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

2009 U.S. DOE HYDROGEN PROGRAM and VEHICLE TECHNOLOGIES ANNUAL MERIT REVIEW and PEER EVALUATION MEETING

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Sandia National Laboratories

May 18-22, 2009

Crystal City, VA

Project ID: #stp_48_allendorf

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Overview

Timeline

Project start date: September 2008
Project end date: September 2011
Percent complete: 25%

Barriers

(A) System weight and volume

(C) Efficiency

(P) Lack of understanding of hydrogen physisorption and chemisorption

Partners

Mark Allendorf (PI) Sandia. MOFs and related templates

Eric Majzoub, Univ. MO, St. Louis. BCP templates, ionic hydride modeling

Jeffery Grossman, U. C. Berkeley. Model benchmarking, non-ionic hydride modeling

Julie Herberg, LLNL. NMR characterization

Terry Udovic, NIST. Neutron spectroscopies

Richard Behrens, Sandia. Desorption kinetics and framework stability

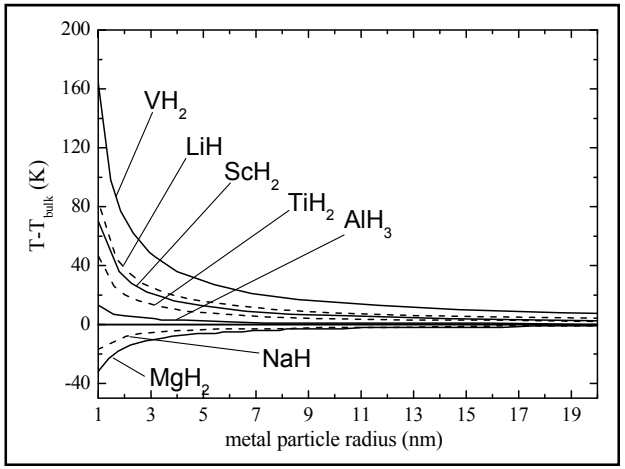
Budget

- Total project funding through FY09:
  - **DOE share: $760 K**
  - **Contractor share: $56 K**
- Funding received in FY08: $240 K
- Funding for FY09: $520 K

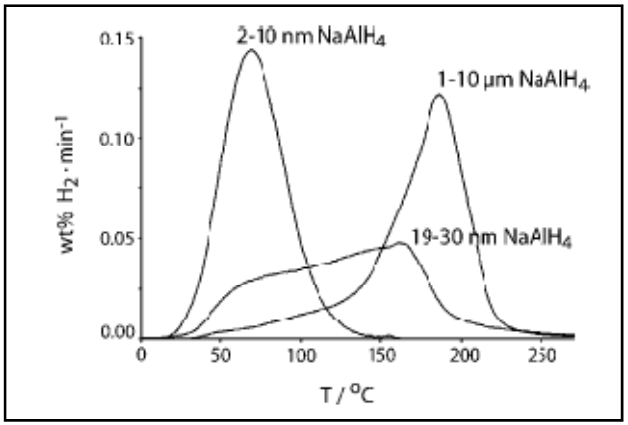
Relevance: Decreasing T(1 bar) would make some metal hydrides much more attractive for hydrogen storage

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 FY09**
  - Demonstrate and downselect infiltration methods
  - Measure desorption kinetics for MgH_2 and $NaAlH_4$ nanoparticles and $LiBH_4$ thin films
  - Benchmark DFT and atomistic nanoparticle models using Quantum Monte Carlo (QMC)
  - Quantify effect of nanoparticle size on ΔH°_d using MgH_2 as initial example



Predicted hydride destablization as a function of particle size, using the Wolfe construction
Johnson, Sholl et al. *Nanotechnology* in press



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

Relevance (cont): This project addresses several key barriers to on-board hydrogen storage

- **Key challenges:** 1) develop synthetic routes that provide controlled size and composition; 2) stabilize particles over time; and 3) develop computational tools that can accurately address micro-to-meso particle sizes.
- **Potential impact on barriers and targets**
  - **(A) System weight/volume:** Some high wt-% hydrides could be useable if T(1 bar) could be shifted to a more favorable value; for example:

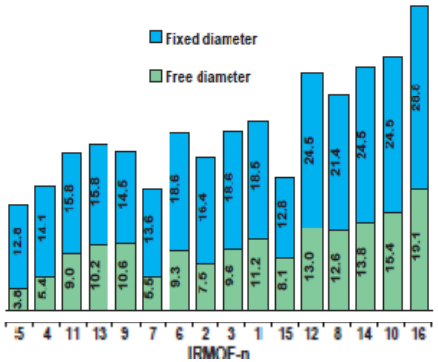
	Wt%	ΔH°_d	T(1 bar)	
MgH_2	7.6	75	570 K	Too stable
$LiBH_4$	13.9	97	685 K	Too stable
AlH_3	10.0	12	58 K	Too unstable

  - **(C) Efficiency:** Lower ΔH°_d would reduce heat management issues
  - **(P) Lack of understanding:** What has the greatest influence: size or local environment, in destabilizing hydride nanoparticles?

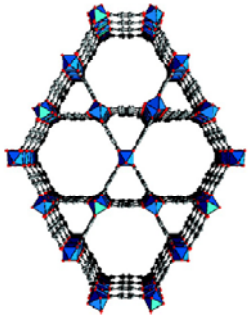
Approach: Use novel *ordered* frameworks to create a suite of templates to *systematically probe* nanoscale effects

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

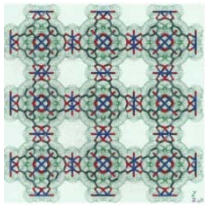
IRMOF entrance (green) and interior (blue) pore diameters



