

Tunable Thermodynamics and Kinetics for Hydrogen Storage: Nanoparticle Synthesis Using Ordered Polymer Templates

2011 U.S. DOE HYDROGEN PROGRAM ANNUAL MERIT REVIEW and PEER EVALUATION MEETING

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Sandia National Laboratories

May 9 – 13, 2011
Washington, DC

Project ID: ST027

Timeline

Project start date: September 2008
 Project end date: September 2011
 Percent complete: 86%

Barriers

- (A) System weight and volume
- (C) Efficiency
- (P) Lack of understanding of hydrogen physisorption and chemisorption

Budget

- Total project funding through FY10:
 - DOE share: \$2010 K
 - Contractor share: \$159 K
- Total funding for FY11: \$580 K

Research Team

Sandia

MOFs and related templates

- M. Allendorf (PI)
- S. Maharrey, R. Behrens – kinetics
- V. Stavila – PCT, melt infiltration

Univ. MO, St. Louis (Prof. E. Majzoub)

BCP templates, hydride modeling

MIT (Prof. J. Grossman, L. Wagner)

Model benchmarking, hydride modeling

NIST (Terry Udovic) *neutron spectroscopies*

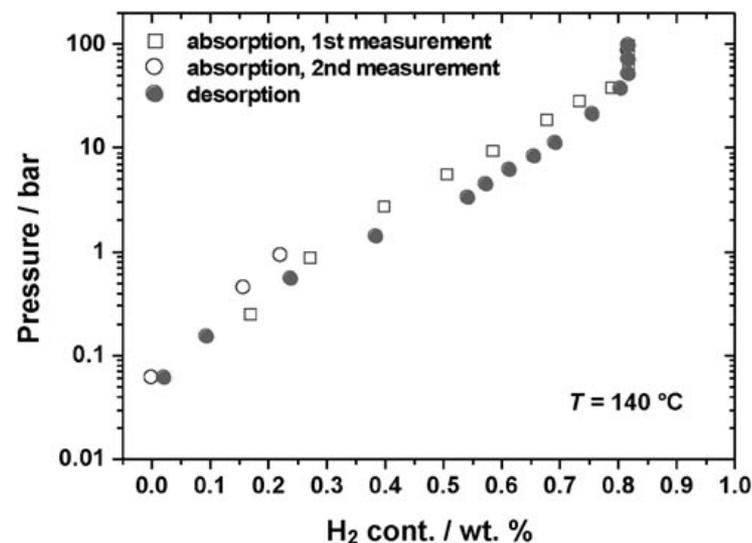
Relevance: Decreasing $T(1 \text{ bar})$ would make some metal hydrides much more attractive for hydrogen storage

Theory and experiment suggest nanoscale hydride particles are destabilized relative to bulk, but the origin of this effect is unclear. Both size and local environment may play a role.

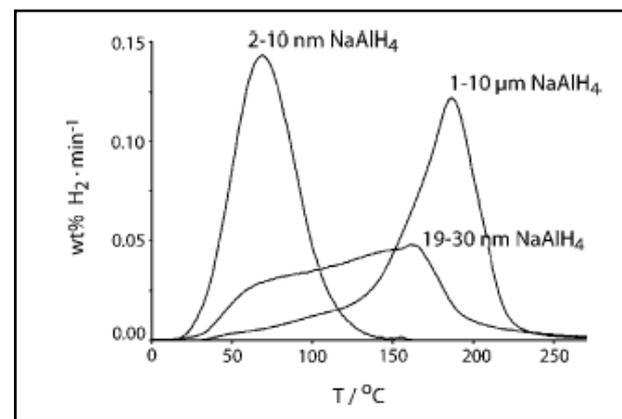
Overall Project Objective: Achieve tunable thermodynamics for hydrogen storage materials by controlling nanoparticle size, composition, and environment

Key Goals for FY10–11

- √ Demonstrate effect of size on complex hydride thermodynamics
 - √ NaAlH_4 in MOF templates
 - √ LiBH_4 in HCP templates
 - MgH_2 , LiNH_2 , $\text{Li}_4\text{BN}_3\text{H}_{10}$, and $\text{Ca}(\text{BH}_4)_2$
- √ Demonstrate compositional tuning effect by:
 - √ Predict Mg-Al-H phase diagram
 - Infiltrate templates and measure H_2 desorption
- Complete and submit journal articles
 - 2 published; 2 submitted



H_2 desorption: NaAlH_4 – infiltrated porous carbon (0.5 – 4 nm)
Lohsdrom et al. *ChemPhysChem* 2010



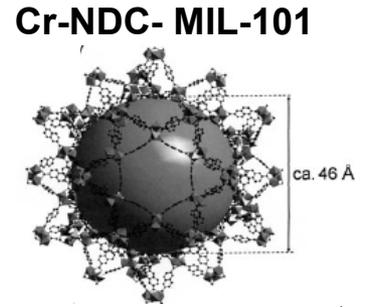
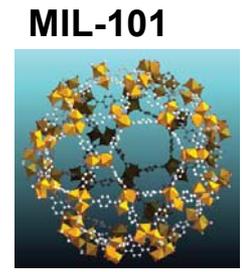
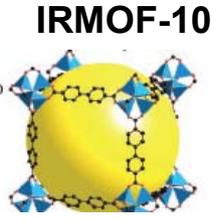
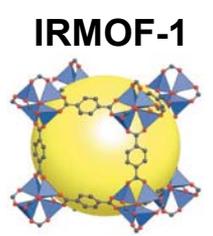
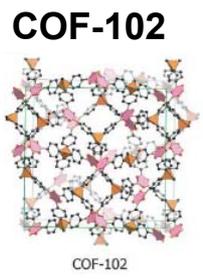
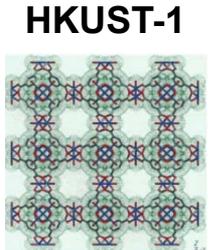
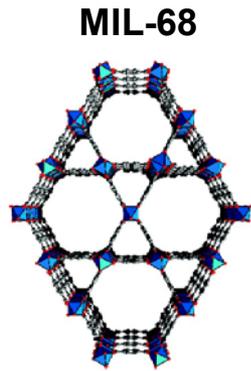
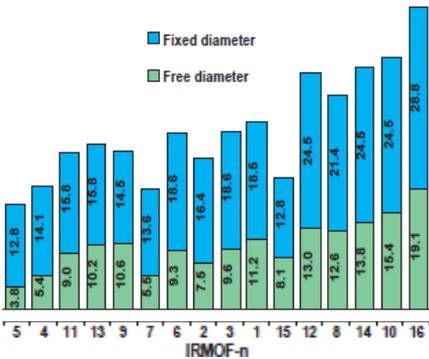
H_2 desorption from NaAlH_4 – infiltrated carbon nanofibers 3

Wagemans et al. *JACS* 2008

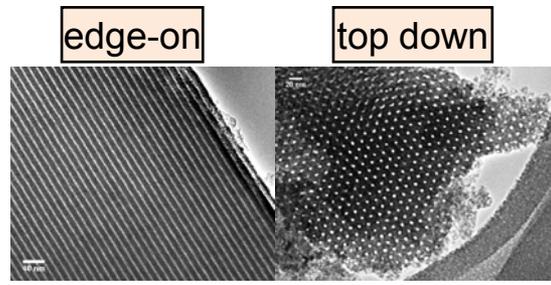
Approach: Use novel *ordered* frameworks to create a suite of templates to *systematically probe* nanoscale effects

MOFs, COFs, ZIFs, and block copolymers can be used to create a suite of templates with micro- to meso-scale pores

IRMOF entrance (green) and interior (blue) pore diameters



BCP and crosslinked phenolic resins



Meng, et al., *Chem. Mater.*, **18**, 4447-4464, (2006)

