Design of Novel Multi-Component Metal Hydride-Based Mixtures for Hydrogen Storage

C. Wolverton (PI), H. Kung
Northwestern University

V. Ozolins
UCLA

A. Sudik, J. Yang
Ford Motor Company

ST028

Overview

Timeline

- Project Start Date: 9/1/08 (Funding started Feb. 09)
- Project End Date: 8/31/13
- ~40% complete

Budget

- Total Budget: $2714K
  - DOE Share: $2160K
  - Contractors Share: $554K
- Funding for FY10: $450K
- Funding for FY11: $400K (anticipated)

Barriers

- Barriers addressed
  - P. Lack of Understanding of Hydrogen Physisorption and Chemisorption
  - A. System Weight and Volume
  - E. Charging/Discharging Rates

Partners

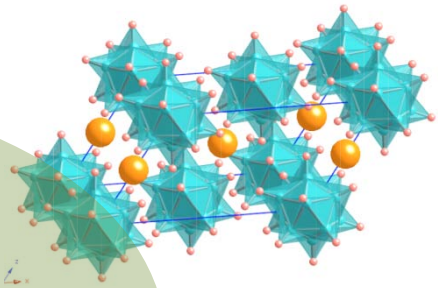
- Northwestern University
- UCLA
- Ford Motor Company
- Project lead: Northwestern University

Relevance - Project Objectives

- **Our project: 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

Approach

Our approach involves a powerful blend of:
1) H2 Storage measurements and characterization, 2) State-of-the-art computational modeling, 3) Detailed catalysis experiments, 4) In-depth automotive perspective



Hydrogen Storage Measurements and Auto Perspective (Sudik and Yang, Ford)

Computational Prediction of Novel Reactions (Wolverton, Ozolins)

Kinetics/Catalysis Experiments (Kung, NU)

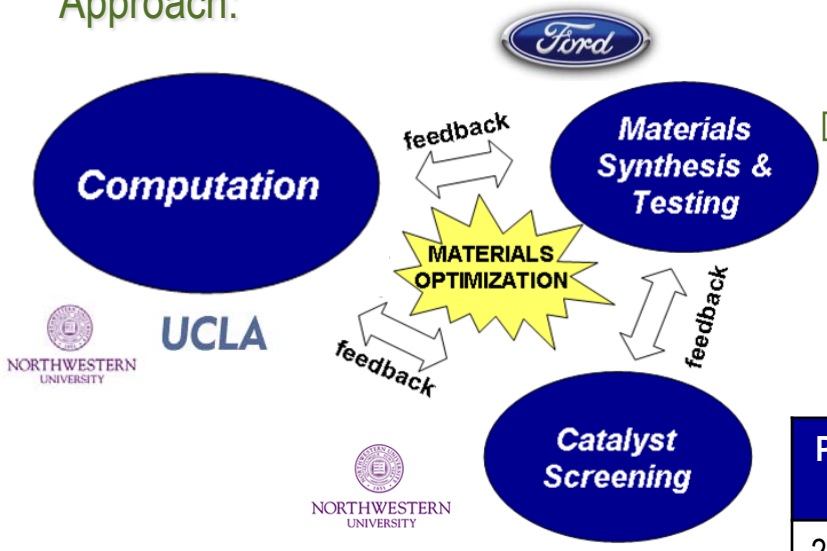
NORTHWESTERN UNIVERSITY

UCLA

Ford

Technical Accomplishments: Experimental Screening & Testing of Theoretical Predictions

Approach:



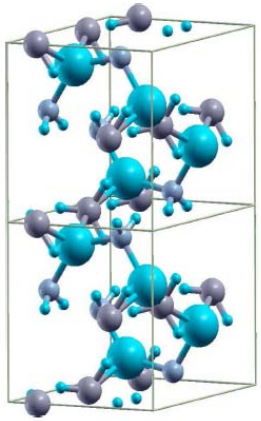
Experimental Objectives:

- Synthesize, characterize, and test promising storage reactions predicted by computation
- Interface with kinetics-focused work to provide materials of interest for catalysis studies and assist in detailed testing of catalyzed reactions.

Predicted Compositions of Interest	Experimental Status
$2(NH_4)_2B_{12}H_{12}$	Material received from OSU (Zhao)
$5Mg(BH_4)_2 + 2LiBH_4$	Material prepared & experiments initiated
$6Mg(BH_4)_2$	Deferred given existing literature data
$Mg(BH_4)_2 + Mg(NH_2)_2$	Material prepared & experiments initiated
$5MgH_2 + MgB_{12}H_{12}$	Deferred given existing literature data

= current experimental focus

PEGS Predicted Mg-B-N-H Structure



$Mg(BH_4)(NH_2)$-PEGS (4 f.u.)
Space group: Ima2 (46)
a=8.83 Å, b=6.53 Å, c=6.34 Å

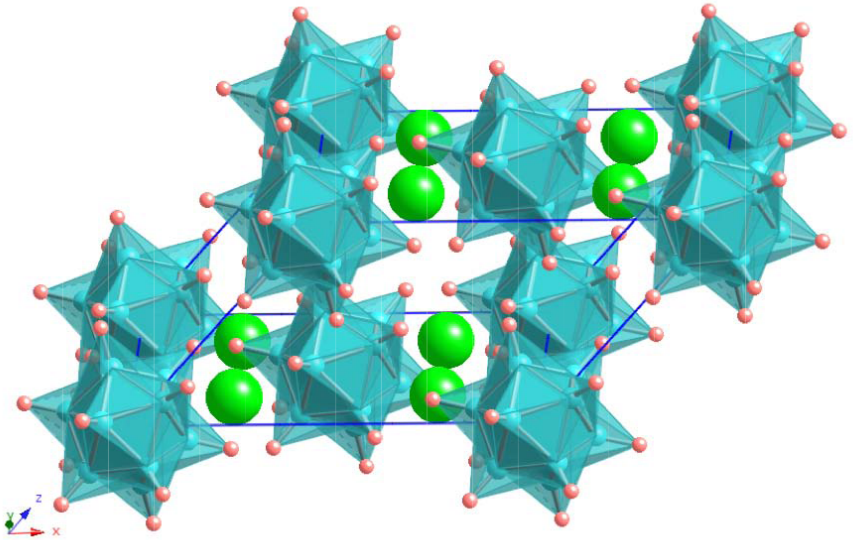
Guiding Questions:

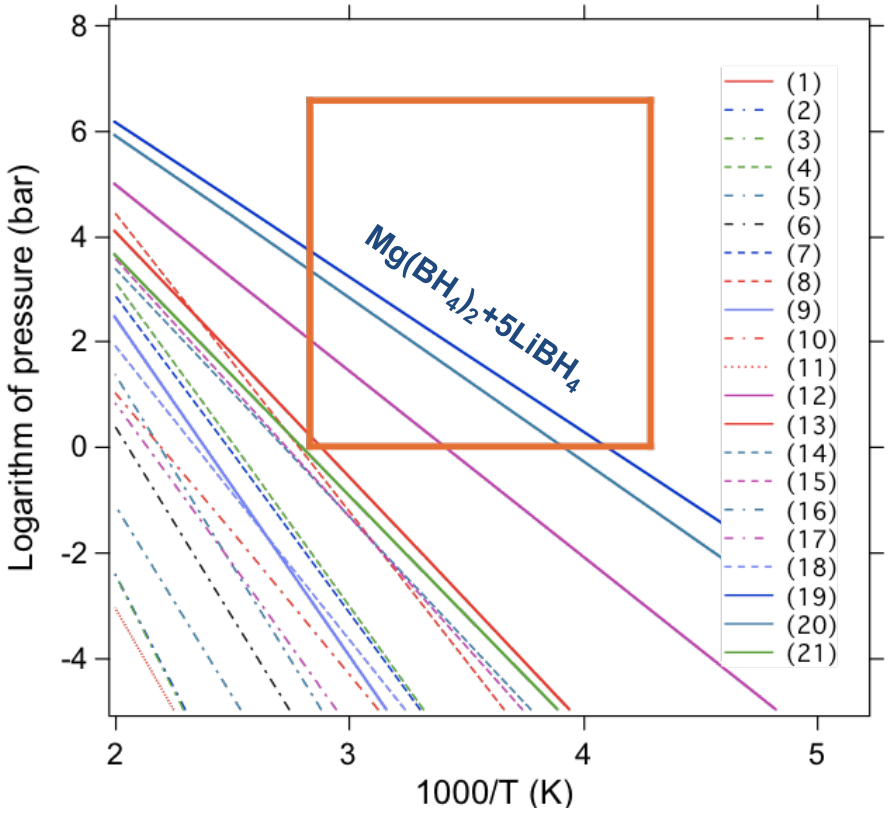
- Is there experimental evidence of a new reactant structure (e.g., Mg-B-N-H)?
- What is the experimentally observed desorption pathway?
- How do these results compare with predictions?

Technical Accomplishments: Experimental Testing of Predicted Reactions

$$5Mg(BH_4)_2 + 2LiBH_4 \xrightarrow{-29\ ^oC} Li_2B_{12}H_{12} + 5MgH_2 + 13\ H_2 \qquad 8.4\ wt.\%\ H_2$$

