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

Overview

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 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

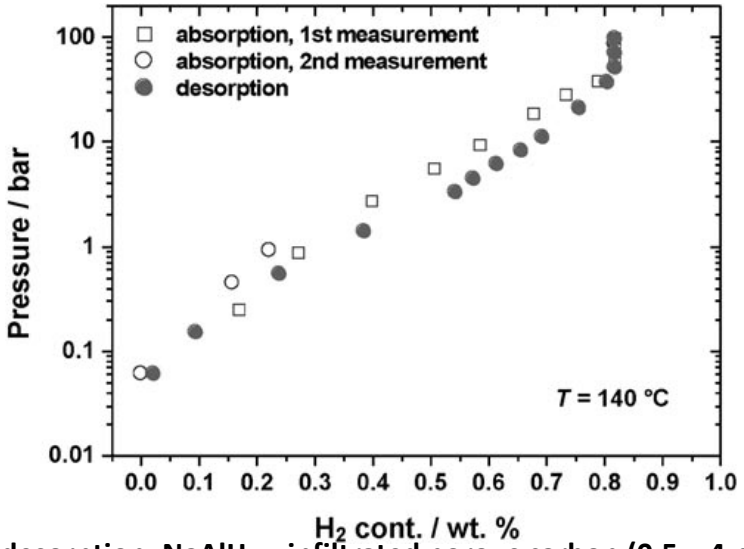
- √ $NaAlH_4$ in MOF templates
- √ $LiBH_4$ in HCP templates
- • MgH_2, $LiNH_2$, $Li_4BN_3H_{10}$, and $Ca(BH_4)_2$

√ Demonstrate compositional tuning effect by:

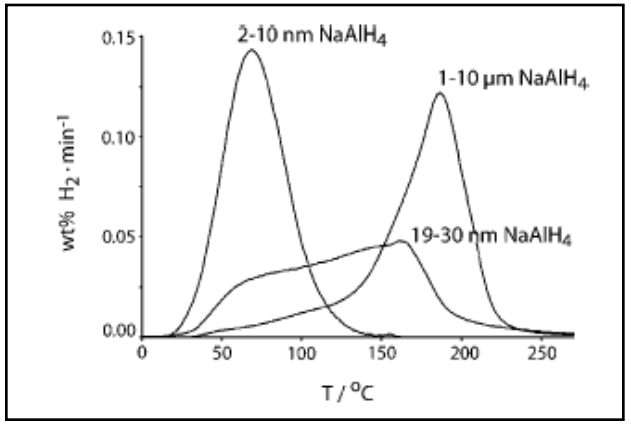
- √ Predict Mg-Al-H phase diagram
- • Infiltrate templates and measure H_2 desorption

• Complete and submit journal articles

- • 2 published; 2 submitted



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

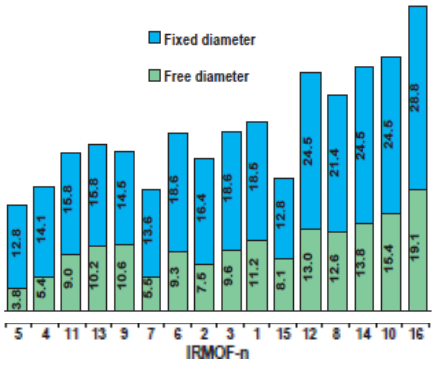


H_2 desorption from $NaAlH_4$ – infiltrated carbon nanofibers
Wagemans et al. *JACS* 2008

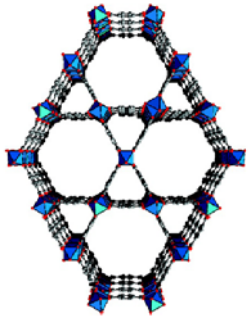
Approach: Use novel *ordered* frameworks to create a suite of templates to *systematically probe* nanoscale effects

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

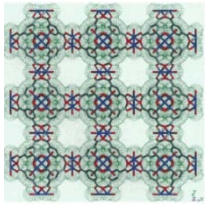
IRMOF entrance (green) and interior (blue) pore diameters



MIL-68



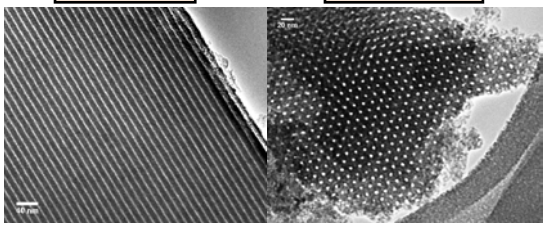
HKUST-1



BCP and crosslinked phenolic resins

edge-on

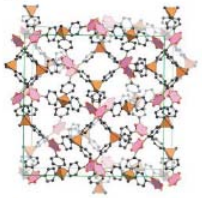
top down



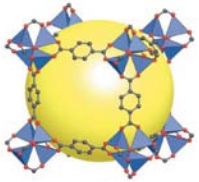
Meng, et al., *Chem. Mater.*, ***18,*** 4447-4464, (2006)

20 Å – 200 Å

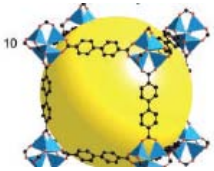
COF-102



IRMOF-1



IRMOF-10



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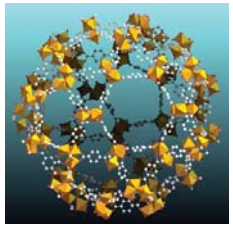
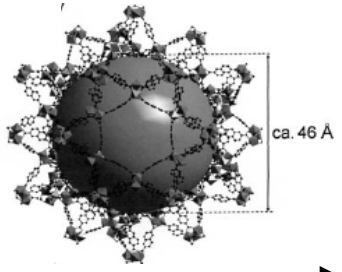


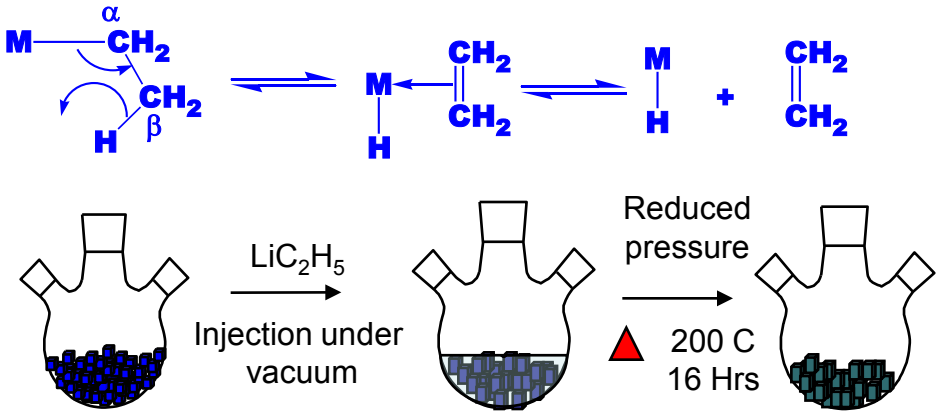
Cr-NDC- MIL-101



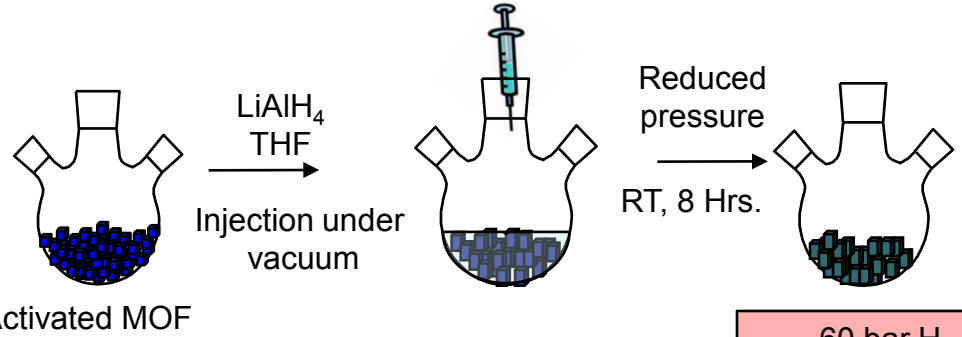
10 Å 20 Å 30 Å 40 Å 50 Å

Approach: Hydride infiltration methods for MOFs

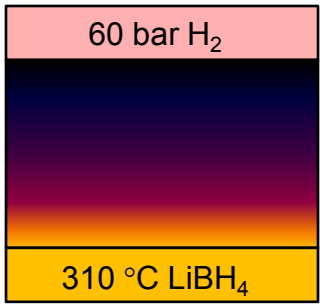
Simple hydrides (LiH, MgH_2)

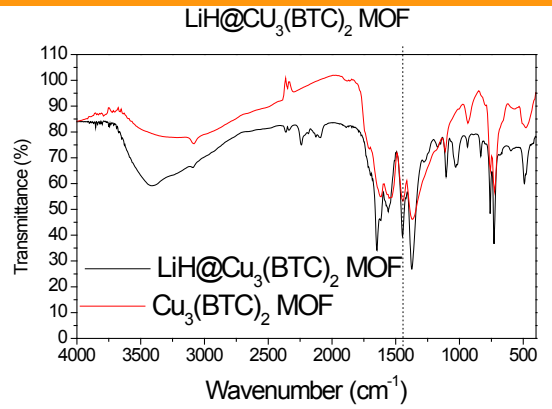


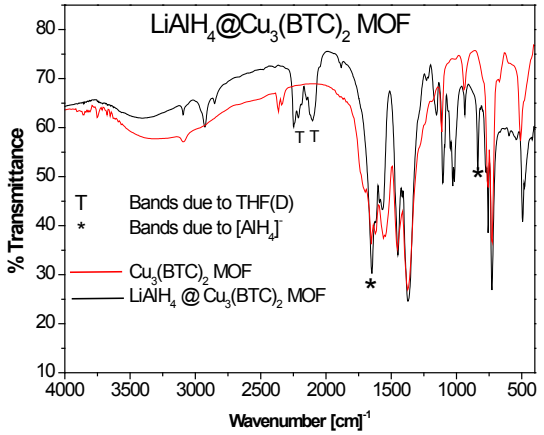
Complex hydrides ($LiAlH_4$, $NaAlH_4$)