20 Å – 200 Å

10 Å

20 Å

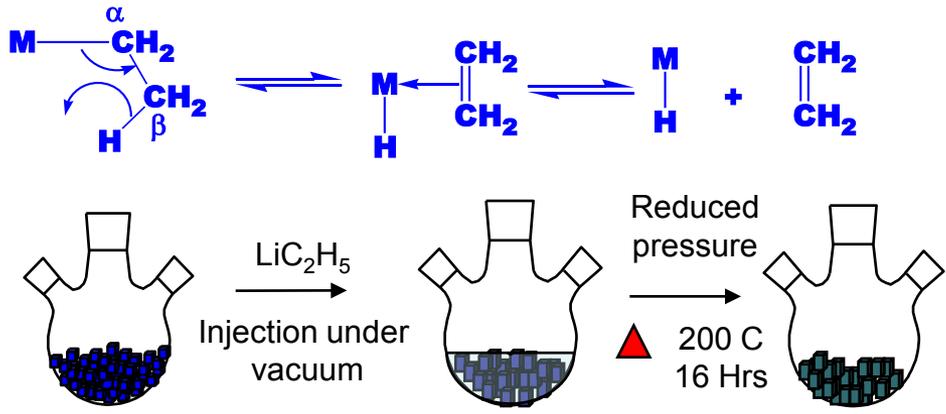
30 Å

40 Å

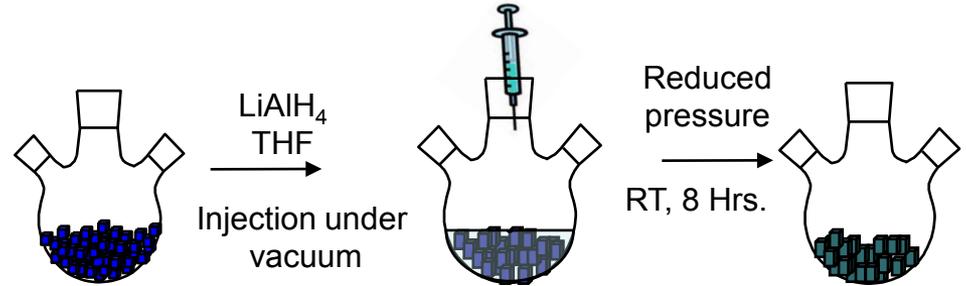
50 Å

Approach: Hydride infiltration methods for MOFs

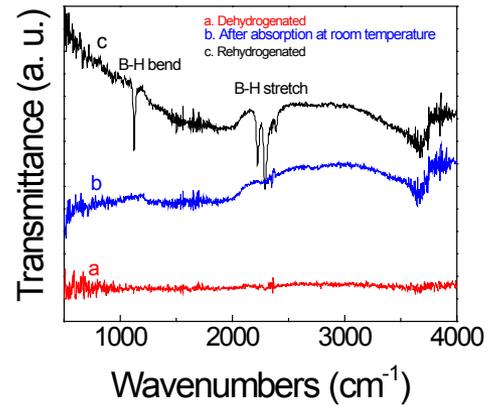
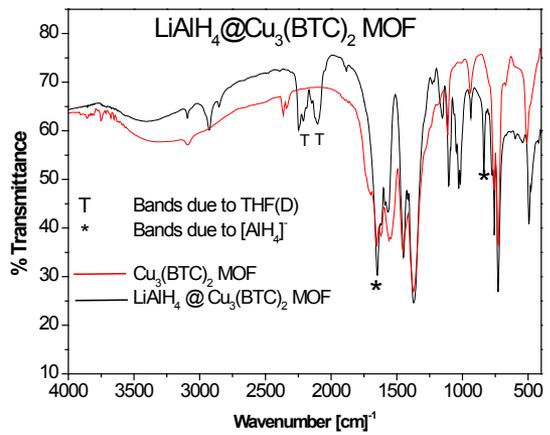
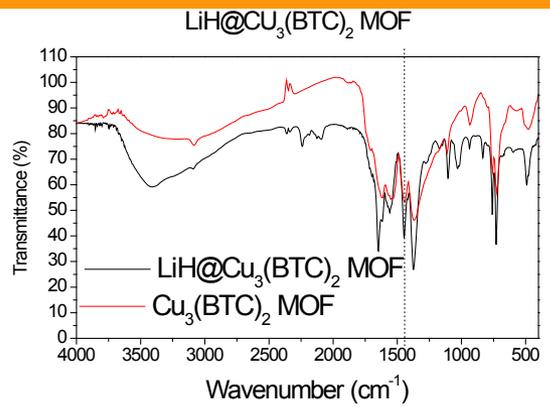
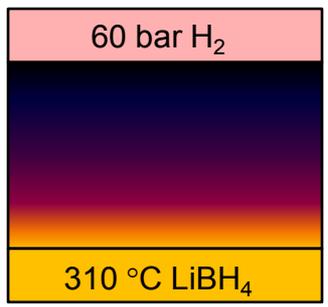
Simple hydrides (LiH, MgH₂)



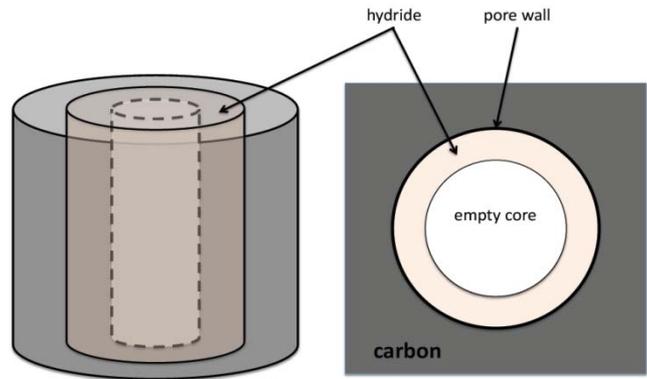
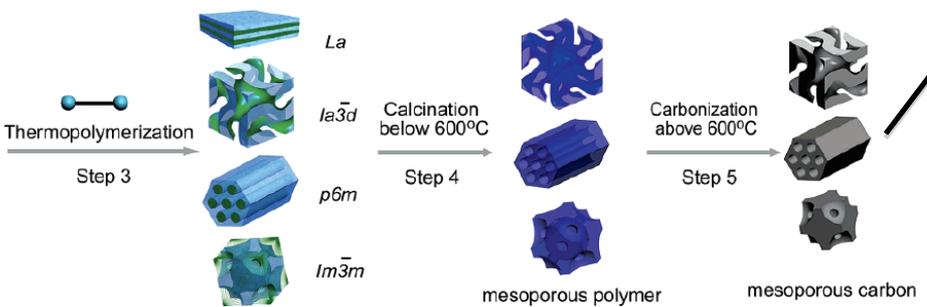
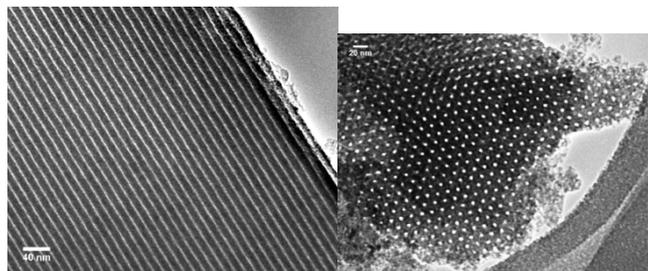
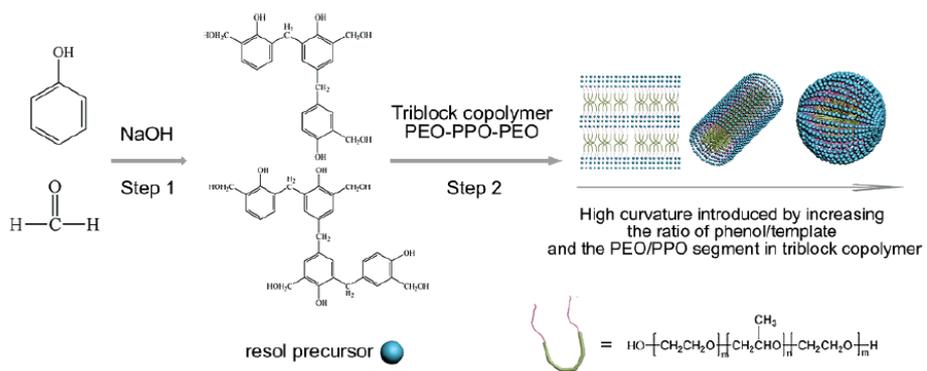
Complex hydrides (LiAlH₄, NaAlH₄)



Melt infiltration/porous C (LiBH₄)



Approach: nanoporous carbon preparation procedure produces high quality cylindrical pore structure

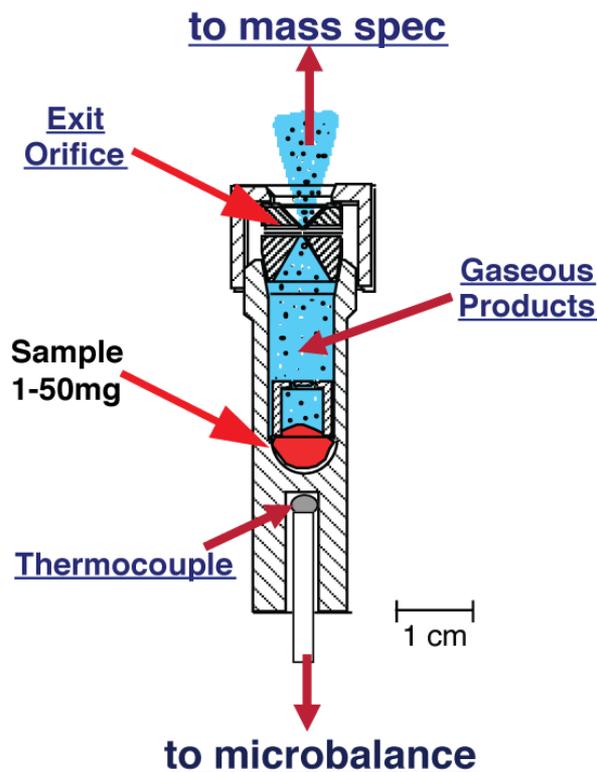


Meng, et al., *Chem. Mater.*, **18**, 4447-4464, (2006)



hexagonal column carbons
 surface area: 600--1200 m²/g
 pore volume: 0.3—0.75 cc/g

Approach: Detect all gas-phase species evolved during hydride decomposition using molecular-beam mass spec



- Knudsen effusion cell + furnace + microbalance
- Modulated molecular beam mass spectrometer
- High accuracy FTMS also available for species identification

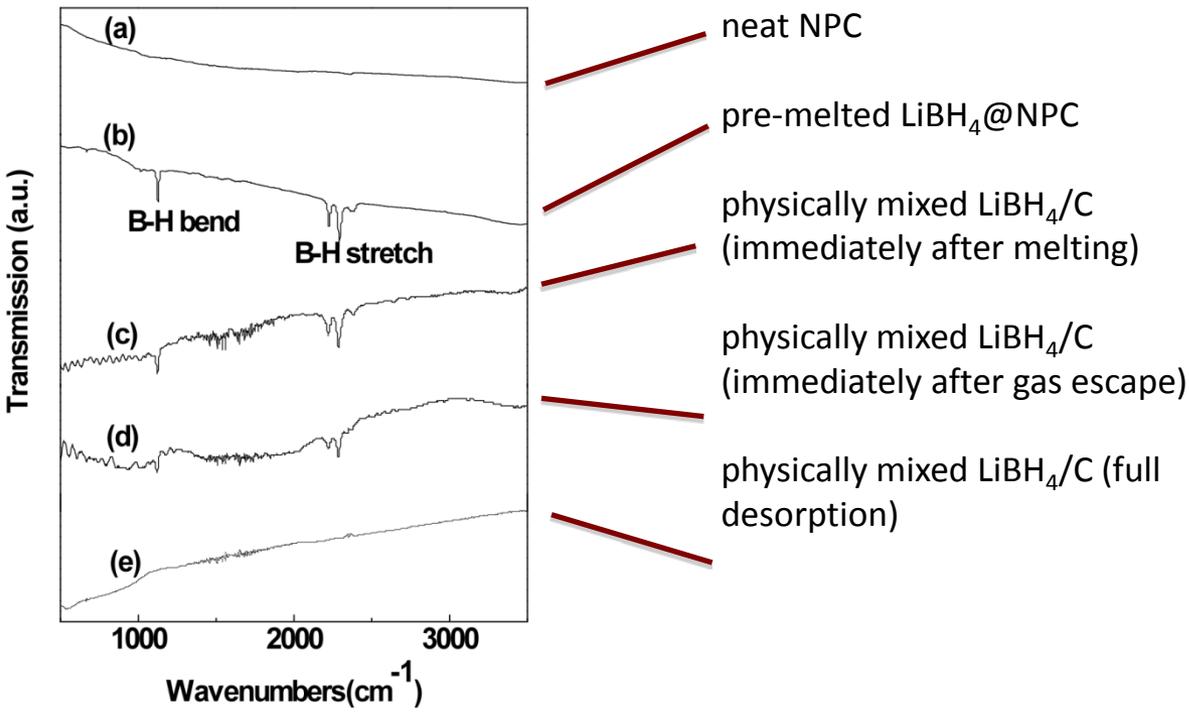
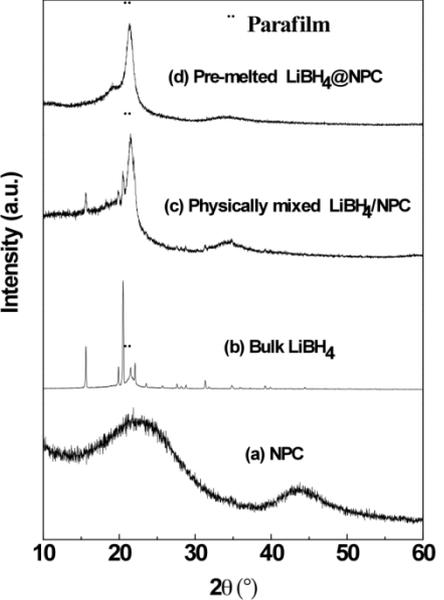
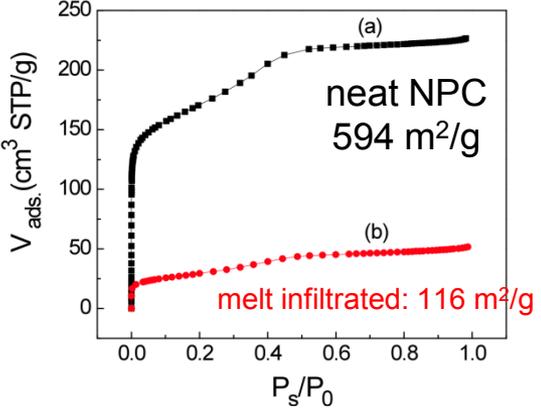
Analysis of solid-state data