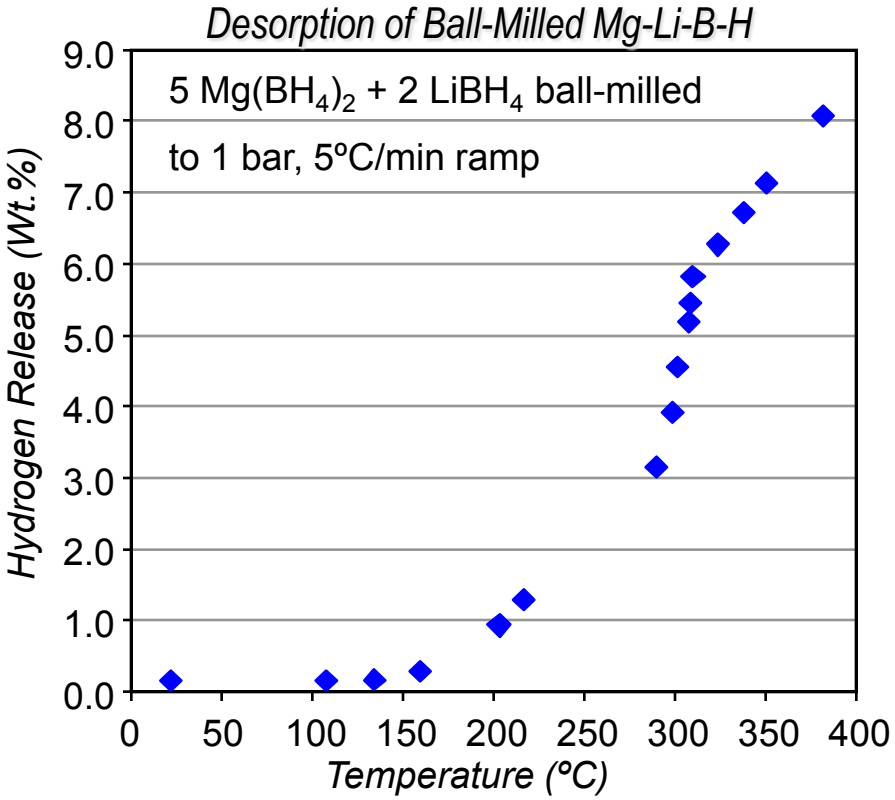
$Li_2B_{12}H_{12}$

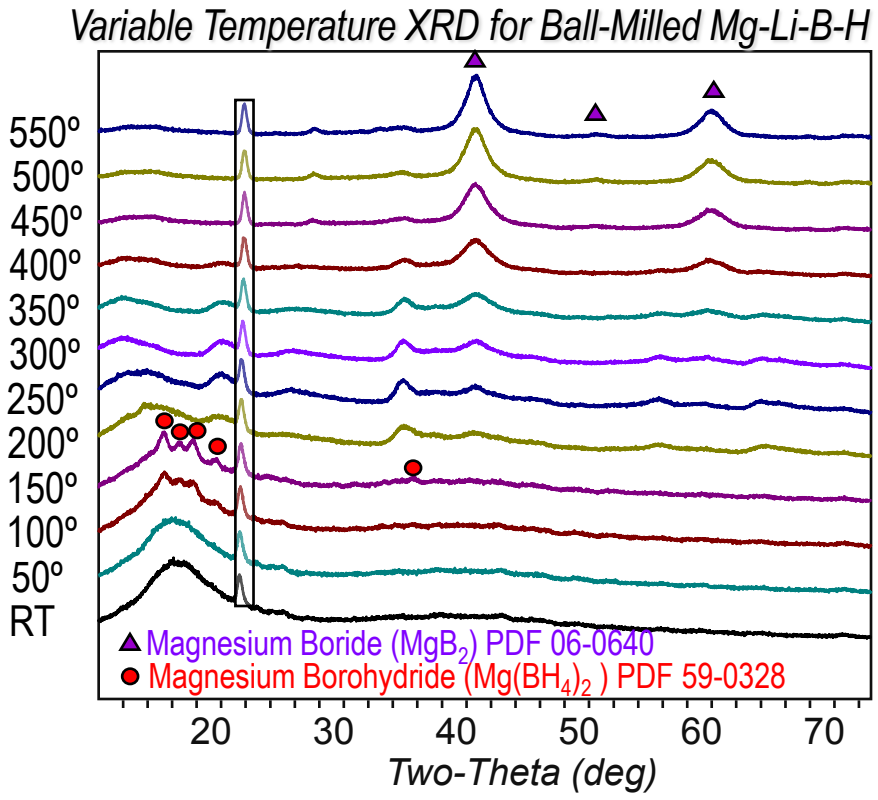




V. Ozolins, E. H. Majzoub, and C. Wolverton, JACS **131** (1), 230-237 (2009).

Synthesis and Characterization of $5Mg(BH_4)_2 + 2LiBH_4$

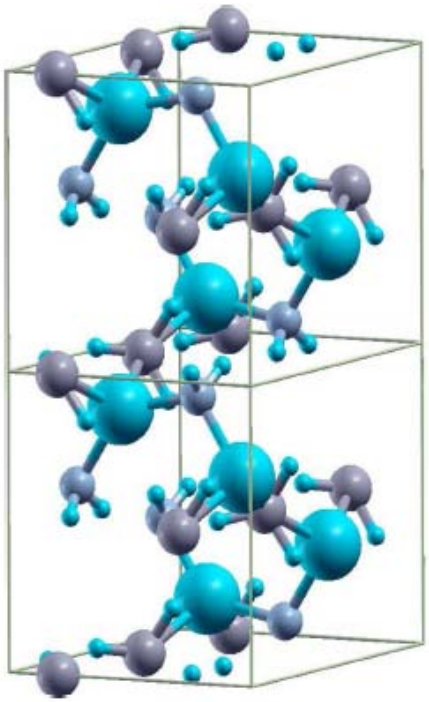




- At least two desorption steps evident (onsets of ~175 and 325ºC)
- VT-XRD data reveals 1st step corresponds, in part, to the disappearance of $Mg(BH_4)_2$ phase and the 2nd step to the possible formation of MgB_2
- More data necessary to determine specific experimental pathway for comparison with predicted pathway

Technical Accomplishments: Experimental Testing of Predicted Compounds

Previously, no known quarternary borohydride/amide compounds in Mg-B-N-H system



$Mg(BH_4)(NH_2)$-PEGS (4 f.u.)
Space group: Ima2 (46)
a=8.83 Å, b=6.53 Å, c=6.34 Å

$Mg(BH_4)_2 + Mg(NH_2)_2 \rightarrow MgBNH_6$

kJ/(mol Mg)	ΔE_{Static}	$\Delta H_{ZPE}^{T=0K}$	$\Delta H^{T=300K}$
$Mg(BH_4)(NH_2)$	-9.75	-8.18	-8.63

New, predicted compound stable w.r.t. $Mg(BH_4)_2 + Mg(NH_2)_2$

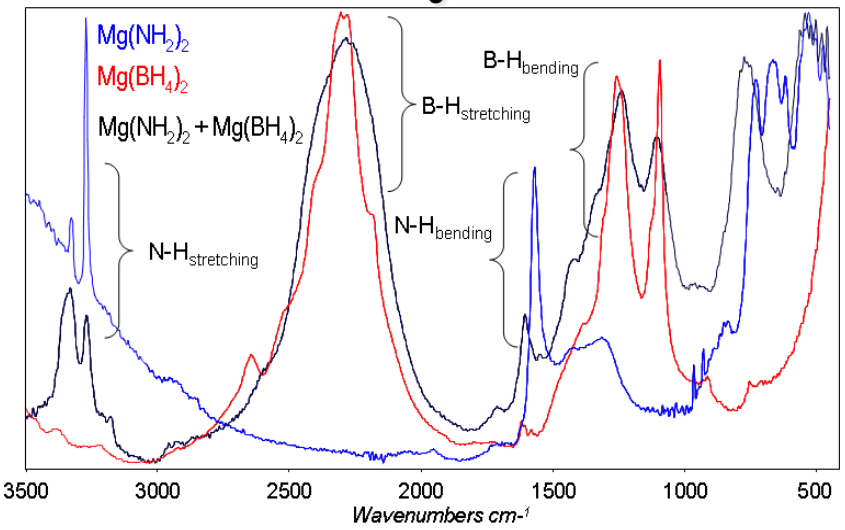
Y.-S. Zhang and C. Wolverton, unpublished (2011).

Synthesis & Characterization of $Mg(NH_2)_2 + Mg(BH_4)_2$ Mixture

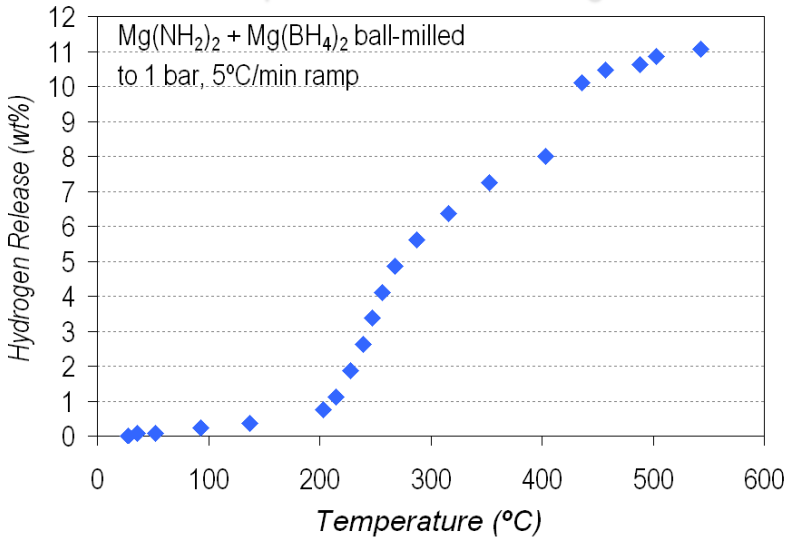
Synthesis:

- 1:1 ratio of $Mg(NH_2)_2$:$Mg(BH_4)_2$ ball-milled (Spex) for 5 hrs
- $Mg(NH_2)_2$ synthesized from MgH_2 and NH_3; $Mg(BH_4)_2$ purchased from Aldrich
- Preliminary hydrogen release & phase characterization performed at Ford; Samples sent from Ford to Northwestern U. for catalyst development

