

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

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# Overview

## ■ Timeline

- Start : 7/1/07
- Finish: 7/1/10
- 100% Complete

## ■ Budget

- \$1.26M Total Program
- DOE: \$1.01M
  - SNL: \$360k
  - Cost share: 20% (31% UTRC \$)
- FY07: \$168k
- FY08: \$482k
- FY09: \$460k
- FY10: \$147k

## ■ 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

## 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.
- Develop doped, functionalized, and catalyzed frameworks.

# Challenges & Objectives

## Objectives (cont.):

- Tune hydride / framework interactions to:
  - Decrease desorption temperature for highly stable compounds.
  - Stabilize unstable high capacity compounds and eliminate ligands.
  - Influence desorption product formation to improve reversibility.
- Develop and apply atomic modeling techniques to evaluate and design local interactions by surface functionalization to achieve reversibility.
- 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.

# Areas of Focus

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

	Description
<b>Hydride Candidates</b>	<ul style="list-style-type: none"> <li>Examined composites with <math>\text{Ca}(\text{BH}_4)_2</math> and <math>\text{Mg}(\text{BH}_4)_2</math>, reversible borohydrides with high theoretical capacity, which are overly stable.</li> <li>Examined <math>\text{NaTi}(\text{BH}_4)_4</math> as a high capacity candidate which is unstable and requires stabilization by ligands.</li> </ul>
<b>Atomic / Thermodynamic Modeling</b>	<ul style="list-style-type: none"> <li>Explored heterogeneous catalysis of hydride reversibility by modeling <math>\text{H}_2</math> dissociation, H migration, and rehydrogenation.</li> <li>Investigated <math>\text{NaTi}(\text{BH}_4)_4</math> stabilization on <b>functionalized</b> surfaces.</li> </ul>
<b>Nano-Framework Development</b>	<ul style="list-style-type: none"> <li>Evaluated influence of framework chemistries on hydride candidates, with a focus on <b>oxides</b> and <b>carbons</b> with different functional surfaces.</li> <li>Heterogeneously catalyzed frameworks to promote <math>\text{H}_2</math> dissociation.</li> </ul>
<b>Hydride Incorporation</b>	<ul style="list-style-type: none"> <li>Investigated both melt- and solution-based incorporation methods.</li> <li>Focused on <b>solution-based</b> incorporation methods for hydride.</li> </ul>
<b>Characterization</b>	<ul style="list-style-type: none"> <li>Screened combined hydride / framework candidates for chemical compatibility to ensure framework integrity and cyclability.</li> <li>Characterized hydride-incorporated frameworks.</li> </ul>

\* Blue highlighting was focused work in 2009/2010.



# Milestones

Date	Major Milestone or Go / No Go Decision in FY 2009
2009 Q2	Evaluated H <sub>2</sub> desorption/absorption performance of Ca(BH <sub>4</sub> ) <sub>2</sub> in C aerogels.
2009 Q3	Synthesized platinum catalyzed nano-framework structure.
2009 Q3	Achieved incorporation of Ca(BH <sub>4</sub> ) <sub>2</sub> in C aerogel at 39 wt% loading level by solution method.
2009 Q3	Go/No go decision to proceed with a modified plan.
2009 Q4	Incorporation of Ca(BH <sub>4</sub> ) <sub>2</sub> in Pt-catalyzed ZrO <sub>2</sub> aerogel.
2009 Q4	Evaluated and characterized Ca(BH <sub>4</sub> ) <sub>2</sub> in Pt-catalyzed ZrO <sub>2</sub> aerogel.
2010 Q1	Incorporation of Mg(BH <sub>4</sub> ) <sub>2</sub> in C aerogel at 47.7 wt% loading level.
2010 Q2	Evaluated H <sub>2</sub> desorption/absorption performance of Mg(BH <sub>4</sub> ) <sub>2</sub> -C aerogel composite.
2010 Q3	Final report

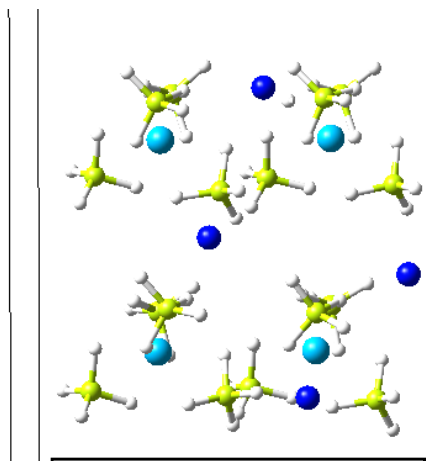
 Completed

# Atomic Modeling

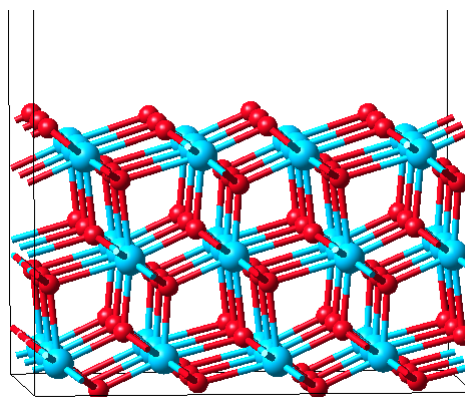


Methodology:

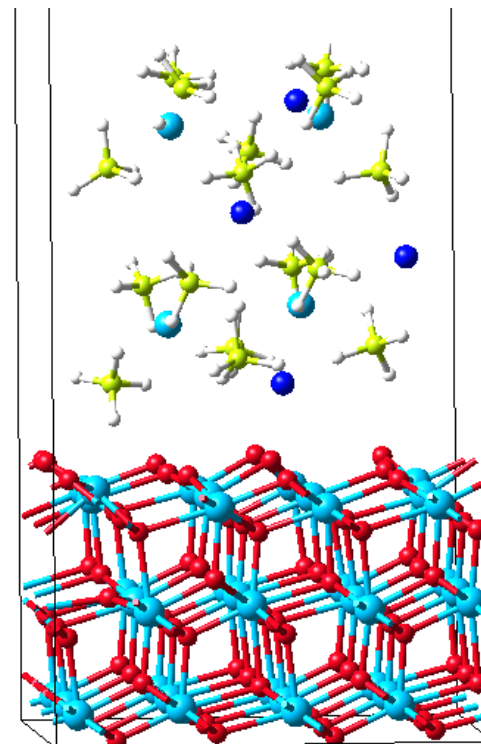
VASP density functional theory atomic modeling investigations of  $\text{NaTi}(\text{BH}_4)_4$  stabilization within functionalized  $\text{ZrO}_2$  nano-frameworks.



