design approach to improve sorption reaction behavior in a number of ways. The objectives of the current effort are to:

- Examine a variety of framework chemistries and hydride / framework combinations to make a relatively broad assessment of the method's potential.
- These chemistries include doped, functionalized, and catalyzed frameworks.

Challenges & Objectives

Objectives (cont.):

- Tune hydride / framework interactions to:
  - Decrease desorption temperature for highly stable compounds.
  - Stabilize high capacity compounds, resulting in ligand elimination.
  - Influence desorption product formation to improve reversibility.
- Develop and apply atomic modeling techniques in evaluating and designing the local surface interactions.
- Activate H_2 dissociation on highly dispersed catalytic sites.
- Maintain nano-scale phase domains during cycling.
- As part of the MHCoE, focus on improving the performance of material candidates within the center, which have been borohydrides to date.

Plan / Approach

Combine *computational* and *experimental* methods to design & synthesize hydride / nano-framework composites.

	Description
Hydride Candidates	▪ Examine composites with $Ca(BH_4)_2$, a reversible borohydride with 9.6 wt% theoretical capacity, which is overly stable. ▪ Examine $NaTi(BH_4)_4$ as a high-capacity candidate which is unstable and requires ligands to stabilize.
Atomic / Therm. Modeling	▪ Evaluate hydride-framework interactions: associative stabilization, decomposition/side-products, dehydrogenation, to guide experiments. ▪ Explore heterogeneous catalysis of hydride reversibility by modeling H_2 dissociation, H migration, and rehydrogenation.
Nano-Framework Development	▪ Evaluate a range of framework chemistries, with a focus on oxides and (functionalized) carbons, for their influence on the hydride candidates. ▪ Catalyze the nano-frameworks to promote H_2 dissociation.
Hydride Incorporation	▪ Employ both melt and solution based incorporation methods. ▪ Focus on solution-based incorporation methods for unstable hydrides.
Characterization	▪ Screen hydride / framework combination candidates for chemical compatibility, to ensure framework integrity and cyclability. ▪ Examine hydride-incorporated frameworks.

Milestones

Date	Milestone or Go / No Go Decision
2008 Q1	Select advanced nano-framework structure
2008 Q1	Demonstrate synthesis of desired nano-framework structure
2008 Q1	Synthesize top Sandia candidate hydride material
2008 Q2	Synthesize top UTRC / Albemarle candidate hydride material
2008 Q4	Evaluate relative performance of framework / catalysts
2008 Q4	Synthesize optimal catalyzed nano-framework structure
2009 Q1	Demonstrate loading of UTRC / Albemarle hydride into framework
2009 Q2	Demonstrate loading of Sandia hydride into framework
2009 Q3	Go / No Go on whether to proceed with original plan or redirect based on: > 50% hydride deposition into the catalyzed framework materials Reasonable absorption/desorption behavior for at least one cycle Performance relative to the state-of-the-art material shows promise

To date greater emphasis has been placed on evaluating uncatalyzed systems.

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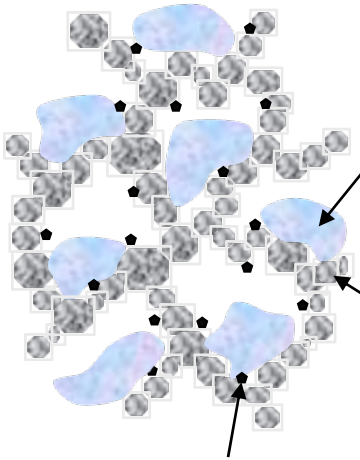
Atomic Modeling

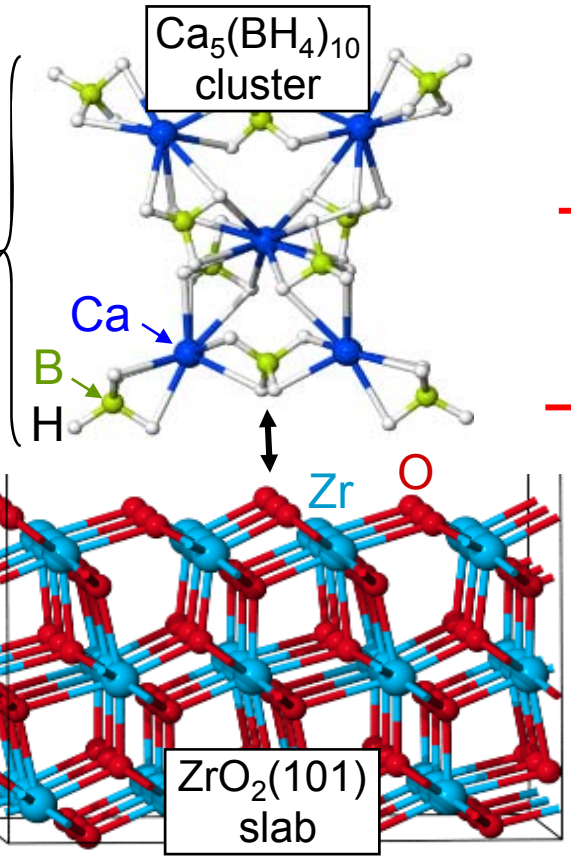
Concept

Hydride-filled nano-framework



loaded metal catalyst

Materials



Role

Conduct atomic modeling to investigate and prescreen:

→ Hydride thermodynamics

→ Interfacial physi-/chemisorption reactions influence on hydride stability and dehydrogenation

→ Nano-framework stability and modification:
a) doping to tune reactivity
b) loading with H_2 activation catalysts for reversibility
c) surface functionalization

Density Functional Theory
Ground State Minimization

Direct Method Lattice Dynamics
Thermodynamic Property Prediction

Exploratory mechanistic simulations to guide material selection & design.

Experimental

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Solid State Processing

- Rapid, low cost screening for undesired reaction products between hydrides and framework and impact on reversibility

Nano-Framework

- Synthesize and characterize uncatalyzed and catalyzed nano-frameworks

aspen aerogels

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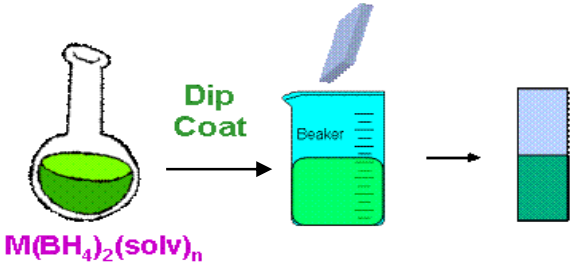
Solution Based Incorporation

- Solvated hydride
- Solvents selected for ease of removal



High-Pressure station

- Solid state reactions
- Wide range of P and T (20,000 psi, 600°C)
- Autoclave with six samples capability

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$NaTi(BH_4)_4$*DME Synthesis

- Synthesize $NaTi(BH_4)_4$*DME by solution based processing
- Incorporation in aerogel

Summary

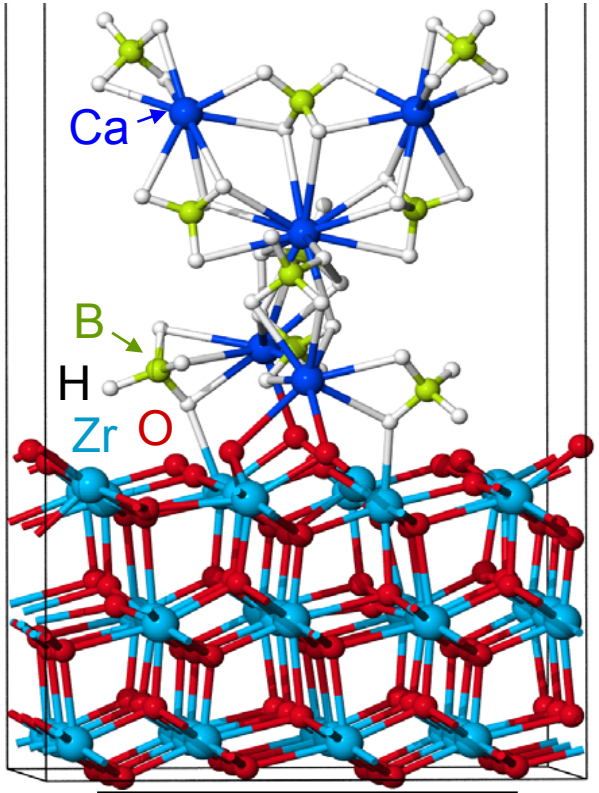
Last Year:

- Down selected ZrO_2 as most stable oxide nano-framework material using $LiBH_4$ as baseline hydride.

This Year:

- **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 Y_2O_3 stabilized ZrO_2 (YSZ) 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 (dimethoxy ether) in aerogels.

