

# Catalyzed Nano-Framework Stabilized High Density Reversible Hydrogen Storage Systems

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Corporation

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# 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](http://www.eere.energy.gov/hydrogenandfuelcells/mypp)

## ■ Partner Participation

- United Technologies Research Center (Project Lead)
- Sandia National Laboratories
- Albemarle Corporation
- 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<sub>2</sub> 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
<b>Hydride Candidates</b>	<ul style="list-style-type: none"> <li>Examine composites with <math>\text{Ca}(\text{BH}_4)_2</math>, a reversible borohydride with 9.6 wt% theoretical capacity, which is overly stable.</li> <li>Examine <math>\text{NaTi}(\text{BH}_4)_4</math> as a high-capacity candidate which is unstable and requires ligands to stabilize.</li> </ul>
<b>Atomic / Therm. Modeling</b>	<ul style="list-style-type: none"> <li>Evaluate hydride-framework interactions: associative stabilization, decomposition/side-products, dehydrogenation, to guide experiments.</li> <li>Explore heterogeneous catalysis of hydride reversibility by modeling <math>\text{H}_2</math> dissociation, H migration, and rehydrogenation.</li> </ul>
<b>Nano-Framework Development</b>	<ul style="list-style-type: none"> <li>Evaluate a range of framework chemistries, with a focus on <b>oxides</b> and (functionalized) <b>carbons</b>, for their influence on the hydride candidates.</li> <li><b>Catalyze</b> the nano-frameworks to promote <math>\text{H}_2</math> dissociation.</li> </ul>
<b>Hydride Incorporation</b>	<ul style="list-style-type: none"> <li>Employ both melt and <b>solution</b> based incorporation methods.</li> <li>Focus on solution-based incorporation methods for unstable hydrides.</li> </ul>
<b>Characterization</b>	<ul style="list-style-type: none"> <li>Screen hydride / framework combination candidates for chemical compatibility, to ensure framework integrity and cyclability.</li> <li>Examine hydride-incorporated frameworks.</li> </ul>

# Milestones

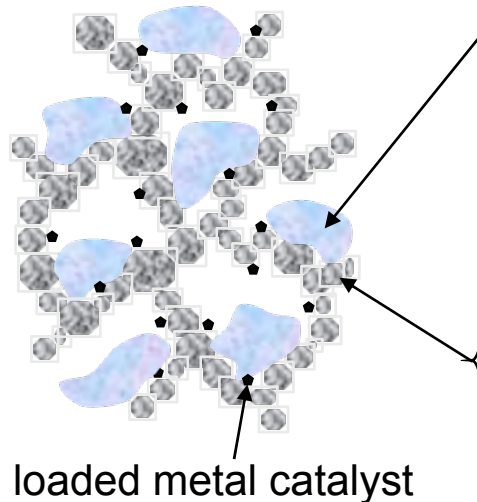
Date	Milestone or Go / No Go Decision
2008 Q1	Select advanced nano-framework structure
2008 Q1	Demonstrate synthesis of desired nano-framework structure
2008 Q1	Synthesize top Sandia candidate hydride material
2008 Q2	Synthesize top UTRC / Albemarle candidate hydride material
2008 Q4	Evaluate relative 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.

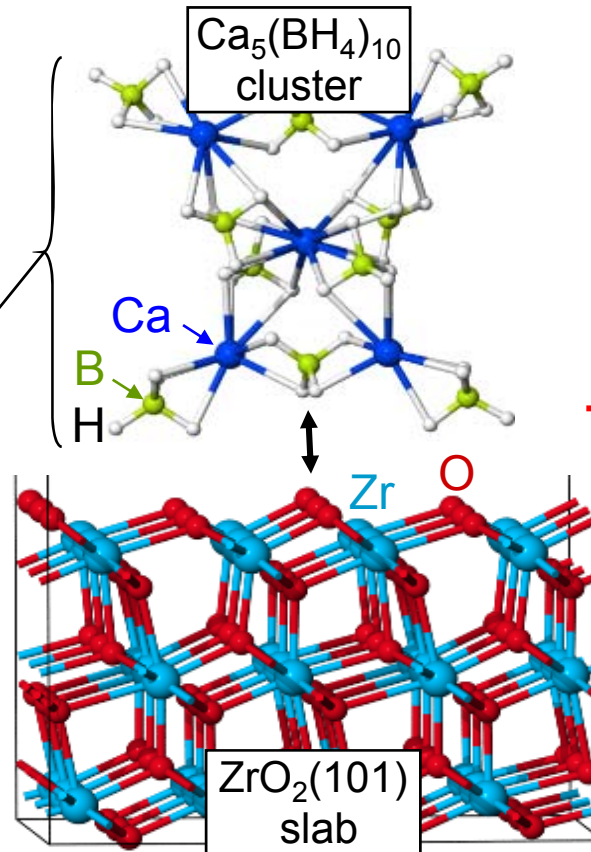
# Atomic Modeling

## Concept

Hydride-filled nano-framework



## 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<sub>2</sub> 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