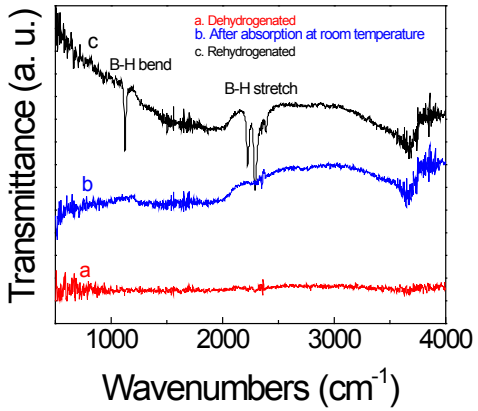


Melt infiltration/porous C ($LiBH_4$)

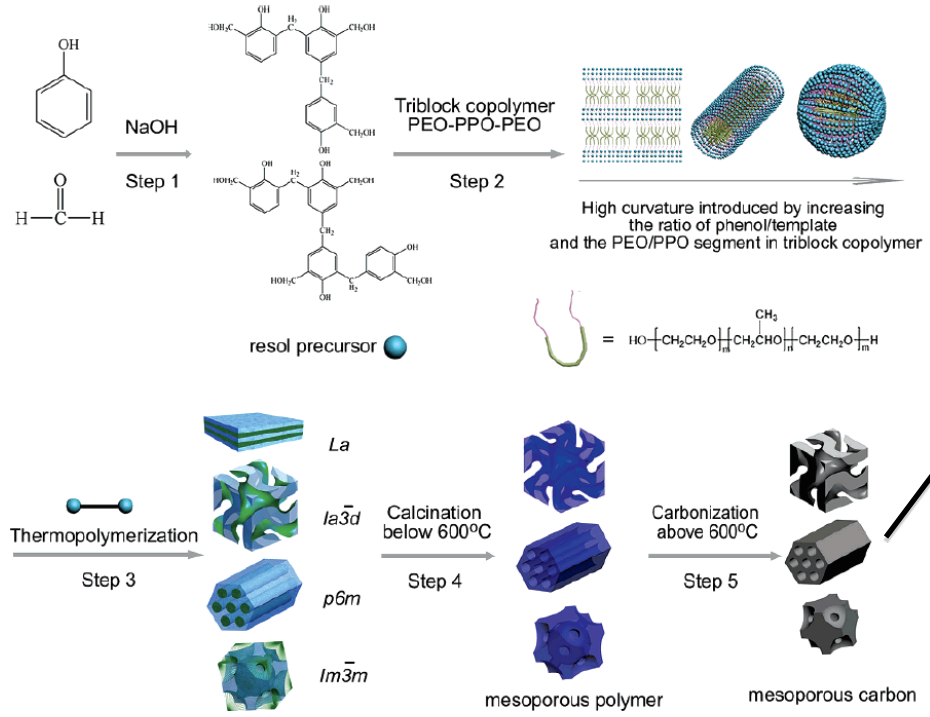


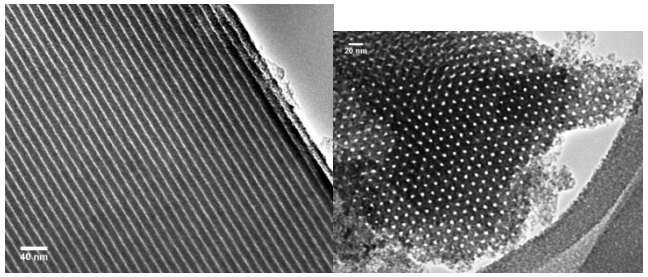


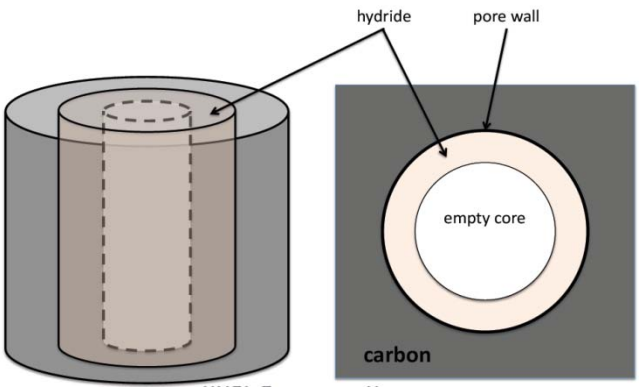




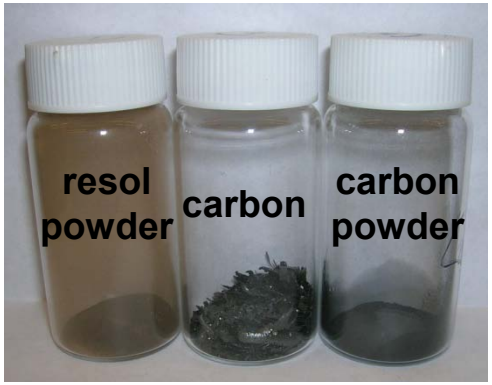
Approach: nanoporous carbon preparation procedure produces high quality cylindrical pore structure





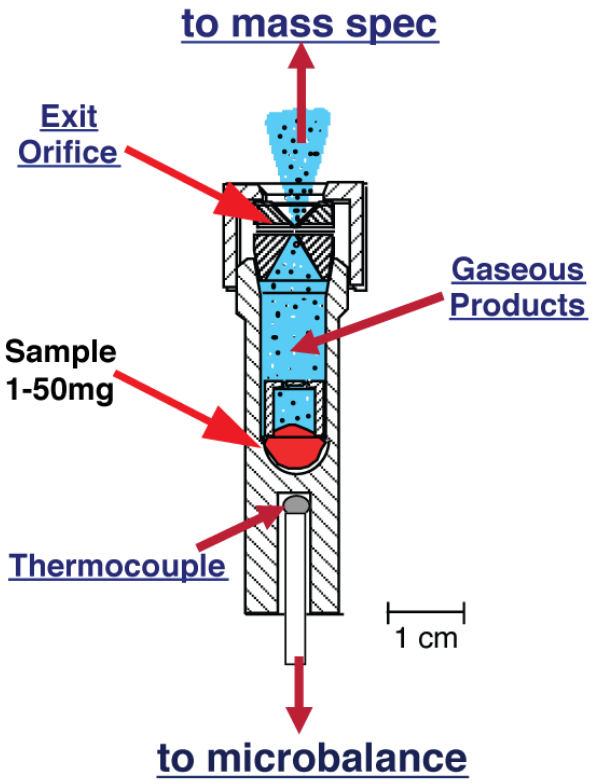


Meng, et al., *Chem. Mater.*, ***18,*** 4447-4464, (2006)



hexagonal column carbons
surface area: 600--1200 m^2/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

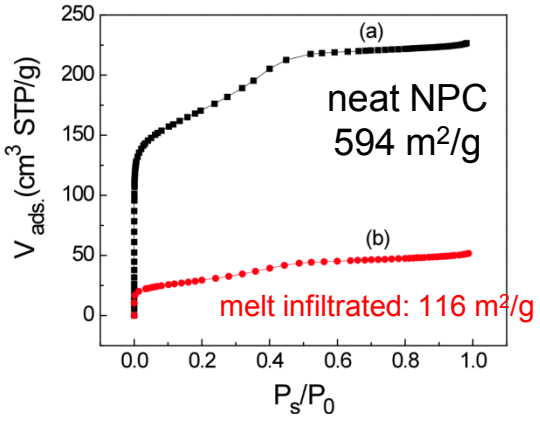
- Concepts can be applied to any measure of the extent of reaction (α).
- Large palette of validated integral and differential expressions already exist.

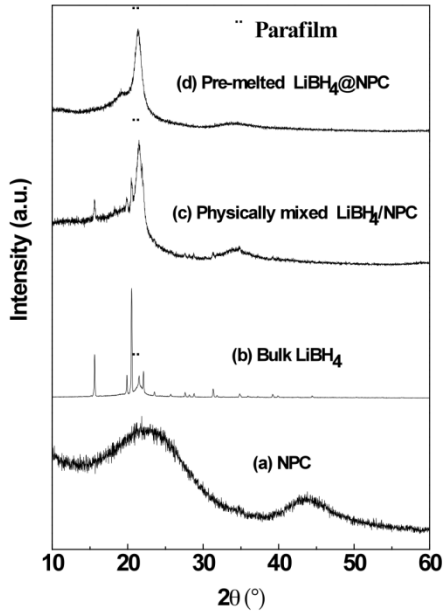
model	differential form $f(\alpha) = 1/k\ d\alpha/dt$	integral form $g(\alpha) = kt$
nucleation models		
power law (P2)	$2\alpha^{1/2}$	$\alpha^{1/2}$
power law (P3)	$3\alpha^{2/3}$	$\alpha^{1/3}$
power law (P4)	$4\alpha^{3/4}$	$\alpha^{1/4}$
Avrami–Erofeyev (A2)	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
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)	$\alpha(1-\alpha)$	$\ln[\alpha/(1-\alpha)] + c^a$
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)	$(1-\alpha)^3$	$(1/2)[(1-\alpha)^{-2}-1]$

