

## IV.A.2 Efficient Discovery of Novel Multicomponent Mixtures for Hydrogen Storage: A Combined Computational/Experimental Approach

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Contract Number: DE-FC36-08GO18136

Project Start Date: September 1, 2008  
Project End Date: July 31, 2013

### Fiscal Year (FY) 2011 Objectives

The objective of the project is to discover novel mixed hydrides for hydrogen storage, which enable the DOE 2010 system-level goals. Our goal is to find a material that desorbs 8.5 wt% H<sub>2</sub> or more at temperatures below 85°C. The research project will combine first-principles calculations of reaction thermodynamics and kinetics with material and catalyst synthesis, testing, and characterization. We will combine materials from distinct categories to form novel multicomponent reactions. Examples of systems to be studied include mixtures of complex hydrides and chemical hydrides and novel multicomponent complex hydride materials and reactions.

### Technical Barriers

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

- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (A) System Weight and Volume
- (E) Charging/Discharging Rates

### Technical Targets

This study is aimed at fundamental insights into new materials and the thermodynamic and kinetic aspects of H<sub>2</sub> release and reabsorption from them. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

- Specific energy: 1.5 kWh/kg
- Energy density: 0.9 kWh/L

### FY 2011 Accomplishments

- Synthesis and characterization of two predicted promising hydride mixtures: 5LiBH<sub>4</sub> + 2Mg(BH<sub>4</sub>)<sub>2</sub> and Mg(BH<sub>4</sub>)<sub>2</sub> + Mg(NH<sub>2</sub>)<sub>2</sub>.
- Prediction of new previously-unknown MgBNH<sub>6</sub> compound, stable with respect to Mg(BH<sub>4</sub>)<sub>2</sub> + Mg(NH<sub>2</sub>)<sub>2</sub>.
- Proposed new metal-carbon catalyst: Tested on NaAlH<sub>4</sub>, and applied to Mg(BH<sub>4</sub>)<sub>2</sub> + Mg(NH<sub>2</sub>)<sub>2</sub>; Effective catalyst - lowers desorption temperature of both reactions, and reduces formation of NH<sub>3</sub> in the latter case.
- Predicted new CaB<sub>2</sub>H<sub>6</sub> product in decomposition of Ca(BH<sub>4</sub>)<sub>2</sub>.
- Predicted structure of AlB<sub>4</sub>H<sub>11</sub> polymeric compound.
- Found new low-energy decomposition product of amidoborane reactions; found stability trends in ammonia-borane reactions to tailor ΔH to choice of metal cation.
- Extended prototype electrostatic ground state (PEGS) and grand-canonical linear programming (GCLP) to apply to nano-confined materials. Explored nano NaAlH<sub>4</sub> and LiBH<sub>4</sub> reactions.
- Developed predictive models of kinetics of mass transport. Application to NaAlH<sub>4</sub> and extension to borohydrides (in progress).



### Introduction

The 2010 and 2015 FreedomCAR/DOE targets for hydrogen storage systems are very challenging, and cannot be met with existing materials. The vast majority of the work to date has delineated materials into various classes, e.g., complex and metal hydrides, chemical hydrides, and sorbents. However, very recent studies indicate that mixtures of storage materials, particularly mixtures between various classes, hold promise to achieve technological

attributes that materials within an individual class cannot reach. Our project involves a systematic, rational approach to designing novel multicomponent mixtures of materials with fast hydrogenation/dehydrogenation kinetics and favorable thermodynamics using a combination of state-of-the-art scientific computing and experimentation. Specifically, we focus on combinations of materials from distinct categories to form novel multicomponent reactions.