## Solid State Processing

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

## Nano-Framework

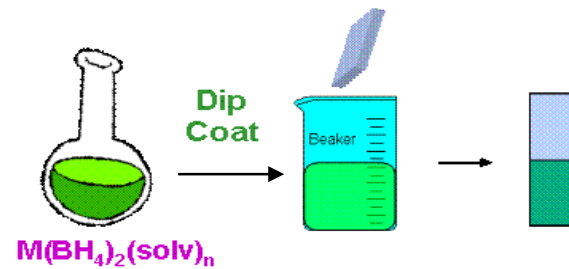
- Synthesize and characterize uncatalyzed and catalyzed nano-frameworks

aspen|aerogels



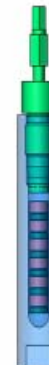
## Solution Based Incorporation

- 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



## NaTi(BH<sub>4</sub>)<sub>4</sub>\*DME Synthesis

- Synthesize NaTi(BH<sub>4</sub>)<sub>4</sub>\*DME by solution based processing
- Incorporation in aerogel



# Summary

## Last Year:

- Down selected  $\text{ZrO}_2$  as most stable oxide nano-framework material using  $\text{LiBH}_4$  as baseline hydride.

## This Year:

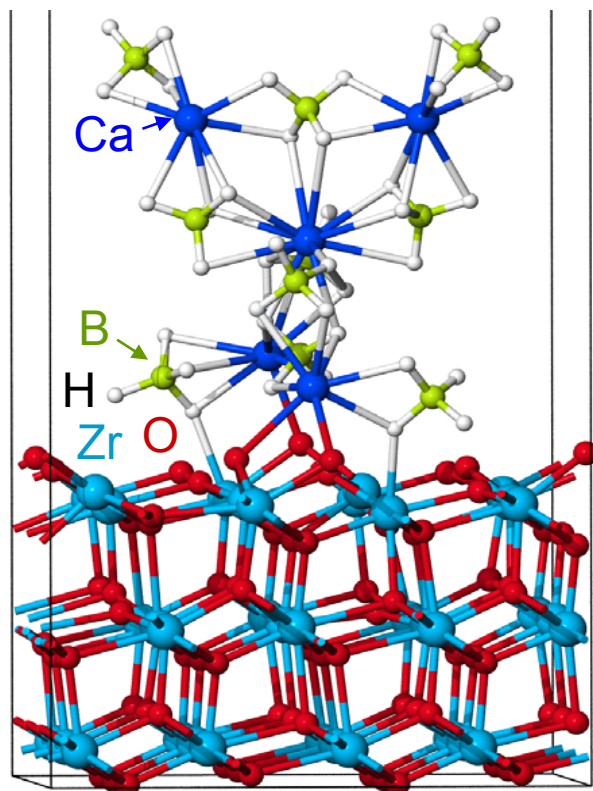
### ▪ Atomic Modeling:

- Evaluated interaction of  $\text{Ca}(\text{BH}_4)_2$  with  $\text{ZrO}_2$  framework and its impact on  $\text{Ca}(\text{BH}_4)_2$  dehydrogenation.
- Investigated the effect of Pt catalyzed  $\text{ZrO}_2$  on hydrogen dissociation and  $\text{Ca}(\text{BH}_4)_2$  rehydrogenation.