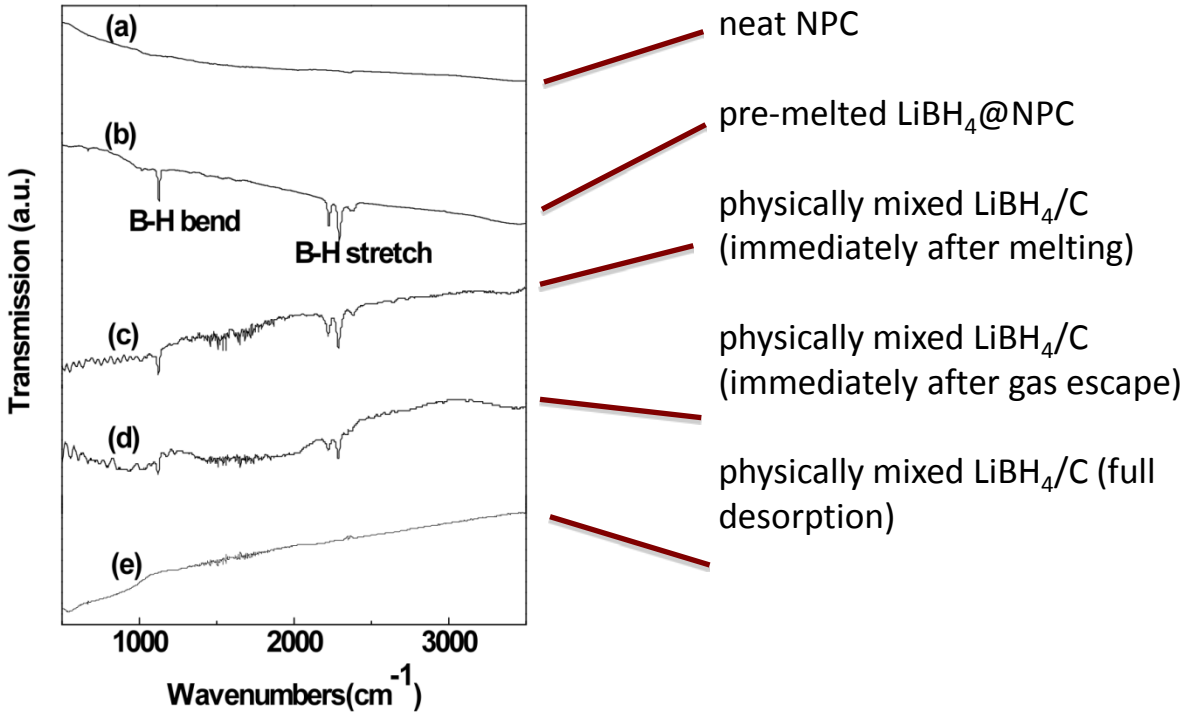
Khawam and Flanagan, *J. Phys. Chem. B*, **110**, 17315 (2006)

Technical accomplishment: Nano-confined $LiBH_4$

Characterization indicates successful infiltration of $LiBH_4$ in cylindrical-pore carbons





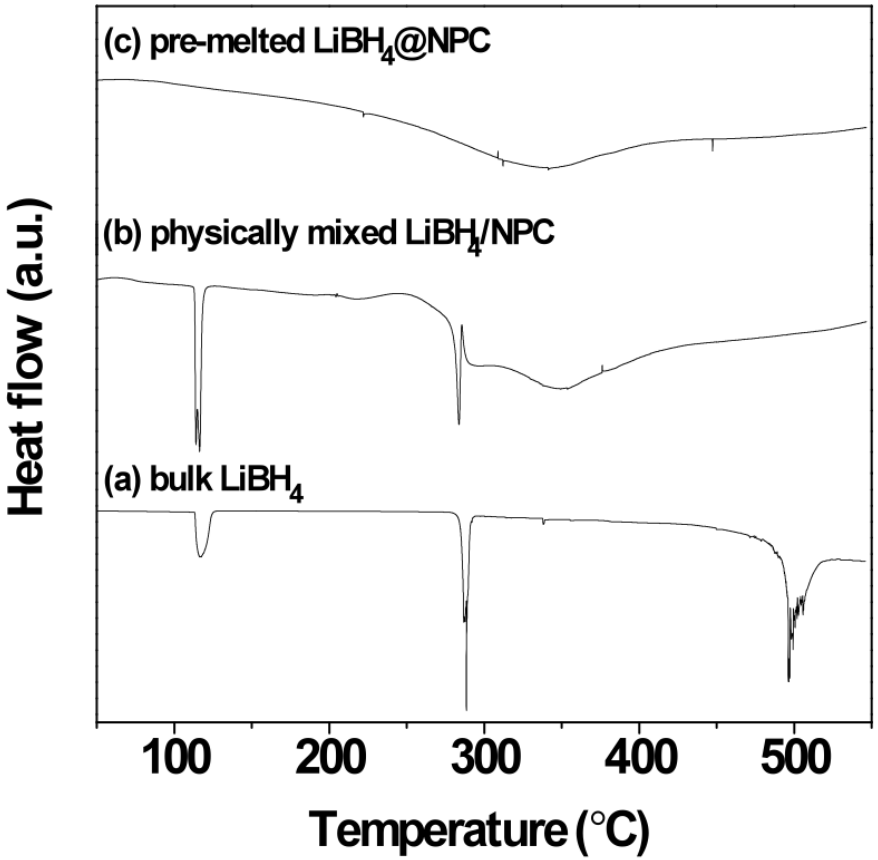


- Pore volume decrease post infiltration
- FTIR indicates B-H bands ($[BH_4]^-$ anions) in infiltrated samples
- $LiBH_4$ is still present in the infiltrated samples

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

Size-dependent thermodynamics: infiltrated $LiBH_4$ in porous carbon is non-crystalline

Differential scanning calorimetry



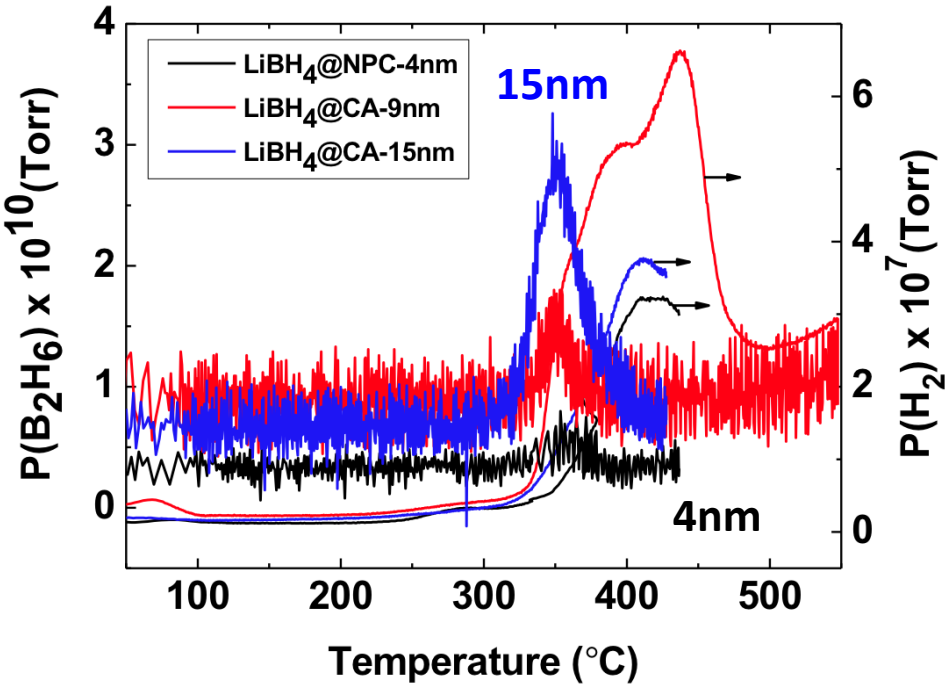
Bulk $LiBH_4$:
- Solid-solid phase transition ~110°C
- Solid-melt transition ~280°C
- Decomposition above 450°C

$LiBH_4$@carbon:
- No ortho-hex phase transition
- No melting endotherm
- Decomposition starts ***before*** melting

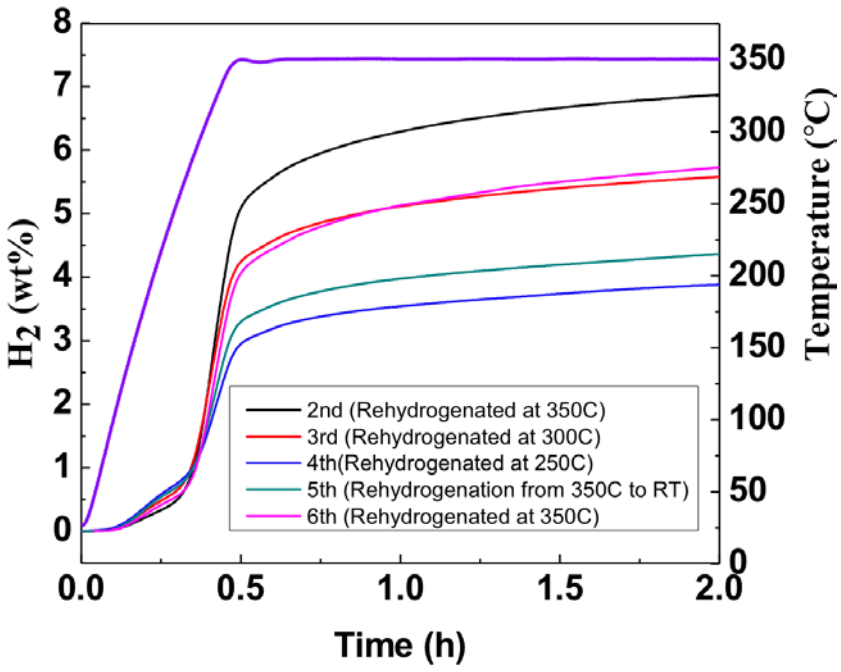
Results indicate ***lower onset temperature of decomposition*** than previous measurements on $LiBH_4$ in 4 nm nano-porous silica-templated carbons. (Janot, et al., *J. Pow. Src.*, **189**, 902, 2009)