## Approach

We use the accurate predictive power of first-principles modeling to understand the thermodynamic and microscopic kinetic processes involved in hydrogen release and uptake and to design new material/catalyst systems with improved properties. Detailed characterization and atomic-scale catalysis experiments elucidate the effect of dopants and nanoscale catalysts in achieving fast kinetics and reversibility. And, state-of-the-art storage experiments give key storage attributes of the investigated reactions, validate computational predictions, and help guide and improve computational methods. In sum, our approach involves a powerful blend of: 1)  $H_2$  storage measurements and characterization, 2) state-of-the-art computational modeling, 3) detailed catalysis experiments, and 4) in-depth automotive perspective.

## Results (Selected Examples)

### Reaction Pathway Characterization for $Mg(NH_2)_2$ - $Mg(BH_4)_2$

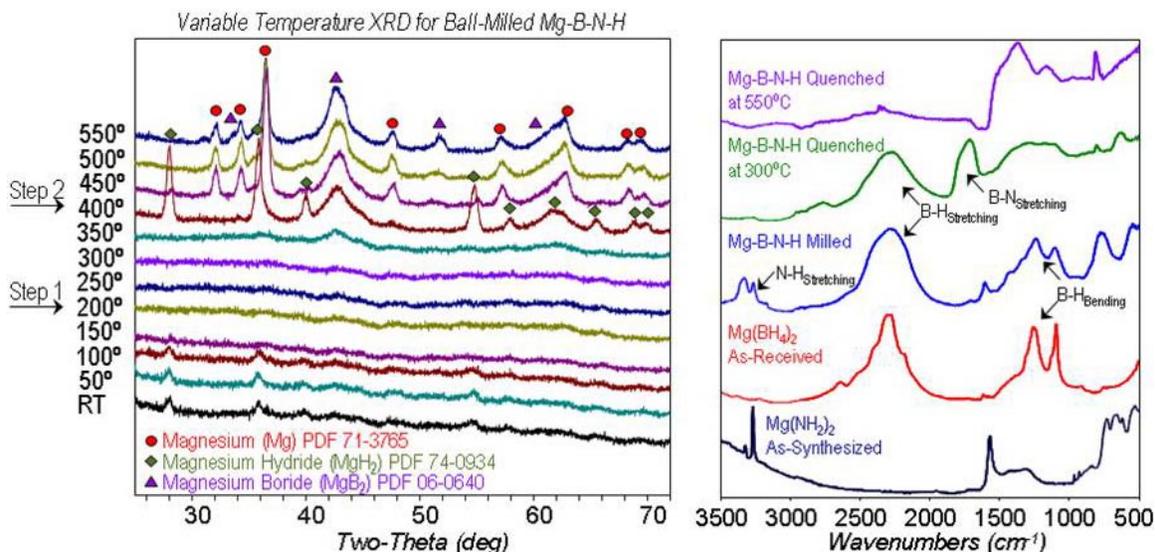
We have performed initial characterization experiments of the reaction pathway for the  $Mg(NH_2)_2$ - $Mg(BH_4)_2$

mixture. In particular, we have collected new in situ X-ray diffraction (XRD) and quenched Fourier transform infrared (FT-IR) data (Figure 1) toward characterization of the 2-step hydrogen desorption pathway which releases a total of ~11 wt% when heated to 550°C. From these new data, we propose that the first hydrogen release step (room temperature to 300°C and ~7 wt%) involves consumption of an amide reactant and formation of a product phase that involves boron-nitrogen bonding (infrared data). The second hydrogen release step (>300° and 4 wt%) involves decomposition of the B-N phase from step 1 and the formation of Mg and  $MgB_2$  (infrared and XRD data). More experimental data and on-going computational studies are needed to determine the specific experimental and computational pathways from potential reactant hydride formation through complete dehydrogenation.

### Facilitating Dehydrogenation of Complex Hydrides Using a Novel Metal-Carbon Catalyst

We have demonstrated that our metal-carbon catalysts are effective for facilitating dehydrogenation of solid-state hydrides, using  $NaAlH_4$  as a model compound. The catalyst, comprised of metal nanoparticles and carbon support, serves multiple functions including nano-compartment of hydride, sites for nucleation, and hydrogen transport.