FT-IR of Ball-Milled Mg-B-N-H vs. Reactants



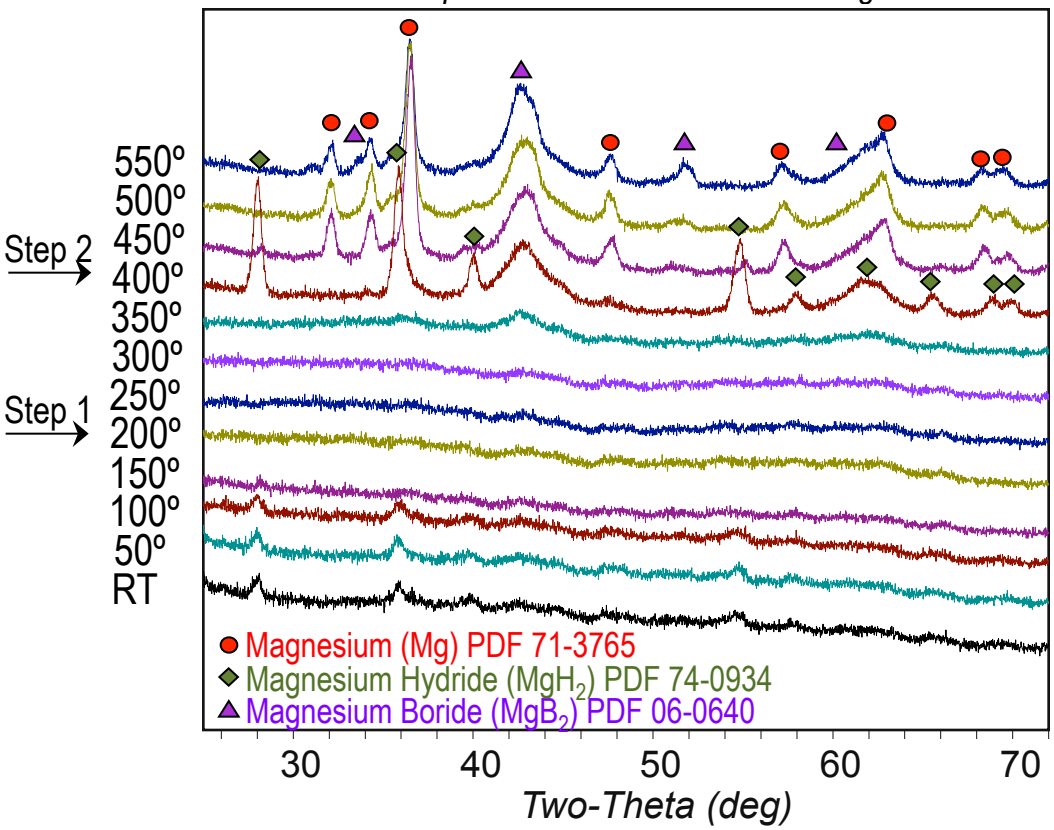
Desorption of Ball-Milled Mg-B-N-H



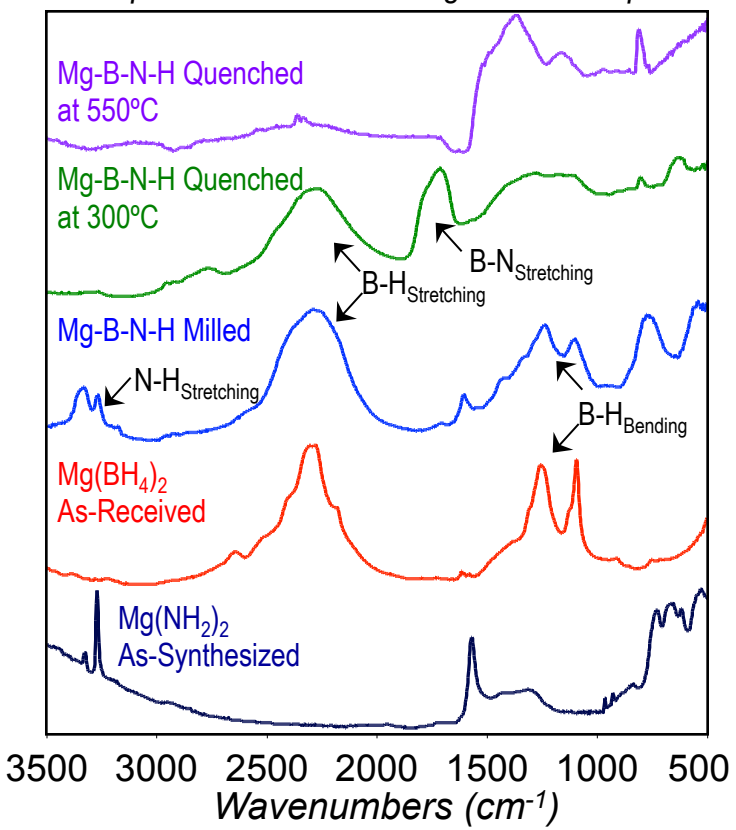
- FT-IR data suggests NH_2^- and BH_4^- units are in the same environment as in individual reactants
- Desorption occurs in two steps (200 & 400ºC onsets) with a total of ~11 wt% released (10.9 wt% theo.)

Characterization of the Reaction Pathway for $Mg(NH_2)_2 + Mg(BH_4)_2$

Variable Temperature XRD for Ball-Milled Mg-B-N-H



IR Spectra for Quenched Mg-B-N-H Samples



Preliminary Conclusions:

- Step 1: Involves consumption of amide and formation of a B-N phase (IR)
- Step 2: Involves decomposition of B-N phase and MgH_2 to form Mg and MgB_2 (IR & XRD)
- More data necessary to determine specific experimental pathway for comparison with predicted pathway.

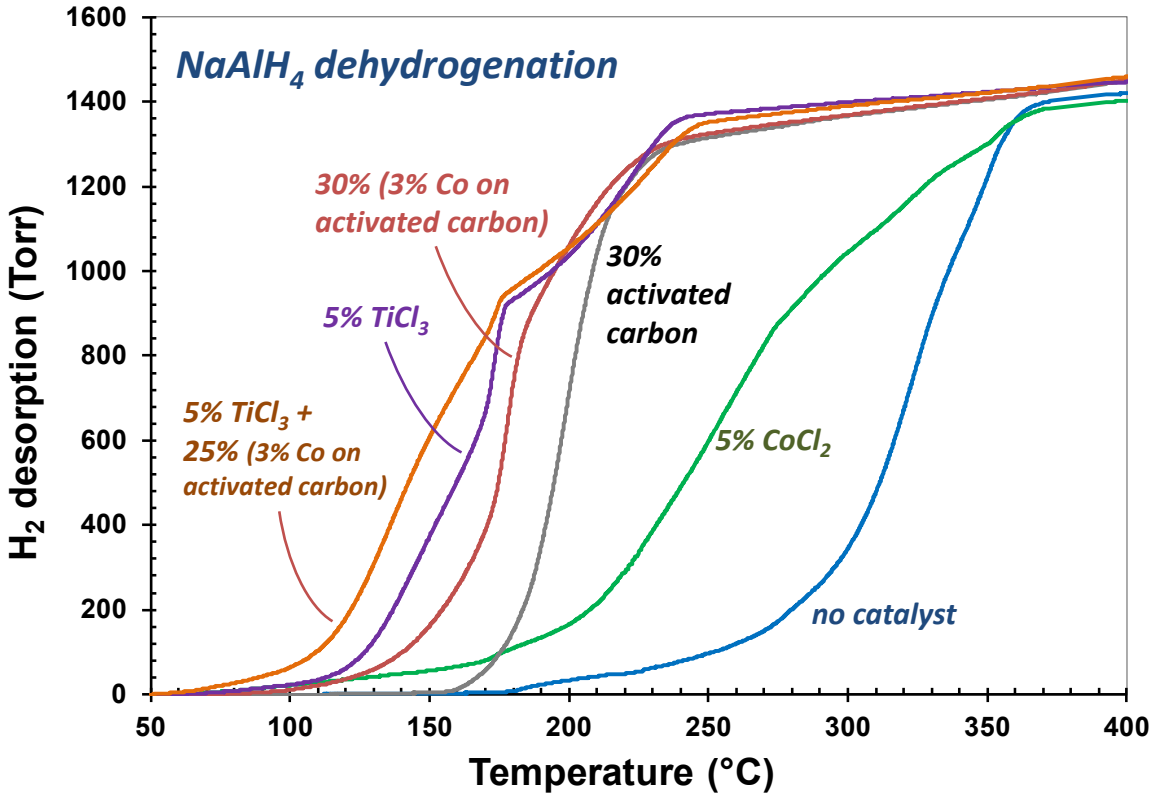
Technical Accomplishments: New Metal–Carbon Catalyst

Problems with the conventional Ti metal catalyst

- only works for few hydrides (component-specific)
- catalyst loses activity upon repeated cycling

Objective—to develop a new form of catalyst

- applicable to any solid-state hydrides
- catalyze de-/re-hydrogenation without specific interactions with hydrides (e.g., compound formation)
- easily prepare in a reproducible manner for optimizing, fine-tuning the composition and functionality



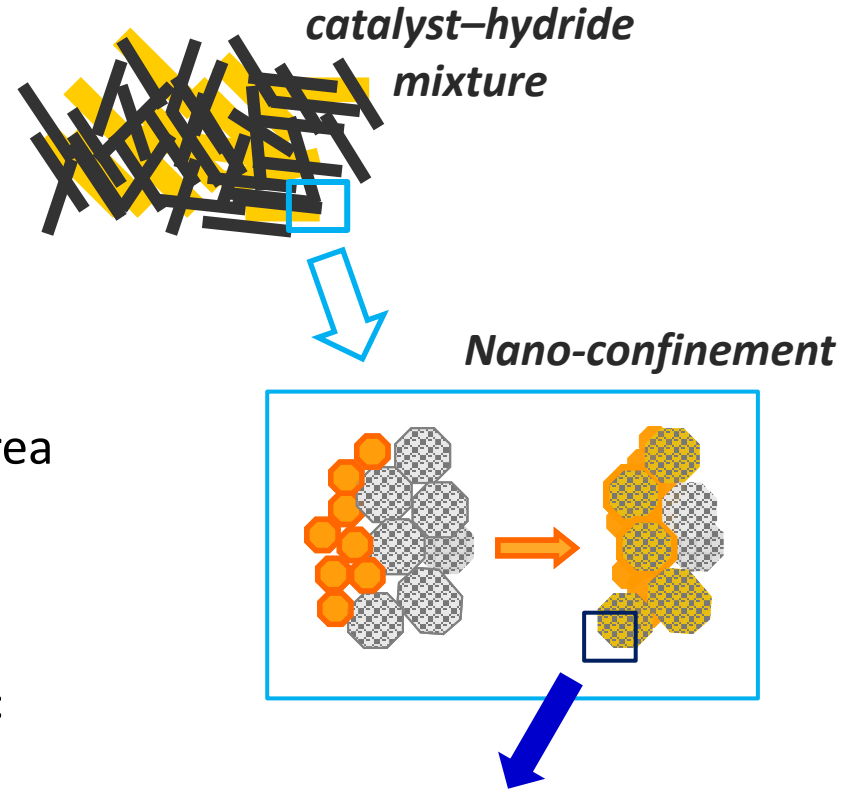
Initial observation

- well studied $NaAlH_4$ is used as a test case
- cobalt on activated carbon exhibits a high activity for dehydrogenation
- adding new catalyst (cobalt on activated carbon) further enhances the dehydrogenation kinetics of Ti-catalyzed $NaAlH_4$