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



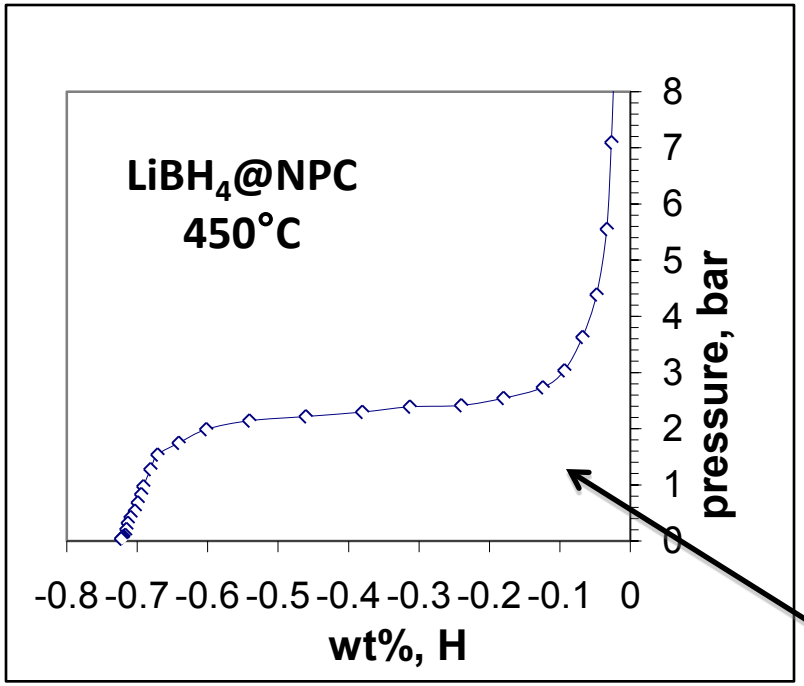
Smaller pore size lowers B_2H_6 release

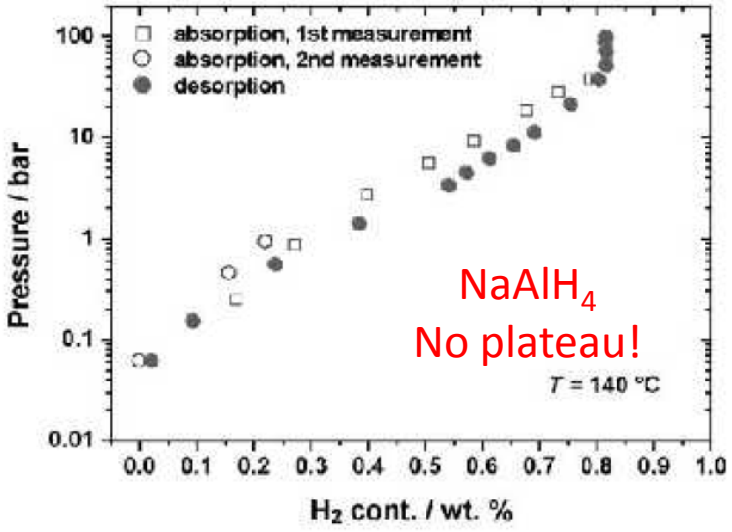


Demonstrated low temperature reversibility

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 $LiBH_4$



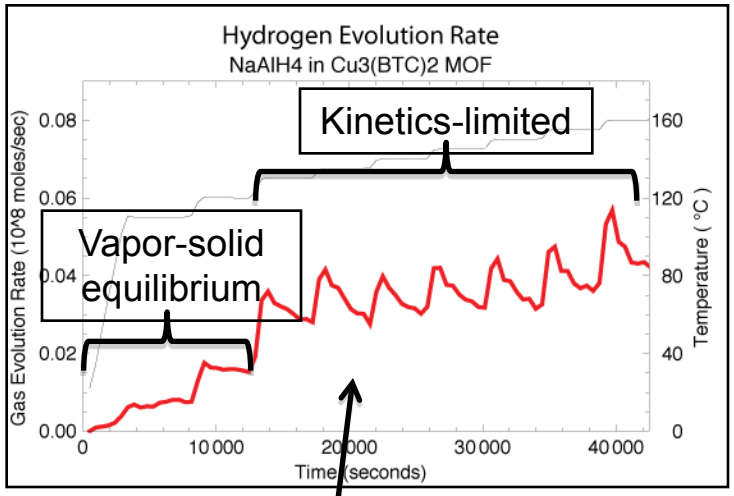


Lohstroh, et al., Chem Phys Chem, **11**, 789, 2010

- 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)

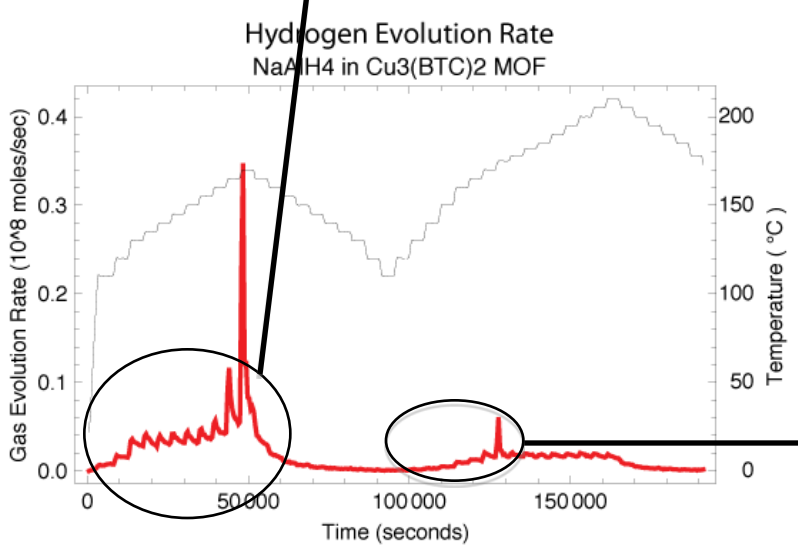


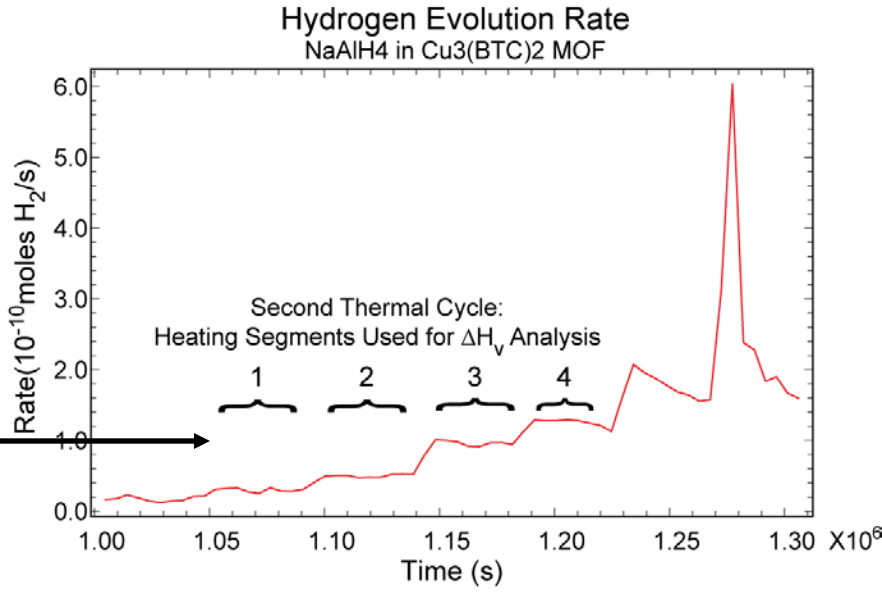
H_2 desorption measurements:

- Varied sample size
- Varied orifice diameter

Two desorption regimes:

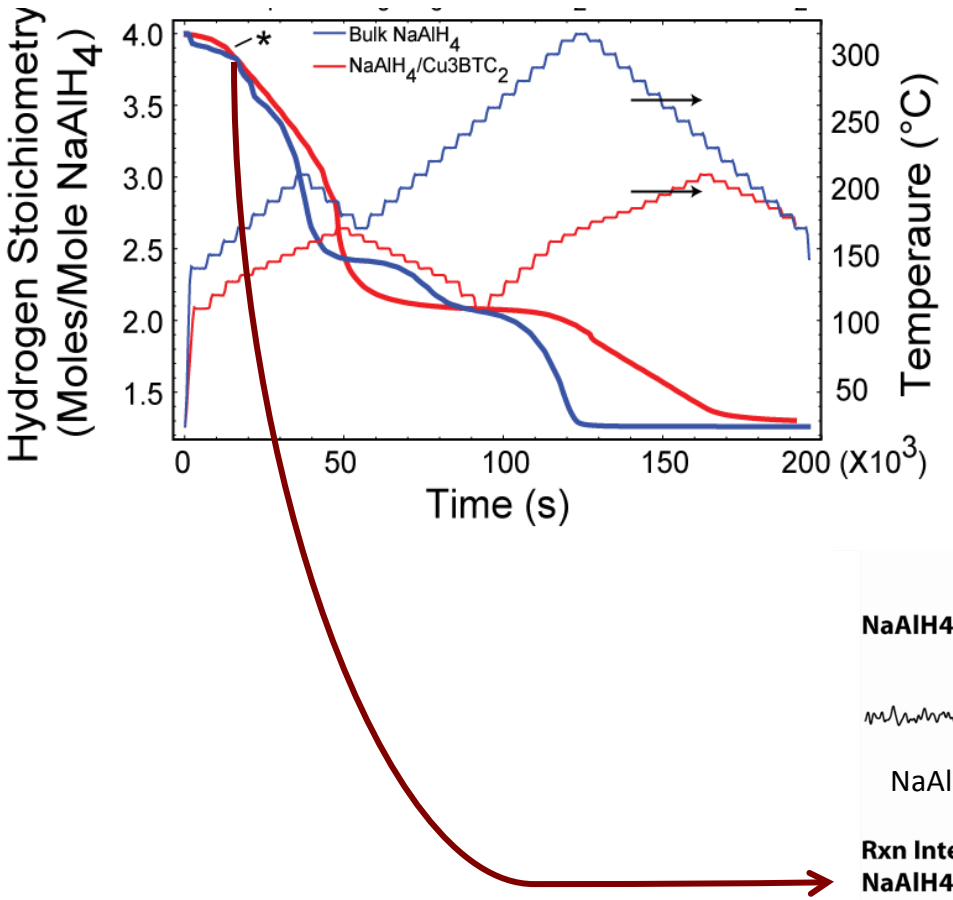
- < 110 ^{0}C: vapor-solid equilibrium
  - Results independent of sample and orifice size
- 110 – 170 ^{0}C: kinetics-limited