For low-melting point hydrides such as  $NaAlH_4$ , mixing the hydride with carbon materials such as activated carbon with high surface area and highly porous structure can significantly lower the dehydrogenation temperature (>100°C). The effect of carbon is mostly due to the nanostructuring of the hydride. As  $NaAlH_4$  melts and diffuses into micropores of carbon,  $NaAlH_4$  is confined into a



**FIGURE 1.** (a) In situ XRD data for ball-milled  $Mg(NH_2)_2$ - $Mg(BH_4)_2$  mixture (heating rate 1°C/min) (b) FT-IR data for ball-milled  $Mg(NH_2)_2$ - $Mg(BH_4)_2$  comparing reactants ( $Mg(NH_2)_2$ , navy) and  $Mg(BH_4)_2$ , (red) with ball-milled mixture (blue) and quenched samples at 300°C (green) and 550°C (purple).

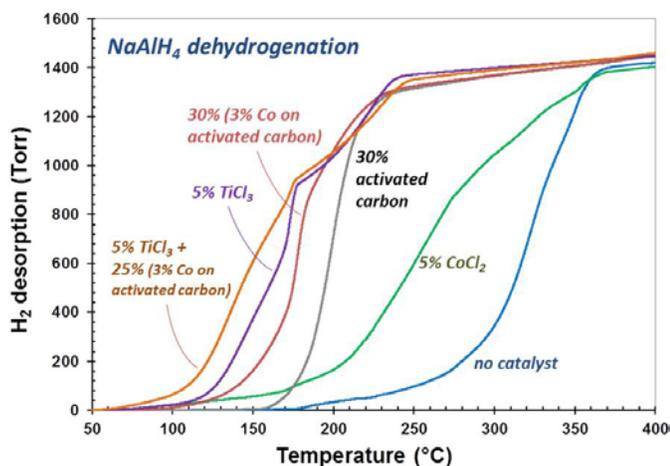


FIGURE 2. The Dehydrogenation of  $\text{NaAlH}_4$  using Different Catalysts

nano-size region and starts to dehydrogenate at a lower temperature as a result.

Adding a small amount of transition metal such as cobalt on the carbon can further enhance the catalytic effect. Mixing with such cobalt-carbon catalyst,  $\text{NaAlH}_4$  starts to dehydrogenate below its melting point. This enhanced effect could be attributed to hydrogen spillover facilitated by metal nanoparticles—the hydrogen atoms dehydrogenated from hydride migrate to hydride-carbon surface and recombine on the metal surface to desorb into gas phase. The cobalt-carbon catalyst can catalyze  $\text{NaAlH}_4$  dehydrogenation below  $130^\circ\text{C}$ . Typically it can only be done by using Ti-based catalysts, which catalyzed the reaction through forming Ti-Al intermediates to facilitate hydrogen transportation. However, unlike Ti-based catalysts deactivate due to  $\text{TiAl}_3$  formation after several dehydrogenation–rehydrogenation cycles, cobalt-carbon catalysts do not interact with hydride to form intermediates and catalyze the dehydrogenation under a different working principle. As a result, we observed synergistic effect from combining cobalt-carbon and  $\text{TiCl}_3$  catalysts for  $\text{NaAlH}_4$ —dehydrogenation starts even below  $100^\circ\text{C}$  (Figure 2).

As shown in Figure 3 and 4, the evidence of  $\text{NaAlH}_4$  dehydrogenated below its melting point when catalyzed by a cobalt-carbon catalyst was provided by in situ XRD study of  $\text{NaAlH}_4$  dehydrogenation from room temperature to  $450^\circ\text{C}$ . As can be seen in Figure 3,  $\text{NaAlH}_4$  without catalyst melted at  $222^\circ\text{C}$  and no diffraction pattern can be detected (flat line). The subsequent diffraction patterns indicate the dehydrogenation began at a temperature above the melting point. In contrast,  $\text{NaAlH}_4$  catalyzed by cobalt-carbon catalyst started to dehydrogenate at a temperature as low as  $192^\circ\text{C}$  and resulted in phase transformation of  $\text{NaAlH}_4$  as can be seen in Figure 4.