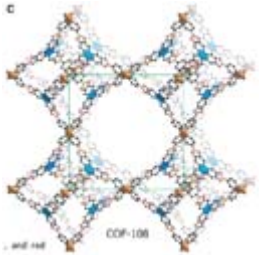
MIL-68



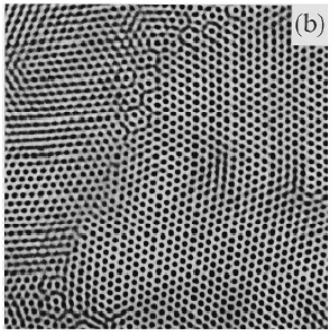
HKUST-1



COF-108

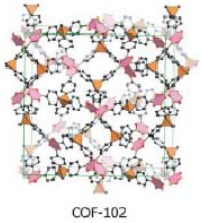


polystyrene-polybutadiene BCP

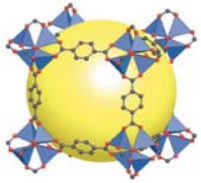


50 Å – 300 Å

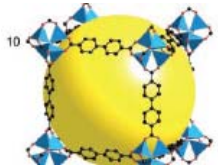
COF-102



IRMOF-1



IRMOF-10



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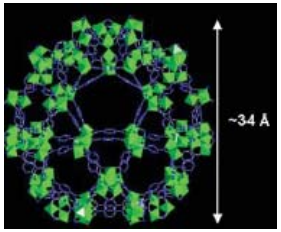
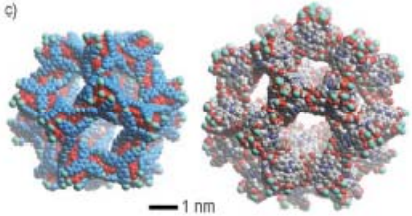


$\{Tb_{16}(TATB)_{16}\}$

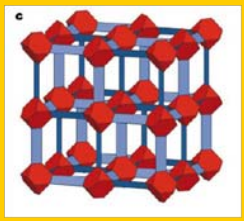


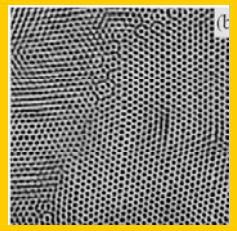
10 Å 20 Å 30 Å 40 Å 50 Å

Approach (cont.) Nanoparticle synthesis is supported by a strong foundation of modeling and characterization

Template design, synthesis, activation

MOFs (SNL) | BCP (UMSL)





Infiltration, reduction, stabilization (SNL,UMSL)

Particle properties
Template structures

Particle thermodynamics
Optimal compositions

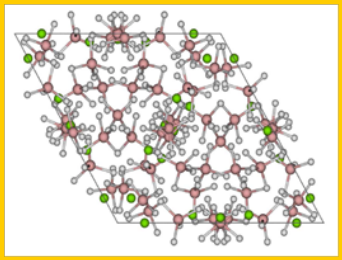
Samples

- Size and composition
- Framework stability
- Desorption kinetics and thermodynamics

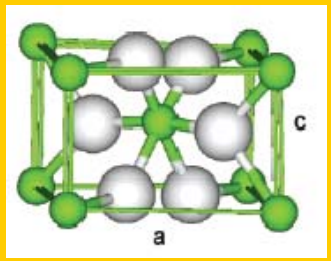
Theory (UCB, UMSL)

- Tool development: DFT, QMC, NanoPEGS
- Model validation and benchmarking
- Synthetic design

Ionic materials

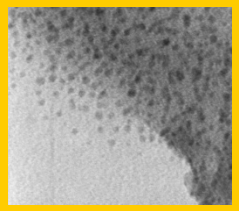


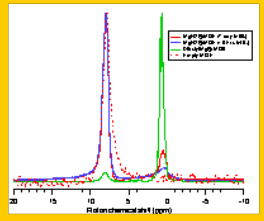
Covalent materials



Characterization Tools:

- MAS-NMR (LLNL)
- QCM+Molecular-beam MS (SNL)
- QENS, IENS,PGA,SANS (NIST)
- FE-TEM (SNL)





Approach (cont.) Task Structure and Project Deliverables

Task 1	Nanoparticle synthesis and characterization (SNL, UMSL, LLNL, NIST) • 1 -5 nm: Sandia • 5 – 20 nm: UMSL • NIST: x-ray, neutron, gamma methods • LLNL: MAS-NMR
Task 2	Sorption measurements and kinetics (UMSL, SNL)
Task 3	Theoretical Modeling for Rational Design of Particles (UCB, UMSL) • Benchmarking, validation, simple hydrides: UCB • Strongly ionic materials: UMSL
Task 4	Project management (SNL)

Technical objectives

- **Task 1:** Optimized nanoparticle synthetic procedures, suitable for further development and scale up, for one simple hydride (e.g. MgH_2) and one complex hydride (e.g. $NaAlH_4$)
- **Task 2:** Quantified size and composition dependencies of nanoparticle dehydrogenation thermodynamics and kinetics
- **Task 3:** Validated computational modeling approaches predicting to the properties of hydride nanoparticles

Our approach compliments ongoing work in the DOE Hydrogen Storage Program and elsewhere by developing highly ordered platforms for nanoparticle synthesis and validated theoretical approaches that enable systematic tuning of nanoparticle thermodynamics and kinetics

Project accomplishment: kickoff meeting and effective communication channels established

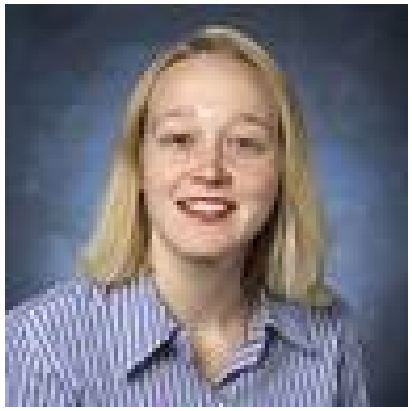
- Oct. 2008: Team kickoff meeting
- Web Sharepoint site established for team data sharing
- PI visits to all team sites
- Biweekly conference calls for team updates

Prof. Eric Majzoub (UMSL)

PI: Dr. Mark Allendorf (Sandia)

Dr. Richard Behrens and STMBMS team (Sandia)

Dr. Jeffery Grossman (UC Berkeley)

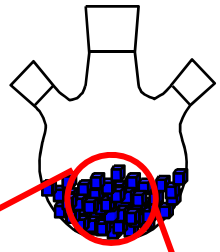


Dr. Julie Herberg (LLNL)

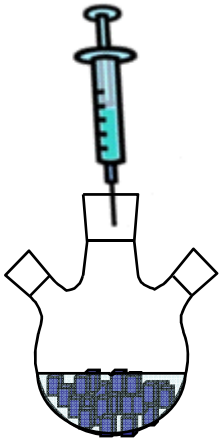
Technical Accomplishment: Infiltration methods developed for $NaAlH_4$ and MgH_2 using MOF templates

Solution-based infiltration route for $NaAlH_4$

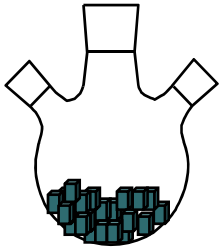
Activated $Cu_2(BTC)_3$ MOF (HKUST-1)
(evacuated at 110 °C)



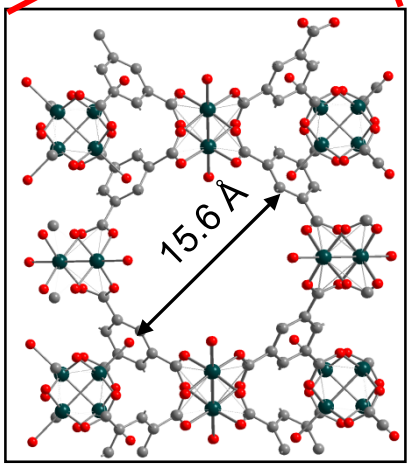
$NaAlH_4$.THF
Injection under vacuum



Reduced pressure
110 ° C
8 Hrs.