- Concepts can be applied to any measure of the extent of reaction (α).
- Large palette of validated integral and differential expressions already exist.

model	differential form $f(\alpha) = 1/k \, d\alpha/dt$	integral form $g(\alpha) = kt$
nucleation models		
power law (P2)	$2\alpha^{1/2}$	$\alpha^{1/2}$
power law (P3)	$3\alpha^{2/3}$	$\alpha^{1/3}$
power law (P4)	$4\alpha^{3/4}$	$\alpha^{1/4}$
Avrami-Erofeyev (A2)	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
Avrami-Erofeyev (A3)	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
Avrami-Erofeyev (A4)	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
Prout-Tompkins (B1)	$\alpha(1-\alpha)$	$\ln[\alpha/(1-\alpha)] + c'$
geometrical contraction models		
contracting area (R2)	$2(1-\alpha)^{1/2}$	$1 - (1-\alpha)^{1/2}$
contracting volume (R3)	$3(1-\alpha)^{2/3}$	$1 - (1-\alpha)^{1/3}$
diffusion models		
1-D diffusion (D1)	$1/(2\alpha)$	α^2
2-D diffusion (D2)	$-[1/\ln(1-\alpha)]$	$((1-\alpha)\ln(1-\alpha)) + \alpha$
3-D diffusion-Jander (D3)	$[3(1-\alpha)^{2/3}]/[2(1-(1-\alpha)^{1/3})]$	$(1 - (1-\alpha)^{1/3})^2$
Ginstling-Brounshtein (D4)	$3/[2((1-\alpha)^{-1/3} - 1)]$	$1 - (2/3)\alpha - (1-\alpha)^{2/3}$
reaction-order models		
zero-order (F0/R1)	1	α
first-order (F1)	$(1-\alpha)$	$-\ln(1-\alpha)$
second-order (F2)	$(1-\alpha)^2$	$[1/(1-\alpha)] - 1$
third-order (F3)	$(1-\alpha)^3$	$(1/2)[(1-\alpha)^{-2} - 1]$

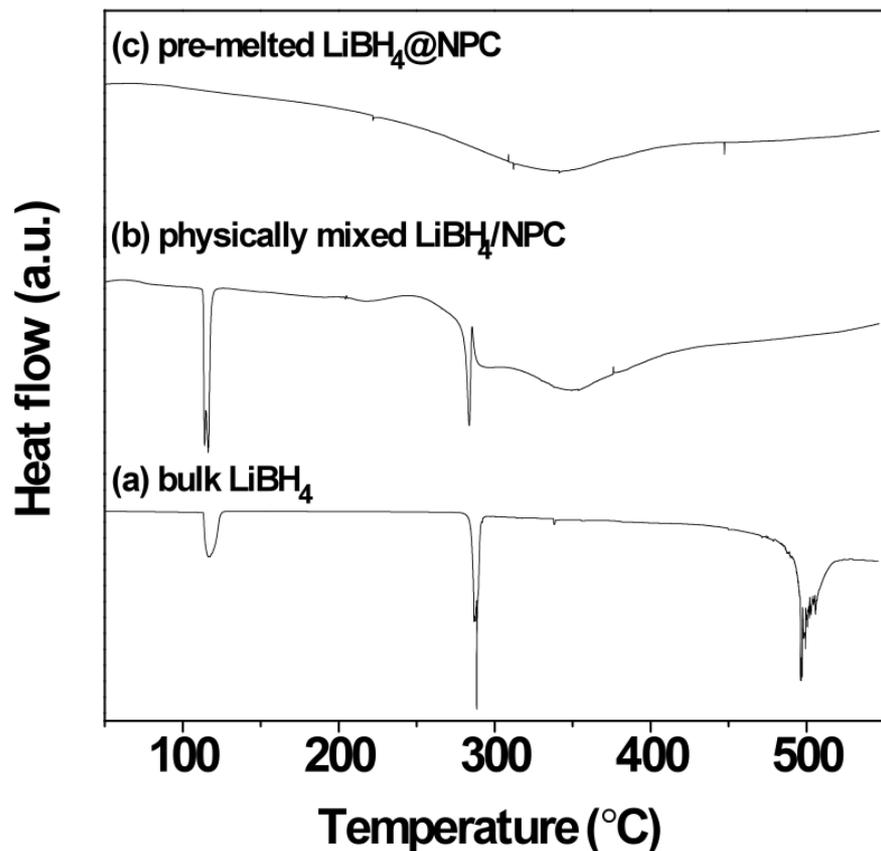
Technical accomplishment: Nano-confined LiBH_4

Characterization indicates successful infiltration of LiBH_4 in cylindrical-pore carbons



- Pore volume decrease post infiltration
- FTIR indicates B-H bands ($[\text{BH}_4]^-$ anions) in infiltrated samples
- LiBH_4 is still present in the infiltrated samples

Differential scanning calorimetry



Bulk LiBH_4 :

- Solid-solid phase transition $\sim 110^\circ\text{C}$
- Solid-melt transition $\sim 280^\circ\text{C}$
- Decomposition above 450°C

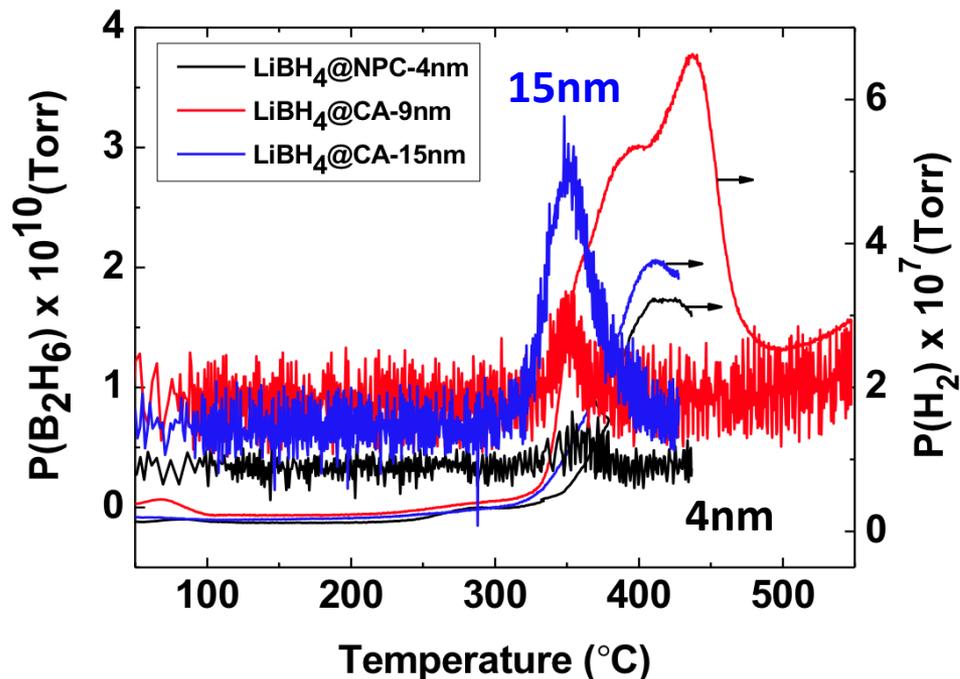
LiBH_4 @carbon:

- No ortho-hex phase transition
- No melting endotherm
- Decomposition starts *before* melting

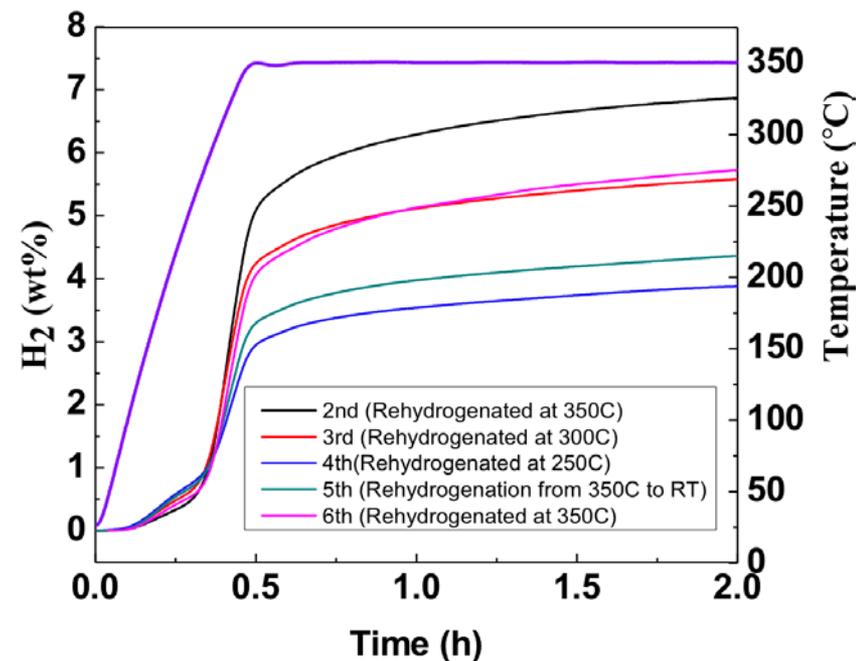
Results indicate *lower onset temperature of decomposition* than previous measurements on LiBH_4 in 4 nm nano-porous silica-templated carbons. (Janot, et al., *J. Pow. Src.*, **189**, 902, 2009)

Technical accomplishment: Nano-confined LiBH_4 in porous carbon (2 nm) (cont.)