**4[NaTi(BH<sub>4</sub>)<sub>4</sub>]  
Cluster**



**ZrO<sub>2</sub>P<sub>4</sub><sub>2</sub>/NMCZ  
(101) Slab Surface**



**NaTi(BH<sub>4</sub>)<sub>4</sub> / ZrO<sub>2</sub>  
Interface**

Approach:

Survey functional group interactions with or at:

High capacity hydride compounds [ $\text{NaTi}(\text{BH}_4)_4$ ]

Nano-framework surfaces [tetragonal  $\text{ZrO}_2^*$ ]

Hydride-loaded nano-framework interface [ $\text{NaTi}(\text{BH}_4)_4\text{-ZrO}_2$ ]

\*  $\text{ZrO}_2$  was selected due to its stability against hydride (slide #9) .

## Experimentation

### Solid-State Processing

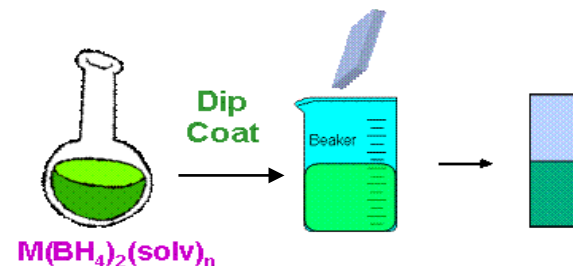
- Rapid screening of hydride – framework reactivity to down-select framework material

### Nano-Framework

- Synthesize and characterize uncatalyzed and catalyzed nano-frameworks

### Solution Based Incorporation

- Solvated hydride
- Solvents selected for ease of removal



### High-Pressure Station for Melt Based Incorporation

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



### $NaTi(BH_4)_4$ \*DME Synthesis

- Solution-based synthesis processing
- Incorporation in aerogel



# Summary of Accomplishments

## 1<sup>st</sup> Year:

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

## 2<sup>nd</sup> Year:

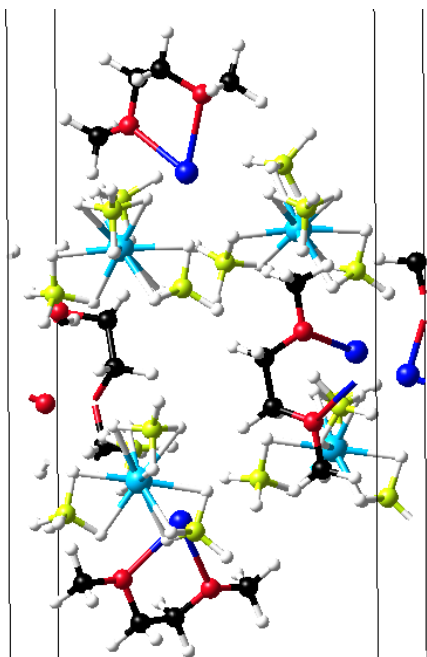
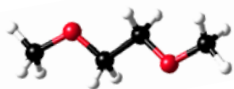
- Evaluated interaction of  $\text{Ca}(\text{BH}_4)_2$  with  $\text{ZrO}_2$  surface and effect of Pt-catalyzed  $\text{ZrO}_2$  on  $\text{H}_2$  dissociation and  $\text{Ca}(\text{BH}_4)_2$  rehydrogenation by atomic modeling.
- Investigated the reactivity of  $\text{Ca}(\text{BH}_4)_2$  with functionalized carbon aerogels and  $\text{Y}_2\text{O}_3$ -stabilized  $\text{ZrO}_2$  (YSZ) and the impact of uncatalyzed nano-framework materials on  $\text{Ca}(\text{BH}_4)_2$  rehydrogenation.
- Incorporated  $\text{Ca}(\text{BH}_4)_2$  and  $\text{NaTi}(\text{BH}_4)_4$ \* dimethoxyethane (DME) in aerogels.

## 3<sup>rd</sup> Year: (This Year)

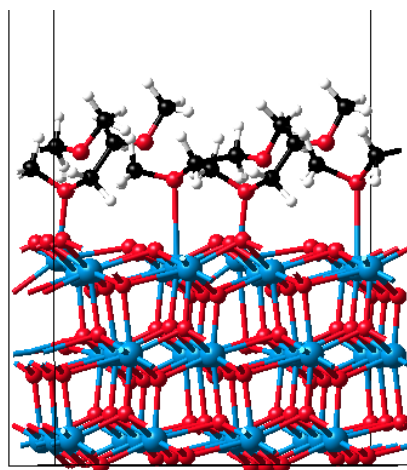
- Atomic modeling investigation of  $\text{NaTi}(\text{BH}_4)_4$  stabilization on functionalized nano-framework surface.
- Optimized incorporation of  $\text{Ca}(\text{BH}_4)_2$  and  $\text{Mg}(\text{BH}_4)_2$  in C and Pt-catalyzed  $\text{ZrO}_2$  aerogels using solution method for high hydride loading.
- Examined  $\text{H}_2$  desorption and absorption properties of  $\text{Ca}(\text{BH}_4)_2$  and  $\text{Mg}(\text{BH}_4)_2$ -aerogel composites.

# Benchmark: DME-Functionalized NaTi(BH<sub>4</sub>)<sub>4</sub>, ZrO<sub>2</sub>, & Interface

Functionalization with  
DME = CH<sub>3</sub>OC<sub>2</sub>H<sub>4</sub>OCH<sub>3</sub>

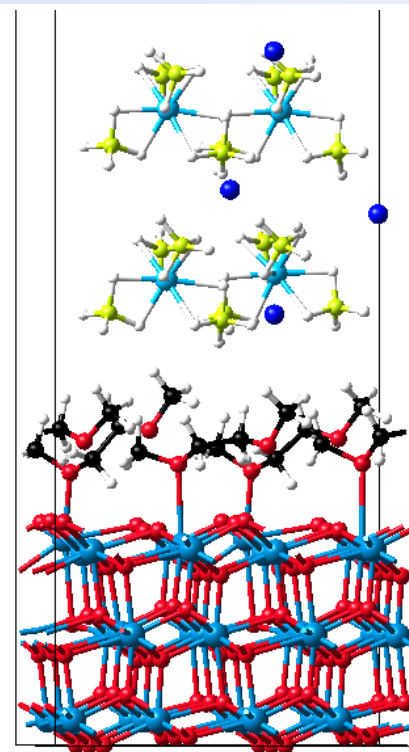


4[NaTi(BH<sub>4</sub>)<sub>4</sub>] \* 4 DME



0.33 ML DME on ZrO<sub>2</sub>

ML = monolayer



NaTi(BH<sub>4</sub>)<sub>4</sub> -  
0.33 ML DME \* ZrO<sub>2</sub>

Predicted Adsorption Enthalpy,  $\Delta H_{\text{ads}} = E_{\text{adsorbate*substrate}} - (E_{\text{substrate}} + E_{\text{adsorbate}})$