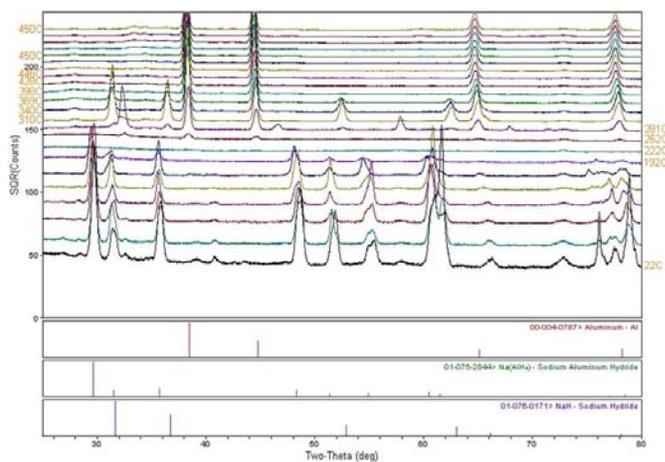


FIGURE 3. In Situ XRD of  $\text{NaAlH}_4$  Dehydrogenation Without Catalyst

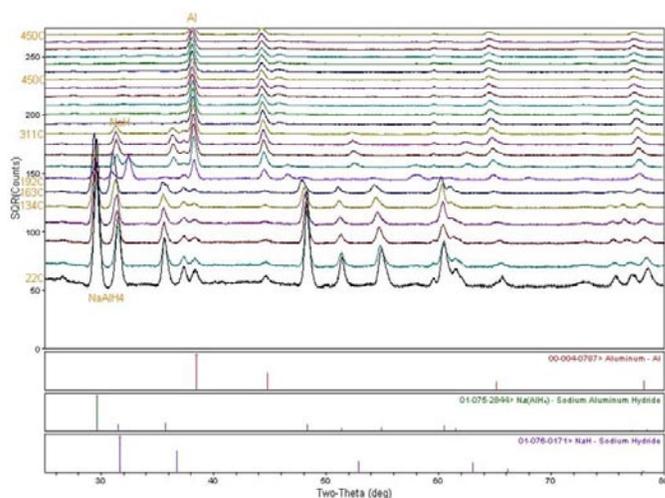


FIGURE 4. In Situ XRD of  $\text{NaAlH}_4$  Dehydrogenation with 30% 3Co-AC-IWI- $350^\circ\text{C}$

Using PEGS to Help Deduce Amorphous Hydride Structures: The Polymeric Structure of  $\text{AlB}_4\text{H}_{11}$  (collaboration with Ji-Cheng Zhao at Ohio State University)

The group of Prof. Zhao at Ohio State University synthesized the  $\text{AlB}_4\text{H}_{11}$  compound through the reaction  $2\text{Al}(\text{BH}_4)_3 + \text{B}_2\text{H}_6 \rightarrow 2\text{AlB}_4\text{H}_{11} + 4\text{H}_2$ . The  $\text{H}_2$  reversibility of the new compound is observed at mild conditions:  $200^\circ\text{C}$  and 90 bar  $\text{H}_2$ , but its amorphous structure is unknown.