Atomic Modeling of $Ca(BH_4)_2*ZrO_2$ Dehydrogenation

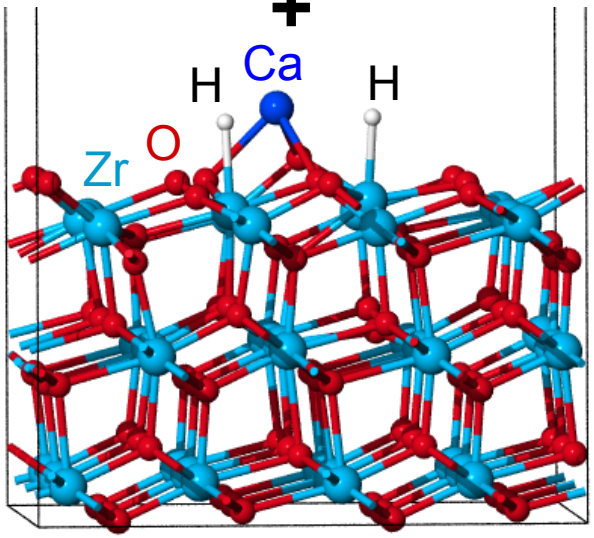


Fully hydrided $Ca_5(BH_4)_{10} * ZrO_2$ interface

$Ca_5(BH_4)_{10}*ZrO_2$ dehydrogenation →

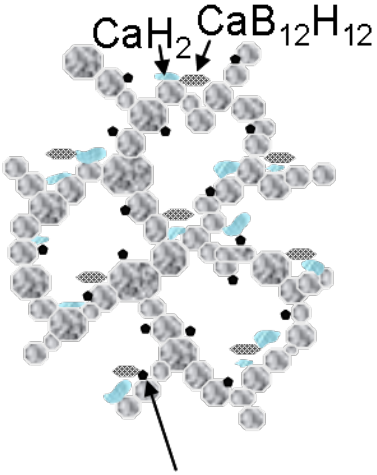
$\{3^1/_6CaH_2 + {}^5/_6CaB_{12}H_{12} + 10\ {}^5/_6H_2\}$ desorbed products

+



Dehydrided interface with most favorable adsorbed CaH_2 product

Dehydrogenation products in nano-framework

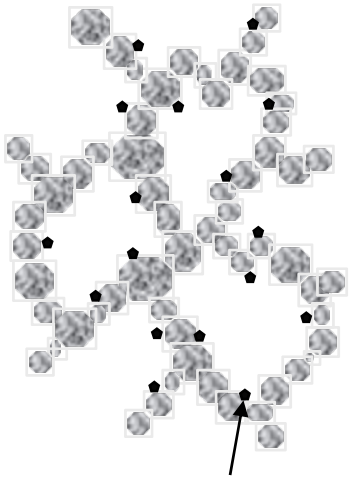


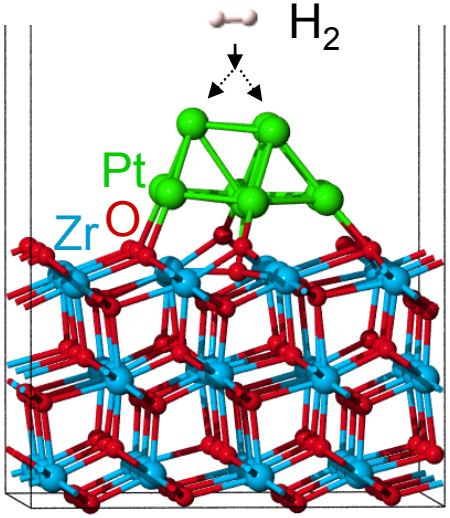
When interfaced with ZrO_2, $Ca(BH_4)_2$ was predicted to have:

* Increased dehydrogenation enthalpy, with an increase of < +14 kJ/m H_2.
* The same order of favorability for competing dehydrogenation reactions.

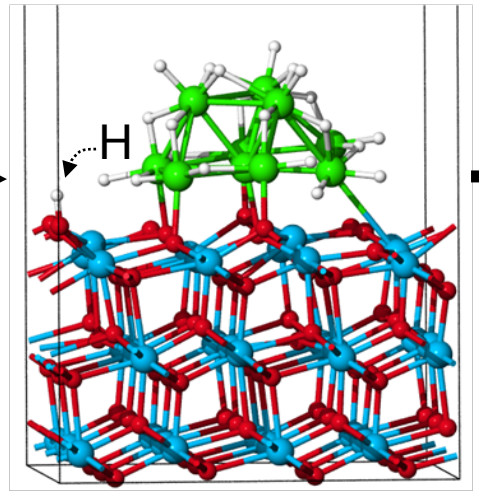
Atomic Modeling of Pt Catalyzed Rehydrogenation

Catalyzed nano-framework

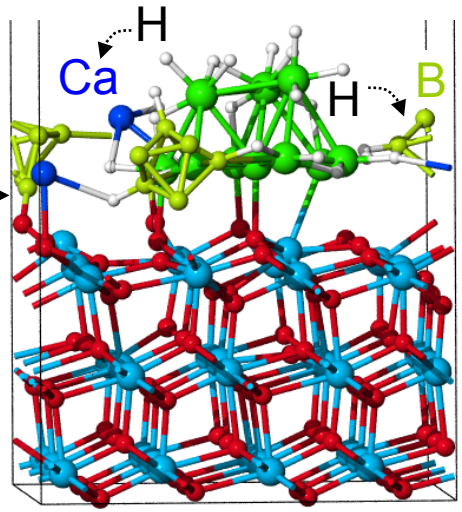




Spontaneous H_2 dissociation and H adsorption on ZrO_2 supported Pt_{10} nano-raft