$\Delta H_{\text{ads}}$   
(kJ/mol)      -305  
Strong

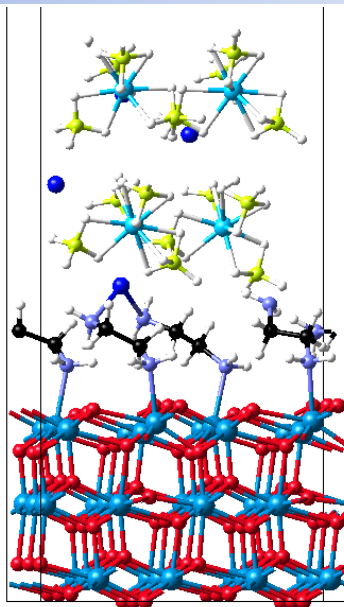
-55  
Weak

104  
Unfavorable

DME stabilizes neat NaTi(BH<sub>4</sub>)<sub>4</sub>, but DME – ZrO<sub>2</sub> associative interactions too weak to form a reversible hydride interface.

# Survey of Multi-Functional Agent Adsorption Interactions

Selected surface agents having multiple functional groups of varying chemistry, capable of simultaneously interacting with hydride and nano-framework.



**Functionalization with Ethylenediamine (EDA):**

←  $\text{NaTi}(\text{BH}_4)_4$

← **0.33 ML EDA**  
 $\text{EDA} = \text{H}_2\text{NC}_2\text{H}_4\text{NH}_2$

←  $\text{ZrO}_2$

Functionalization with Surface Agent Candidate	$\text{NaTi}(\text{BH}_4)_4$ (1 : 1)	$\text{ZrO}_2$ (0.33 ML)	$\text{NaTi}(\text{BH}_4)_4/\text{ZrO}_2$ (0.33 ML)
	$\Delta H_{\text{ads total}}$ (kJ/mole)		
oxalic acid (OXA) = $\text{HOOC}\text{COOH}$	-235.8	-536.4	-453.5
glycolic acid (GLA) = $\text{HOOC}\text{CH}_2\text{OH}$	-293.1	-565.0	-410.9
ethylenediamine (EDA) = $\text{H}_2\text{NC}_2\text{H}_4\text{NH}_2$	-338.5	-302.5	-377.2
hexamethylenetetramine (HMTA) = $(\text{CH}_2)_6\text{N}_4$	-177.1	-172.3	-309.1
triethylenediamine (TEDA) = $\text{C}_6\text{H}_{12}\text{N}_2$	-72.5	-129.8	-236.8

- Carboxylate groups chemisorb too strongly on  $\text{ZrO}_2$ .
- Amines have balanced associative interactions at interface.

## Modeling of Hydride Reversibility at Functionalized Interfaces

Favorable scenarios for functionalized NaTi(BH<sub>4</sub>)<sub>4</sub> **dehydrogenation** (deh) :

$$\Delta H_{\text{deh.}} (\text{kJ/mole} \cdot \text{H}_2) = \Sigma[\text{E}_{\text{deh. products}}] - \text{E}_{\text{functionalized NaTi(BH}_4)_4 (/ \text{ZrO}_2)}$$

**Neat** – without ZrO<sub>2</sub> nano-framework

**Full** – within ZrO<sub>2</sub> nano-framework, multi-functional agents retained on ZrO<sub>2</sub>

**Partial** – within ZrO<sub>2</sub> nano-framework, 2Na + 2H products adsorbed on ZrO<sub>2</sub>

Multi-functional Surface Agent Candidate	Dehydrogenation, $\Delta H_{\text{deh}}$ (kJ/Mole*H <sub>2</sub> )		
	Neat	Full	Partial
none	<b>26.1</b>	27.3	-
dimethoxyethane (DME) = CH <sub>3</sub> OC <sub>2</sub> H <sub>4</sub> OCH <sub>3</sub>	37.8	19.9	<b>13.7</b>
oxalic acid (OXA) = HOOC-COOH	35.1	<b>22.9</b>	36.9
glycolic acid (GLA) = HOOC-CH <sub>2</sub> -OH	37.3	<b>20.1</b>	32.4
ethylenediamine (EDA) = H <sub>2</sub> NC <sub>2</sub> H <sub>4</sub> NH <sub>2</sub>	39.1	<b>28.9 *</b>	35.1
hexamethylenetetramine (HMTA) = (CH <sub>2</sub> ) <sub>6</sub> N <sub>4</sub>	44.2	31.3	<b>30.9 **</b>
triethylenediamine (TEDA) = C <sub>6</sub> H <sub>12</sub> N <sub>2</sub>	28.9	30.2	<b>27.9</b>

Nano-framework functionalization demonstrated to improve hydride stability:

\* EDA is retained by nano-framework, stabilizes without reducing H<sub>2</sub> capacity.