The PEGS method has been proved to be effective in the prediction of most “simple” complex hydrides with well-known anion geometries, like  $\text{Mg}(\text{BH}_4)_2$ . For the current  $\text{AlB}_4\text{H}_{11}$  stoichiometry, the structure of the  $[\text{B}_4\text{H}_{11}]^{3-}$  anion geometry structure is presently unknown. Therefore, in the PEGS simulations, we split the  $\text{AlB}_4\text{H}_{11}$  into different small known fragments,  $\text{Al} + [\text{BH}_4] + [\text{BH}_3] + 2[\text{BH}_2]$  or

$[\text{AlH}_4]+3[\text{BH}_2]+[\text{BH}]$ . Surprisingly, after the PEGS and density functional theory (DFT), the fragments of B except  $[\text{BH}_4]$  bond together to form a larger B cluster. In the low-energy structure at one formula unit (fu), it contains Al,  $[\text{BH}_4]$  and  $[\text{B}_3\text{H}_7]$  clusters, and they form a  $-\text{Al}[\text{BH}_4]-[\text{B}_3\text{H}_7]-$  polymer chain, which is consistent with the experimental evidence (e.g., nuclear magnetic resonance and other measurements performed at Ohio State). Comparing the theoretical phonon density of states (pDOS) calculations and experimental neutron vibration spectra, we find that our pDOS is in overall agreement with the experimental peaks.

Subsequently, experiments confirmed our PEGS prediction that there are two kinds of B clusters,  $[\text{BH}_4]$  and  $[\text{B}_3\text{H}_7]$ , but also suggest two kinds of Al environments that our initially predicted structure doesn't have, since we only performed calculations of one formula unit (and hence, only one Al atom). Therefore, we believe the two anion groups ( $[\text{BH}_4]$  and  $[\text{B}_3\text{H}_7]$ ) are correct and implement these into the PEGS code, and increased the cell size to two formula units. At 2 fu, a new low-energy  $\text{AlB}_4\text{H}_{11}$  structure is predicted, which is  $\sim 400$  meV/fu lower than the previous one. In this new structure, it still shows the  $-\text{Al}[\text{BH}_4]-[\text{B}_3\text{H}_7]-$  polymer chain, and Al clearly has two kinds of surroundings. Its pDOS is in excellent agreement with the experimental neutron vibration spectra. The PEGS predicted  $\text{AlB}_4\text{H}_{11}$  structure is therefore in excellent agreement with all the experimental data obtained. PEGS has previously been shown to provide accurate predictions of complex hydrides with well-known anion geometries. However, in this work, we extend the method and successfully apply it to cases where the anion geometry is unknown.

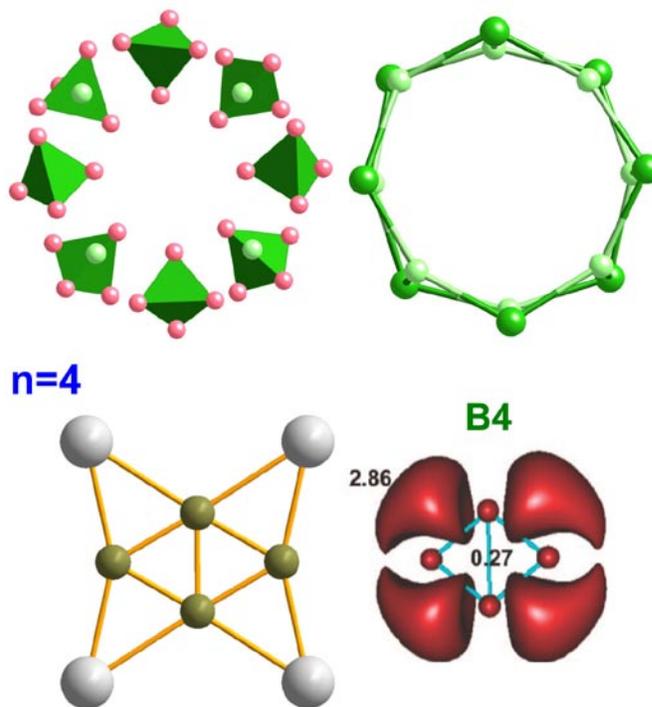
### Computational Studies of Finite Size Effects in Lithium Borohydride Nanoclusters