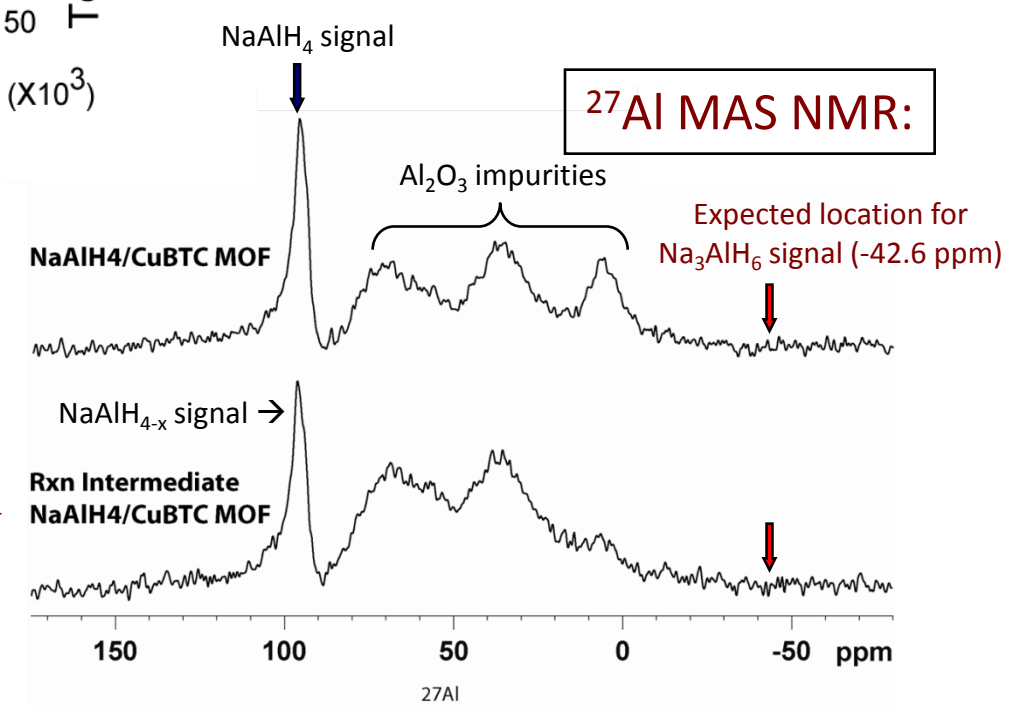
Technical accomplishment: Nano-confined $NaAlH_4$ (cont.)

Reaction path modification: NMR shows no evidence for Na_3AlH_6



Experiment:

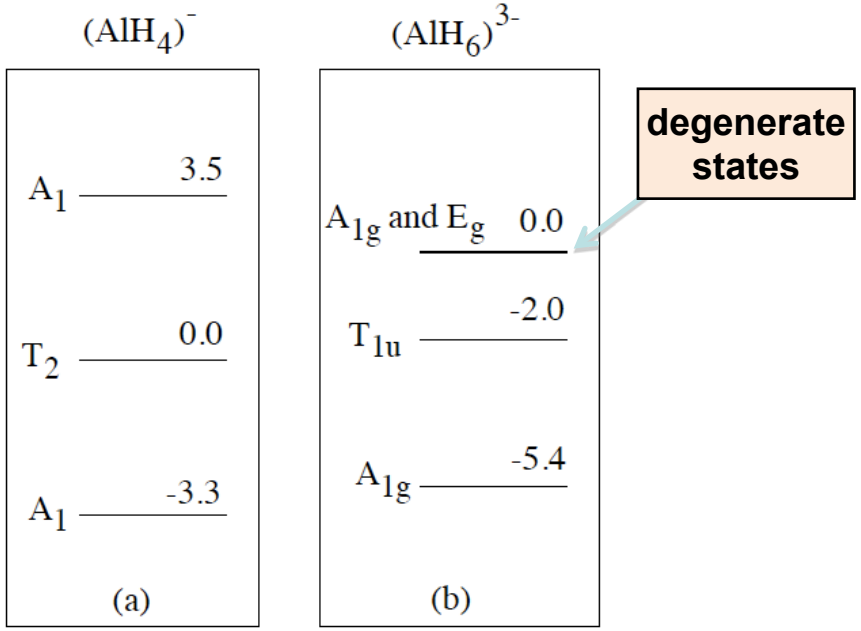
- Heat sample to 150 °C to initiate reaction
- Stop heating; remove sample for NMR



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

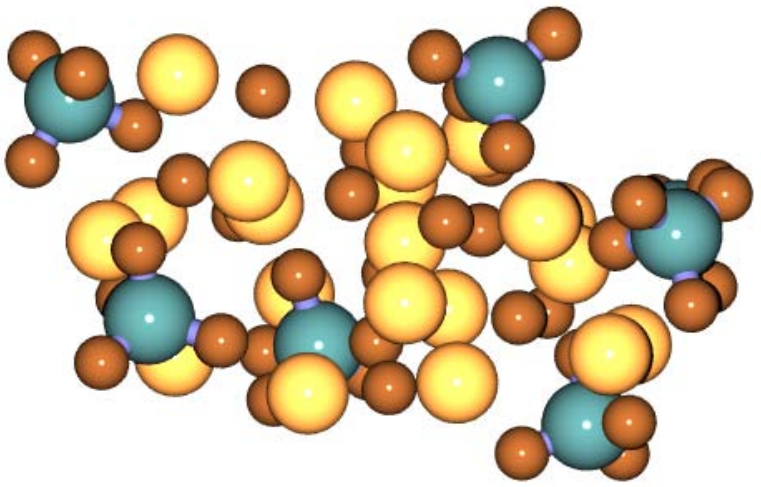
Reaction path modification: Theory supports absence of $(Na_3AlH_6)_n$ decomposition intermediates

Degenerate states in $(AlH_6)^{3-}$ anion result in destabilizing Jahn-Teller distortion



Electronic structure of isolated anions (charge compensated)*

$(Na_3AlH_6)_7$



Relaxes to NaH + $NaAlH_4$

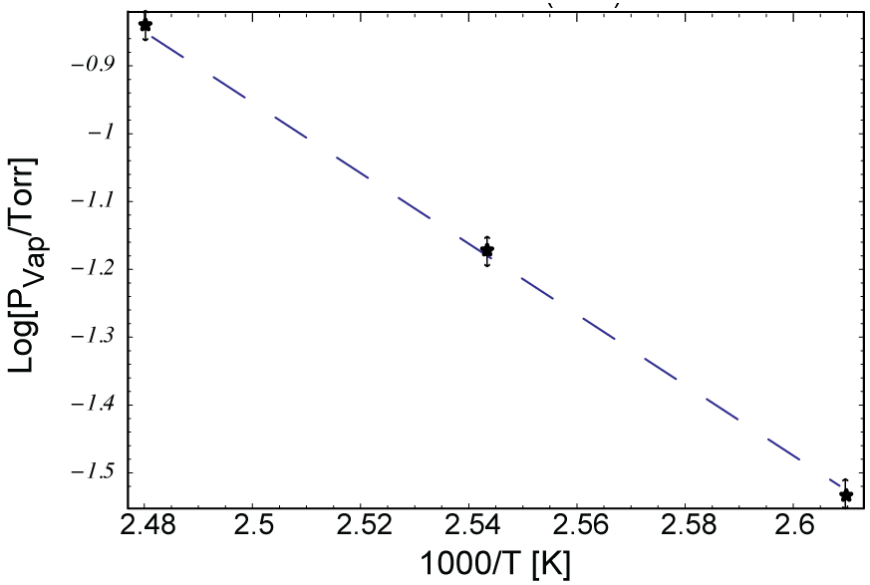
*Ozolins, V.; Udovic, T.; Majzoub, E.H.; J. Al. Comp, (2004) **375**, 1-10

Absence of Na_3AlH_6 decomposition intermediates agrees with NMR and other experimental results

Thermodynamics of H_2 desorption: vapor-equilibrium analysis

$NaAlH_4$@Cu-BTC (1.3 nm pores)

STMBMS data



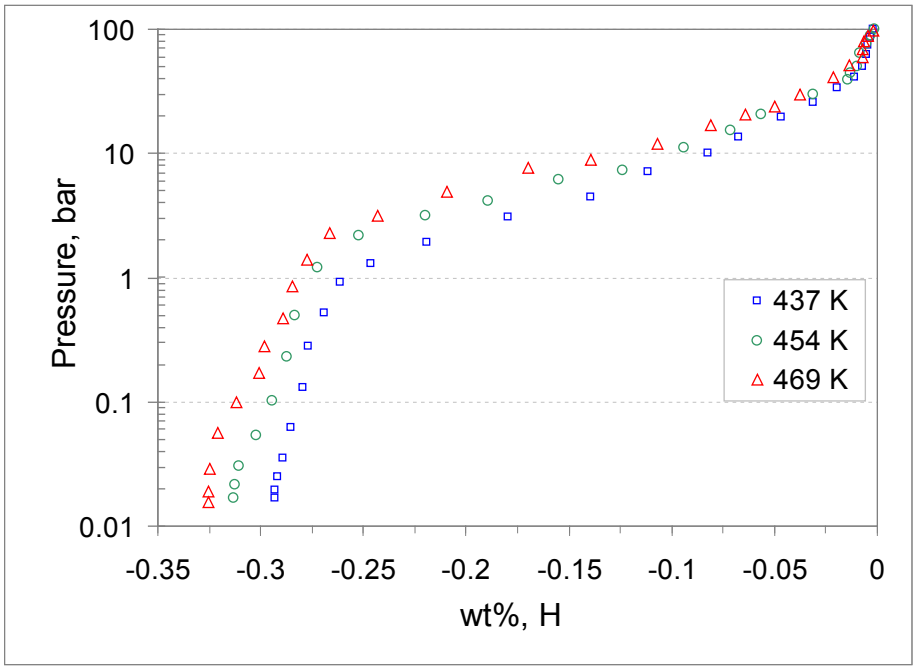
$\Delta H^o_{desorp} = 47.3 \pm 0.12$ kJ/mol-H_2