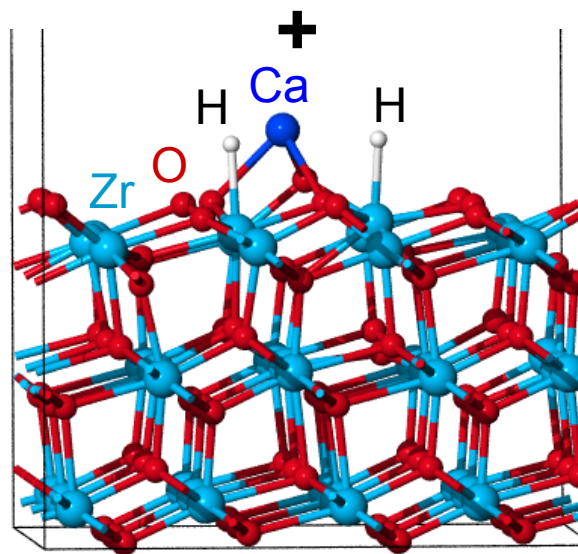
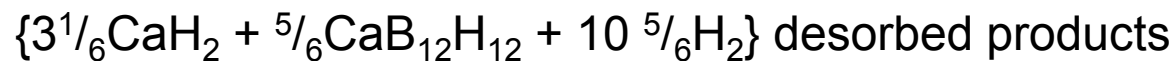
### ▪ Framework and Hydride (Experimental):

- Conducted evaluation of the reactivity of  $\text{Ca}(\text{BH}_4)_2$  with  $\text{Y}_2\text{O}_3$  stabilized  $\text{ZrO}_2$  (YSZ) and functionalized carbon aerogels.
- Identified the impact of uncatalyzed framework materials on  $\text{Ca}(\text{BH}_4)_2$  rehydrogenation.
- Incorporated  $\text{Ca}(\text{BH}_4)_2$  and  $\text{NaTi}(\text{BH}_4)_4^*$  DME (dimethoxy ether) in aerogels.

# Atomic Modeling of $\text{Ca}(\text{BH}_4)_2 \cdot \text{ZrO}_2$ Dehydrogenation

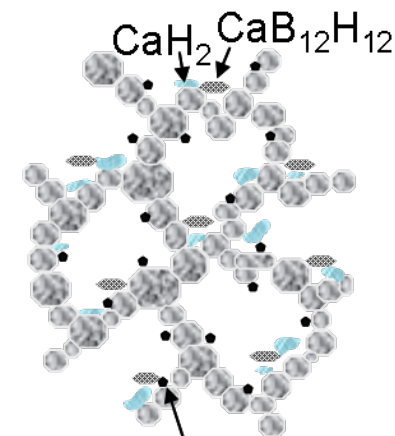


Fully hydrided  
 $\text{Ca}_5(\text{BH}_4)_{10} \cdot \text{ZrO}_2$   
interface



Dehydrided interface  
with most favorable  
adsorbed  $\text{CaH}_2$  product

Dehydrogenation  
products in  
nano-framework



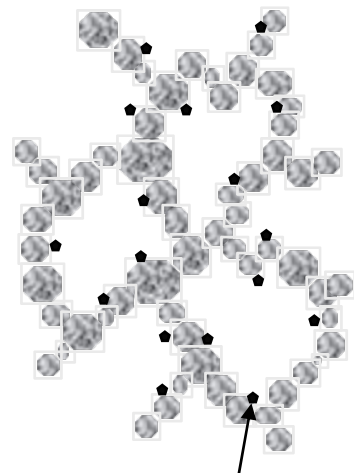
loaded metal catalyst

When interfaced with  $\text{ZrO}_2$ ,  $\text{Ca}(\text{BH}_4)_2$  was predicted to have:

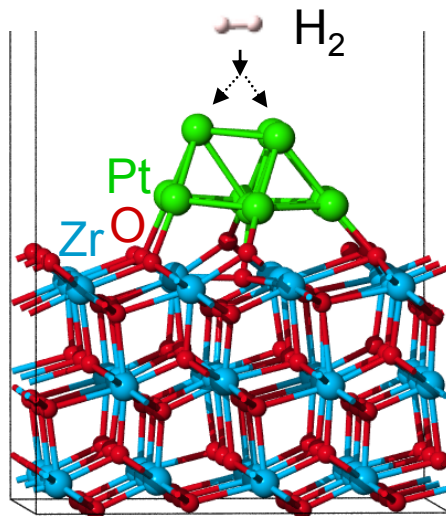
- \* Increased dehydrogenation enthalpy, with an increase of  $< +14 \text{ kJ/m H}_2$ .
- \* The same order of favorability for competing dehydrogenation reactions.