Preliminary observation justifies further investigation in order to

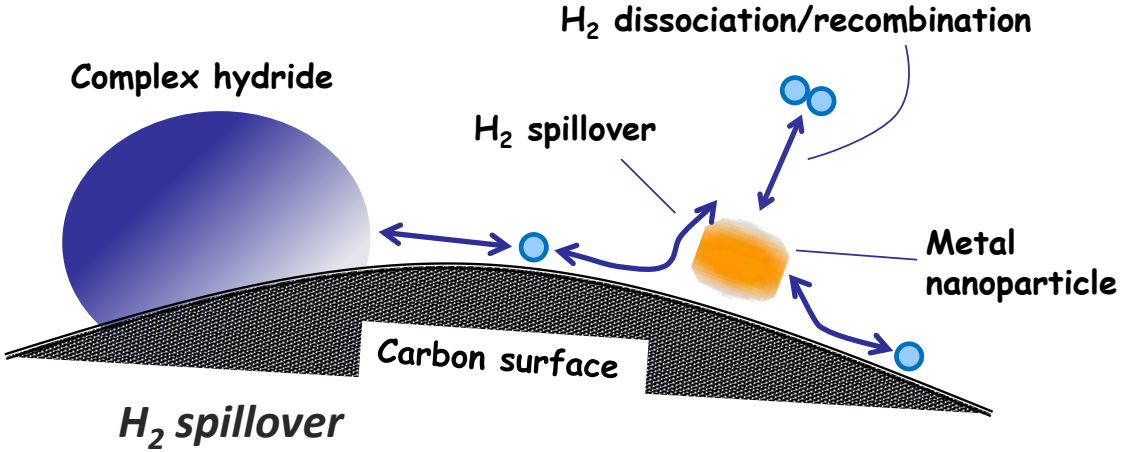
—understand the phenomena

—optimize the catalytic system

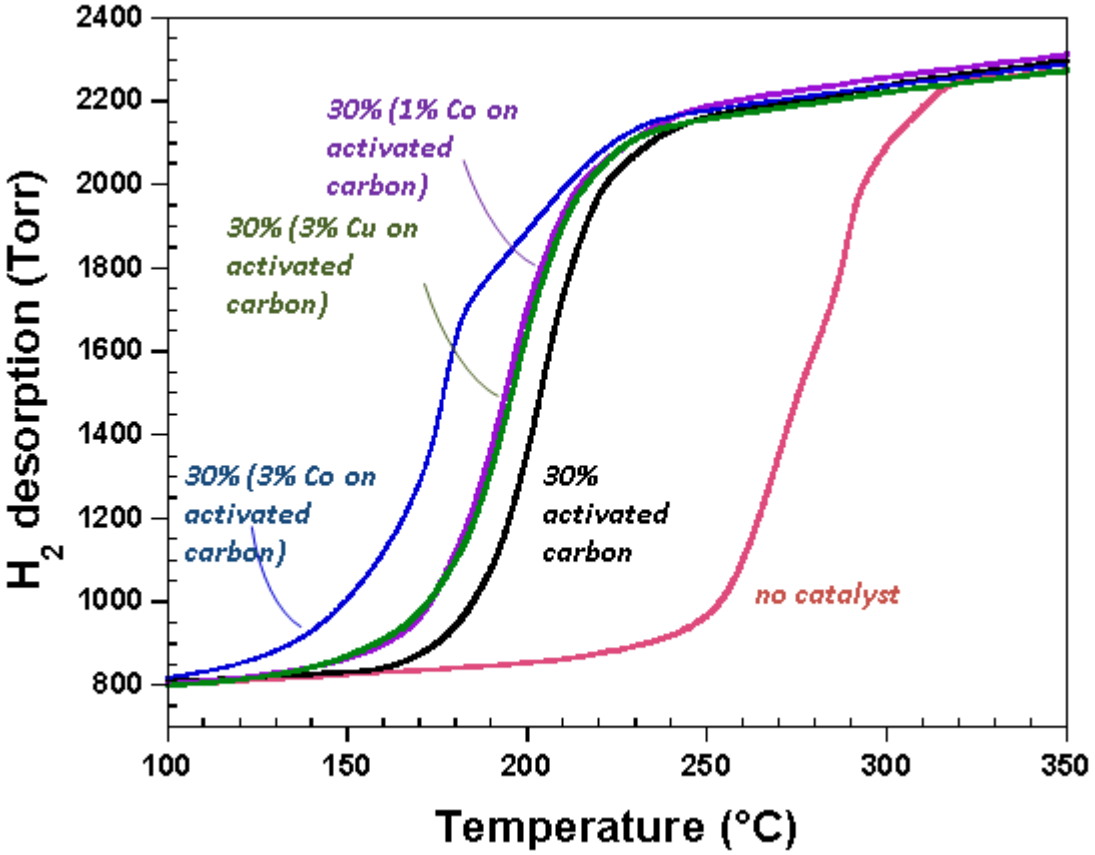


Proposed catalytic actions

- carbon substrate for large contact area with hydrides
- porous carbon introduces nano-confinement effect
- adding metal NPs enhances catalytic activity, possibly by spillover effect



Technical Accomplishments: New Metal–Carbon Catalyst Test Case: $NaAlH_4$

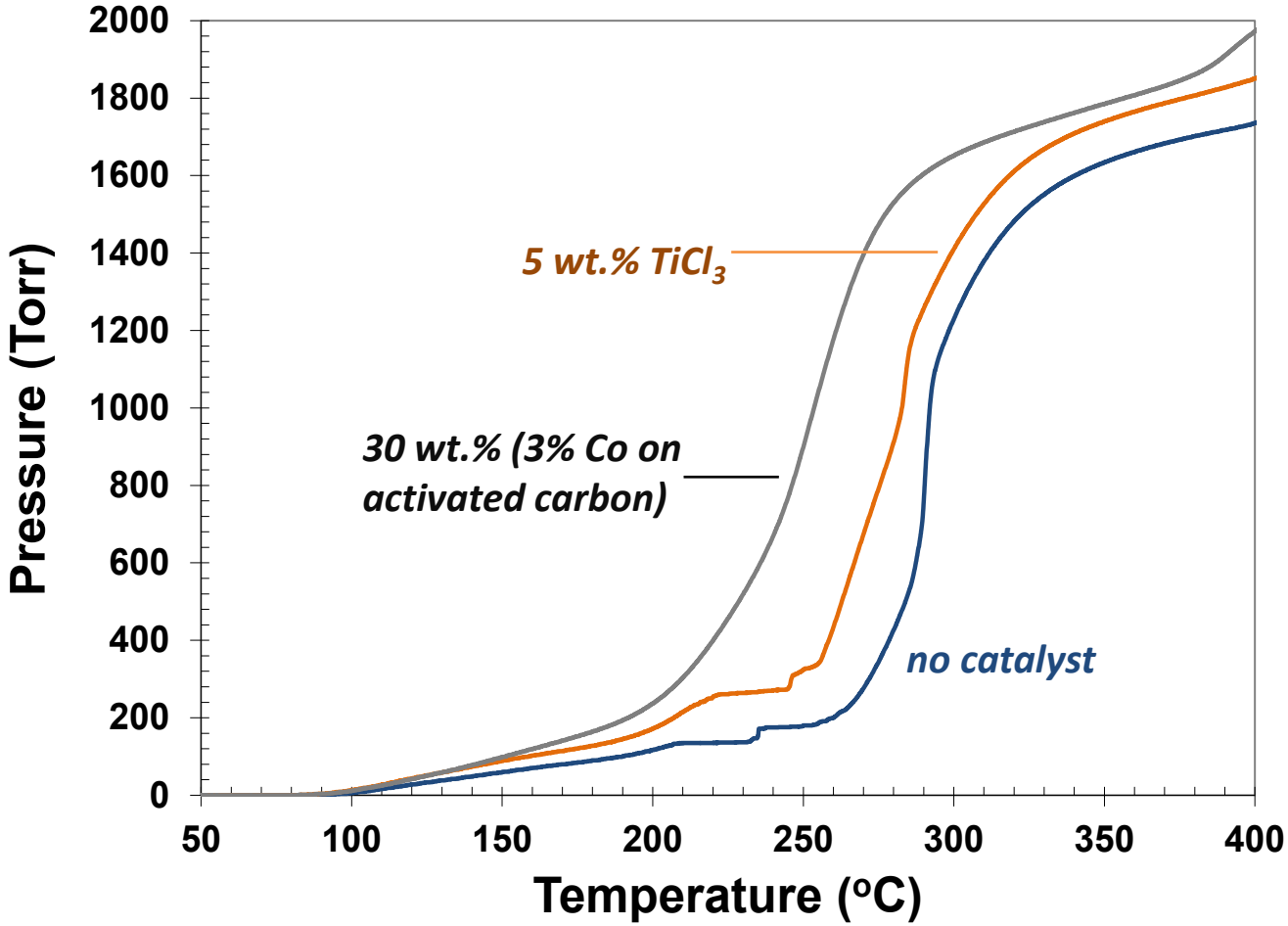


Higher loading cobalt on a high surface area, porous carbon material enhances dehydrogenation

Summary

- Various forms of carbon are catalysts for $NaAlH_4$.
- Catalytic effect: activated carbon > MWCNTs> graphite nanoplatelets > graphite flakes.
- Adding 1 to 3 wt.% metal (Co or Cu) to carbon further enhances catalytic effect, and Co> Cu.
- Dehydrogenated sample can be re-hydrogenated.

$Mg(NH_2)_2 + Mg(BH_4)_2$ Thermal Decomposition: Effect of Catalyst (30% (3% Co-activated carbon) and $TiCl_3$)



Sample mass: 83 mg ($Mg(NH_2)_2$+$Mg(BH_4)_2$
Initial pressure: << 1 Torr
Ramping rate: 5°C/min

Effect of Catalyst in $Mg(NH_2)_2$–$Mg(BH_4)_2$ Thermal Decomposition:

Pressure measurement with in-line gas phase FT-IR

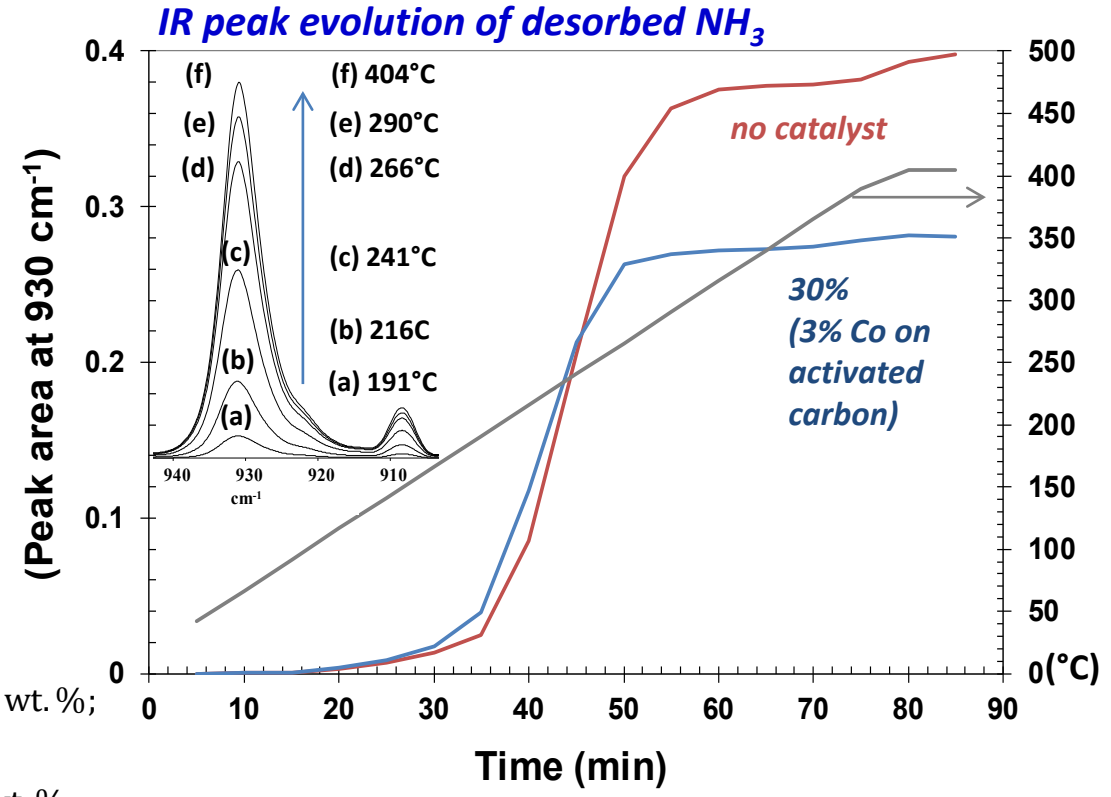
Reaction conditions:

Sample mass: 59 mg

Catalyst mass: 25.3 mg (30 wt.% (3% Co on activated carbon)

Initial pressure: << 1 Torr

Ramping rate: 5°C/min



H_2 release estimated by mass change:

Pristine $Mg(NH_2)_2$–$Mg(BH_4)_2$:

$$H_2 = \frac{total\ mass\ lost\ -estimated\ NH_3}{sample\ mass\ (active\ material)} = \frac{5.0-0.8\ mg}{59.0\ mg} = \mathbf{7.1}\ \text{wt.\%};$$

$$NH_3 = \frac{estimated\ NH_3}{sample\ mass\ (active\ material)} = \frac{0.8\ mg}{59.0\ mg} = \mathbf{1.4}\ \text{wt.\%};$$

Catalyzed $Mg(NH_2)_2$–$Mg(BH_4)_2$:

$$H_2 = \frac{total\ mass\ lost\ -estimated\ NH_3}{sample\ mass\ (active\ material)} = \frac{7.9-0.6\ mg}{59.0\ mg} = \mathbf{12.4}\ \text{wt.\%};$$

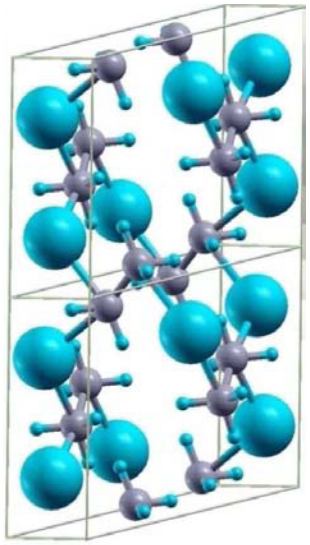
$$NH_3 = \frac{estimated\ NH_3}{sample\ mass\ (active\ material)} = \frac{0.6\ mg}{59.0\ mg} = \mathbf{1.0}\ \text{wt.\%};$$

Assuming mass lost due to NH_3 and H_2 formation only—catalyzed sample released more H_2 and less NH_3!

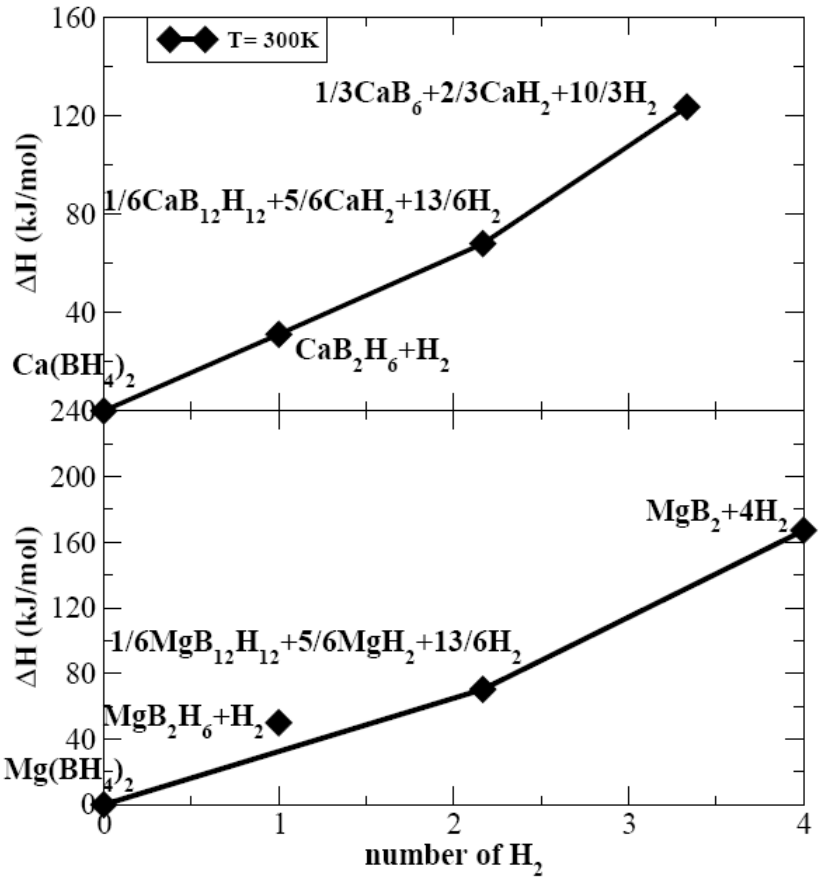
Technical Accomplishments: New Theoretical Predictions

- New borohydride compounds
  - CaB_2H_6 and MgB_2H_6
  - AlB_4H_{11}
- Decomposition products in metal amidoboranes
- Properties of nano-confined materials
- Diffusion & mass transport (required for fast kinetics)

Technical Accomplishments: Prediction of New Mg-B-H and Ca-B-H Decomposition Pathways



New predicted B_2H_6 intermediate: Stable decomposition product in Ca $(BH_4)_2$, but not in $Mg(BH_4)_2$



Y.-S. Zhang, E.H. Majzoub, V. Ozolins, and C. Wolverton, Phys Rev B **82**, 174107 (2010).

Technical Accomplishments: New metal borohydride: AlB_4H_{11}

In collaboration with Xuenian Chen and JiCheng Zhao (OSU)

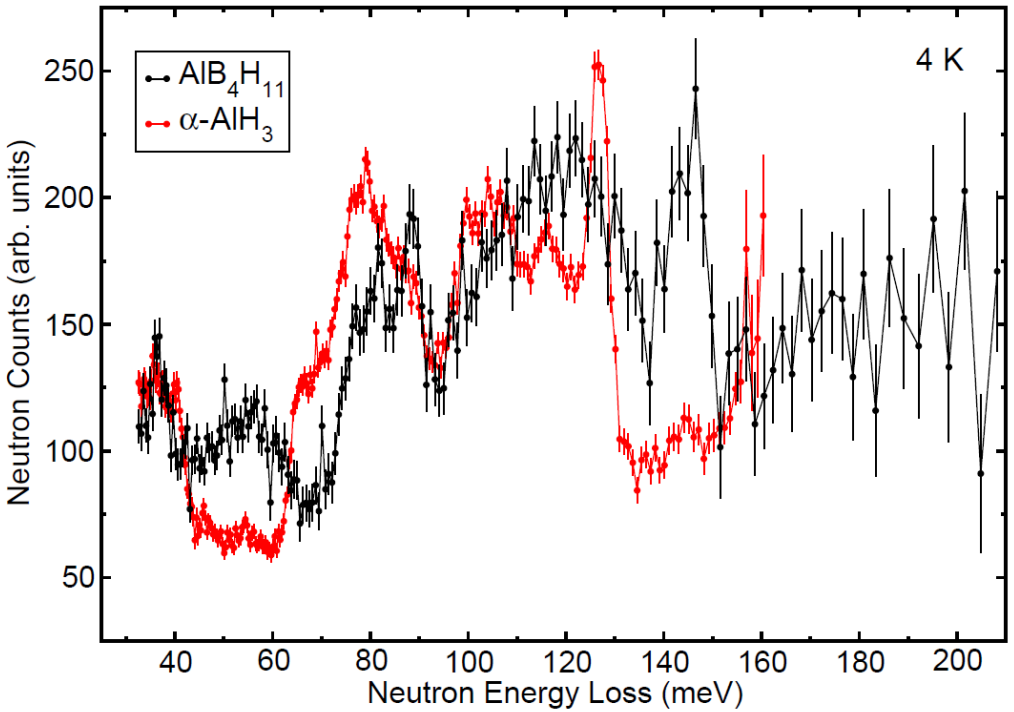
- **AlB_4H_{11} synthesis:**
  $2Al(BH_4)_3+B_2H_6 \rightarrow 2AlB_4H_{11}+4H_2$

- **AlB_4H_{11} reversibility observed for at mild conditions: 200C, 90 bar H2, 5hr**

- **But the structure of AlB_4H_{11} is experimentally unknown: amorphous and polymeric**

- **A great challenge for computational approaches**

J. –C. Zhao, *et al.* J. Phys. Chem. C. 113, 2 (2009)

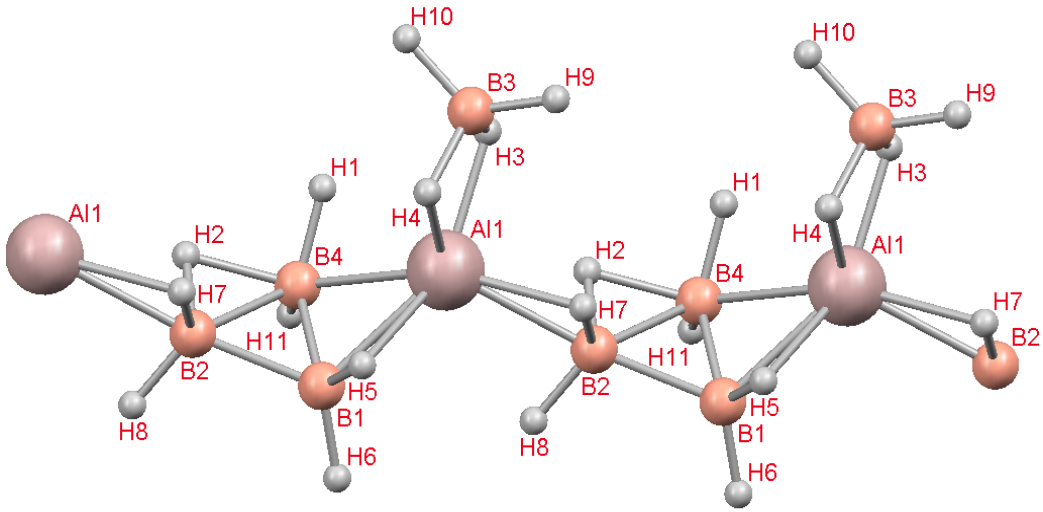


Can we use PEGS+DFT to predict the structure? Or at least help interpret the experimental data?