Exothermic H saturation of Pt_{10} surface and migration to ZrO_2 support

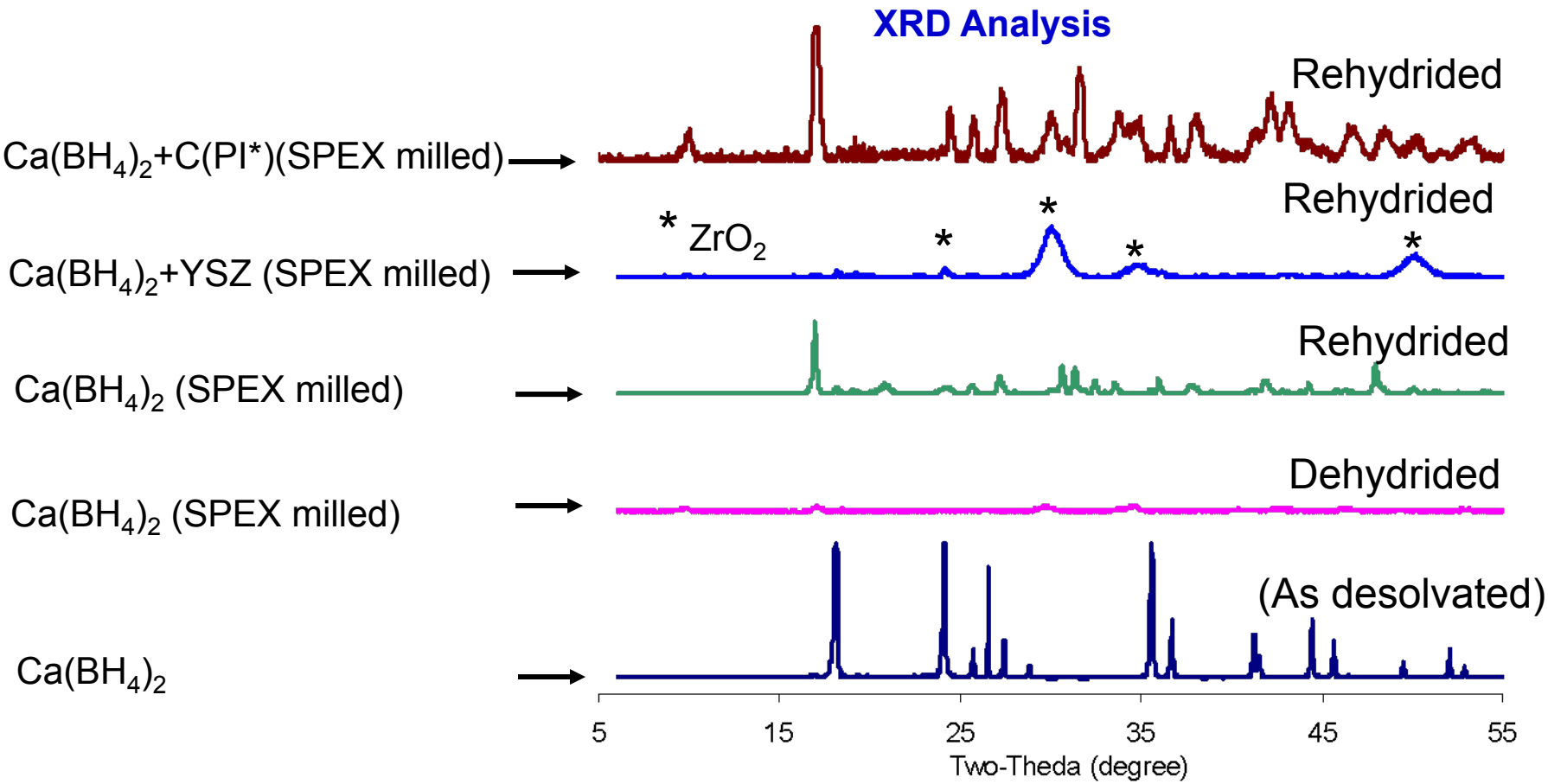


Spontaneous initiation of CaB_6 rehydrogenation adjacent to H-saturated Pt_{10}

Modeling investigations demonstrated utility of H_2 activation catalysts to:

* Facilitate formation, adsorption, and transfer of atomic H,
* Enhance binding and rehydrogenation of dehydrogenated phases.

$Ca(BH_4)_2$ – Framework Interaction



(* PI: Polyimide derived C aerogel, Dehydriding: 350ºC/1 bar, Rehydriding: 350ºC/190 bar)

- $Ca(BH_4)_2$ (low temperature phase) formed in recharged $Ca(BH_4)_2$ and $Ca(BH_4)_2$-C systems, but not in recharged $Ca(BH_4)_2$-YSZ.
- Small amount of products from $Ca(BH_4)_2$ reaction with C framework.