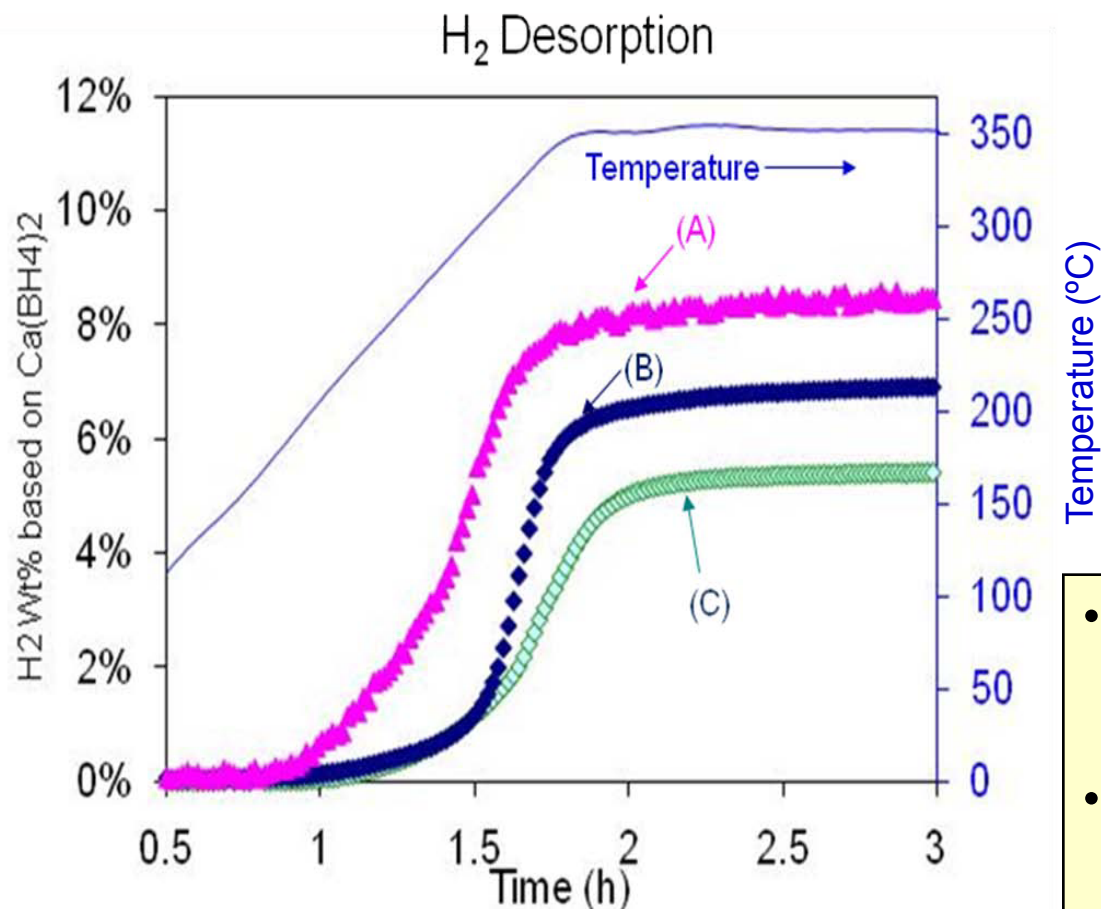
\*\* HMTA offers best stability within nano-framework, but may volatilize with H<sub>2</sub>.

# Ca(BH<sub>4</sub>)<sub>2</sub> Incorporation in C Aerogel

**Ca(BH<sub>4</sub>)<sub>2</sub> Precursors Investigated:** Ca(BH<sub>4</sub>)<sub>2</sub>\*2THF

**Monolithic Carbon Aerogels :** derived from polyimide (PI) and phenolic (PF) polymers

**Ca(BH<sub>4</sub>)<sub>2</sub> incorporation :** 39.0 wt% (solution method)



**A:** Ca(BH<sub>4</sub>)<sub>2</sub> incorporated in C (PI) aerogels.

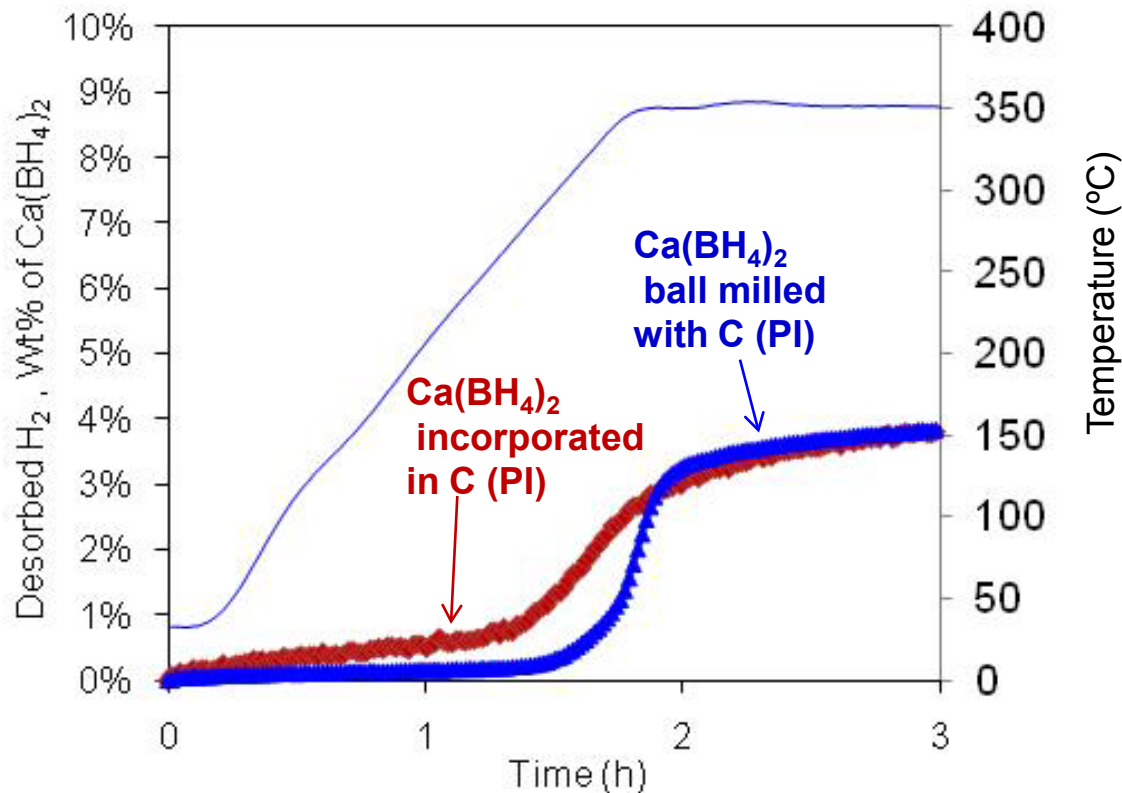
**B:** Ca(BH<sub>4</sub>)<sub>2</sub> SPEX milled with C(PI) aerogels.

**C:** SPEX milled Ca(BH<sub>4</sub>)<sub>2</sub>.

- Incorporation of Ca(BH<sub>4</sub>)<sub>2</sub> in C aerogel (both PI and PF) enhances desorption kinetics.
- Desorption capacity was also increased.
- Trace amount of organics is detected in desorbed H<sub>2</sub>.