Reducing the size of the bulk solids to the nanoscale regime is one approach that may allow for engineered equilibrium pressures and reaction kinetics that are more suitable for on-board hydrogen storage. First principles calculations on  $\text{MgH}_2$  nanoparticles, for example, indicate that significant lowering of the desorption enthalpy is possible with decreasing cluster size [1]. Recent experimental work has demonstrated considerable changes in kinetics for hydrogen storage materials when incorporated in nanoporous frameworks. These frameworks include high surface area carbon aerogels [2,3], block-copolymer-templated highly ordered carbons [4], and metal-organic-frameworks (MOFs) [5].

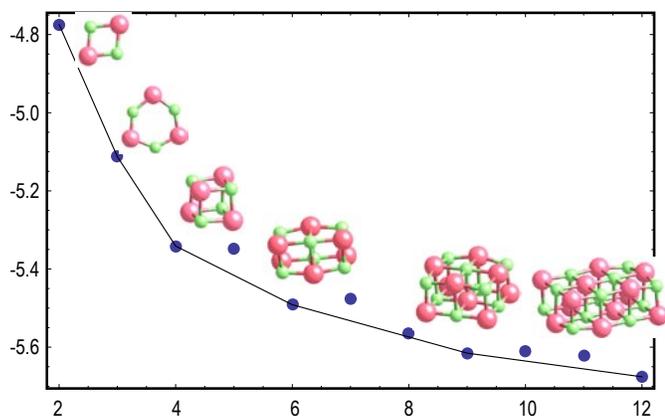
In collaboration with Profs. Eric Majzoub from University of Missouri, St. Louis and Feng-Chuan Chuang from National Sun Yat-Sen University in Taiwan we are addressing the intrinsic reaction thermodynamics and decomposition pathways of gas-phase lithium borohydride clusters in the few nanometer size regime; such clusters can be synthesized in nanopores of high-surface-area carbons and MOFs, and are currently under investigation in the Northwestern group. We have recently generalized the

GCLP method to determine thermodynamically preferred decomposition pathways in finite-size systems, which allows us to obtain the phase diagram of small, free clusters of complex hydrides [6]. In the case of  $(\text{NaAlH}_4)_n$  clusters with  $n \leq 8$  we found that decomposition pathways of free-standing clusters are drastically different from those of bulk sodium alanate, favoring hydrogen release in a one-step reaction leading to the formation of mixed  $(\text{AlNa})_n$  nanoclusters. We also predicted nanocluster analogues of bulk destabilized reactions between simple hydride ( $\text{NaH}$  and  $\text{AlH}_3$ ) and complex hydride ( $\text{NaAlH}_4$ ) nanoclusters. It is of considerable interest whether similar phenomena can be found in materials with higher hydrogen content than sodium alanate.

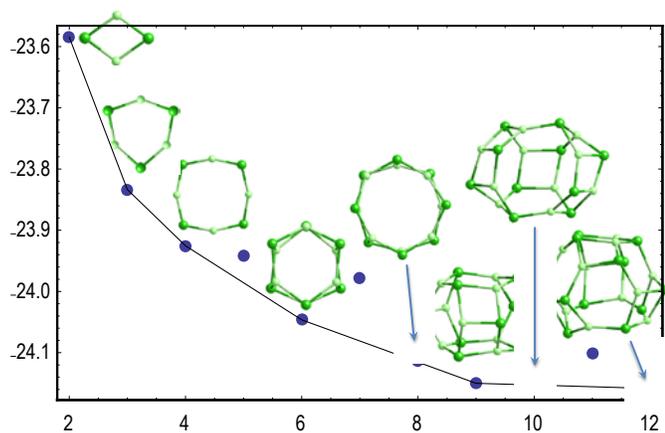
Using the recently developed PEGS method and genetic algorithm in conjunction with DFT calculations, we predict the structures of small clusters of  $\text{LiBH}_4$  and its decomposition products ( $\text{Li}$ ,  $\text{B}$ ,  $\text{Li}_n\text{B}_n$ ,  $\text{LiH}$ ) with up to 12 Li and B atoms. A few representative structures are shown in Figures 5, 6 and 7. Just like the case for the bulk  $\text{LiBH}_4$  compound, our preliminary results indicate that the decomposition pathway of  $\text{LiBH}_4$  nanoclusters with  $N \geq 6$  involves the formation of closoboranes based on  $(\text{B}_n\text{H}_n)^{2-}$  anions. The calculated decomposition enthalpies are shown in Figure 8 as functions of the cluster size. These results demonstrate that lithium borohydride nanoclusters have higher enthalpies of hydrogen release than bulk materials, suggesting that any destabilization observed in recent experiments must come due to strong interaction effects with