# Atomic Modeling of Pt Catalyzed Rehydrogenation

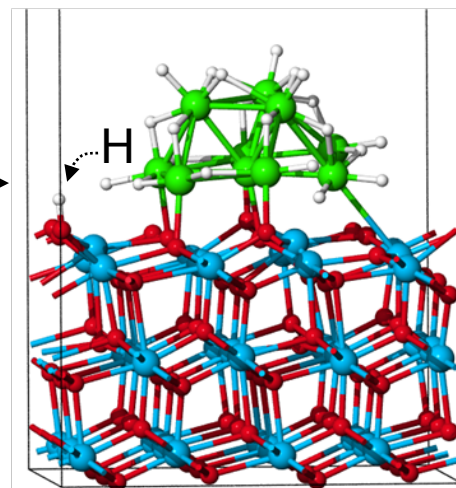
Catalyzed  
nano-framework



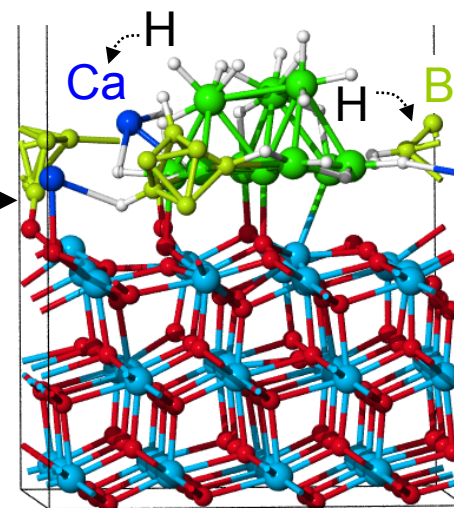
loaded metal  
catalyst



Spontaneous  
H<sub>2</sub> dissociation  
and H adsorption  
on ZrO<sub>2</sub> supported  
Pt<sub>10</sub> nano-raft



Exothermic H  
saturation of  
Pt<sub>10</sub> surface and  
migration to  
ZrO<sub>2</sub> support