# Ca(BH<sub>4</sub>)<sub>2</sub>-C Aerogel Composite

Second H<sub>2</sub> desorption after recharging at 350 °C / 190 bar H<sub>2</sub>



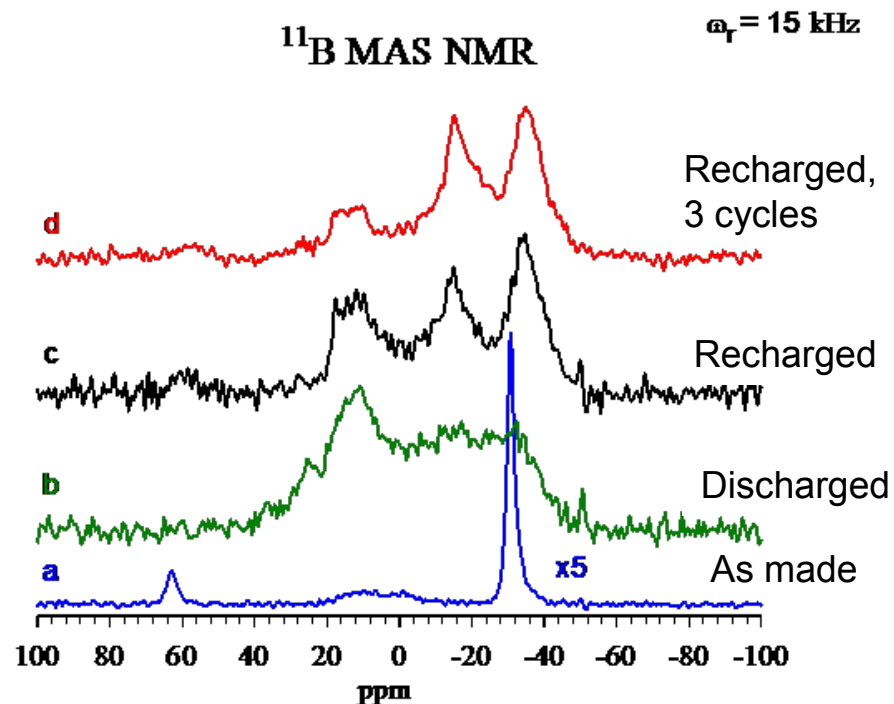
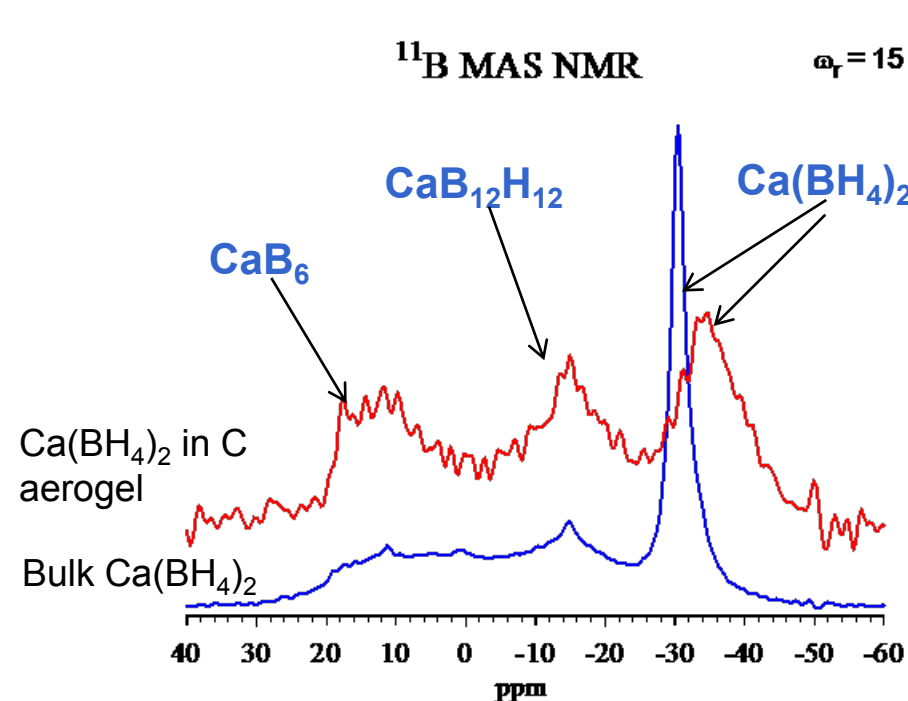
- No significant increase in the absorption capacity.
- H<sub>2</sub> desorbed at low temperature after recharging.
- H<sub>2</sub> desorption kinetics was enhanced similar to the first desorption.
- Trace amount of reaction products from reacting with framework.

## Solid-State NMR Characterization\*

\* Solid-State NMR conducted by Sonjong Hwang, California Institute of Technology.