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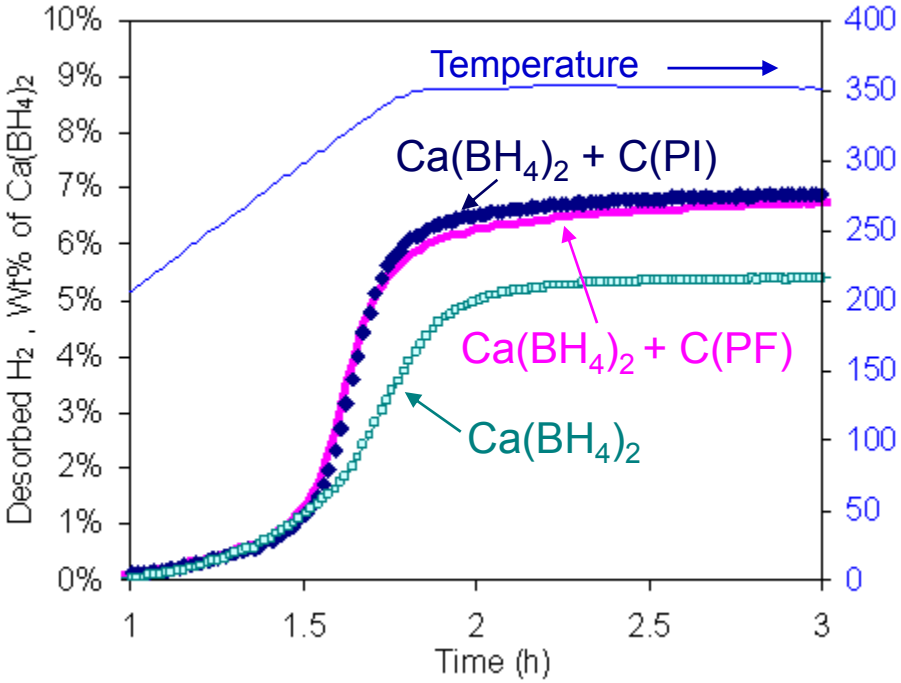
H_2 Desorption of $Ca(BH_4)_2$ Mixed with C Aerogels

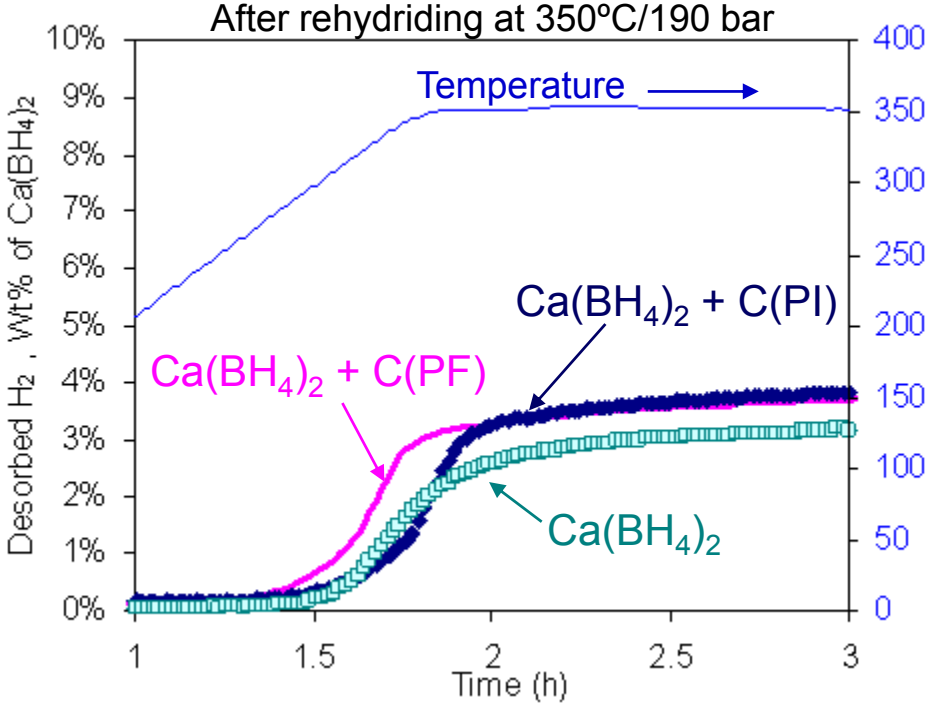
High Energy SPEX Milled

1st Desorption



2nd Desorption

After rehydriding at 350ºC/190 bar



PI: Polyimide derived, PF: Polyphenolic derived

$Ca(BH_4)_2$: C = 1 : 1 (mole ratio)

- Enhanced desorption was observed in $Ca(BH_4)_2$ - C systems.
- C aerogel from PF has faster $Ca(BH_4)_2$ desorption after rehydriding

$Ca(BH_4)_2$ Incorporation (Solution Method)

$Ca(BH_4)_2$ Precursors Investigated:
$Ca(BH_4)_2$*2THF, $Ca(BH_4)_2(py)_4$•py and $Ca(BH_4)_2$*2DME