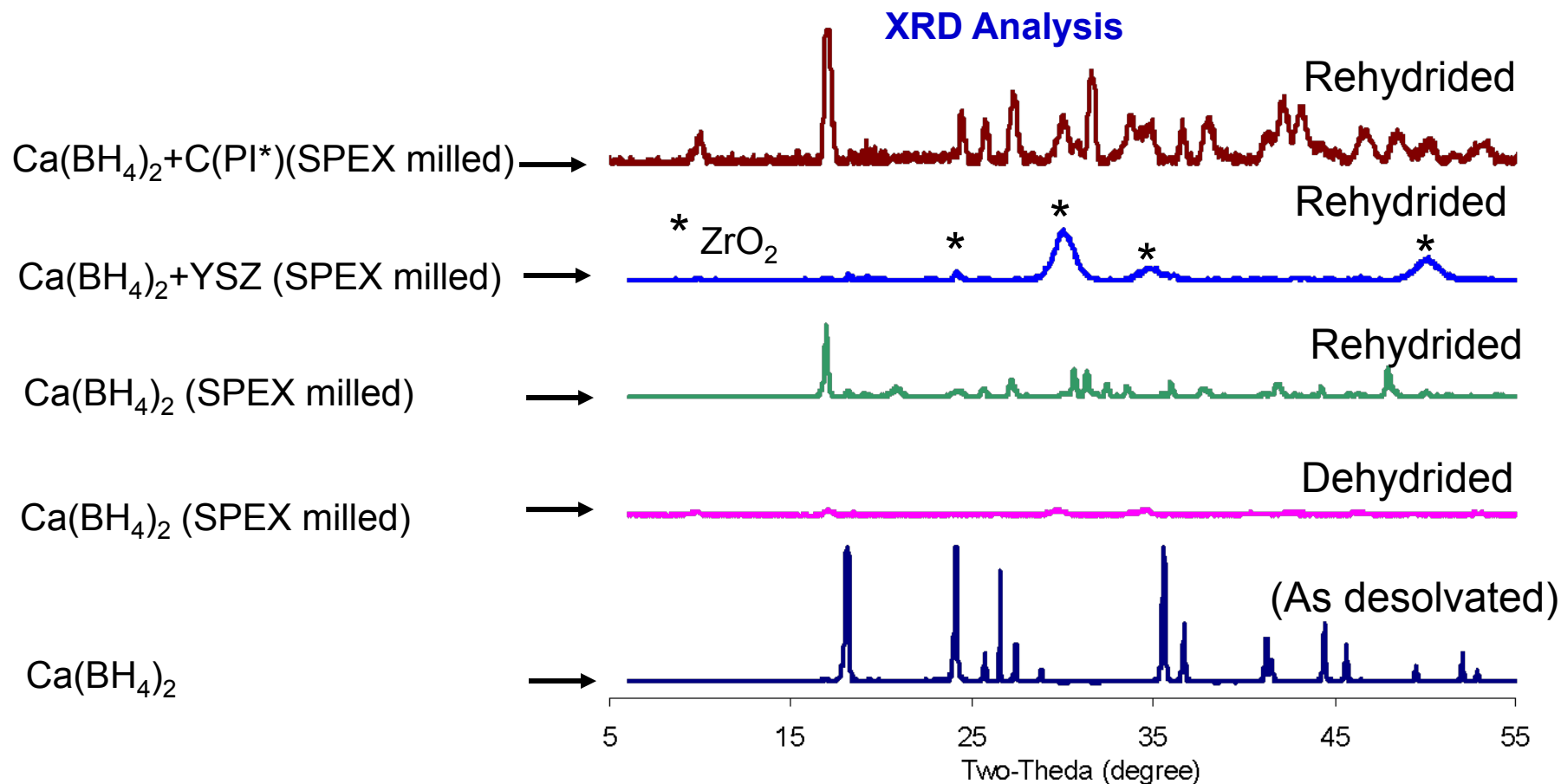


Spontaneous  
initiation of CaB<sub>6</sub>  
rehydrogenation  
adjacent to  
H-saturated Pt<sub>10</sub>

Modeling investigations demonstrated utility of H<sub>2</sub> activation catalysts to:

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

# Ca(BH<sub>4</sub>)<sub>2</sub> – Framework Interaction



(\* PI: Polyimide derived C aerogel, Dehydrating: 350°C/1 bar, Rehydrating: 350°C/190 bar )