### Ca(BH<sub>4</sub>)<sub>2</sub> after Recharging

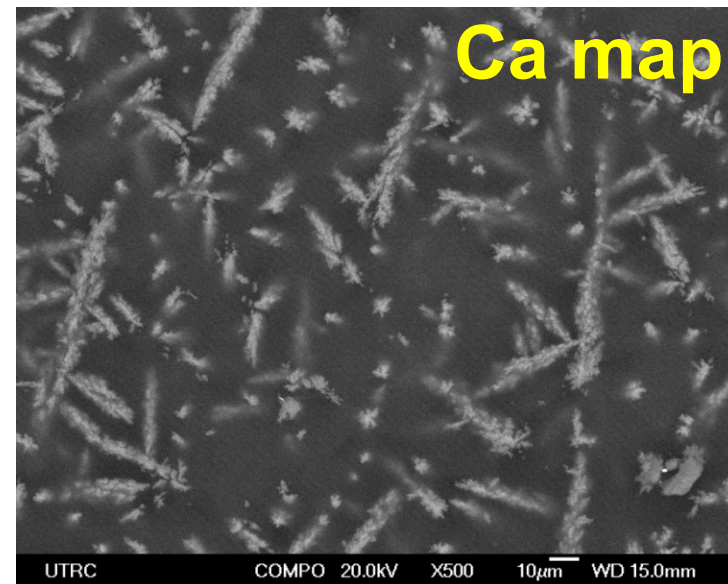
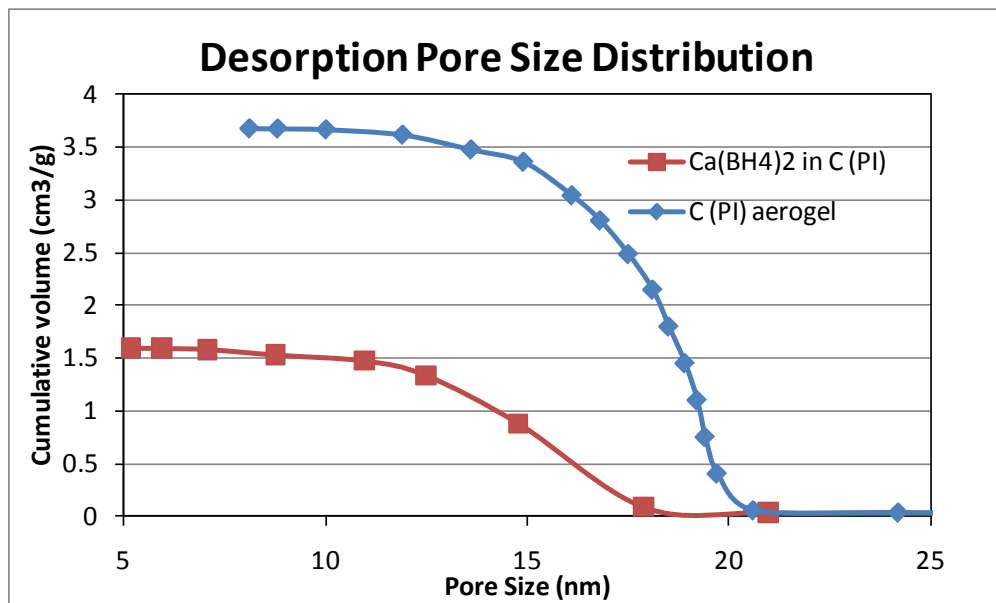
### Ca(BH<sub>4</sub>)<sub>2</sub> in C aerogel



- Solid-State NMR shows the formation of Ca(BH<sub>4</sub>)<sub>2</sub> in C aerogel after recharging. The Ca(BH<sub>4</sub>)<sub>2</sub> peak is broad and slightly shifted from the bulk Ca(BH<sub>4</sub>)<sub>2</sub>.
- The reduced H<sub>2</sub> capacity is attributed to the formation of CaB<sub>12</sub>H<sub>12</sub> upon cycling.
- Small amount of oxide in sample could be caused by THF ligand decomposition.

# Ca(BH<sub>4</sub>)<sub>2</sub> - C Aerogel Composite Characterization

NFS Material	Surface Area m <sup>2</sup> /g	Avg. Pore Size nm	Pore volume cc/g
Carbon Aerogel (PI)	580	25	3.7
Ca(BH <sub>4</sub> ) <sub>2</sub> incorporated Carbon Aerogel (PI)	330	19	1.6



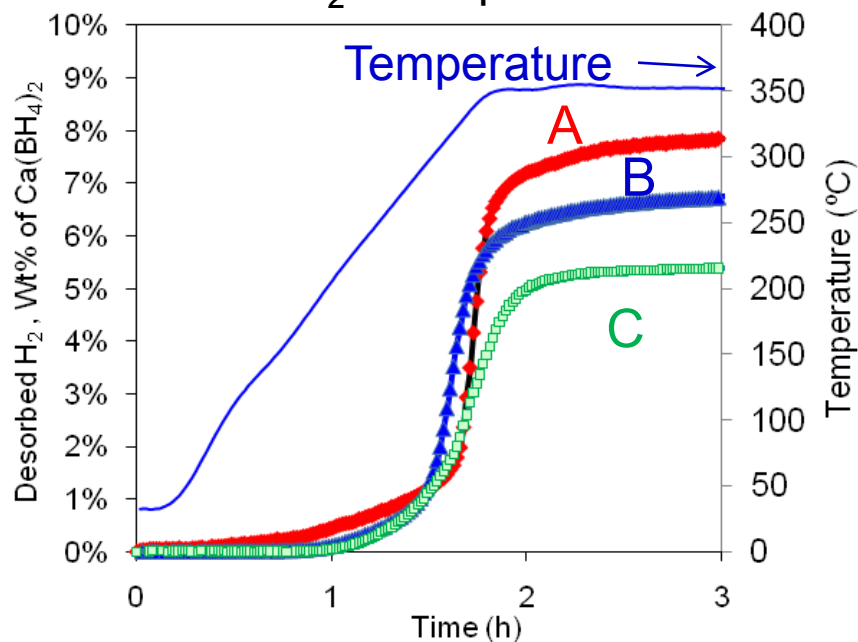
- Significant decrease in surface area, pore sizes, and pore volume.
- Large pores are filled preferentially. The small pores are harder to fill.
- Majority of Ca(BH<sub>4</sub>)<sub>2</sub> particles are within 15-25 nm range.



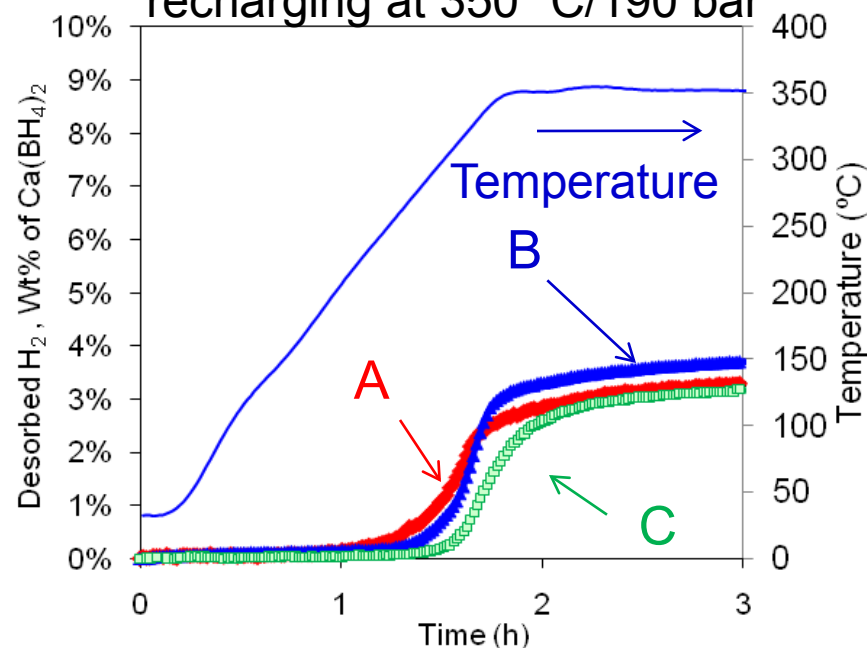
# Catalyzation Effect of Pt-ZrO<sub>2</sub> Nano-Framework