Size-dependent thermodynamics: Decomposition pathway can be tuned by adjusting template pore size



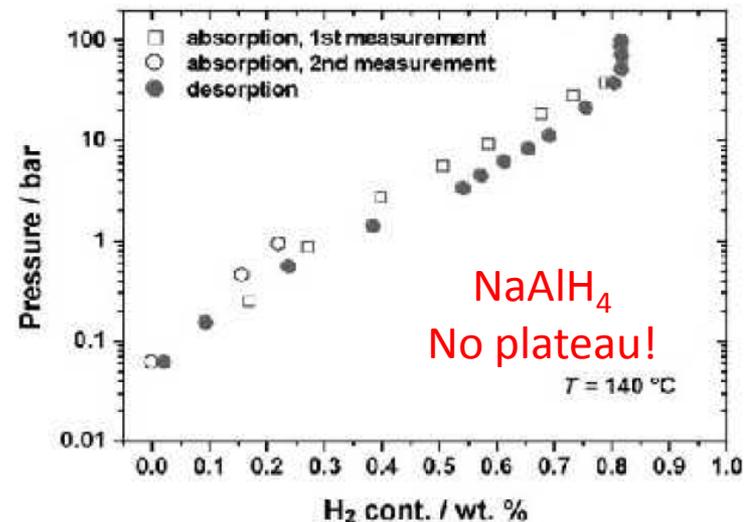
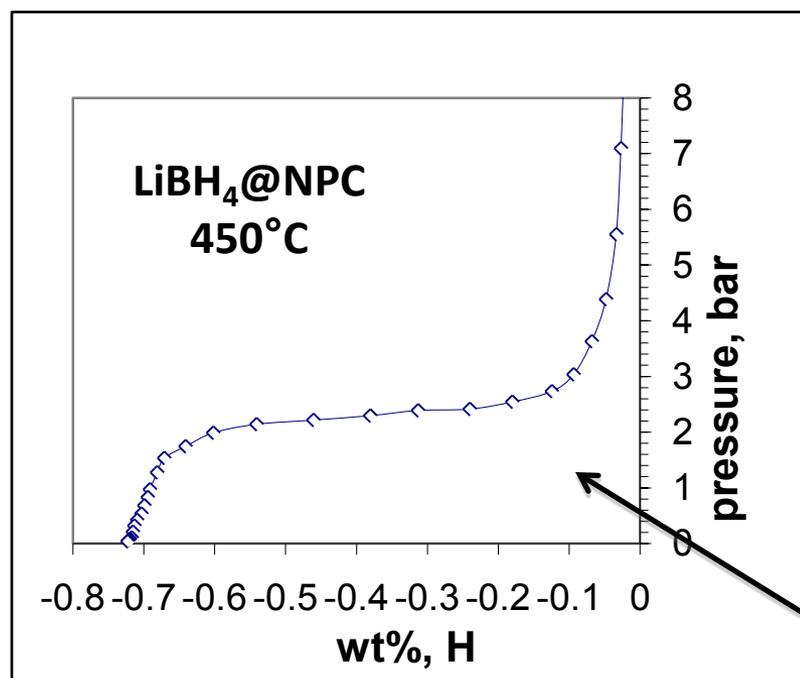
Smaller pore size lowers B_2H_6 release



Demonstrated low temperature reversibility

Technical accomplishment: Nano-confined LiBH_4 in porous carbon (2 nm) (cont.)

Size-dependent thermodynamics: PCT indicates thermodynamics change for nano-confined NaAlH_4 and not LiBH_4

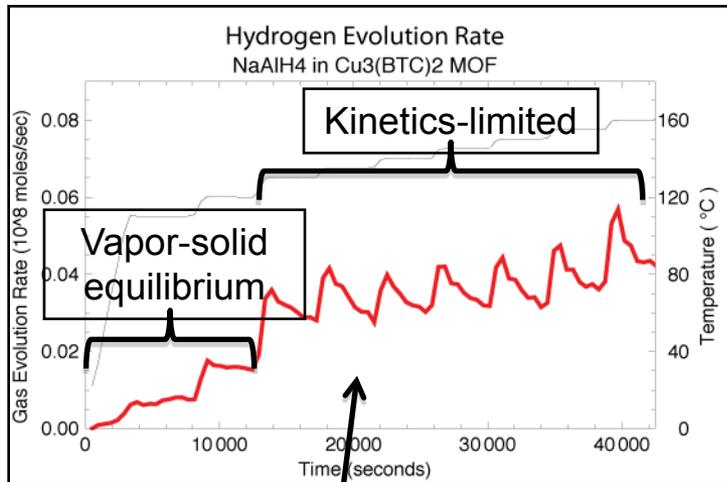


Lohstroh, et al., Chem Phys Chem, **11**, 789, 2010

- 4-nm nanoporous carbon (NPC)
- 20 wt.% LiBH_4
- Flat plateau
- Enthalpy: 75 kJ/mol- H_2

Technical accomplishment: Nano-confined NaAlH_4

H_2 desorption from Cu-BTC MOF (1.3-nm pores)

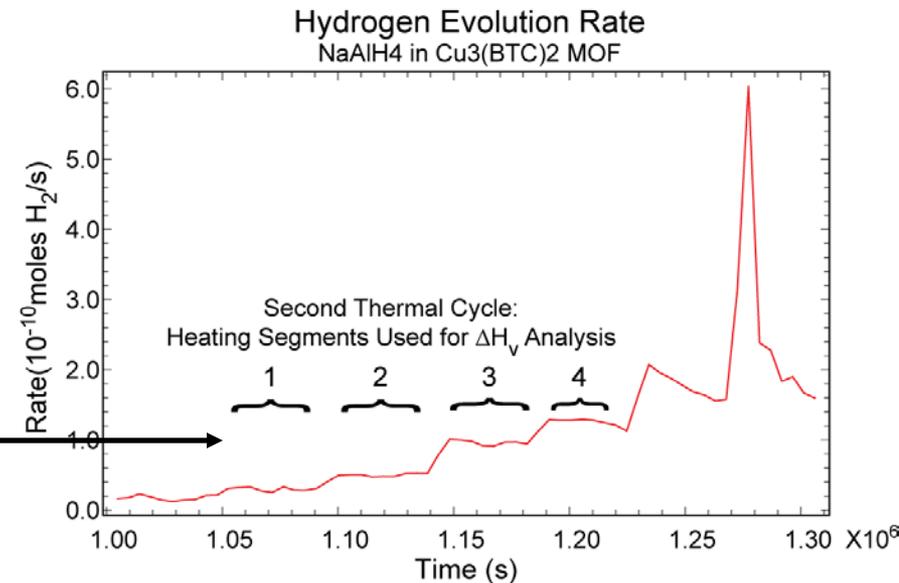
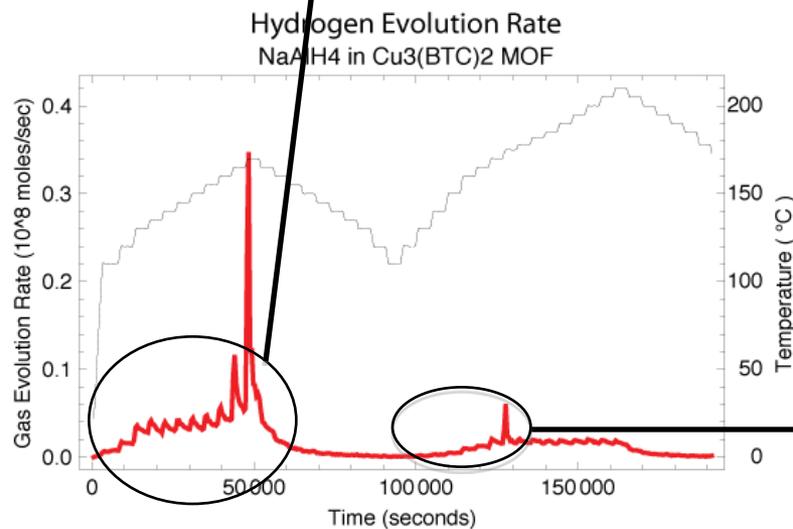


H_2 desorption measurements:

- Varied sample size
- Varied orifice diameter

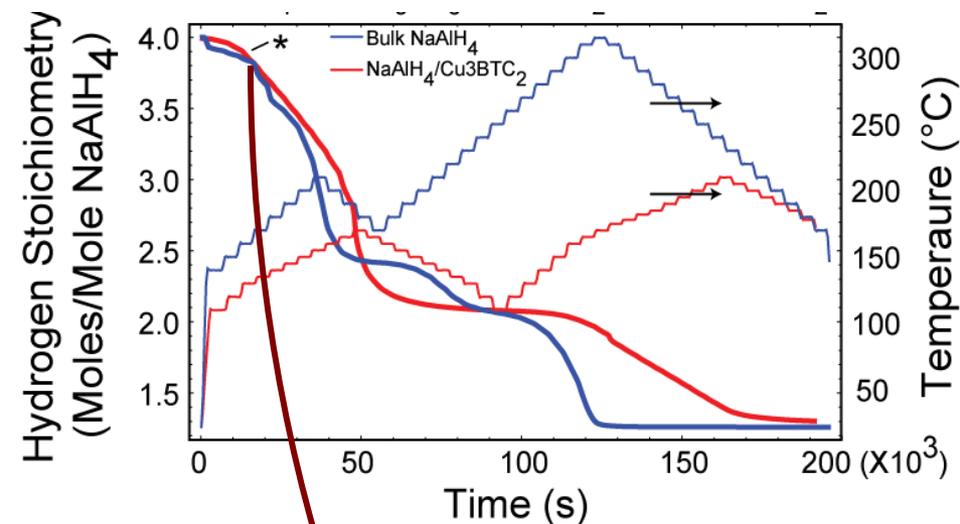
Two desorption regimes:

- $< 110^{\circ}\text{C}$: vapor-solid equilibrium
 - Results independent of sample and orifice size
- $110 - 170^{\circ}\text{C}$: kinetics-limited



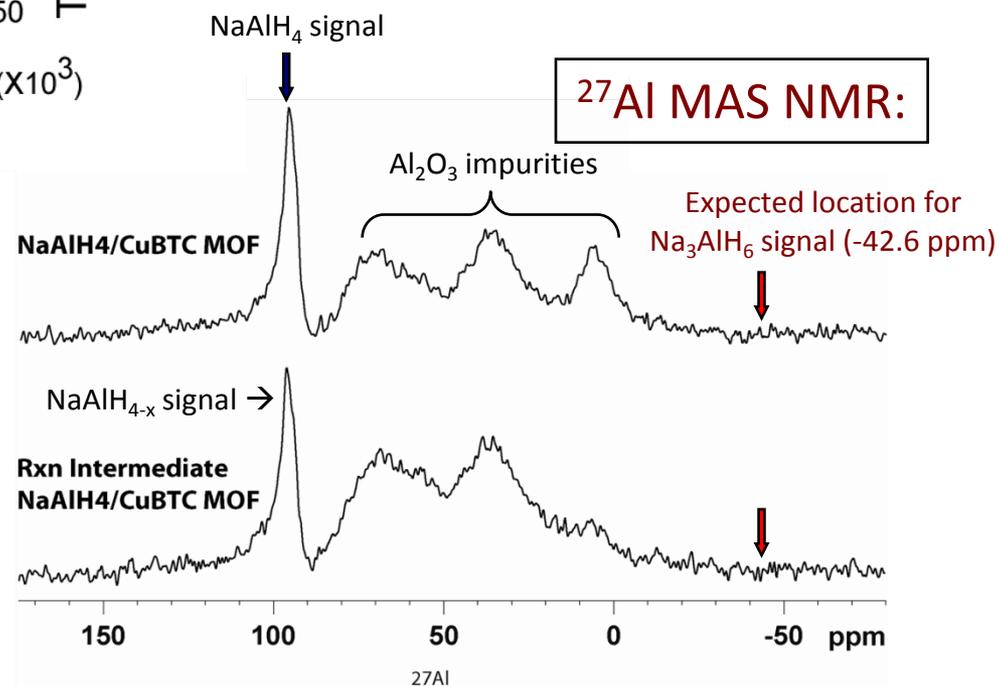
Technical accomplishment: Nano-confined NaAlH_4 (cont.)

Reaction path modification: NMR shows no evidence for Na_3AlH_6



Experiment:

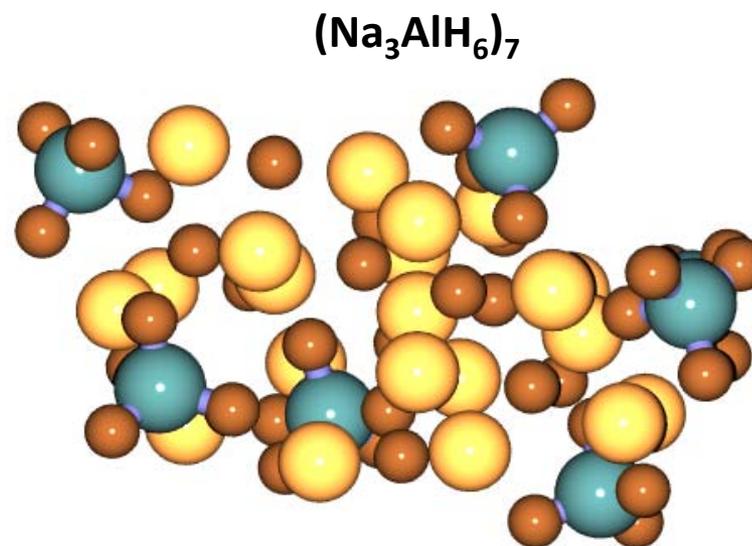
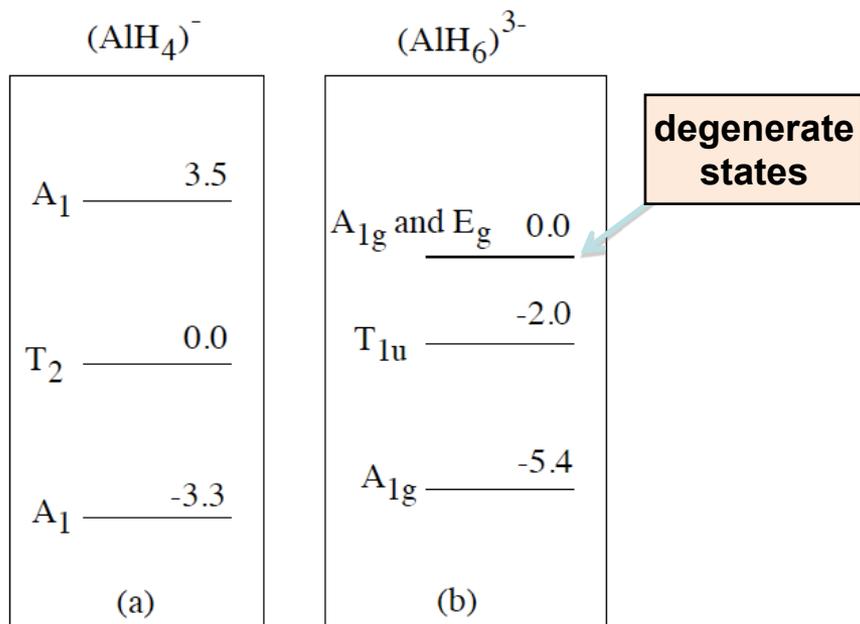
- Heat sample to 150 $^{\circ}\text{C}$ to initiate reaction
- Stop heating; remove sample for NMR



Lack of Na_3AlH_6 NMR signal indicates 1.3 nm NaAlH_4 decomposes in a single-step reaction

Reaction path modification: Theory supports absence of (Na₃AlH₆)_n decomposition intermediates

Degenerate states in (AlH₆)³⁻ anion result in destabilizing Jahn-Teller distortion



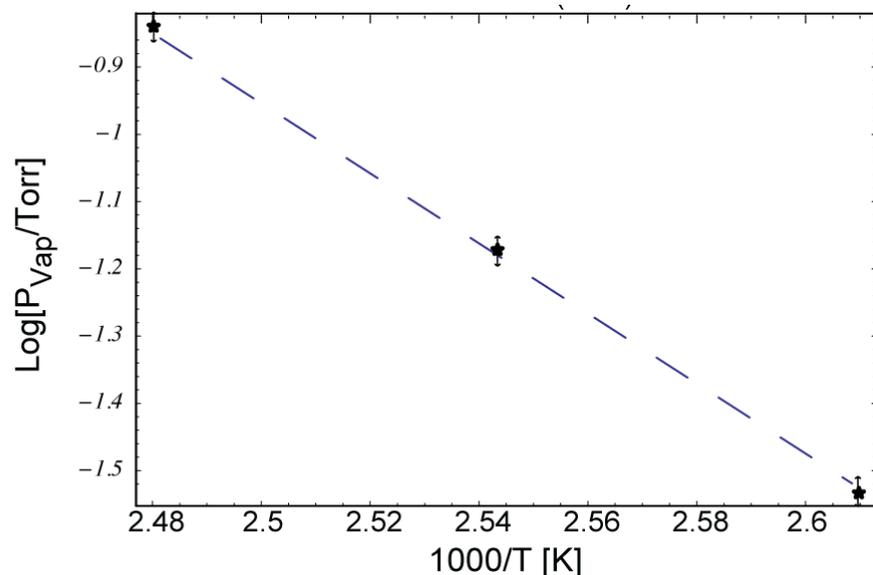
Relaxes to NaH + NaAlH₄

Electronic structure of isolated anions (charge compensated)*

*Ozolins, V.; Udovic, T.; Majzoub, E.H.; J. Al. Comp, (2004) **375**, 1-10

Absence of Na₃AlH₆ decomposition intermediates agrees with NMR and other experimental results

NaAlH_4 @Cu-BTC (1.3 nm pores)
STMBMS data

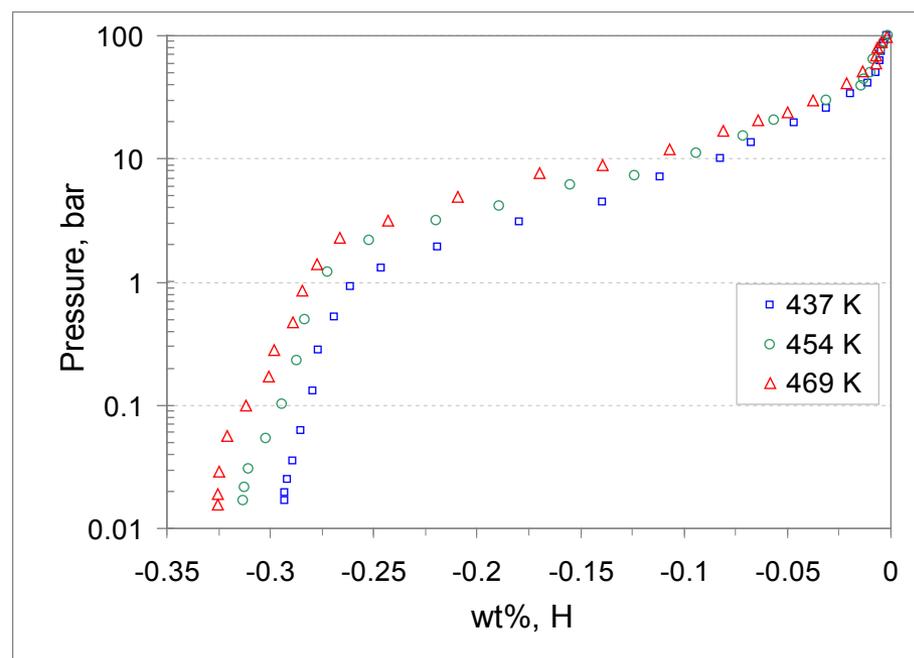


$$\Delta H^{\circ}_{\text{desorp}} = 47.3 \pm 0.12 \text{ kJ/mol-H}_2$$

$$\Delta S^{\circ}_{\text{desorp}} = 110.1 \text{ J/mol-K}$$

(average of 3 experiments)