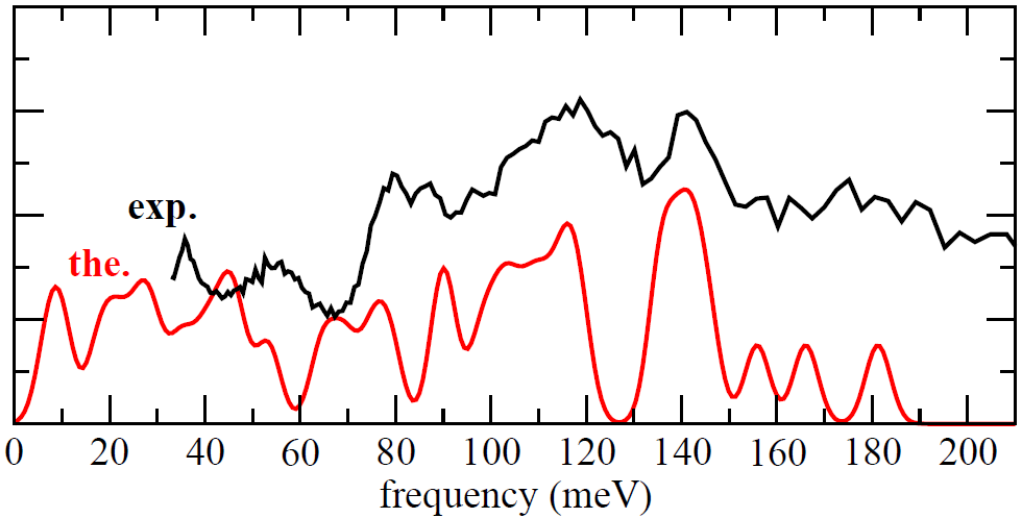
PEGS+DFT Predicted AlB_4H_{11} low-energy structure

In collaboration with Xuenian Chen and JiCheng Zhao (OSU)

Polymeric Chain:
Comprised of
Al, BH_4, BH_3, and BH_2 "units"



Theoretical phonon DOS vs. experimental neutron vibration spectra



Good agreement between theory and experiment.

Theoretical peaks slightly shifted down: possibly due to exchange-correlation functional (overestimation of bond lengths).

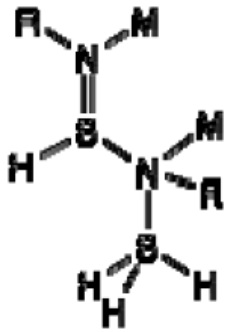
Theoretical structure has provided good guidance to experimental efforts

Technical Accomplishments
Amidoborane Decomposition Products:
Dianion $[NHBHNHBH_3]^{2-}$

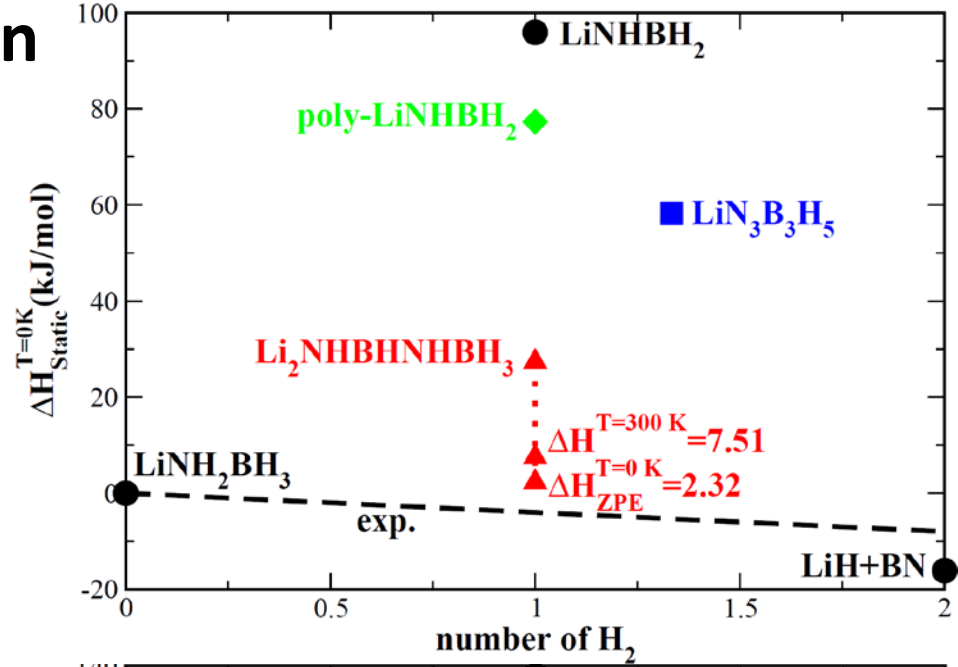
in collaboration with T. Autrey (PNNL)

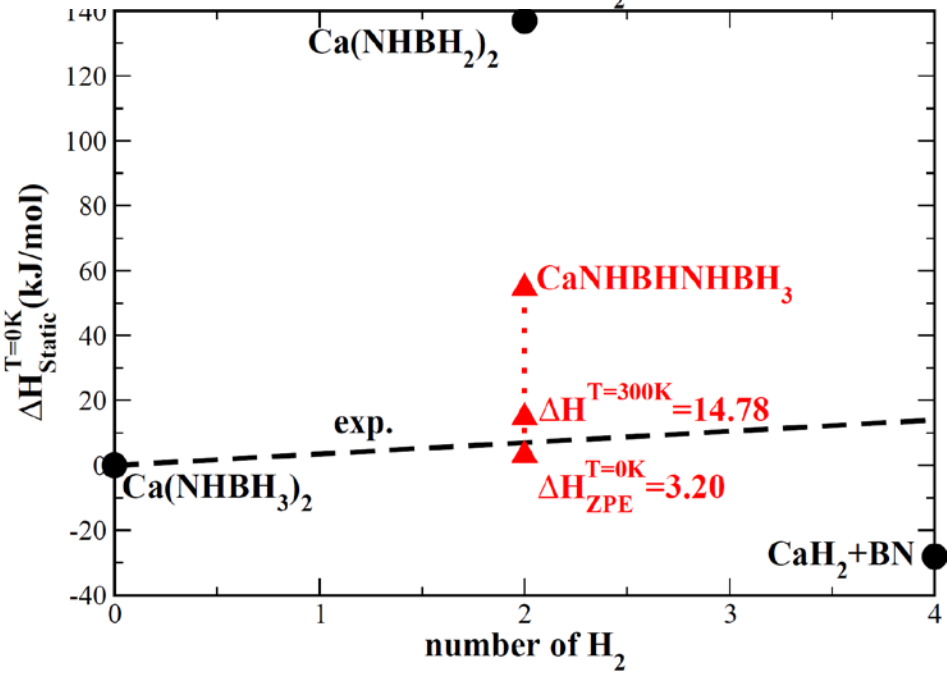
- **B-N-B-N bridge proposed AB decomposition product.**
- **DFT calculations support this proposal:**

$NHBHNHBH_3$ is lowest energy decomposition intermediate (out of many possibilities calculated). Near thermoneutral for LiAB and CaAB



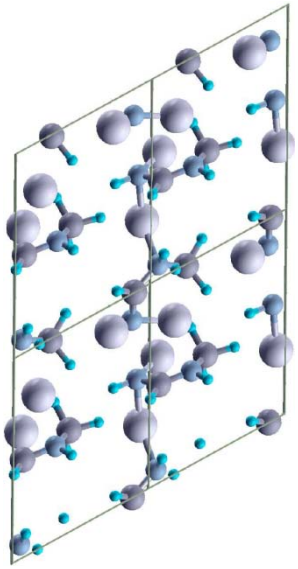
A. T. Luedtke and T. Autrey,
Inorganic Chem. 49, 3905 (2010)