## Ca(BH<sub>4</sub>)<sub>2</sub> SPEX milled with Pt-ZrO<sub>2</sub> nano-framework

First H<sub>2</sub> desorption



Second H<sub>2</sub> desorption after recharging at 350 °C/190 bar



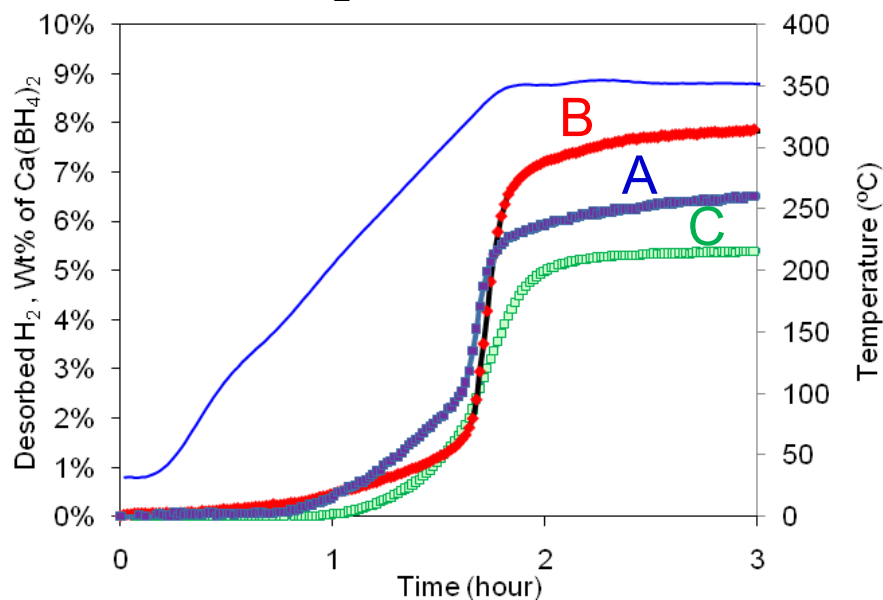
- (A) Ca(BH<sub>4</sub>)<sub>2</sub> SPEX milled with Pt-ZrO<sub>2</sub>.
- (B) Ca(BH<sub>4</sub>)<sub>2</sub> SPEX milled with C (PF).
- (C) Ca(BH<sub>4</sub>)<sub>2</sub> SPEX milled.

Similar to C aerogel, Pt-catalyzed ZrO<sub>2</sub> framework enhances H<sub>2</sub> desorption kinetics of Ca(BH<sub>4</sub>)<sub>2</sub>, especially in second desorption, but does not improve H<sub>2</sub> absorption.

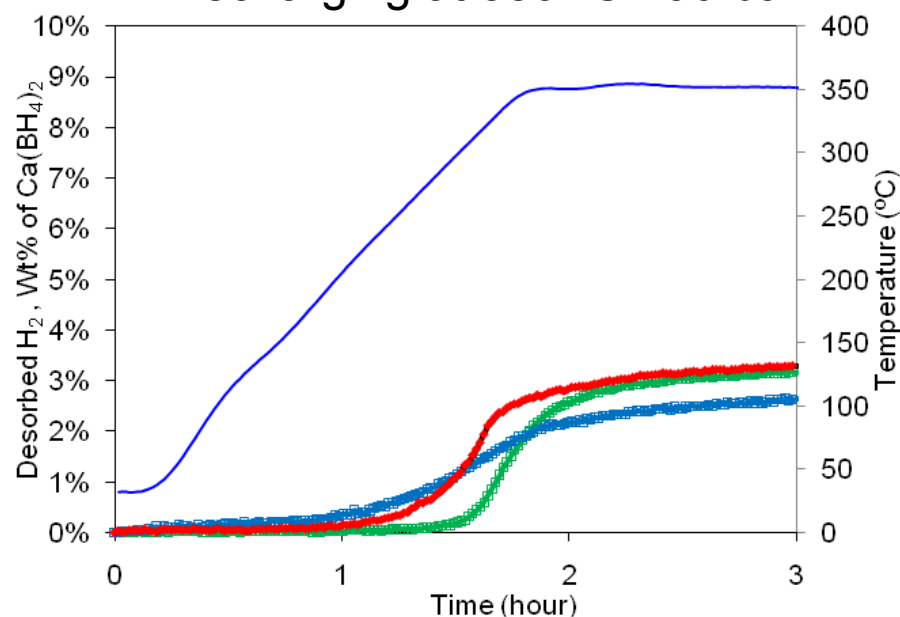
## Ca(BH<sub>4</sub>)<sub>2</sub> Incorporated in Pt–ZrO<sub>2</sub> Nano-Framework