NaAlH_4 @hex-porous carbon (4 nm pores)
PCT data



In contrast to bulk NaAlH_4 , no plateau regions are observed

$$\Delta H^{\circ}_{\text{desorp}} = 35 \pm 3 \text{ kJ/mol-H}_2$$

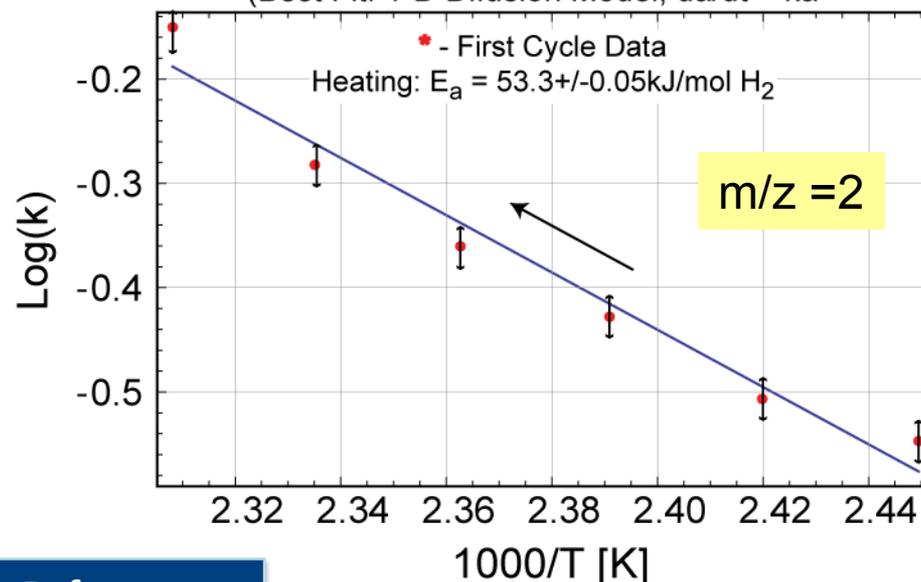
(using center of sloping plateau)

- Mechanism:
Diffusion + solid-state phase change
- 1-D diffusion model fits rate data:
 $da/dt = k(1-a)^{-1}$

Activation Energy Analysis

NaAlH₄ in Cu₃(BTC)₂ MOF

(Best Fit: 1-D Diffusion Model; $da/dt = ka^{-1}$)



Template	E_a (kJ mol ⁻¹)	Reference
CuBTC MOF (1.32 nm)	53	This work
Carbon nanofiber (2 – 10 nm)	58	Baldé et al. JACS 2008
Uncatalyzed bulk	118 – 121	Sandrock et al. 2002

Similar E_a for chemically different templates

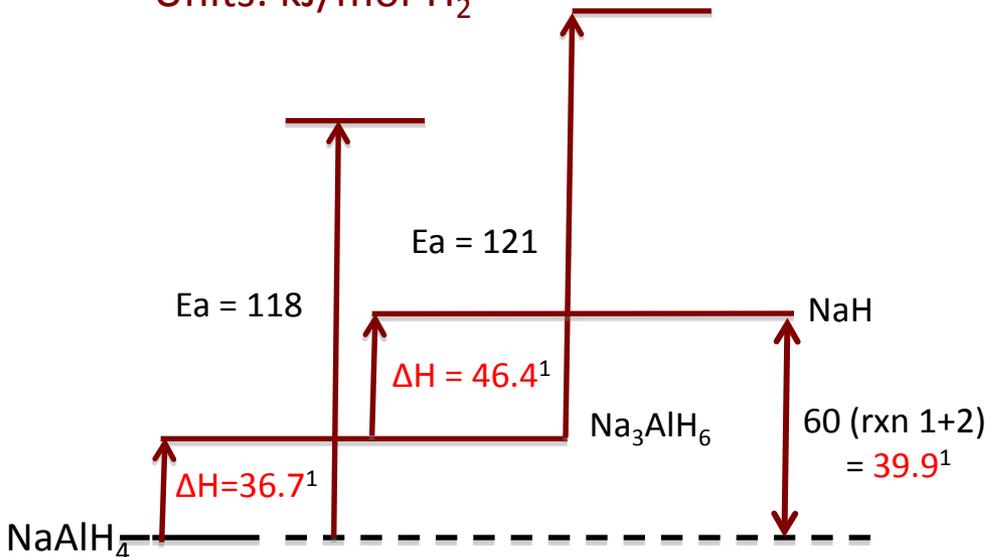
Conclusion: Size has strong effect on desorption kinetics, but local chemical environment must also have an influence

Technical accomplishment: Nano-confined NaAlH₄ (cont.)

Size-dependent thermodynamics: Bulk vs. NaAlH₄@CuBTC (~1.3 nm)

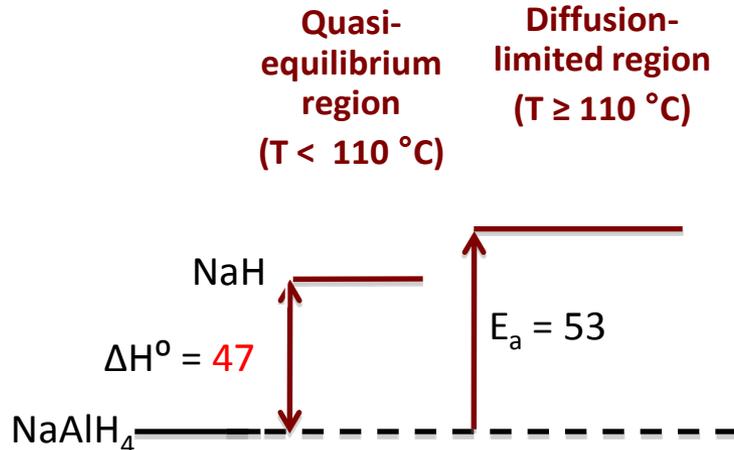
¹Data from Lee et al. (*J. Alloy Comp.* 2006)

NaAlH₄ (bulk)
Units: kJ/mol-H₂



Data from this work

NaAlH₄@Cu-BTC (~1.3 nm)
Units: kJ/mol H₂



Reaction (energies given in kJ/mol-H ₂)	1.3 nm		4 nm		Bulk	
	ΔH°	E _a	ΔH°	E _a	ΔH°	E _a
NaAlH ₄ → NaH + 0.33Al + 1.5H ₂	47	47 - 53	35 ± 10	--	40	121
NaAlH ₄ → 0.33Na ₃ AlH ₆ + 0.67 Al + 1.0H ₂	N/A	N/A	N/A	N/A	37	118

*Value is uncertain due to sloping plateau of PCT curve.

Nanoconfined NaAlH₄ decomposes via a one-step mechanism with a low activation barrier, vs. a 2-step mechanism in bulk: → Implies a 50% increase in accessible capacity at typical fuel cell temps

Grand Canonical Linear Programming (GCLP)* method

Each cluster energy calculated separately
 (NaAlH₄)₁, (NaAlH₄)₂, (NaAlH₄)₃, (NaAlH₄)₄, (NaAlH₄)₅, (NaAlH₄)₆, ...
 (NaH)₁, (NaH)₂, (NaH)₃, (NaH)₄, (NaH)₅, (NaH)₆, (NaH)₇, (NaH)₈, ...
 Al₁, Al₂, Al₃, Al₄, Al₅, Al₆, Al₇, Al₈, Na₁, Na₂, Na₃, Na₄, Na₅, Na₆, Na₇, Na₈, ...
 (NaAl)₁, (NaAl)₂, (NaAl)₃, (NaAl)₄, (NaAl)₅, (NaAl)₆, (NaAl)₇, (NaAl)₈, ...
 (AlH₃)₁, (AlH₃)₂, (AlH₃)₃, (AlH₃)₄, (AlH₃)₅, (AlH₃)₆, (AlH₃)₇, (AlH₃)₈, ...
 (Na₃AlH₆)₁, (Na₃AlH₆)₂, (Na₃AlH₆)₃, (Na₃AlH₆)₄, (Na₃AlH₆)₅, ...

Al	AlH ₃	Na	NaH	NaAlH ₄	AlNa

Ionic Cluster Geometries from PEGS method
 Majzoub, et al., PRB **77** 104115 (2008)

Minimize the Gibbs Free Energy:

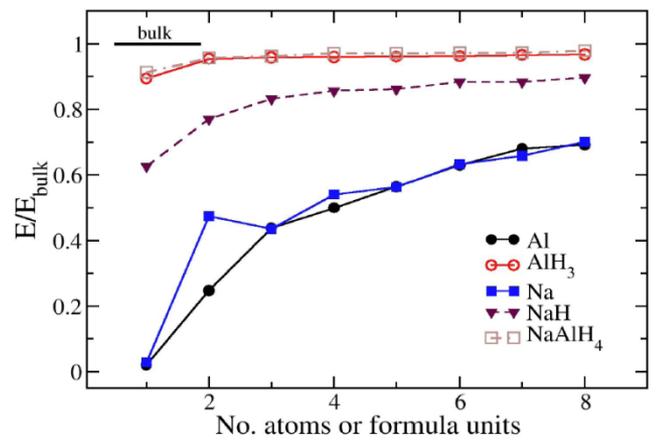
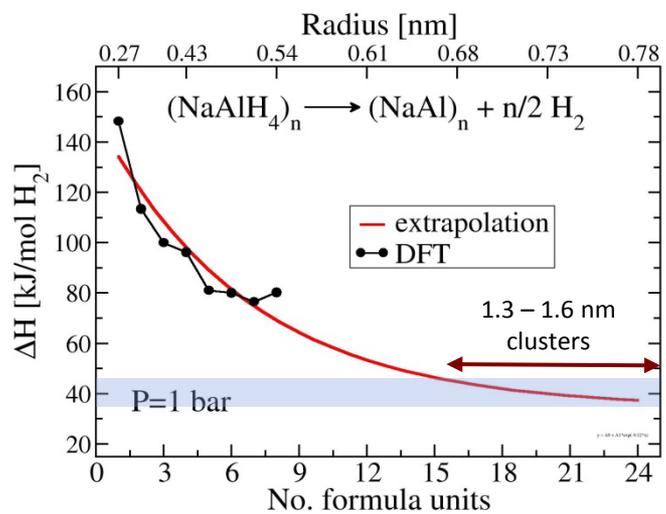
$$G(T, p) = \sum_i x_i F_i(T) - \frac{\mu_{H_2}(T, p)}{2} \sum_i x_i n_i^H$$

Determine the clusters present as a function of composition, temperature, and pressure

*A. Akbarzadeh, V. Ozolinš, C. Wolverton, Adv. Mater. 2007, 19, 3233–3239

Technical accomplishment: Nano-confined NaAlH₄ (cont.)