$NaAlH_4@Cu_2(BTC)_3$



CuBTC MOF. (formula unit = $Cu_2(BTC)_3$
(BTC = 1,3,5-benzenetricarboxylate)

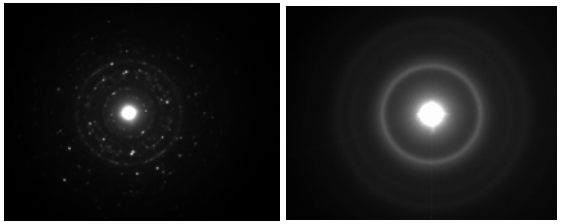
As-synthesized MOF Post activation Post infiltration

Technical Accomplishment: Infiltration methods developed for $NaAlH_4$ and MgH_2 using MOF templates

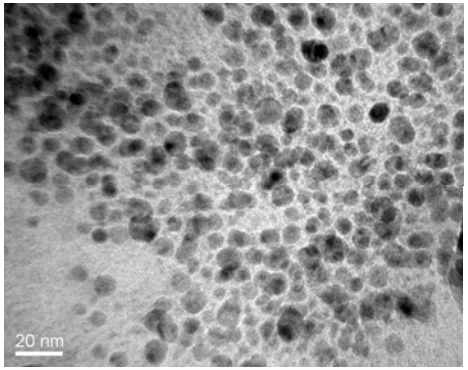
Results for $NaAlH_4$ in CuBTC MOF

- FTIR indicates presence of hydride
- XRD shows framework unaffected by hydride
- ^1H NMR indicates:
  - Free THF in pores (removable by heating)
  - THF coordinated to MOF Cu (visible by NMR)
- Loading: 4.0 ± 0.1 wt% (~ 8 formula units/pore)

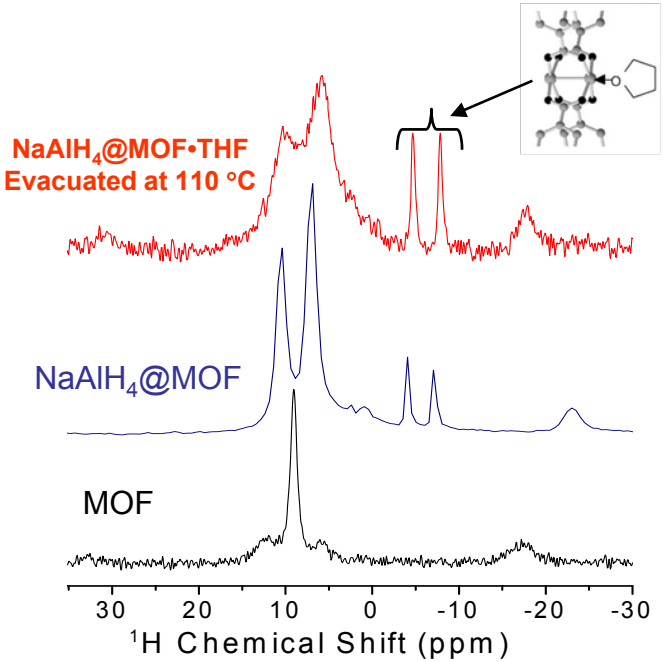
TEM indicates 5 – 10 nm particles, but our work on Ag-infiltrated MOFs shows TEM destroys the framework, allowing particles to agglomerate. *Thus, actual particle sizes are much smaller than indicated by TEM.*

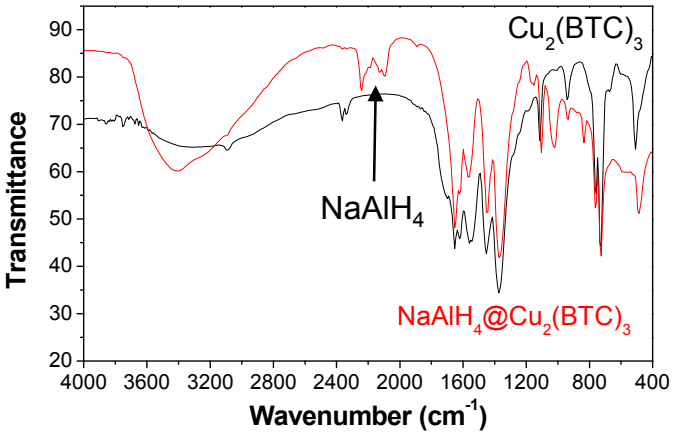


Ag-infiltrated MOF-508 diffraction under TEM beam. t = 0 s (left); t = 60 s (right), showing decomposition of framework and formation of metallic Ag particles