$\Delta S^o_{desorp} = 110.1$ J/mol-K

(average of 3 experiments)

$NaAlH_4$@hex-porous carbon (4 nm pores)

PCT data



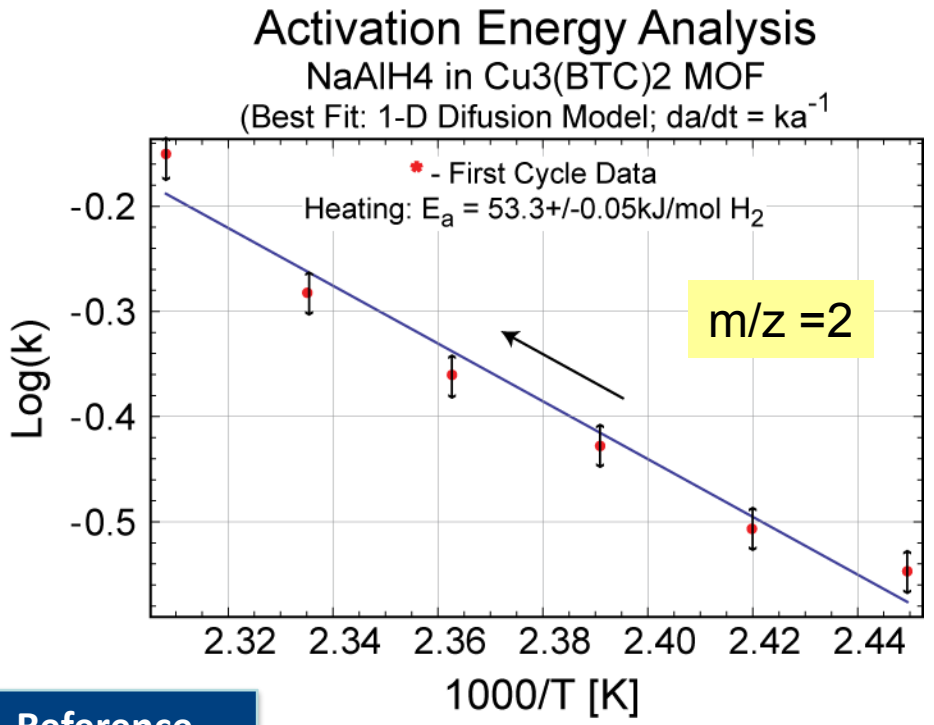
In contrast to bulk $NaAlH_4$, no plateau regions are observed

$\Delta H^o_{desorp} = 35 \pm 3$ kJ/mol-H_2

(using center of sloping plateau)

Kinetics of NaAlH4@Cu-BTC: Dramatic acceleration of H_2 desorption

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



Template	Ea (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

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

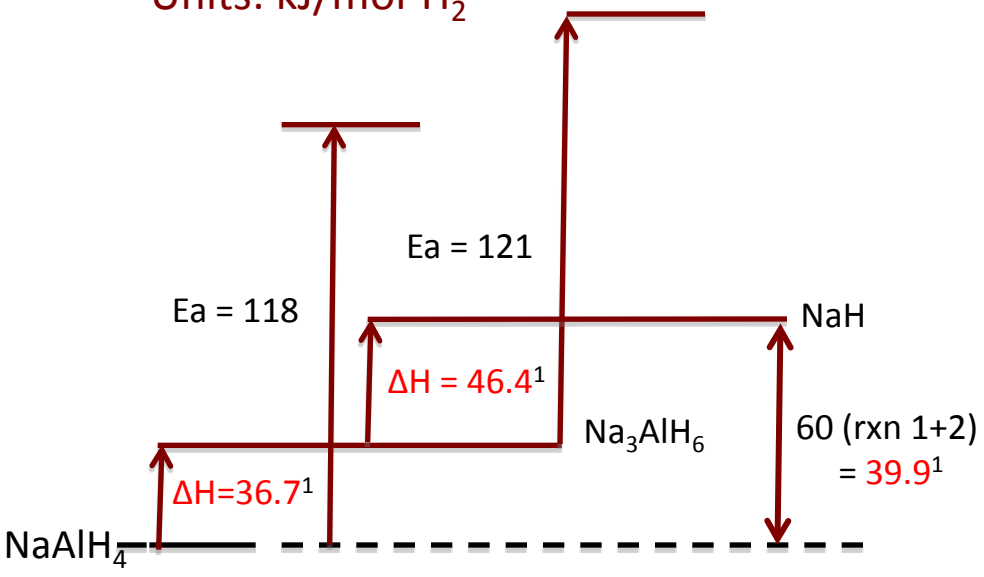
Technical accomplishment: Nano-confined $NaAlH_4$ (cont.)

Size-dependent thermodynamics: Bulk vs. $NaAlH_4$@CuBTC (~1.3 nm)

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

$NaAlH_4$ (bulk)

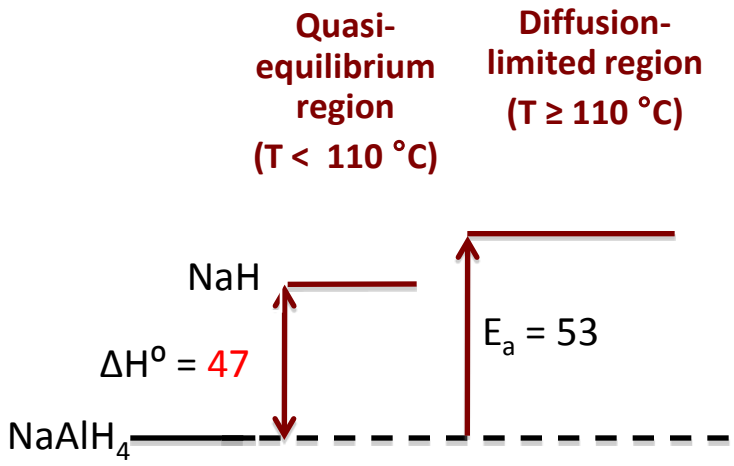
Units: kJ/mol-H_2



Data from this work

$NaAlH_4$@Cu-BTC (~1.3 nm)

Units: kJ/mol H_2



Reaction (energies given in kJ/mol-H_2)	1.3 nm		4 nm		Bulk	
	ΔH^o	E_a	ΔH^o	E_a	ΔH^o	E_a
$NaAlH_4 \rightarrow NaH + 0.33Al + 1.5H_2$	47	47 – 53	35 ± 10	--	40	121
$NaAlH_4 \rightarrow 0.33Na_3AlH_6\ 0.67\ Al + 1.0H_2$	N/A	N/A	N/A	N/A	37	118

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

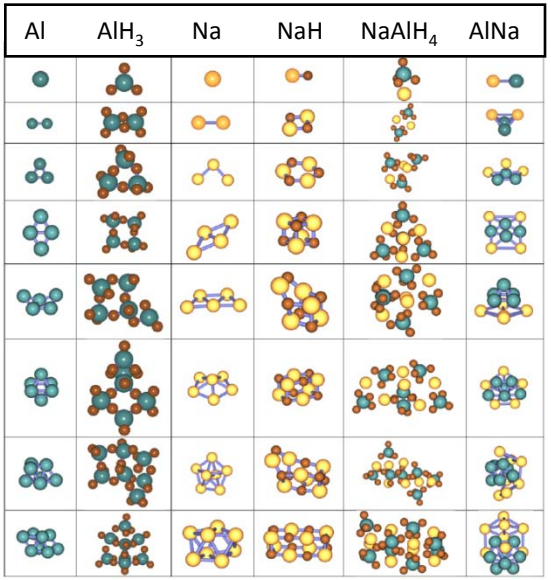
Nanoconfined $NaAlH_4$ decomposes via a <u>one-step mechanism with a low activation barrier</u>, vs. a 2-step mechanism in bulk: → Implies a 50% increase in accessible capacity at typical fuel cell temps

Size-dependent thermodynamics: Na-Al-H nano-cluster phase diagram

Grand Canonical Linear Programming (GCLP)* method

Each cluster energy calculated separately

$(NaAlH_4)\_1$, $(NaAlH_4)\_2$, $(NaAlH_4)\_3$, $(NaAlH_4)\_4$, $(NaAlH_4)\_5$, $(NaAlH_4)\_6$, …
$(NaH)\_1$, $(NaH)\_2$, $(NaH)\_3$, $(NaH)\_4$, $(NaH)\_5$, $(NaH)\_6$, $(NaH)\_7$, $(NaH)\_8$, …
Al_1, Al_2, Al_3, Al_4, Al_5, Al_6, Al_7, Al_8, Na_1, Na_2, Na_3, Na_4, Na_5, Na_6, Na_7, Na_8, …
$(NaAl)\_1$, $(NaAl)\_2$, $(NaAl)\_3$, $(NaAl)\_4$, $(NaAl)\_5$, $(NaAl)\_6$, $(NaAl)\_7$, $(NaAl)\_8$, …
$(AlH_3)\_1$, $(AlH_3)\_2$, $(AlH_3)\_3$, $(AlH_3)\_4$, $(AlH_3)\_5$, $(AlH_3)\_6$, $(AlH_3)\_7$, $(AlH_3)\_8$, …
$(Na_3AlH_6)\_1$, $(Na_3AlH_6)\_2$, $(Na_3AlH_6)\_3$, $(Na_3AlH_6)\_4$, $(Na_3AlH_6)\_5$, …