Size-dependent thermodynamics: tuning NaAlH₄ cluster stability



Ionic clusters rapidly approach their bulk cohesive energy, while small metal clusters do not

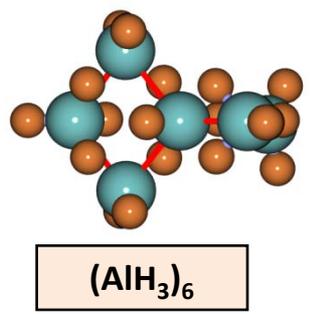
Temperature needed for equilibrium $p(\text{H}_2) = 0.01 \text{ bar}$

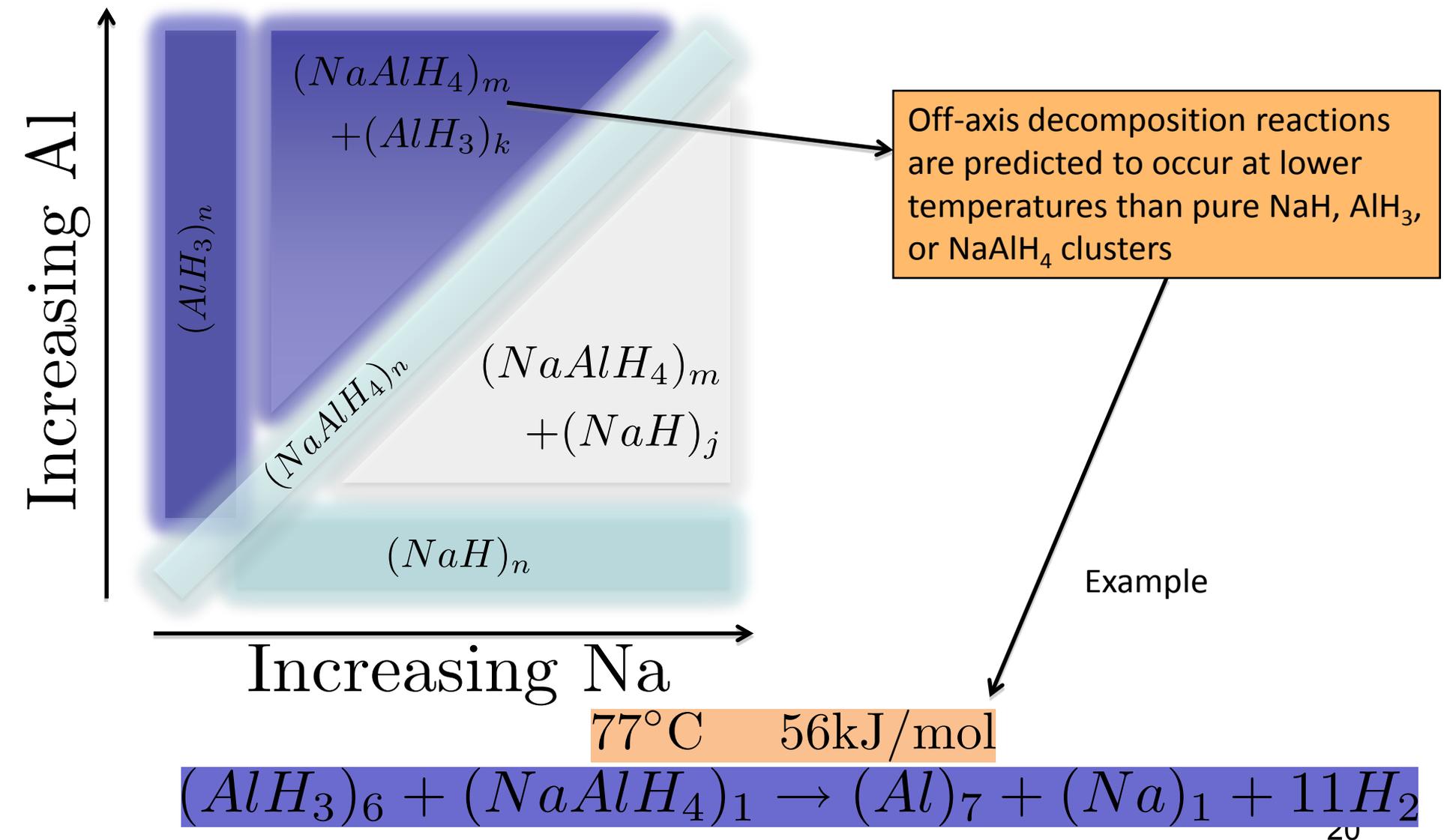
T [°C]	ΔH [kJ/mol H ₂]	reaction
589	161	$(\text{AlH}_3)_1 \rightarrow (\text{Al})_1 + 1.5\text{H}_2$
601	149	$(\text{AlH}_3)_2 \rightarrow (\text{Al})_2 + 3.0\text{H}_2$
388	105	$(\text{AlH}_3)_3 \rightarrow (\text{Al})_3 + 4.5\text{H}_2$
294	92	$(\text{AlH}_3)_4 \rightarrow (\text{Al})_4 + 6.0\text{H}_2$
199	77	$(\text{AlH}_3)_5 \rightarrow (\text{Al})_5 + 7.5\text{H}_2$
114	61	$(\text{AlH}_3)_6 \rightarrow (\text{Al})_6 + 9.0\text{H}_2$
50	52	$(\text{AlH}_3)_7 \rightarrow (\text{Al})_7 + 10.5\text{H}_2$
43	51	$(\text{AlH}_3)_8 \rightarrow (\text{Al})_8 + 12.0\text{H}_2$

Contrast: bulk $\alpha\text{-AlH}_3$ is unstable at STP
 $\sim +7 \text{ kJ/mol H}_2$ for $\text{AlH}_3 \rightarrow \text{Al} + 3/2 \text{H}_2$

T [°C]	ΔH [kJ/mol H ₂]	reaction
151	71	$(\text{NaH})_3 \rightarrow (\text{Na})_3 + 1.5\text{H}_2$
97	68	$(\text{NaH})_4 \rightarrow (\text{Na})_4 + 2.0\text{H}_2$
103	69	$(\text{NaH})_5 \rightarrow (\text{Na})_5 + 2.5\text{H}_2$
117	73	$(\text{NaH})_6 \rightarrow (\text{Na})_6 + 3.0\text{H}_2$
95	66	$(\text{NaH})_7 \rightarrow (\text{Na})_7 + 3.5\text{H}_2$
100	69	$(\text{NaH})_8 \rightarrow (\text{Na})_8 + 4.0\text{H}_2$

$(\text{NaH})_n$ destabilized only < 3 formula units, but $(\text{NaAlH}_4)_n$ and $(\text{AlH}_3)_n$ stability increases as n increases

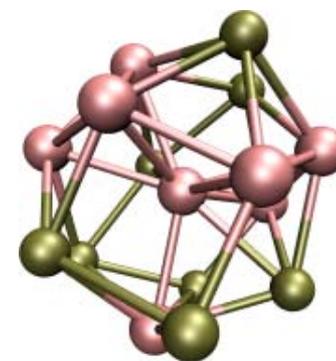
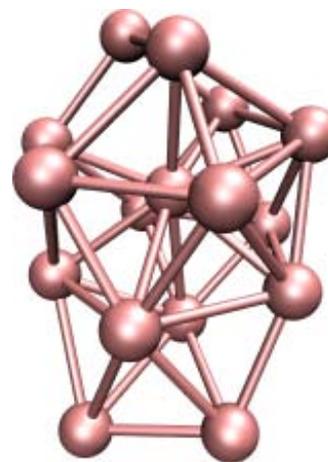
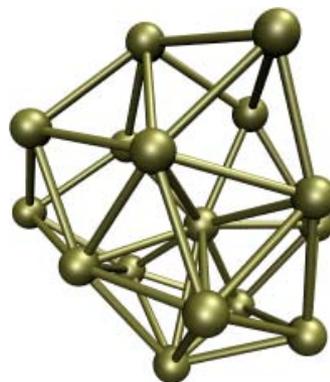
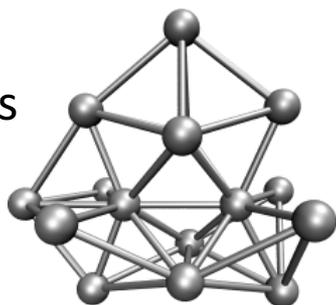




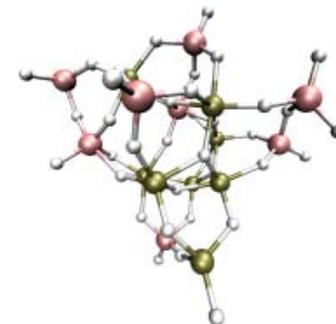
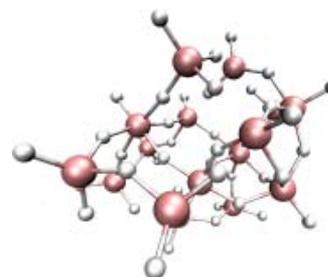
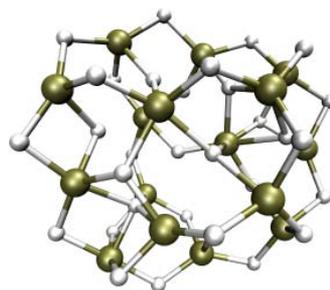
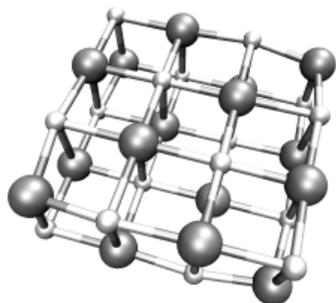
Technical accomplishment: Compositional tuning of thermodynamics