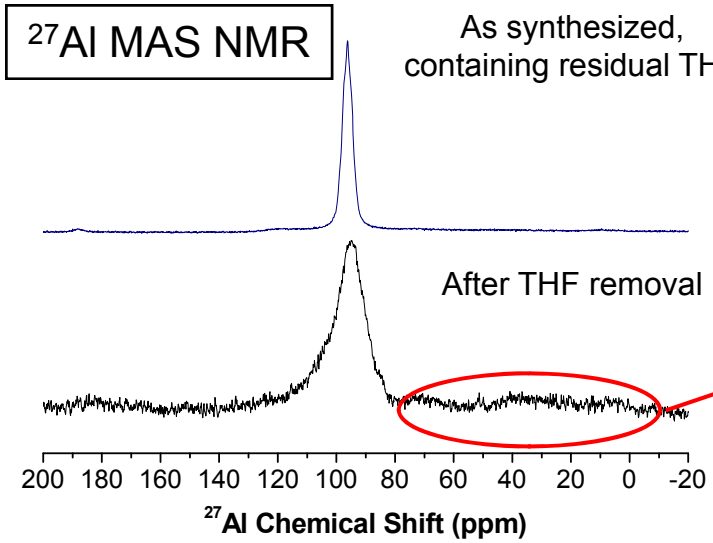
TEM of $NaAlH_4$@CuBTC MOF

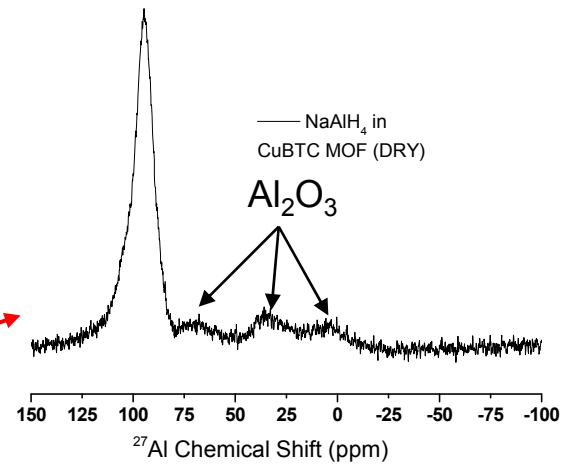




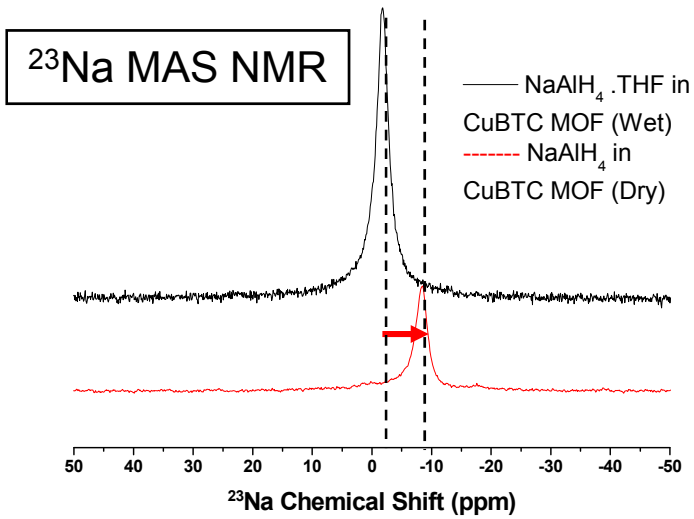
Collaboration of R. Bhakta, B. Jacobs (Sandia) and J. Herberg (LLNL)

Technical Accomplishment (cont): ^{23}Na and ^{27}Al MAS-NMR indicate $NaAlH_4$ clusters are present in the pores



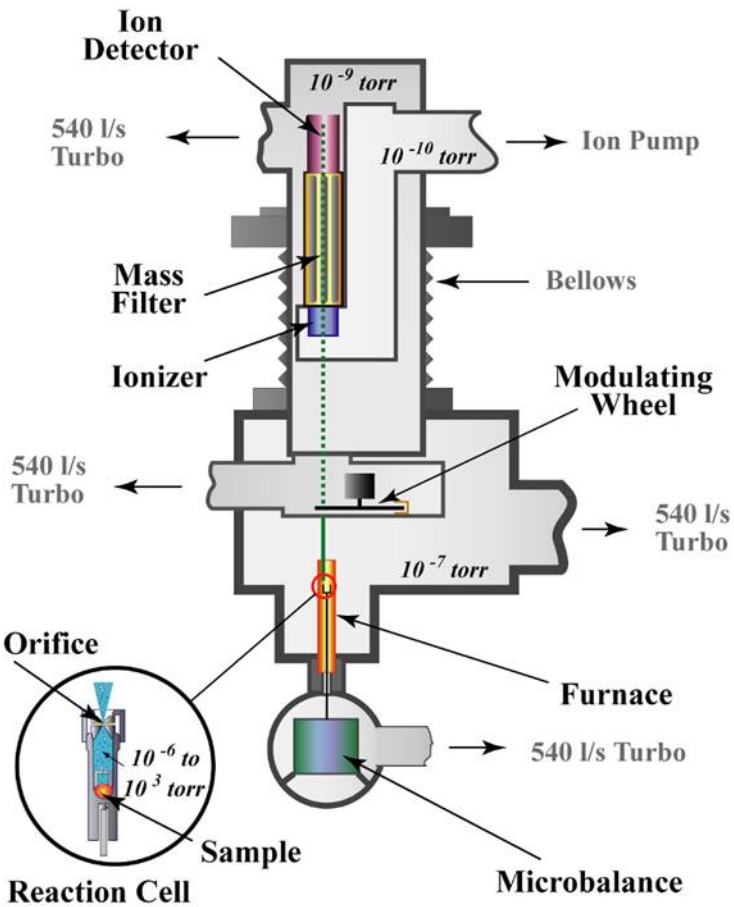


- ^{27}Al MAS NMR
  - Broad resonance ~ 95 ppm suggests decreased mobility in solvent-evacuated case
  - Minor Al_2O_3 impurity sometimes observed
- ^{23}Na MAS NMR
  - Up-field shift upon THF removal may indicate Na in the vicinity of copper



Collaboration of R. Bhakta (SNL) and J. Herberg (LLNL)

New advanced diagnostic capability: Simultaneous thermogravimetric modulated-beam mass spectrometry (STMBMS)



Instrument features:

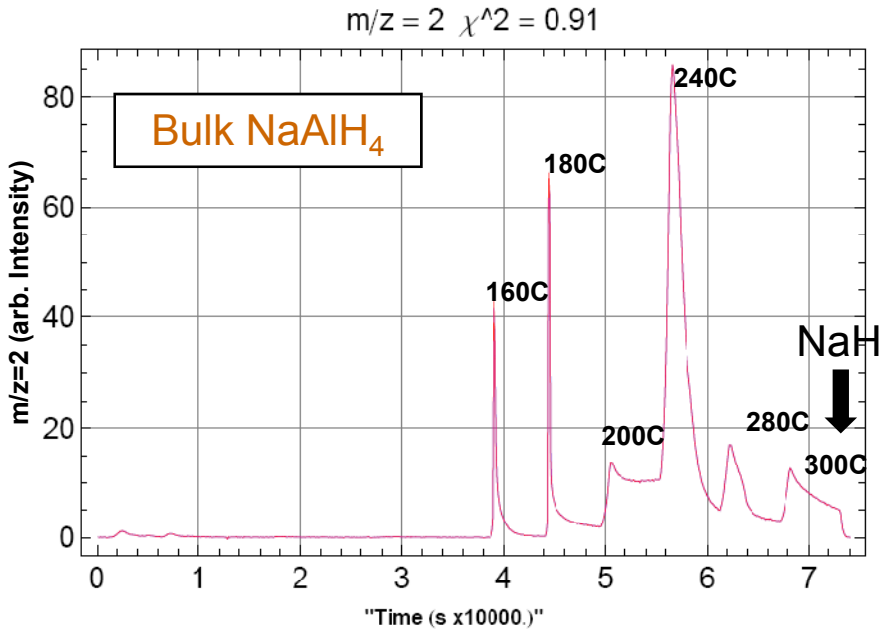
- Knudsen effusion cell installed within a furnace and upon a microbalance
- Simultaneous modulated molecular beam mass spectrometer provides time-dependent species data
- High accuracy FTMS also available for species identification