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

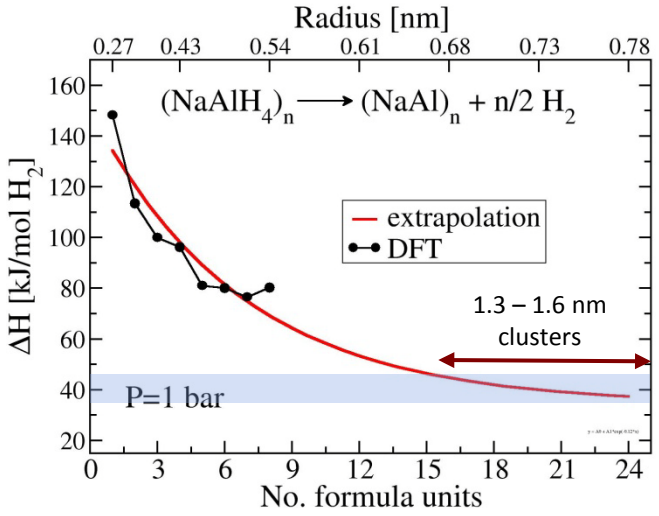
Minimize the Gibbs Free Energy:

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

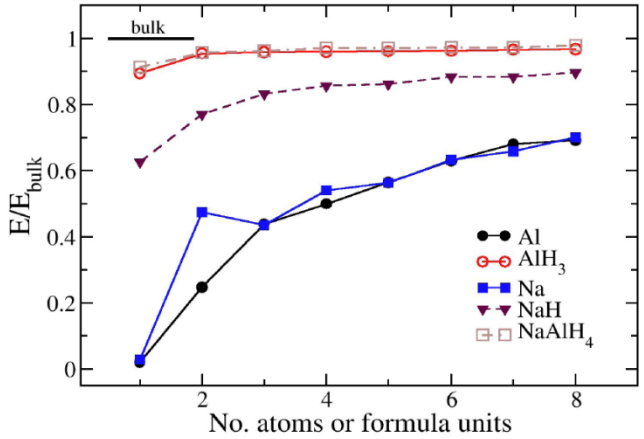
Determine the clusters present as a function of composition, temperature, and pressure

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

Size-dependent thermodynamics: tuning $NaAlH_4$ cluster stability



← Observed Δ*H* range for nano-confined $NaAlH_4$

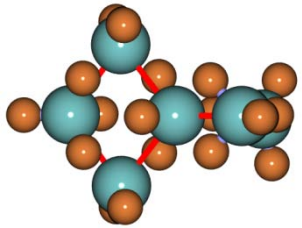


Ionic clusters rapidly approach their bulk cohesive energy, while small metal clusters do not

Temperature needed for equilibrium p(H_2) = 0.01 bar

T [°C]	Δ*H* [kJ/mol H_2]	reaction
589	161	$(AlH_3)_1 \rightarrow (Al)_1 + 1.5H_2$
601	149	$(AlH_3)_2 \rightarrow (Al)_2 + 3.0H_2$
388	105	$(AlH_3)_3 \rightarrow (Al)_3 + 4.5H_2$
294	92	$(AlH_3)_4 \rightarrow (Al)_4 + 6.0H_2$
199	77	$(AlH_3)_5 \rightarrow (Al)_5 + 7.5H_2$
114	61	$(AlH_3)_6 \rightarrow (Al)_6 + 9.0H_2$
50	52	$(AlH_3)_7 \rightarrow (Al)_7 + 10.5H_2$
43	51	$(AlH_3)_8 \rightarrow (Al)_8 + 12.0H_2$
T [°C]	Δ*H* [kJ/mol H_2]	reaction
151	71	$(NaH)_3 \rightarrow (Na)_3 + 1.5H_2$
97	68	$(NaH)_4 \rightarrow (Na)_4 + 2.0H_2$
103	69	$(NaH)_5 \rightarrow (Na)_5 + 2.5H_2$
117	73	$(NaH)_6 \rightarrow (Na)_6 + 3.0H_2$
95	66	$(NaH)_7 \rightarrow (Na)_7 + 3.5H_2$
100	69	$(NaH)_8 \rightarrow (Na)_8 + 4.0H_2$

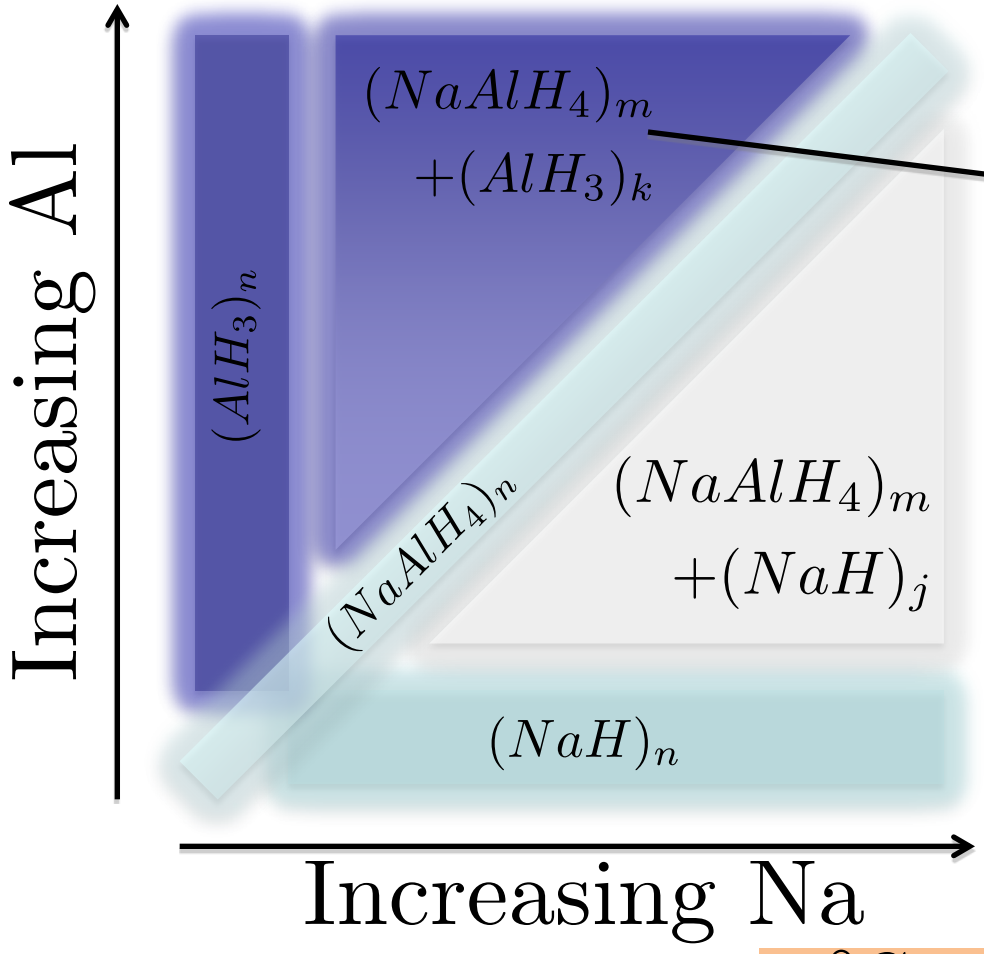
Contrast: bulk α-AlH_3 is unstable at STP
~ +7 kJ/mol H_2 for AlH_3 → Al + 3/2 H_2



$(AlH_3)_6$

$(NaH)_n$ destabilized only < 3 formula units, but $(NaAlH_4)_n$ and $(AlH_3)_n$ stability increases as *n* increases

Thermodynamic destabilization: Na-Al-H nanocluster phase diagram



Off-axis decomposition reactions are predicted to occur at lower temperatures than pure NaH, AlH_3, or $NaAlH_4$ clusters

Example

$77^{\circ}C \quad 56kJ/mol$

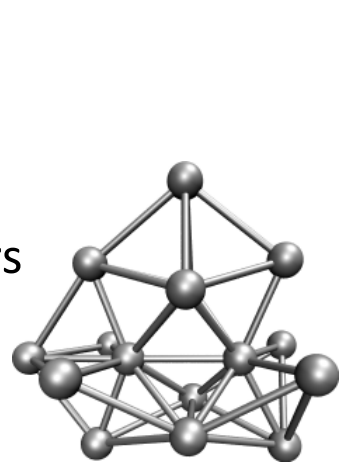
$$(AlH_3)_6 + (NaAlH_4)_1 \rightarrow (Al)_7 + (Na)_1 + 11H_2$$

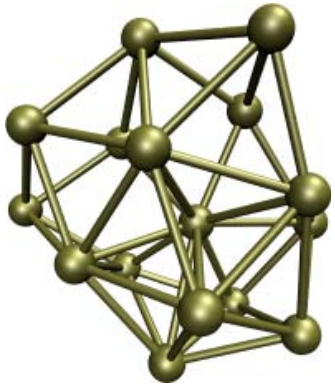
Technical accomplishment: Compositional tuning of thermodynamics

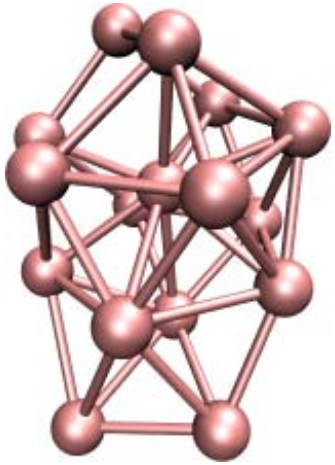
Quantum Monte Carlo predictions of cluster stability