Solvent: THF and Pyridine

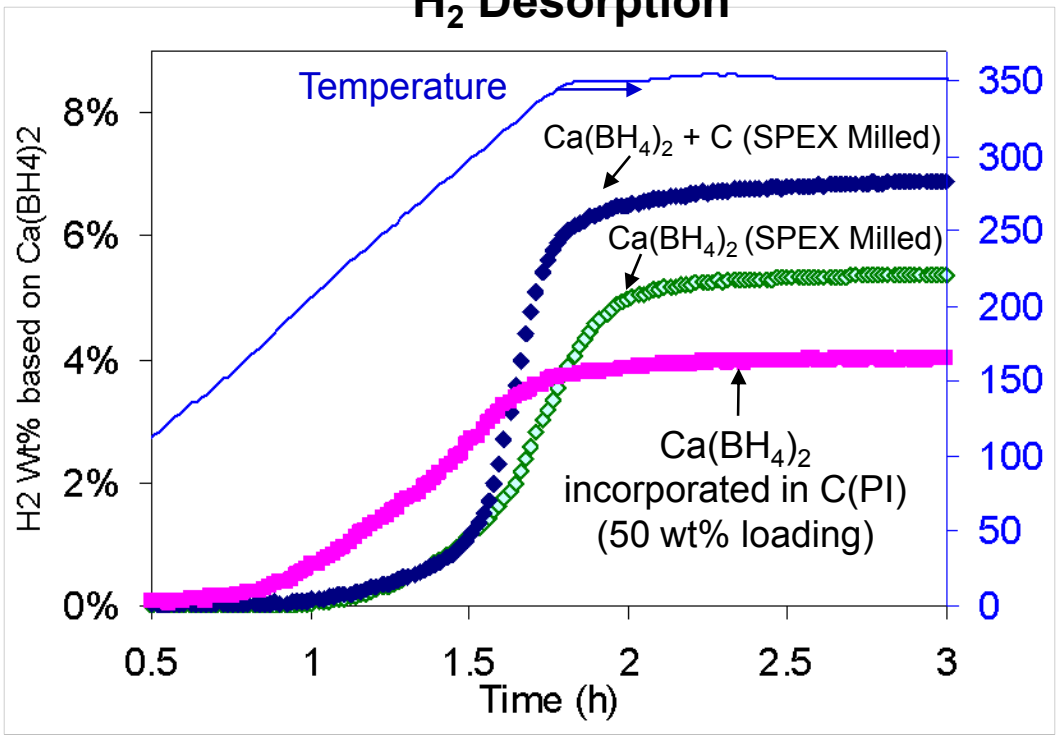
Aerogels: Carbon (PI) (583 m^2/g, 25 nm pore size, 3.67 cc/g pore volume)
Y-stabilized ZrO_2 (138 m^2/g, 12 nm pore size, 0.72 cc/g pore volume)

Incorporation methods for C aerogel:

- Dissolve $Ca(BH_4)_2$*2THF in THF
- Submerge for 48 h
- Remove aerogel from solvent
- Remove solvent from aerogel at 160ºC/vacuum for 24h

- Incorporation of $Ca(BH_4)_2$ in C aerogel lowered H_2 desorption temperature.
- Desorption capacity needs to be optimized.

H_2 Desorption



$Ca(BH_4)_2$ Incorporation (Melting Method)

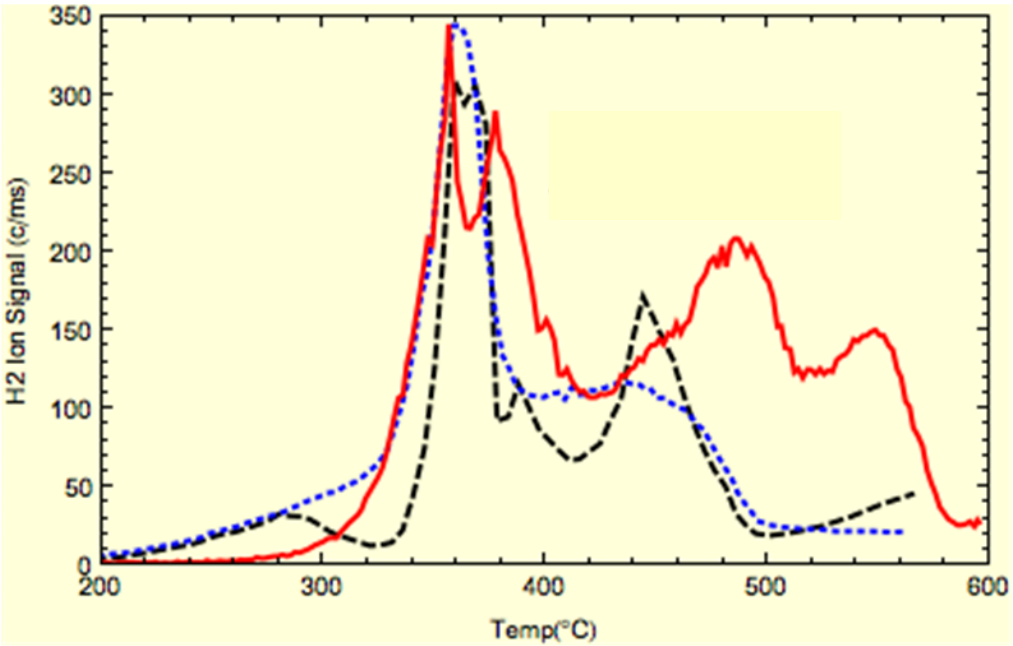
Approach similar to John Vajo et al., HRL