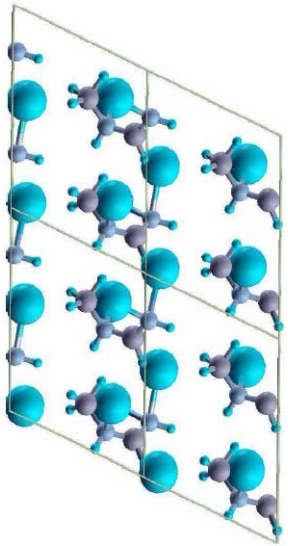


Technical Accomplishment: Stability Trends in Amidoboranes

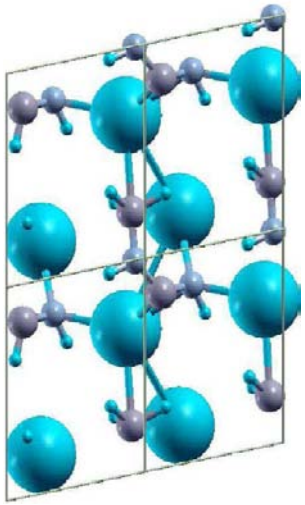
Tailoring ΔH by Changing Metal Cations



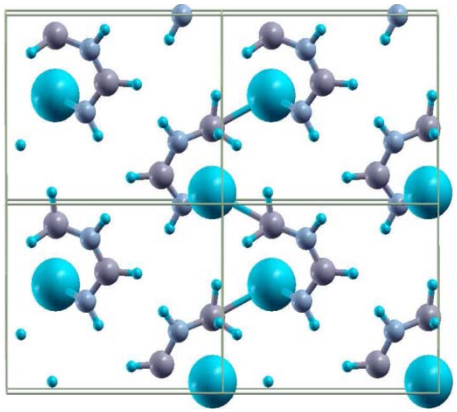
$LiNHBHNHBH_3$



$NaNHBHNHBH_3$

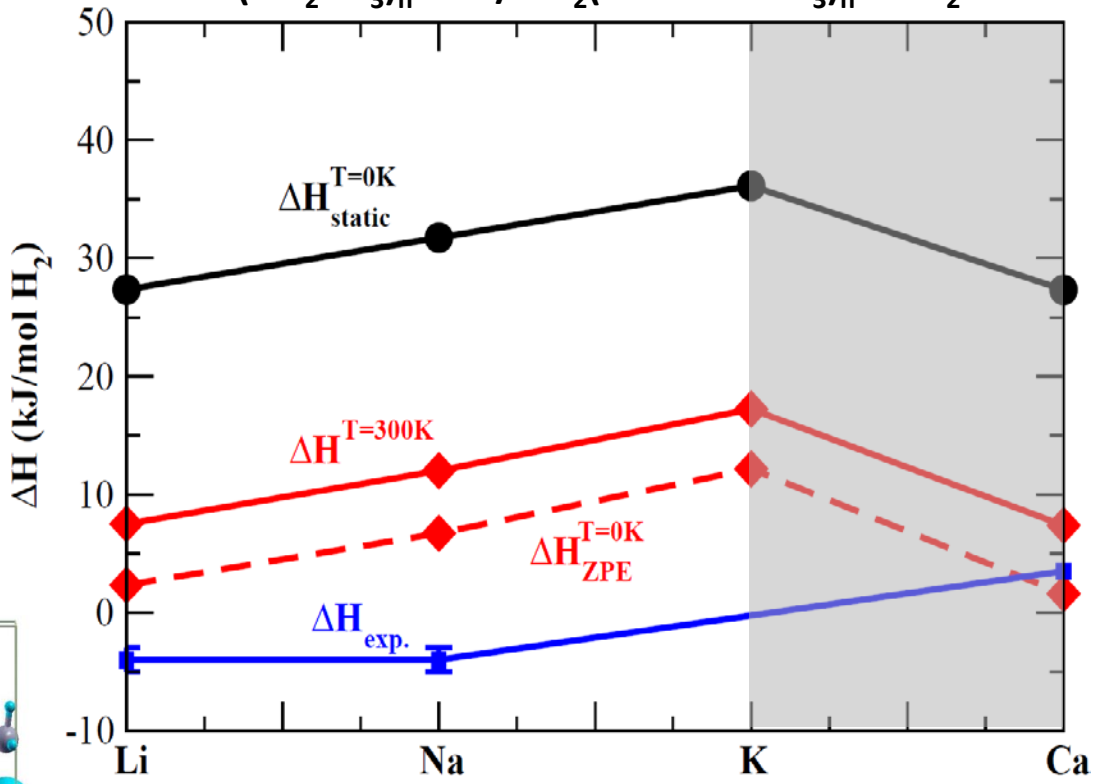


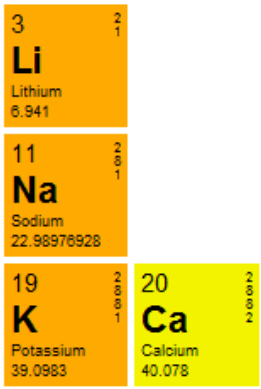
$KNHBHNHBH_3$



$Ca(NHBHNHBH_3)_2$

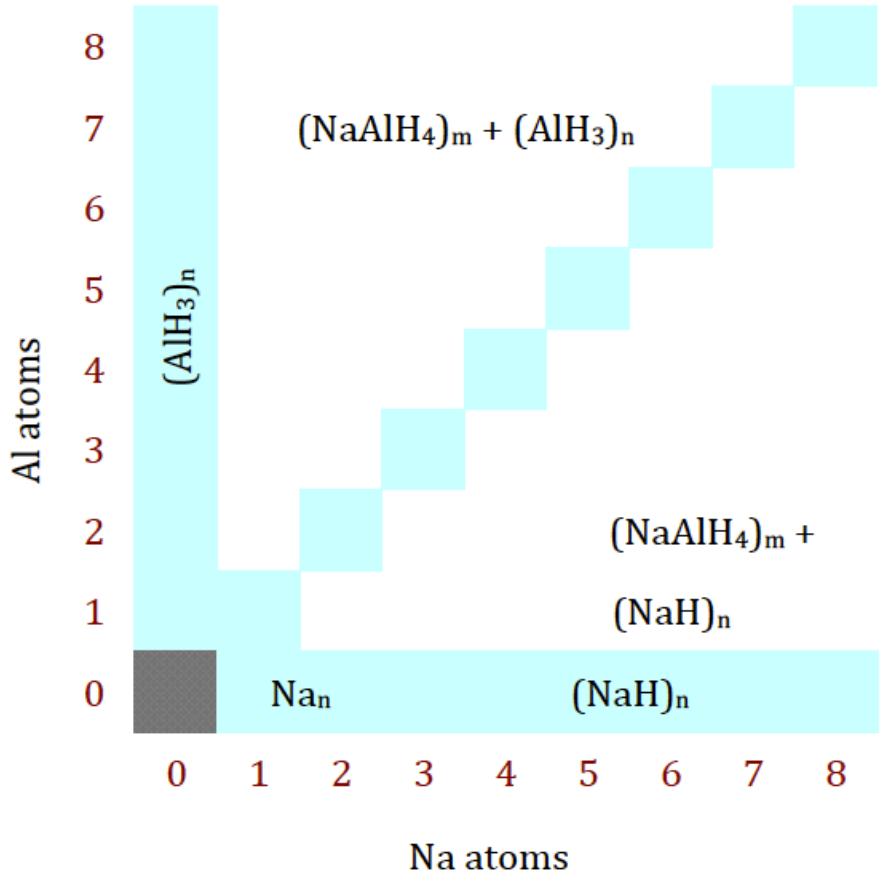
$M(NH_2BH_3)_n \rightarrow 1/2M_2(NHBHNHBH_3)_n + nH_2$

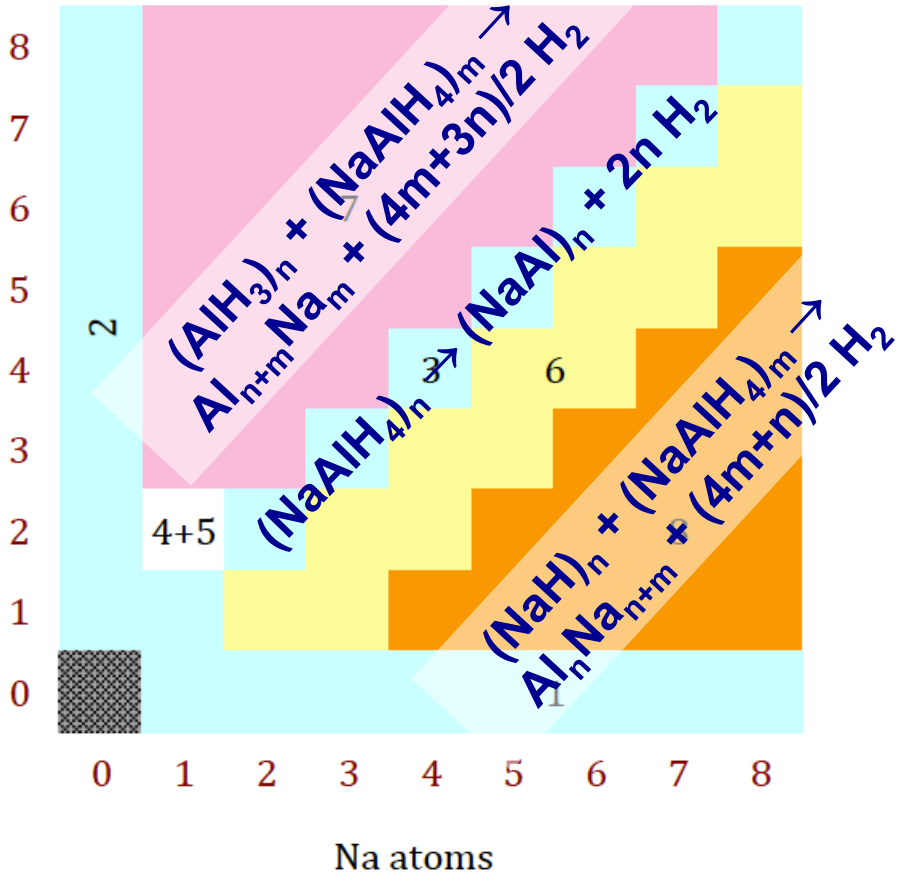




Stability Trends: AB becomes more stable as metal cation moves down a column or moves to left in a row of the periodic table

Development of nanoPEGS and nanoGCLP

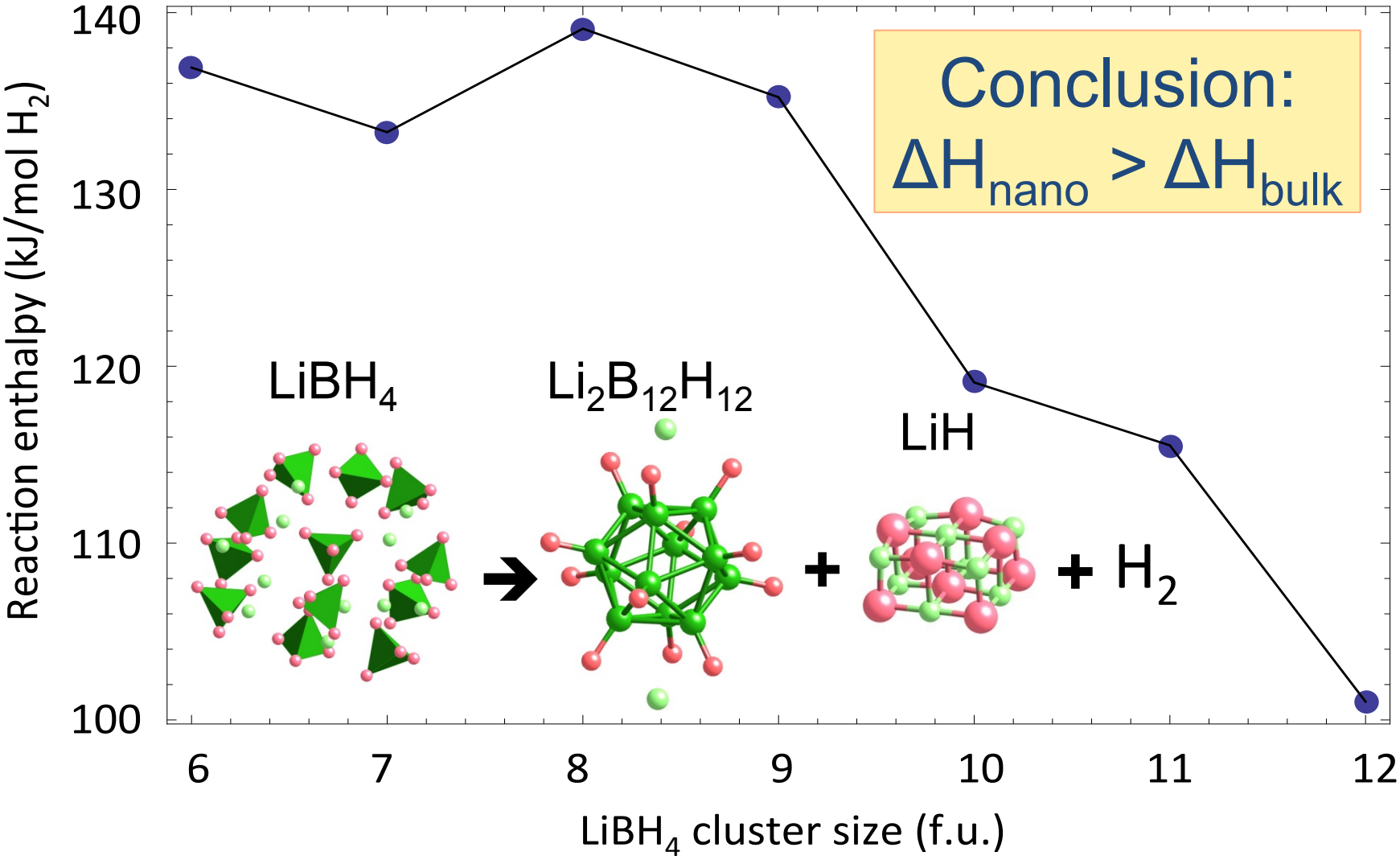




- Improved PEGS to handle nanoparticles using Wang-Landau Monte Carlo
- Generalized grand-canonical linear programming (GCLP) to nanoclusters
- Predicted phase diagrams & decomposition pathways of nano-$NaAlH_4$
- Predicted nanoparticle analogues of destabilized reactions