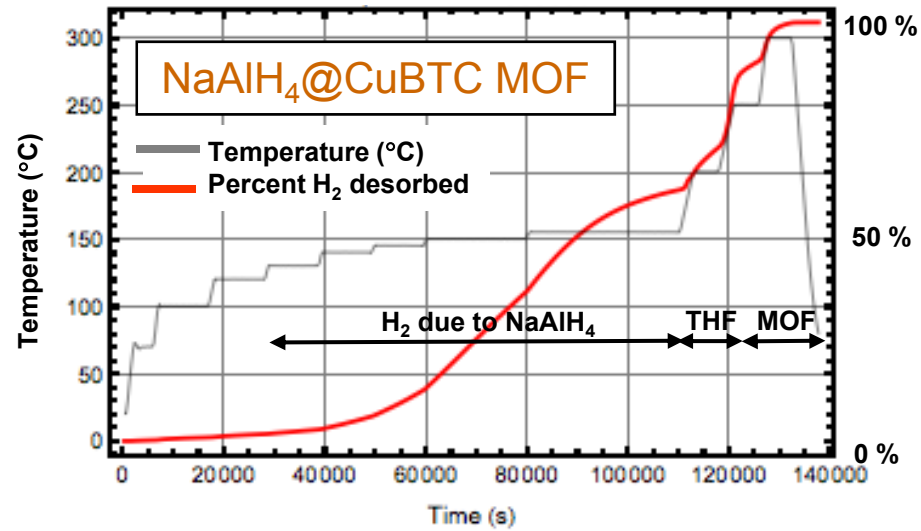
Data from each of these components is correlated and analyzed to determine reaction processes and kinetics

Experiment objectives

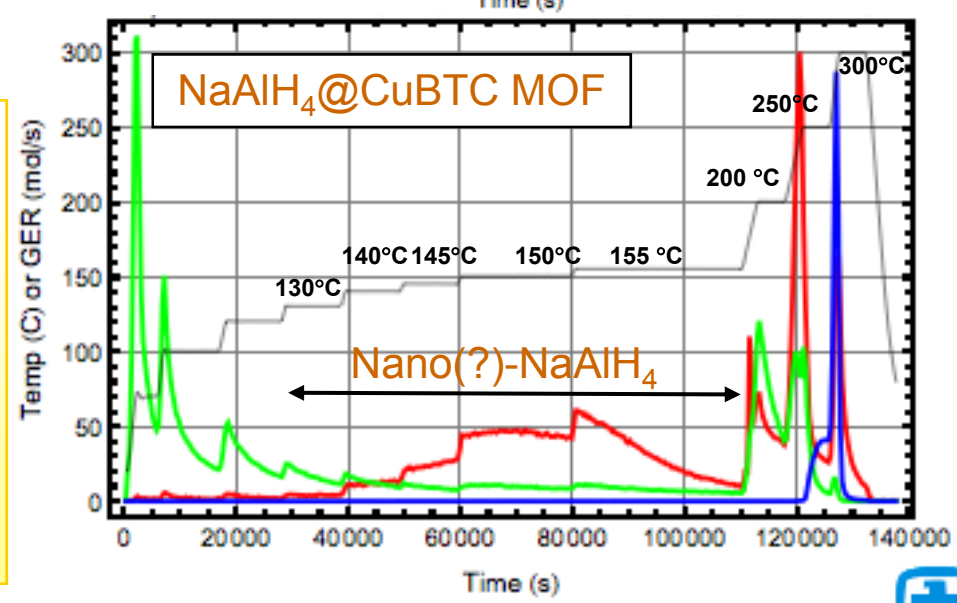
- Identify thermal decomposition products
- Measure product formation rates
- Correlate ion signals with sample mass loss
- Develop hydride decomposition mechanisms

Technical Accomplishment (cont): STMBMS data provide strong evidence that $NaAlH_4$@CuBTC MOF is kinetically destabilized





- Infiltration from deuterated solvent (TDF) shows 130 – 155 °C H_2 must be from $NaAlH_4$, not solvent or template decomposition
- Template decomposes at T ≥ 250 °C
- These results are strong evidence that nanoscale $NaAlH_4$ particles, which could be as small as 1.5 nm in this template, are destabilized relative to bulk

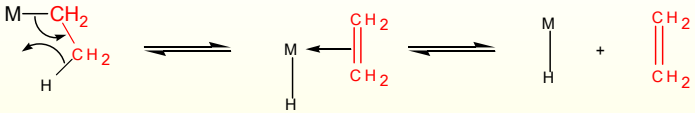


Green: THF; Red: H_2; Blue: CO_2

Collaboration of R. Bhakta and R. Behrens, Sandia

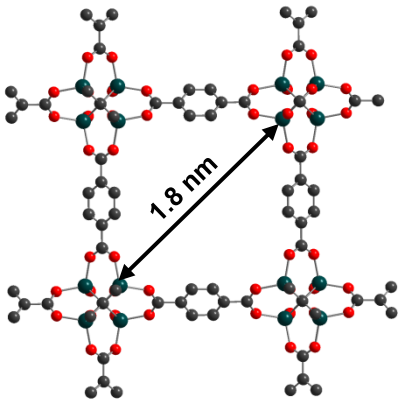
Technical Accomplishment (cont): Preliminary data indicate that nanoscale MgH_2 particles were formed within MOF-5

- MgH_2 infiltration using dibutylmagnesium ($Mg(C_4H_9)_2$) followed by heating to induce β-hydride elimination