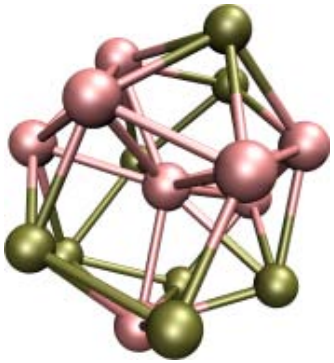
Metallic clusters

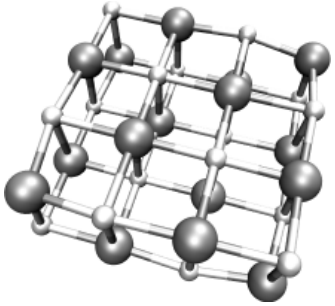
Metal-hydride clusters

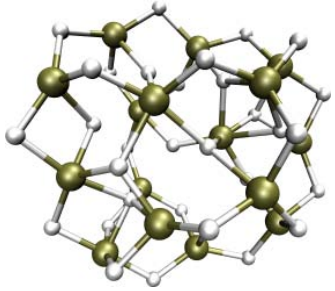


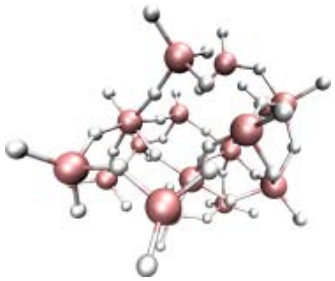


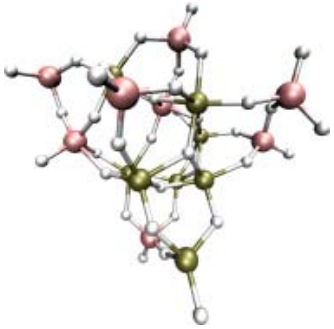








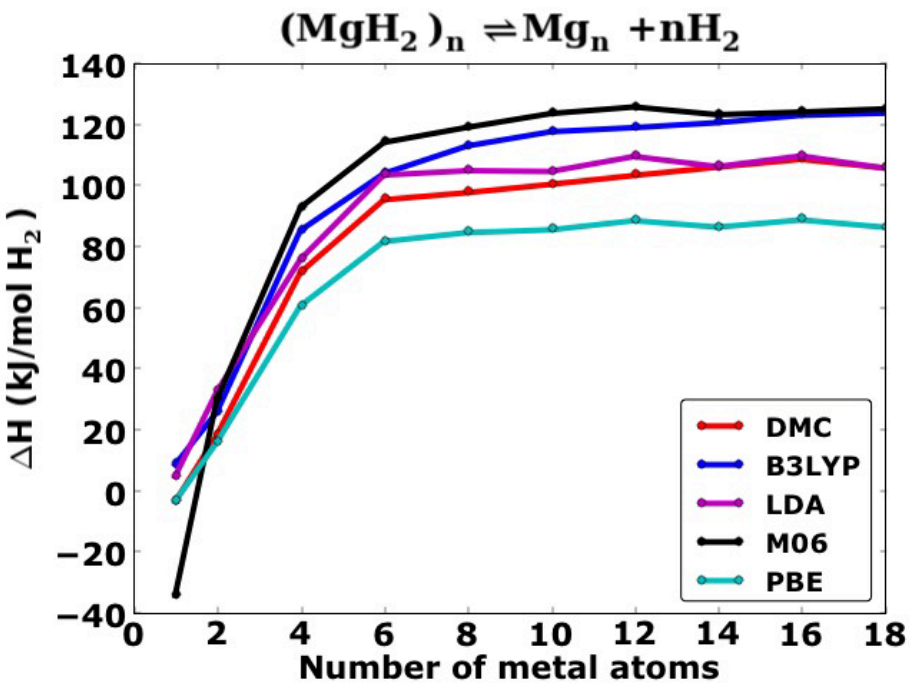


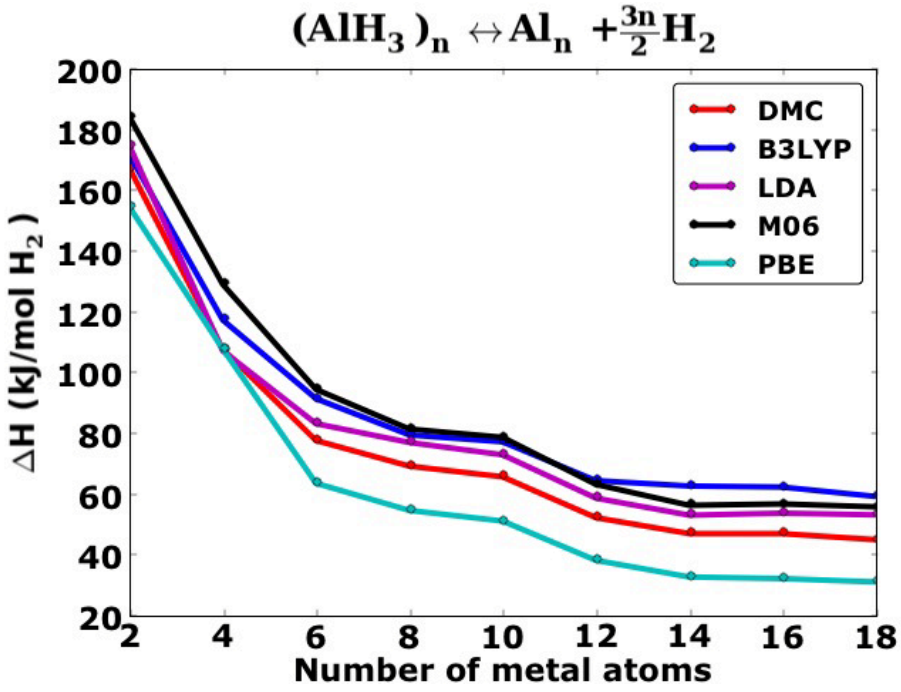


Li_{16} Mg_{16} Al_{16} $(MgAl)_{16}$

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

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



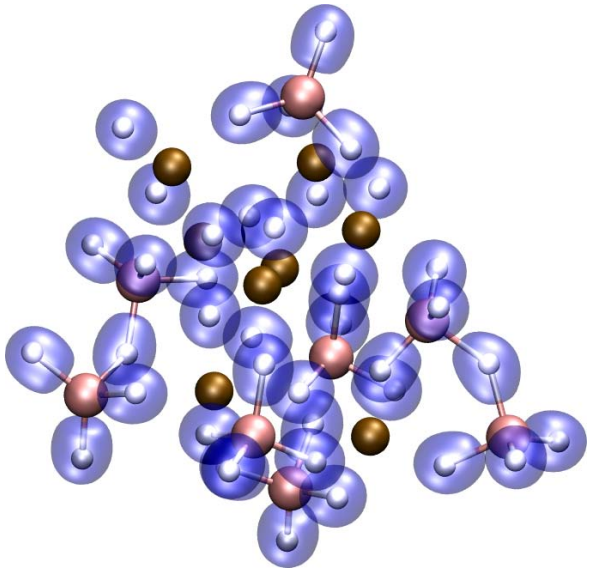


$(MgH_2)_n$ clusters are destabilized only at very small sizes

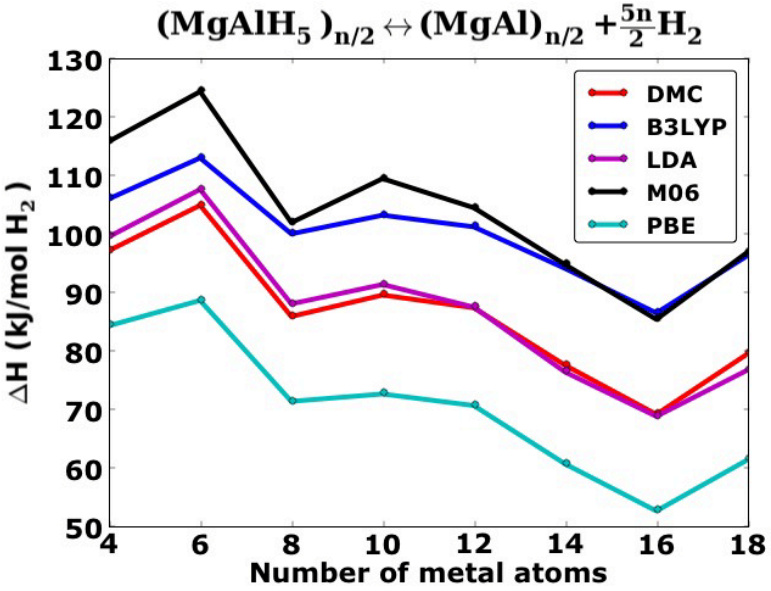
$(AlH_3)_n$ clusters are stabilized at small sizes

Mg-Al-H nanoclusters are destabilized relative to MgH_2

$(AlMgH_5)_8$ clusters are very ionic; note highly localized charges



Comparison of DFT functionals with highly accurate Diffusion Monte Carlo calculations



	ΔH (kJ/mol)
$(MgH_2)_8$	~ 100
$(AlH_3)_8$	~ 40
$(AlMgH_5)_8$	~ 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 $Ca(BH_4)_2$ nanoparticle desorption kinetics in MOFs and nanoporous carbons
  - Complete measurements of $Li_4BN_3H_{10}$ 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 $NaAlH_4$@MOF
  - Thermodynamics of $LiBH_4$@HPC and $NaAlH_4$@HPC
  - Use of MOFs as templates for metal hydrides

Collaborations

Project Team:

- ***Prof. Jeffery Grossman, MIT Mater. Sci. Eng.*** (subcontract to Sandia). Lead investigator, non-ionic hydrides and code validation (project funds1 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 relative magnitudes