### 22.3 wt% of Ca(BH<sub>4</sub>)<sub>2</sub> Incorporated in Pt–ZrO<sub>2</sub>

First H<sub>2</sub> desorption



Second H<sub>2</sub> desorption after recharging at 350 °C/190 bar

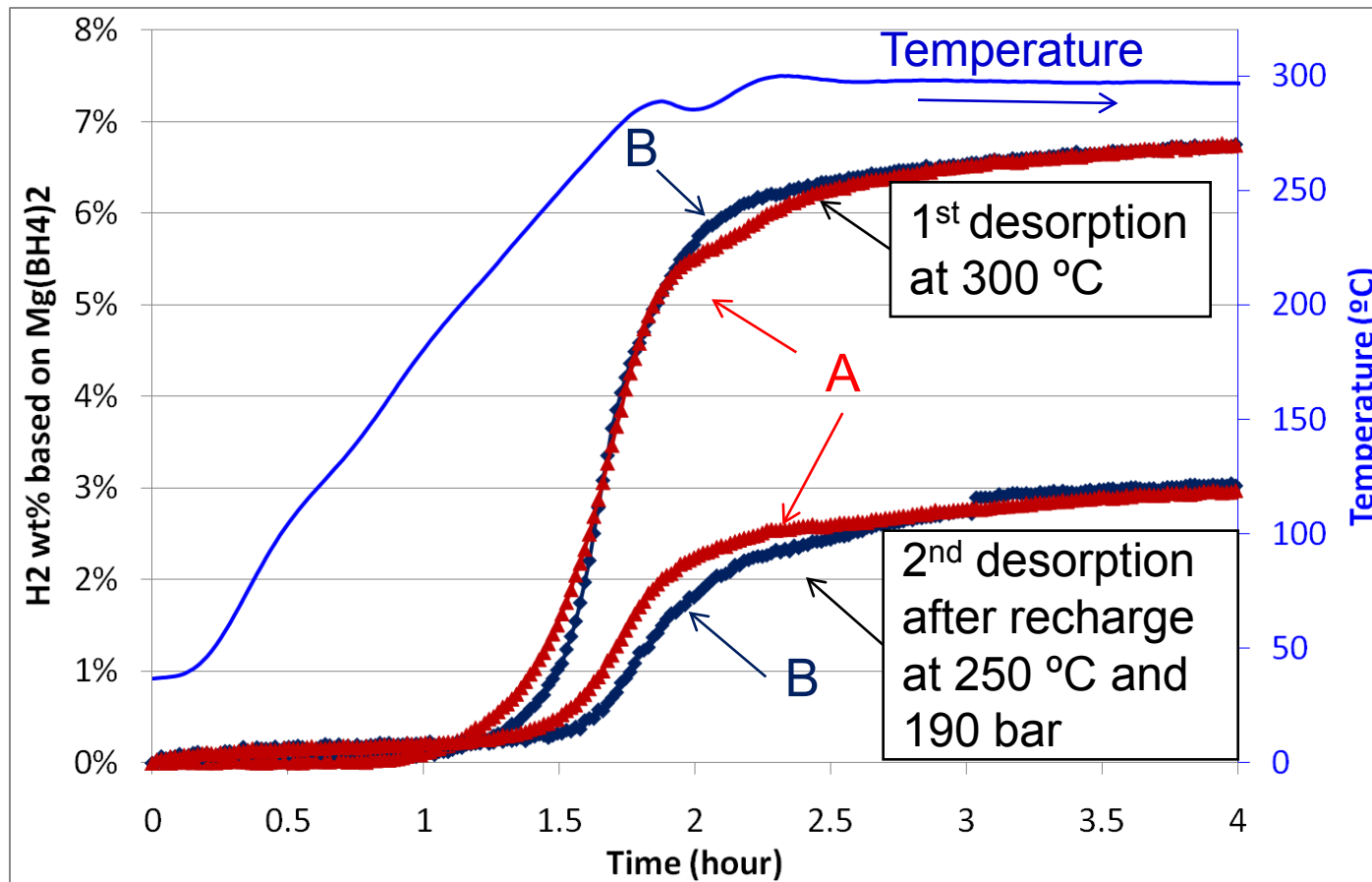


- (A) Ca(BH<sub>4</sub>)<sub>2</sub> incorporated in Pt–ZrO<sub>2</sub> aerogel.
- (B) Ca(BH<sub>4</sub>)<sub>2</sub> SPEX milled with Pt–ZrO<sub>2</sub> aerogel.
- (C) SPEX milled Ca(BH<sub>4</sub>)<sub>2</sub>.

- Incorporation of Ca(BH<sub>4</sub>)<sub>2</sub> in Pt–catalyzed ZrO<sub>2</sub> nano-framework improves H<sub>2</sub> desorption kinetics compared to the SPEX milled materials.
- Pt –ZrO<sub>2</sub> aerogel does not improve H<sub>2</sub> absorption.

## Mg(BH<sub>4</sub>)<sub>2</sub>\* Incorporated in C Aerogel

\* Mg(BH<sub>4</sub>)<sub>2</sub> was provided by J. C. Zhao, Ohio State University.



- (A) Mg(BH<sub>4</sub>)<sub>2</sub> incorporated in C (PF) aerogel (47.7 wt%).  
 (B) Bulk Mg(BH<sub>4</sub>)<sub>2</sub> SPEX milled with C (PF) aerogel.

Incorporation of Mg(BH<sub>4</sub>)<sub>2</sub> in C aerogel slightly improved H<sub>2</sub> desorption kinetics compared to bulk material. Some H<sub>2</sub> loss occurred during desolvation. No improvement in H<sub>2</sub> absorption.

# Summary

- Atomic modeling demonstrated enhanced  $\text{NaTi}(\text{BH}_4)_4$  stabilization at nano-framework surfaces modified with multi-functional agents.
- Effective amine multi-functional agents have more balanced interactions with nano-framework and hydride cluster.
- Incorporation of  $\text{Ca}(\text{BH}_4)_2$  and  $\text{Mg}(\text{BH}_4)_2$  in aerogels enhances hydride desorption kinetics. C aerogels are the most suitable nano-framework for hydride kinetic enhancement and high hydride loading.
- Incorporation of  $\text{Ca}(\text{BH}_4)_2$  and  $\text{Mg}(\text{BH}_4)_2$  in nano-frameworks does not improve their  $\text{H}_2$  absorption due to the formation of stable alkaline earth  $\text{B}_{12}\text{H}_{12}$  intermediates upon rehydrogenation.
- This work primarily investigated the effect of nano-framework surface chemistry on hydride properties. The effect of pore size is the focus area of other efforts (e.g., HRL etc.) within the MHCoe. The projects are complementary in gaining an overall understanding of the influence of nano-frameworks on hydride behavior.



# Conclusions and Recommendations

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Nano-framework confinement provides a unique approach to improve hydride properties in following ways:

- Significant decrease in desorption temperature and enhancement of kinetics for highly stable hydrides.
- Stabilization of unstable hydrides through surface functionalization.
- Maintenance of nano-scale phases domain during cycling.

The inability of current aerogels to circumvent the formation of stable alkaline earth  $B_{12}H_{12}$  intermediates is the main cause for reduced absorption capacity of the borohydrides investigated.

## Future Recommendations:

- Apply this approach to reversible hydride systems where improvements in kinetics and cyclability are needed.
- Develop intrinsically functionalized carbon with engineered pore structure to stabilize unstable borohydrides and improve cyclability.



# Collaborations

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- **Sandia National Laboratory, Livermore:** Tim Boyle, Vitalie Stavila, Joe Cordaro, Ewa Rönnebro (now with PNNL)  
Synthesis of mixed–metal borohydrides.
- **Ohio State University:** J. C. Zhao  
Synthesis of borohydrides.
- **California Institute of Technology:** Sonjong Hwang  
Solid state NMR characterization.
- **HRL:** John Vajo  
Discussions on related efforts & exchange of aerogels.
- **Aspen Aerogels:** Wendell Rhine, Sara Rosenberg  
Synthesis and characterization of aerogels.
- **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.