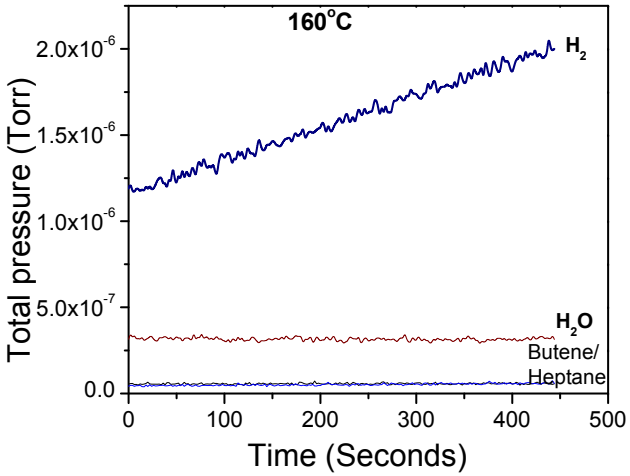


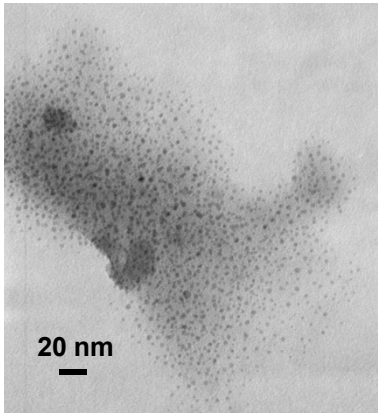
- NMR, FTIR, and PXRD indicate framework is intact
- TEM indicates 1.5 – 4 nm particles (sample pre-oxidized for TEM)
- RGA indicates little residual hydrocarbon or H_2O and H_2 desorption at 160 °C
- STMBMS experiments planned

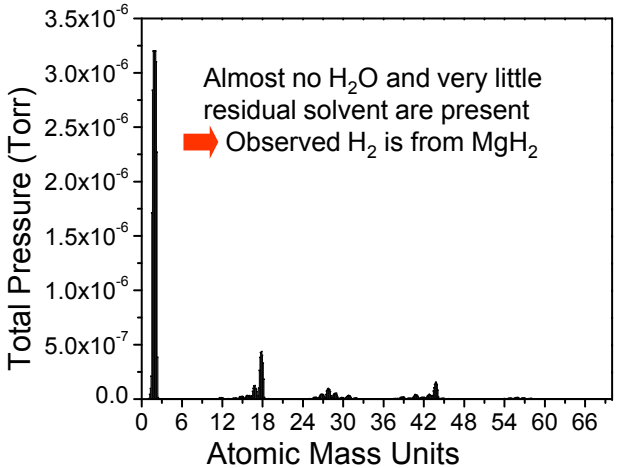
MOF-5 template structure



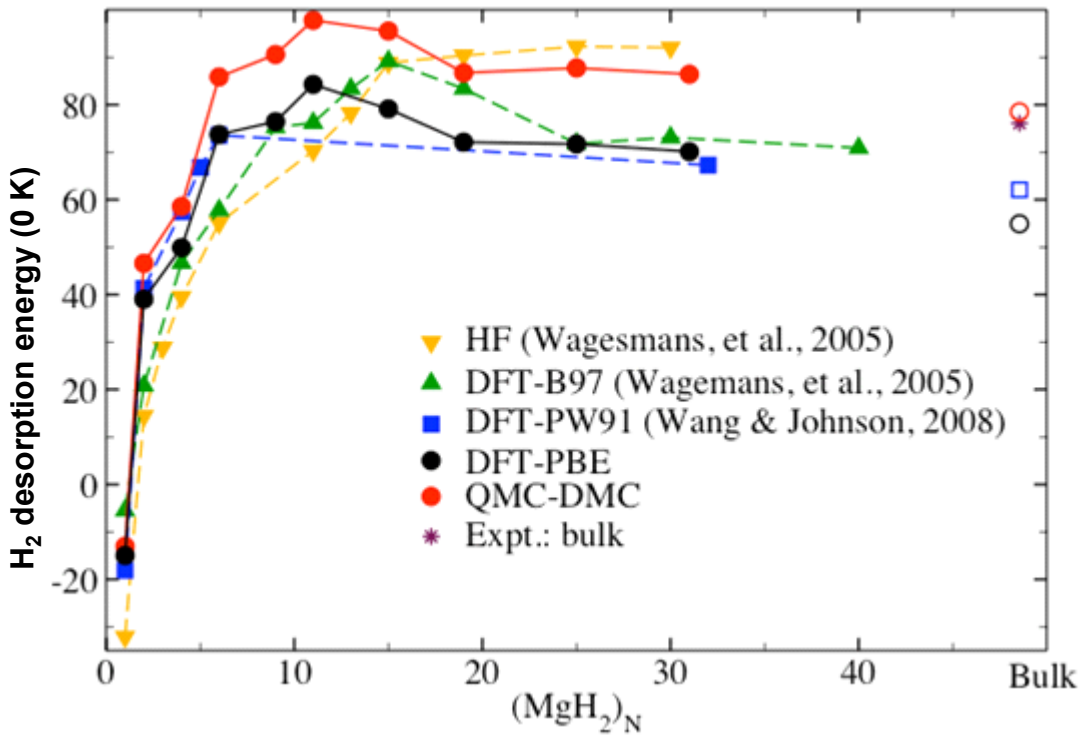
RGA of MgH_2@MOF-5 at 160 °C

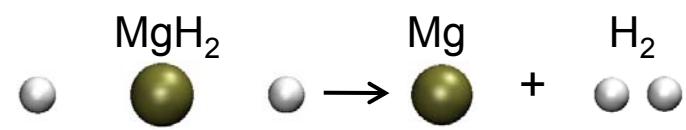






Technical Accomplishment: DFT methods benchmarked against Quantum Monte Carlo, using MgH_2 nanoparticles as a test case