- Ca(BH<sub>4</sub>)<sub>2</sub> (low temperature phase) formed in recharged Ca(BH<sub>4</sub>)<sub>2</sub> and Ca(BH<sub>4</sub>)<sub>2</sub>-C systems, but not in recharged Ca(BH<sub>4</sub>)<sub>2</sub>-YSZ.
- Small amount of products from Ca(BH<sub>4</sub>)<sub>2</sub> reaction with C framework.

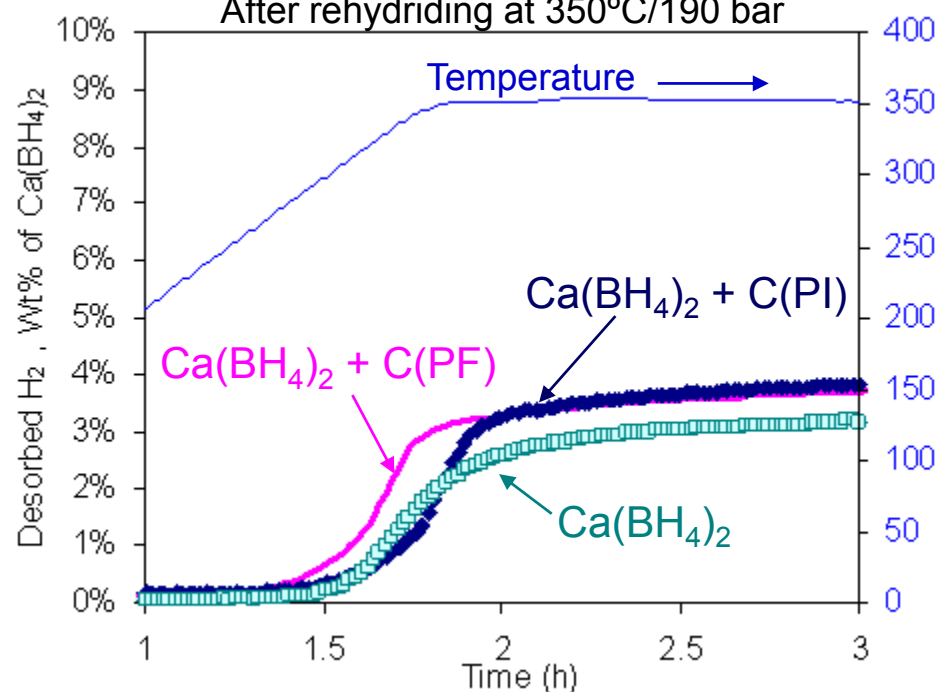
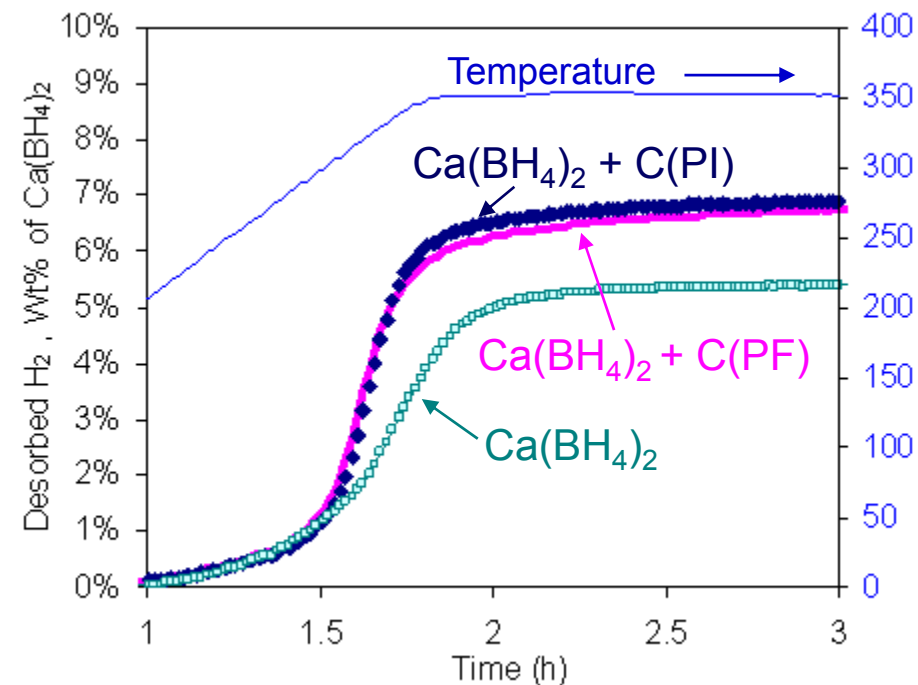
# H<sub>2</sub> Desorption of Ca(BH<sub>4</sub>)<sub>2</sub> Mixed with C Aerogels