- Melt incorporation of $Ca(BH_4)_2$ into four different nano-frameworks at elevated T and P:
  - C-aerogel (from HRL)
  - Polyimide-derived C-aerogel
  - Phenolic-derived C-aerogel
  - Y-stabilized ZrO_2

- From a visual inspection, it appears that $Ca(BH_4)_2$ wets the surface but also may have been infused into the polyimide-derived C-aerogel

Melt incorporation increases the proportion of hydrogen released at elevated temperatures.

H_2 Evolution from $Ca(BH_4)_2$



Simultaneous Thermo-gravimetric Modulated-Beam Mass Spectrometer (STMBMS)

- Red solid line: $Ca(BH_4)_2$ melt - incorporated in C-aerogel (from HRL)
- Black dashed line: Uncatalyzed $Ca(BH_4)_2$
- Blue dotted line: Catalyzed $Ca(BH_4)_2$ by milling

$NaTi(BH_4)_4$*DME Incorporation (Solution Method)

Hydride Precursor: $NaTi(BH_4)_4$•3DME and $NaTi(BH_4)_4$•DME

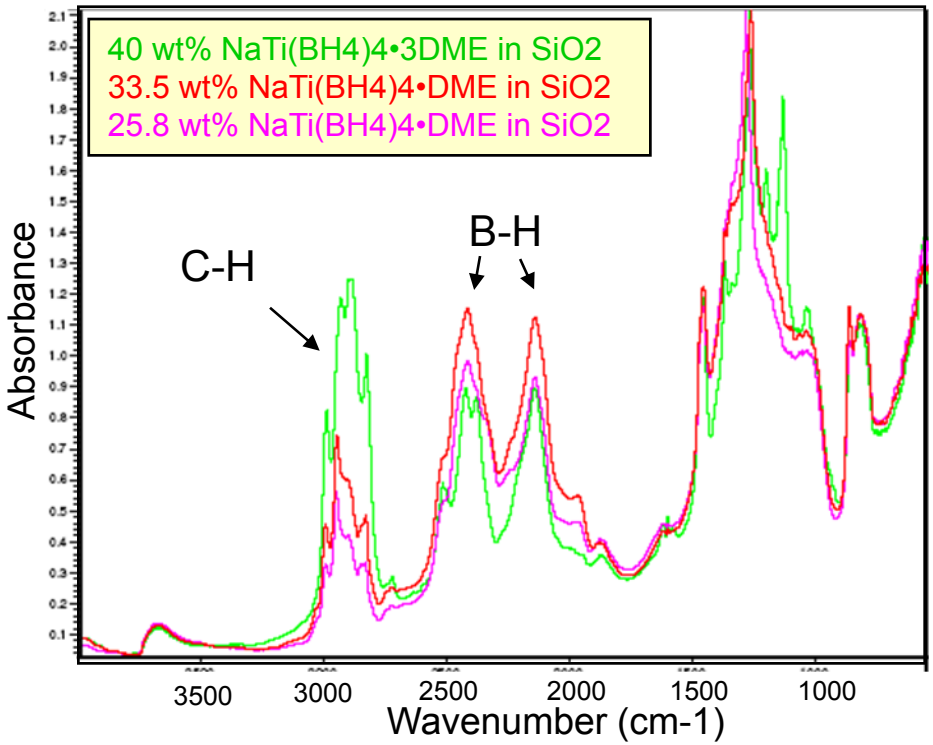
Solvent: DME (Dimethoxyethane)

Aerogel:
- SiO_2 (312m^2/g, 39nm, 1.58cc/g)
- YSZ

Incorporation by solvent route (incipient wetness):
- 40 wt% $NaTi(BH_4)_4$•3DME in SiO_2
- 50 wt% $NaTi(BH_4)_4$•3DME in SiO_2
- 25.8 wt% $NaTi(BH_4)_4$•DME in SiO_2
- 33.5 wt% $NaTi(BH_4)_4$•DME in SiO_2

Stability:
- Baseline precursor material: **< 2 days**
- Incorporated materials **> 10 days**

DRIFTS* of $NaTi(BH_4)_4$ Complexes Incorporated in Silica



* Diffuse Reflectance Infrared Fourier Transform Spectra

- High loading of borohydrides in a SiO_2 aerogel was achieved.
- SiO_2 framework improved stability of unstable hydride, but still not sufficient.