Quantum Monte Carlo predictions of cluster stability

Metallic clusters



Metal-hydride clusters



Li_{16}

Mg_{16}

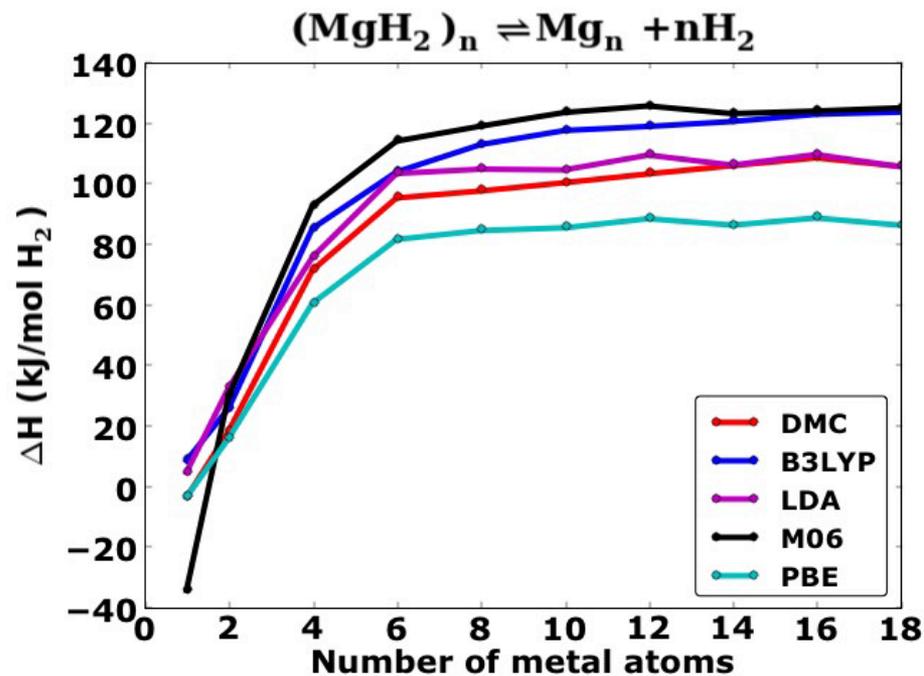
Al_{16}

$(\text{MgAl})_{16}$

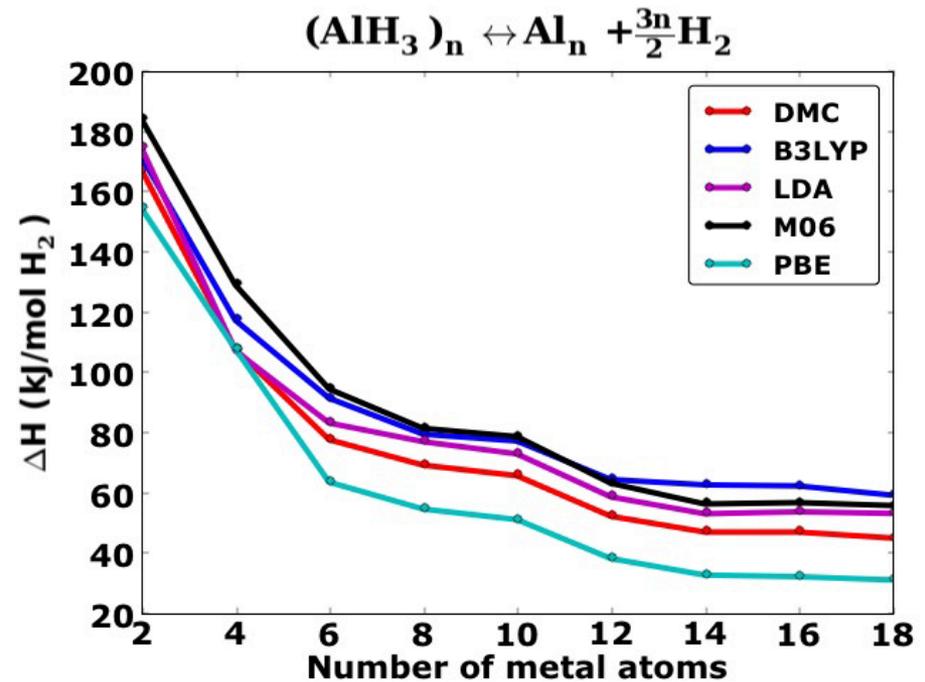
The arrangement of atoms in these clusters is very different from bulk

Technical accomplishment: Compositional tuning of thermodynamics (cont.)

Quantum Monte Carlo predictions of Mg-Al-H nanocluster stability



$(\text{MgH}_2)_n$ clusters are destabilized only at very small sizes



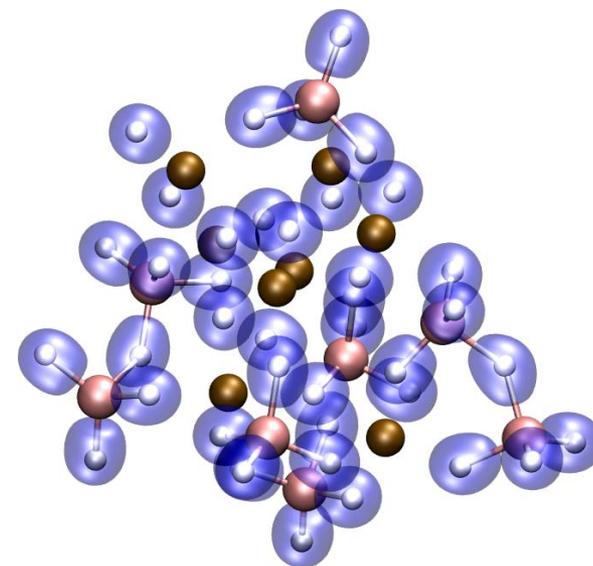
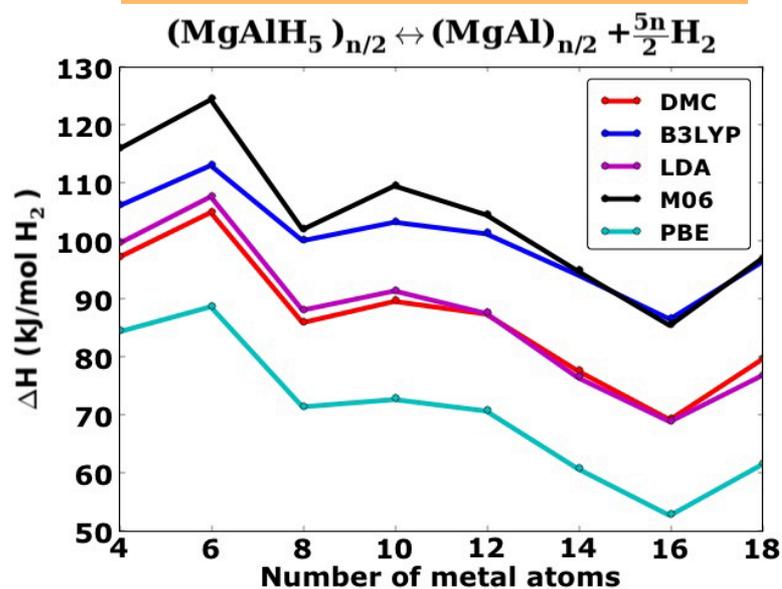
$(\text{AlH}_3)_n$ clusters are stabilized at small sizes

Technical accomplishment: Compositional tuning of thermodynamics (cont.)

Mg-Al-H nanoclusters are destabilized relative to MgH_2

$(\text{AlMgH}_5)_8$ clusters are very ionic;
note highly localized charges

Comparison of DFT functionals
with highly accurate Diffusion
Monte Carlo calculations



	ΔH (kJ/mol)
$(\text{MgH}_2)_8$	~ 100
$(\text{AlH}_3)_8$	~ 40
$(\text{AlMgH}_5)_8$	~ 70

These results support the hypothesis that MgH_2 thermodynamics can be tuned into the appropriate range for hydrogen storage by creating mixed Mg-Al nanoclusters

Future Plans

Remainder of project

- **Nanoparticle synthesis**

- Develop synthetic method to make M-Al hydride combinations
- Complete infiltration of carbon templates with complex hydrides
- Complete investigation of size effects (2 – 15 nm)

- **Dehydrogenation thermodynamics and kinetics**

- Complete measurements of NaAlH_4 , MgH_2 , LiBH_4 , LiNH_2 , and $\text{Ca}(\text{BH}_4)_2$ nanoparticle desorption kinetics in MOFs and nanoporous carbons
- Complete measurements of $\text{Li}_4\text{BN}_3\text{H}_{10}$ desorption; quantify NH_3 and B_2H_6 formation

- **Theory**

- Complete investigation of thermodynamics in mixed-metal Mg-Al-H clusters

- **Publications (currently underway)**

- Theoretical predictions of Li-Mg-Al-H nanocluster thermodynamics
- Thermodynamics and kinetics of $\text{NaAlH}_4@MOF$
- Thermodynamics of $\text{LiBH}_4@HPC$ and $\text{NaAlH}_4@HPC$
- Use of MOFs as templates for metal hydrides



Project Team:

- **Prof. Jeffery Grossman, MIT Mater. Sci. Eng.** (subcontract to Sandia). Lead investigator, non-ionic hydrides and code validation (project funds 1 postdoc)
- **Prof. Eric Majzoub, Univ. of Missouri St. Louis Dept. of Physics** (subcontract to Sandia). Lead investigator, BCP templates, and complex hydride modeling (project funds 1 postdoc) (2 grad students other funds)
- **Dr. Terry Udovic, NIST** (funding from DOE to NIST). Lead investigator, neutron analytical probes.

• Other collaborations:

- **Prof. Ian Robertson, Univ. Illinois U-C (UIUC).** TEM tomographic imaging of infiltrated templates



- **Prof. Roland Fischer, Ruhr Univ. Bochum (Germany).** Leading group worldwide developing MOF infiltration methods. Visited Sandia March 2009; visits by Sandia staff in 2009 and 2010



Summary of Key Results

Relevance: Many attractive hydrides are too stable for practical use; nanoconfinement could mitigate this problem

Approach: Use highly ordered nanoporous materials such as MOFs and BCP to systematically probe the origins of nanohydride destabilization

Technical accomplishments and progress:

- Demonstrated strong size-dependent effects on metal hydride reaction pathway and kinetics as a result of nanoconfinement
- Showed 1 – 4 nm NaAlH_4 nanoclusters decompose in one step with very low activation energy, effectively increasing the storage capacity of this hydride by 50% under fuel-cell conditions
- Predicted MgH_2 hydrogen desorption thermodynamics can be shifted to a more favorable thermodynamic regime by creating Mg-Al-H nanoclusters

Collaborations: Interdisciplinary team effectively integrates experiment and theory



Proposed future research:

- 1) modulate thermodynamics of simple hydrides through compositional tuning
- 2) separate effects of size and pore chemical environment to determine 26 relative magnitudes