High Energy SPEX Milled

## 1<sup>st</sup> Desorption

## 2<sup>nd</sup> Desorption

After rehydrating at 350°C/190 bar



PI: Polyimide derived, PF: Polyphenolic derived  
 Ca(BH<sub>4</sub>)<sub>2</sub> : C = 1 : 1 (mole ratio)

- Enhanced desorption was observed in Ca(BH<sub>4</sub>)<sub>2</sub> - C systems.
- C aerogel from PF has faster Ca(BH<sub>4</sub>)<sub>2</sub> desorption after rehydrating

## Ca(BH<sub>4</sub>)<sub>2</sub> Precursors Investigated:

Ca(BH<sub>4</sub>)<sub>2</sub>\*2THF, Ca(BH<sub>4</sub>)<sub>2</sub>(py)<sub>4</sub>•py and Ca(BH<sub>4</sub>)<sub>2</sub>\*2DME

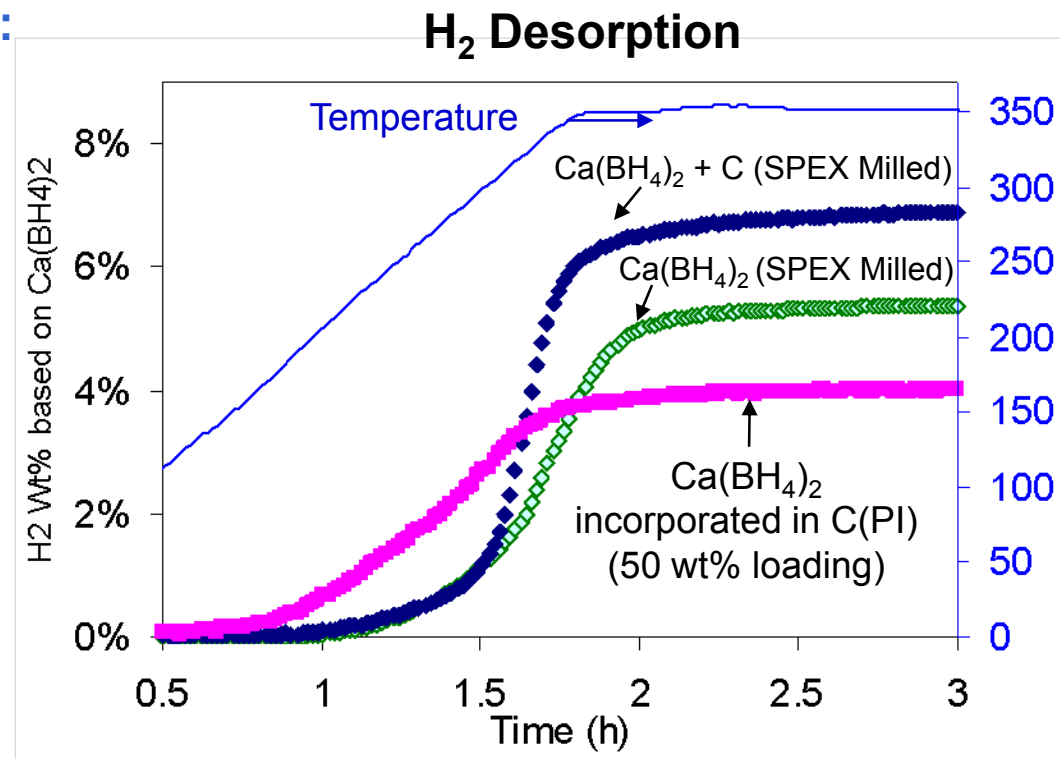
**Solvent:** THF and Pyridine

**Aerogels:** Carbon (PI) (583 m<sup>2</sup>/g, 25 nm pore size, 3.67 cc/g pore volume)  
 Y-stabilized ZrO<sub>2</sub> (138 m<sup>2</sup>/g, 12 nm pore size, 0.72 cc/g pore volume)

## Incorporation methods for C aerogel:

- Dissolve Ca(BH<sub>4</sub>)<sub>2</sub>\*2THF in THF
- Submerge for 48 h
- Remove aerogel from solvent
- Remove solvent from aerogel at 160°C/vacuum for 24h

- Incorporation of Ca(BH<sub>4</sub>)<sub>2</sub> in C aerogel lowered H<sub>2</sub> desorption temperature.
- Desorption capacity needs to be optimized.

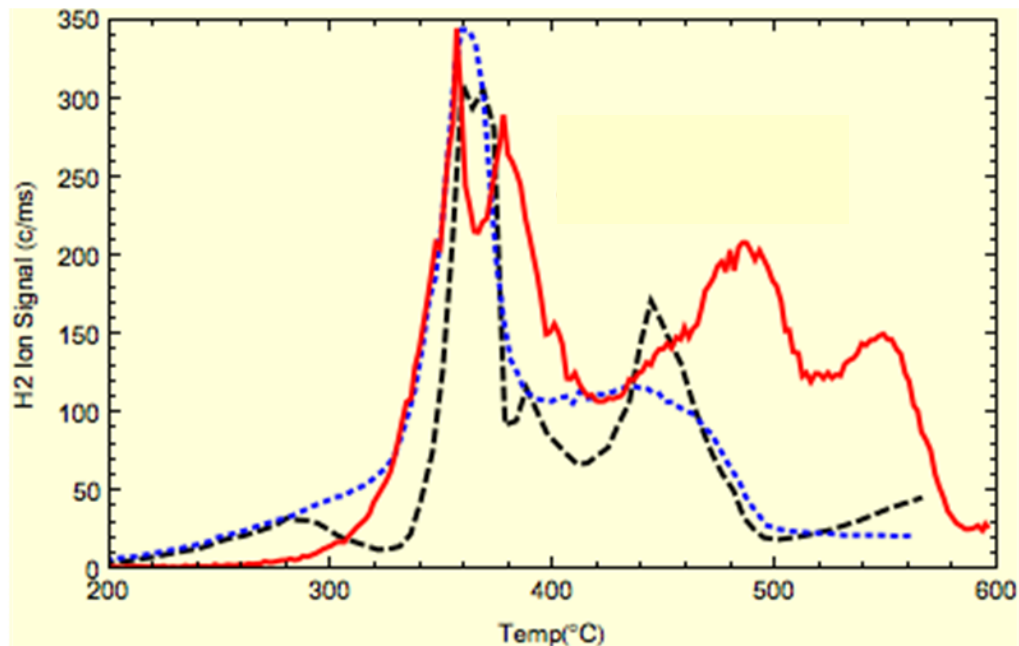


# Ca(BH<sub>4</sub>)<sub>2</sub> Incorporation (Melting Method)

*Approach similar to John Vajo et al., HRL*

- Melt incorporation of Ca(BH<sub>4</sub>)<sub>2</sub> 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<sub>2</sub>
  
- From a visual inspection, it appears that Ca(BH<sub>4</sub>)<sub>2</sub> wets the surface but also may have been infused into the polyimide-derived C-aerogel