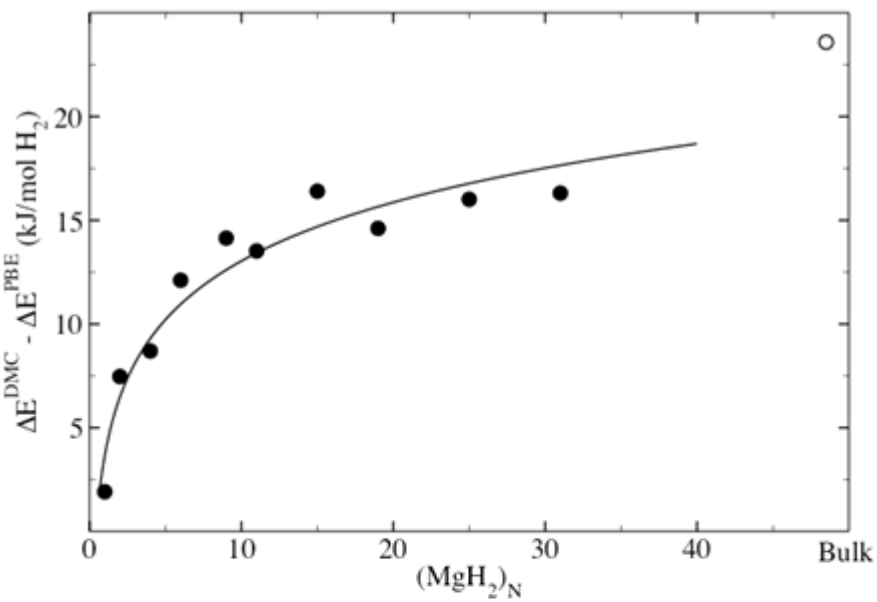
New high-accuracy (TZ) Mg basis sets developed, suitable for use in Siesta, a DFT code capable of modeling large systems (up to $(MgH_2)_{2000}$)

- Decreasing desorption energy as cluster size is reduced predicted by all methods
- However, there is enormous variation in the *quantitative* trends.
- Using quantum Monte Carlo we provide a chemically accurate benchmark

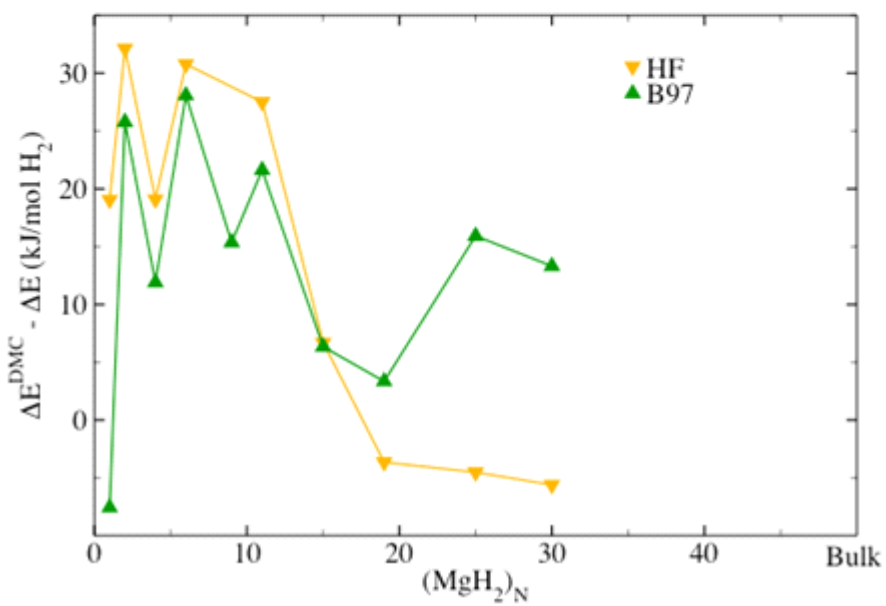
Surprisingly, for small sizes, just as the tunability becomes interesting, QMC shows that all other methods exhibit non-systematic errors

Work by J. Grossman, Z. Wu UCB
Collaboration with D. Johnson, UIUC

Technical Accomplishment (QMC benchmarking, cont.):
Computational error is non-systematic for DFT



- Compute the difference between QMC and other methods as a function of size
- Two important observations:
  1. Strong size-dependence on the error, and
  2. Size dependence is extremely non-uniform from one method to another.



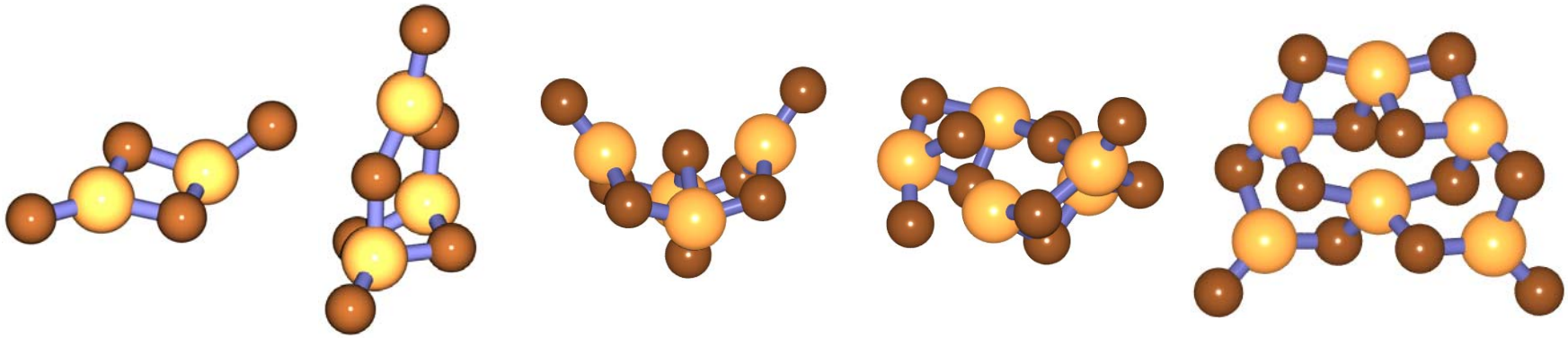
- These results illustrate the need for highly accurate methods to predict desorption tunability.
- Current work is aimed at other clusters (e.g., Na), alloy clusters (e.g., MgAl) and better understanding of failures of traditional theoretical approaches.

BNNI
Berkeley Nanosciences and Nanoengineering Institute

Technical accomplishment: New Nano-PEGS code we developed predicts high-symmetry Mg and MgH_2 cluster geometries

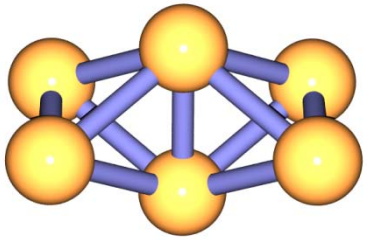
PEGS Hamiltonian

$$E_{\text{tot}} = \sum_{i>j} \frac{Q_i Q_j}{R_{ij}} + \sum_{i>j} \frac{\epsilon_{ss}}{R_{ij}^{12}}$$



2 f.u. 3 f.u. 4 f.u. 5 f.u. 6 f.u.