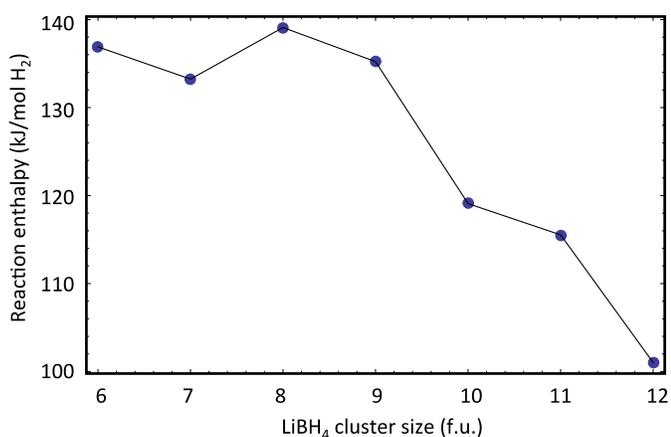
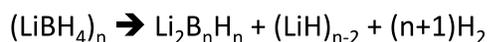
**FIGURE 5.** Top: Structure of  $(\text{LiBH}_4)_8$  cluster found using PEGS and DFT. Bottom: structure of  $\text{Li}_4\text{B}_4$  cluster found using genetic algorithm.



**FIGURE 6.** Energy of LiH clusters versus cluster size. Inset figures show the clusters that lie on the convex hull.



**FIGURE 7.** Energy of LiBH<sub>4</sub> clusters versus cluster size. Inset figures show the clusters that lie on the convex hull. Only Li and B atoms are shown.



**FIGURE 8.** Calculated Decomposition Enthalpies of LiBH<sub>4</sub> Clusters as Functions of Cluster Size

the porous support. These results are in marked contrast to earlier DFT-based findings for metal nanoclusters, which suggested destabilization with decreasing size and the appearance of new decomposition pathways. We are currently in the process of refining the structures of B<sub>n</sub>H<sub>m</sub> nanoclusters using genetic algorithms. Inclusion of B<sub>n</sub>H<sub>m</sub> may yet change the preferred decomposition pathways and somewhat alter the preliminary conclusions reached so far.

## Conclusions and Future Directions

- Experimentally characterize storage properties/reactions of (NH<sub>4</sub>)<sub>2</sub>B<sub>12</sub>H<sub>12</sub> and other predicted reactions; elucidate decomposition pathway for Mg(BH<sub>4</sub>)<sub>2</sub>+Mg(NH<sub>2</sub>)<sub>2</sub> mixture.
- Extend experimental catalyst studies to other predicted promising materials; explore optimal morphology of carbon/metal catalysts.
- Direct computational efforts to focus on kinetics, defects, diffusion/mass transport in promising predicted reactions.
- Continue some computational exploration for: novel BH<sub>4</sub>/NH<sub>2</sub> compounds and reversible reactions, and mixed metal borohydrides.

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