Collaborations

- HRL: John Vajo
  Discussions on related efforts & exchange of aerogels.
- Aspen Aerogels: Wendell Rhine, Sara Rosenberg
  Synthesis and characterization of aerogels.
- LLNL: Ted Baumann
  Discussions on processing of aerogels.
- Ohio State University: J. C. Zhao
  Initiated synthesis of borohydrides.
- Oak Ridge National Laboratory: Gilbert Brown
  Initiated synthesis of borohydrides.
- U Hawaii: Craig Jensen
  Incorporation of $Mg(BH_4)_2$.
- University of Missouri – St. Louis: Eric Majzoub
  Atomic modeling of mixed metal borohydrides.
- Sandia National Laboratory, Livermore: Tim Boyle, Vitalie Stavila, Joe Cordaro, Ewa Rönnebro (now with PNNL)
  Synthesis of mixed metal borohydrides.

Future Work

Atomic Modeling

- Design doped-ZrO_2 to balance interfacial interactions of hydrided and dehydrided storage material candidates.
- Survey influence of candidate ligands on hydride / nano-framework interactions.

Framework and Hydride

- Evaluate the impact of catalyzed nano-frameworks.
- Examine stabilization effect of YSZ and C aerogels on the stability of $NaTi(BH_4)_4$•DME and removal of ligand.
- Consideration of alternate hydride candidates.
- Characterize hydride incorporated in nano-framework (uncatalyzed and catalyzed) with BET, SEM, etc.
- Optimize hydrogen storage performance.

Go / No-Go decision affecting project execution & emphasis in final year.

Summary

To advance the understanding of how nano-frameworks can enhance the performance of storage candidates, a range of material / framework combinations and effects has been investigated including:

- Down-selected functionalized C and ZrO_2 as most suitable framework materials for future catalyzation investigations.
- Simulated the atomic mechanism for heterogeneously catalyzed H_2 dissociation and H transfer to kinetically facilitate rehydrogenation of $Ca(BH_4)_2$ dehydrogenation products.
- Obtained a decrease in H_2 desorption temperature of the stable borohydride $Ca(BH_4)_2$ incorporated in C aerogels by solution based incorporation.
- Demonstrated high loading of $NaTi(BH_4)_4$*ligand in SiO_2 aerogel and improved hydride stability with the aerogel.

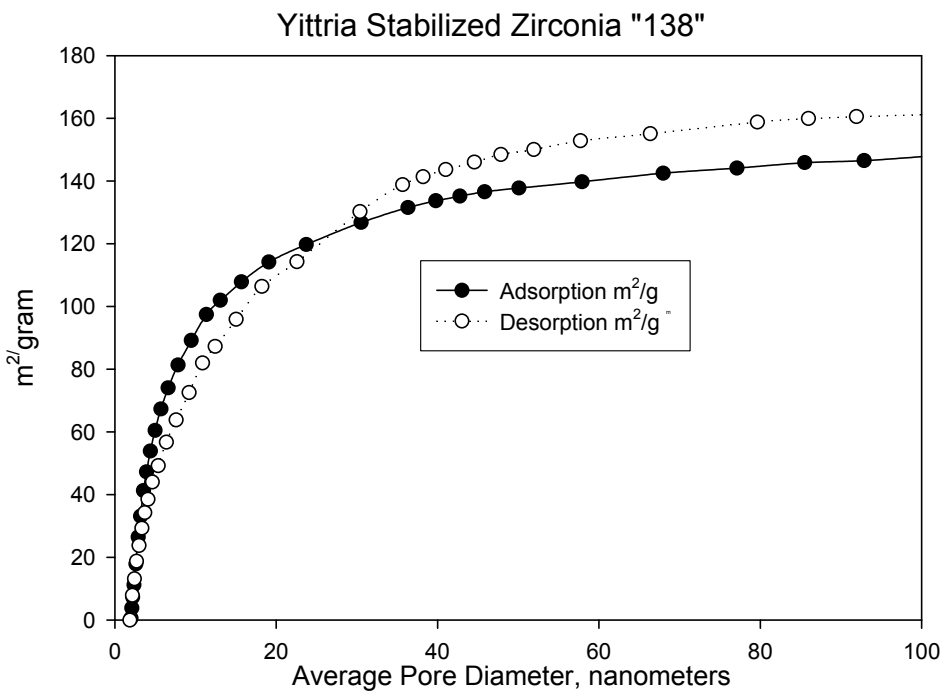
Additional Slides

Framework Characterization

In-house BET Analysis

- Determine pore size distribution and pore volume for nano–framework
- Provide guidance in optimizing calcination conditions
- Evaluate hydride incorporation

Yttria Stabilized Zirconia

Calcination Conditions	Surface Area [m^2/g]	Average Pore Diameter [nm]	Pore Volume [cc/g]
-	417	11.8	1.65
550ºC / 1h	148	11.7	0.72
550ºC / 1h **	199	13.8	0.69
400ºC / 6h	221	15.2	0.92

** Pt loaded YSZ