Lennard-Jones Hamiltonian for Metal and Mixed-Metal Clusters

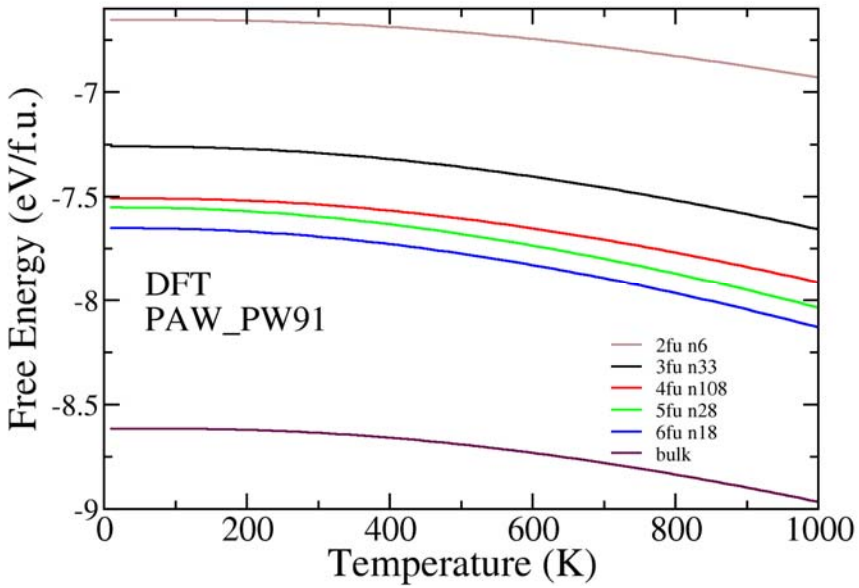


Mg_6

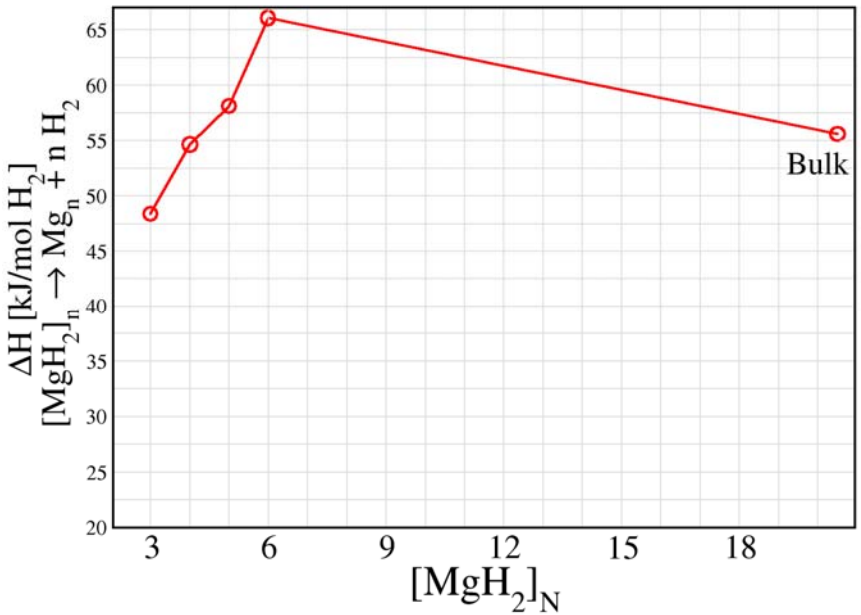
Work by E. Majzoub, UMSL

Technical accomplishment (cont): MgH_2 cluster enthalpies from Nano-PEGS and first-principles DFT

MgH_2 cluster free-energies



MgH_2 cluster enthalpies



- Enthalpies calculated for T=0 K plus zero-point energy
- Smaller clusters calculated to have smaller enthalpy
- Errors in DFT calculations benchmarked against quantum Monte Carlo (QMC)

University of Missouri St. Louis

Collaborations

Project Team:

- ***Dr. Jeffery Grossman, UC Berkeley Nanoscience and Nanoengineering Institute*** (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)
- ***Dr. Julie Herberg, Lawrence Livermore National Laboratory*** (Sandia subcontract). Lead investigator, NMR analysis of metal hydride nanoparticles
- ***Dr. Terry Udovic, NIST*** (funding from DOE to NIST). Lead investigator, neutron analytical probes. Samples currently undergoing neutron diffraction

Other collaborations:

- ***Prof. Ian Robertson, Univ. Illinois U-C (UIUC).*** TEM tomography. Samples currently under examination
- ***Prof. Duane Johnson, UIUC.*** DFT geometries of $(MgH_2)_n$ clusters
- ***Prof. Roland Fischer, Ruhr Univ. Bochum (Germany)***. Infiltration methods. Visited Sandia March 2009; visits by Sandia staff and postdoc planned

Future Plans

Remainder of FY09

- **Nanoparticle synthesis**
  - MOFs: Demonstrate Mg and Li infiltration; downselect infiltration methods
  - BCP: Downselect complex hydride infiltration method for thin films
- **Dehydrogenation thermodynamics and kinetics**
  - $NaAlH_4$ and MgH_2 nanoparticle desorption kinetics
  - Investigate framework reactions with dehydrogenation products
- **Theory**
  - Compute properties of $(MgH_2)_n$, $(NaH)_n$, and LiH nanoparticles
  - Complete DFT and NanoPEGS benchmarking using QMC and coupled-cluster methods

FY10 (Project year 2)

- Develop Al precursor infiltration method; synthesize mixed Mg-Al particles
- Infiltrate 3D BCP templates with complex hydrides
- **Decision point:** Downselect to one simple hydride and one complex hydride
- Measure PCT curves for downselected hydrides
- Predict stability and synthesize mixed-metal nanoparticles
- **Go/No-Go:** Continue compositional tuning effort?

Summary of Key Results

- New highly ordered nanoporous templates enable systematic probing of nanoscale effects
  - Nanoscale $NaAlH_4$ particles (as small as 1.5 nm diameter) exhibit improved H_2 desorption kinetics relative to bulk
  - Preliminary data suggest MgH_2 nanoparticle formation and possibly improved desorption kinetics
- Benchmarking DFT against QMC reveals significant errors that are non-systematic (H_2 desorption energies underpredicted by as much as 30 kJ/mol)
- QMC predicts greatest effect of size is for extremely small particles; e.g. $(MgH_2)_n$, $n \leq 6$)
  - Much smaller than predicted by Wolfe construction approach and observed in experiments
  - Suggests factors other than electronic structure (e.g. surrounding chemical environment) influence stability
- New NanoPEGS code developed and tested for MgH_2 particles
- New mass spec tool (STMBMS) reveals key details of hydrogen desorption process