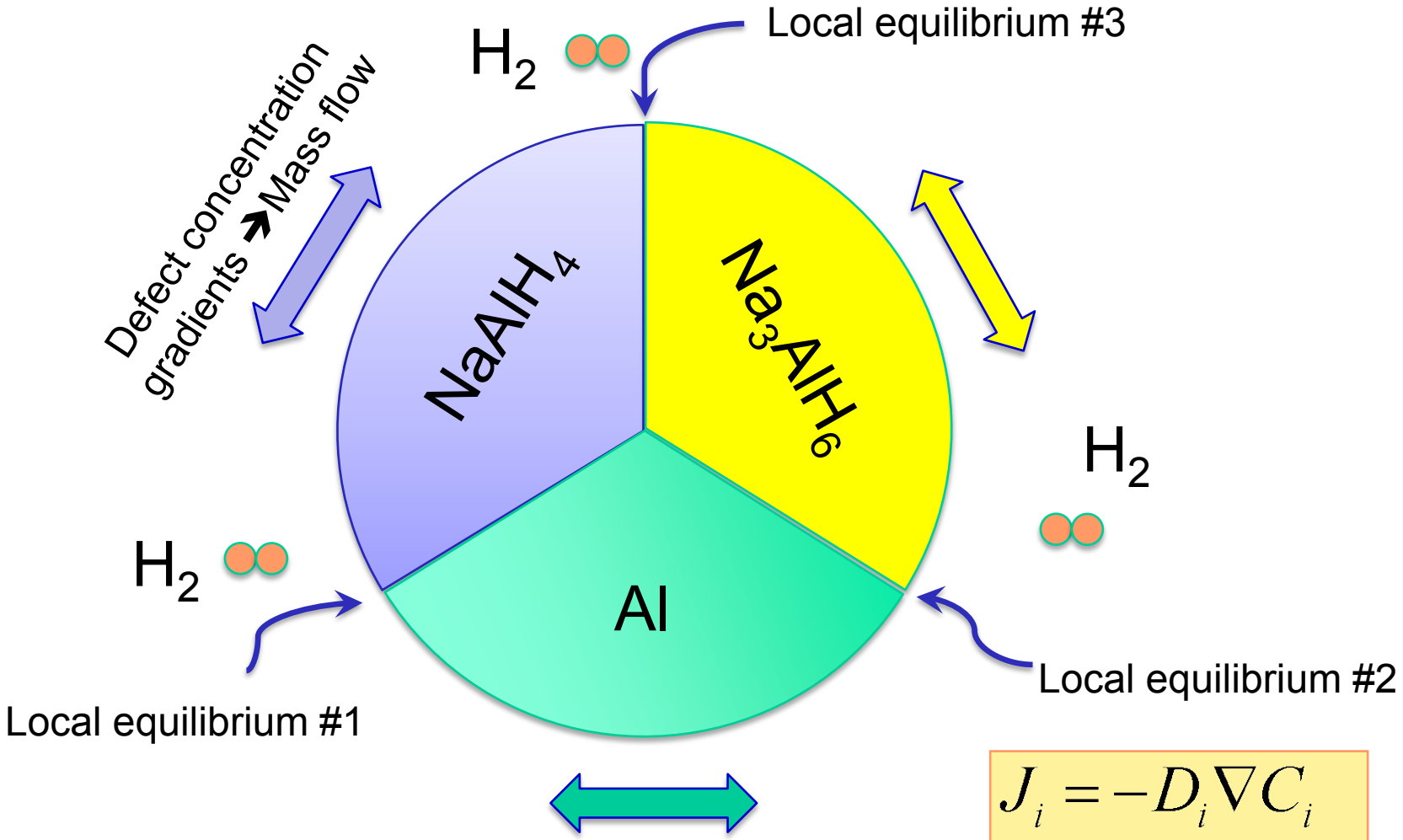
E. H. Majzoub, F. Zhou, and V. Ozolins, J Phys Chem C **115**, 2636–2643 (2011)

Technical Accomplishments: Predicted Decomposition Enthalpies of Free $LiBH_4$ Nanos



In collaboration with E.H. Majzoub (UMSL) and F.-C. Chuang (Nat'l Sun Yat-Sen U)

Technical Accomplishments: Developed Predictive Models for Kinetics of Mass Transport



$$J_i = -D_i \nabla C_i$$

$$\text{Rate} \propto \max J_i$$

K. Michel and V. Ozolins, submitted to J Phys Chem (2011).

Validation of Diffusion-Reaction Model

Incorrect morphology

Na_3AlH_6	$NaAlH_4$	Al

Activation Energy (kJ/mol)	Calculated	
	$T < T_{crit}$	$T > T_{crit}$
$[AlH_3]$	109	172
$[AlH_4]^+$	108	170

Correct morphology

$NaAlH_4$	Na_3AlH_6	Al

Activation Energy (kJ/mol)	Calculated	
	$T < T_{crit}$	$T > T_{crit}$
$[Na]^-$	53 ✔	86 ✔

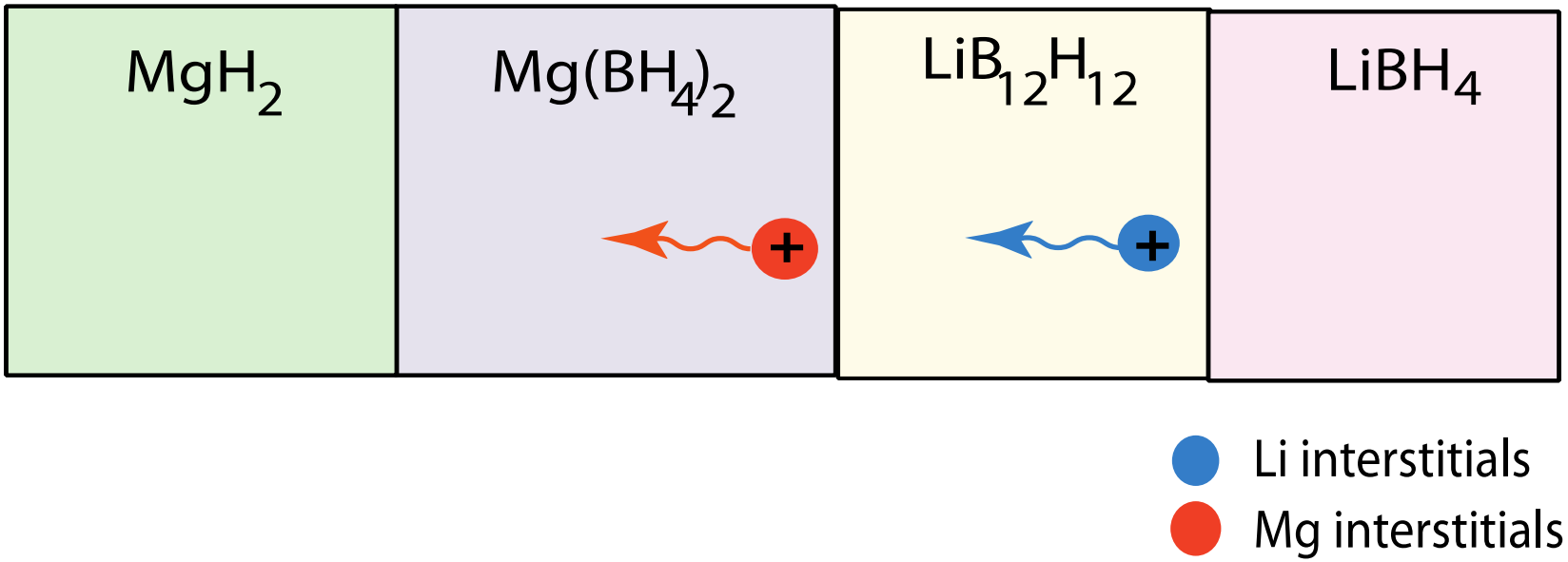
Experimentally Measured Activation Energies (kJ/mol)	Rehydrogenation	Dehydrogenation	
	2 mol % Ti	Undoped	2 mol % Ti
$NaAlH_4 \rightarrow \frac{1}{3}Na_3AlH_6 + \frac{2}{3}Al + H_2$	62 ✔	118	80, 86 ✔

Conclusion: Diffusion of $[Na]^-$ vacancies through Na_3AlH_6 is rate-limiting for both hydrogenation and de-hydrogenation of $NaAlH_4$.

K. Michel and V. Ozolins, submitted to J Phys Chem C (2011).

Work in Progress: Kinetics in Borohydrides

$$5Mg(BH_4)_2 + 2LiBH_4 \rightarrow Li_2B_{12}H_{12} + 5MgH_2 + 13\ H_2$$



Generalized interfacial equilibrium conditions for:

- Two reactants and three products (incl. H_2)
- Four elements (Li, Mg, B, H)

Collaborations

PI's/co-PI's

Chris Wolverton (Northwestern, lead)
Harold Kung (Northwestern)
Vidvuds Ozolins (UCLA, subcontract)
Andrea Sudik (Ford, no-cost collaborator)
Jun Yang (Ford, no-cost collaborator)

Outside Collaborators:

D. Siegel (U. Michigan)
E. Majzoub (UMSL)
G. Ceder, N. Marzari (MIT)
C. Brown (NIST)
T. Burrell (LANL)
T. Autrey (PNNL)
F.-C. Chuang (Nat'l Sun Yat-Sen U)
J. C. Zhao (OSU)

Future Plans

- Experimentally characterized storage properties/reactions of $(NH_4)_2B_{12}H_{12}$ and other predicted reactions; elucidate decomposition pathway for $Mg(BH_4)_2$+$Mg(NH_2)_2$ 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_4/NH_2 compounds and reversible reactions, and mixed metal borohydrides

Summary – Project Overview

- Project focused on design of novel multi-component mixtures for hydrogen storage
- Systems being studied include mixtures of complex hydrides and chemical hydrides involving combinations of B- and N-containing materials
- Powerful blend of: 1) H_2 Storage measurements and characterization, 2) State-of-the-art computational modeling, 3) Detailed catalysis experiments, 4) In-depth automotive perspective

Summary – Technical Accomplishments

- Synthesis and characterization (XRD, IR, TPD) of two predicted promising hydride mixtures: $5LiBH_4 + 2Mg(BH_4)_2$ and $Mg(BH_4)_2 + Mg(NH_2)_2$
- Prediction of new previously-unknown $MgBNH_6$ compound, stable w.r.t. $Mg(BH_4)_2 + Mg(NH_2)_2$
- Proposed new metal-carbon catalyst: Tested on $NaAlH_4$, and applied to $Mg(BH_4)_2 + Mg(NH_2)_2$; Effective catalyst - lowers desorption temperature of both reactions, and reduces formation of NH_3 in the latter case.
- Predicted new CaB_2H_6 product in decomposition of $Ca(BH_4)_2$
- Predicted structure of AlB_4H_{11} polymeric compound
- Found new low-energy decomposition product of amidoborane reactions; found stability trends in AB reactions to tailor ΔH to choice of metal cation
- Extended PEGS and GCLP to apply to nano-confined materials. Explored nano $NaAlH_4$ and $LiBH_4$ reactions
- Developed predictive models of kinetics of mass transport. Application to $NaAlH_4$ and borohydrides (in progress)