## H<sub>2</sub> Evolution from Ca(BH<sub>4</sub>)<sub>2</sub>



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

- Ca(BH<sub>4</sub>)<sub>2</sub> melt - incorporated in C-aerogel (from HRL)
- - - Uncatalyzed Ca(BH<sub>4</sub>)<sub>2</sub>
- ..... Catalyzed Ca(BH<sub>4</sub>)<sub>2</sub> by milling

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

# NaTi(BH<sub>4</sub>)<sub>4</sub>\*DME Incorporation (Solution Method)



**Hydride Precursor:** NaTi(BH<sub>4</sub>)<sub>4</sub>•3DME and NaTi(BH<sub>4</sub>)<sub>4</sub>•DME

**Solvent:** DME (Dimethoxyethane)

**Aerogel:**

- SiO<sub>2</sub> (312m<sup>2</sup>/g, 39nm, 1.58cc/g)
- YSZ

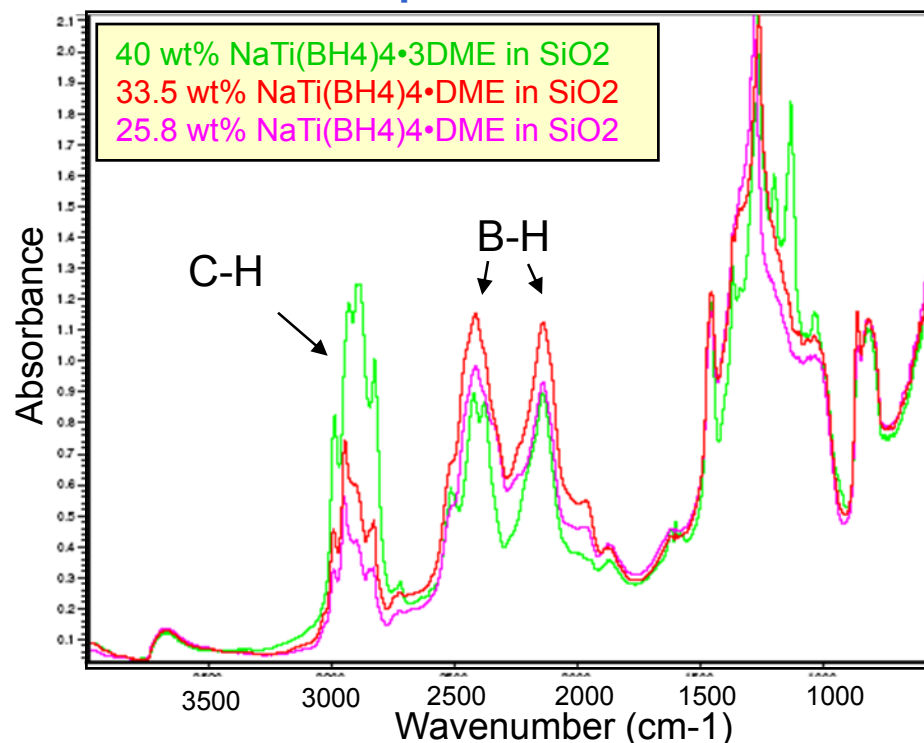
**Incorporation by solvent route (incipient wetness):**

- 40 wt% NaTi(BH<sub>4</sub>)<sub>4</sub>•3DME in SiO<sub>2</sub>
- 50 wt% NaTi(BH<sub>4</sub>)<sub>4</sub>•3DME in SiO<sub>2</sub>
- 25.8 wt% NaTi(BH<sub>4</sub>)<sub>4</sub>•DME in SiO<sub>2</sub>
- 33.5 wt% NaTi(BH<sub>4</sub>)<sub>4</sub>•DME in SiO<sub>2</sub>

**Stability:**

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

**DRIFTS\* of NaTi(BH<sub>4</sub>)<sub>4</sub> Complexes Incorporated in Silica**



\* Diffuse Reflectance Infrared Fourier Transform Spectra

- High loading of borohydrides in a SiO<sub>2</sub> aerogel was achieved.
- SiO<sub>2</sub> framework improved stability of unstable hydride, but still not sufficient.



# Collaborations

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- **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  $\text{Mg}(\text{BH}_4)_2$ .
- **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

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## Atomic Modeling

- Design doped-ZrO<sub>2</sub> 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<sub>4</sub>)<sub>4</sub>•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

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

# Additional Slides

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# 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 <sup>2</sup> /g]	Average Pore Diameter [nm]	Pore Volume [cc/g]
-	417	11.8	1.65
550°C / 1h	148	11.7	0.72
550°C / 1h **	199	13.8	0.69
400°C / 6h	221	15.2	0.92

\*\* Pt loaded YSZ

