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High Throughput Screening of Nanostructured Hydrogen Storage Materials

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Project Started September, 2005

2006 DOE Hydrogen Program Review
May 16 to 19, 2006

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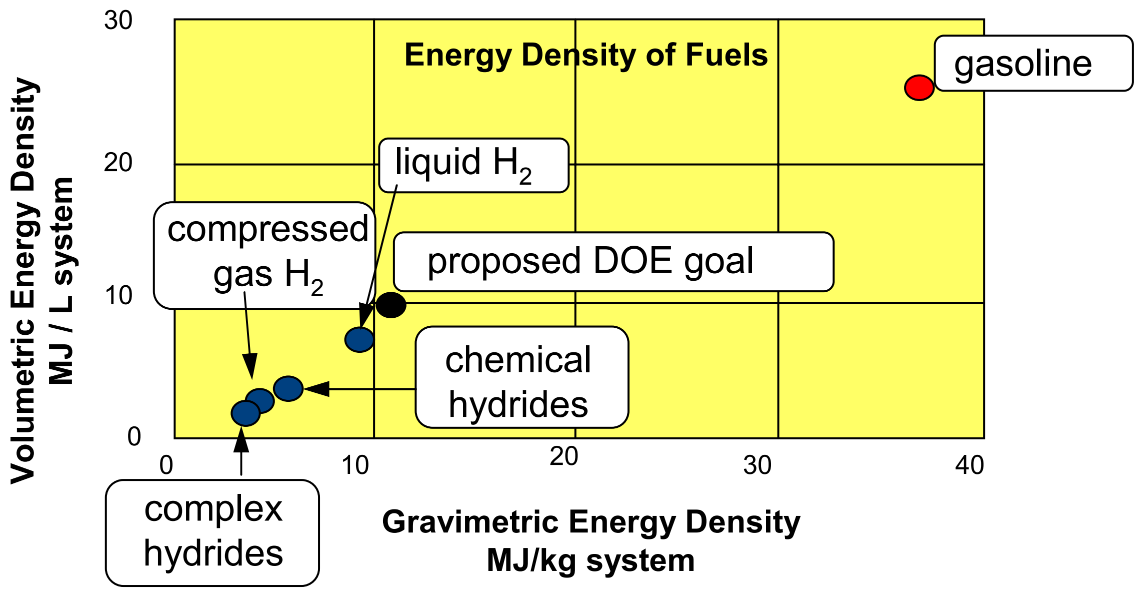
Hydrogen Storage: Challenges



Our Goals:

- Increase storage capacity
- Speed up transport (hydriding and dehydriding time)
- Study thermodynamics (to increase efficiency and improve thermal management)
- Study heat transfer

Heat Transfer Issues

- Hyriding reaction: ~1 MW for 5 min.
- Excessive temperature rise suppresses hydriding reaction.

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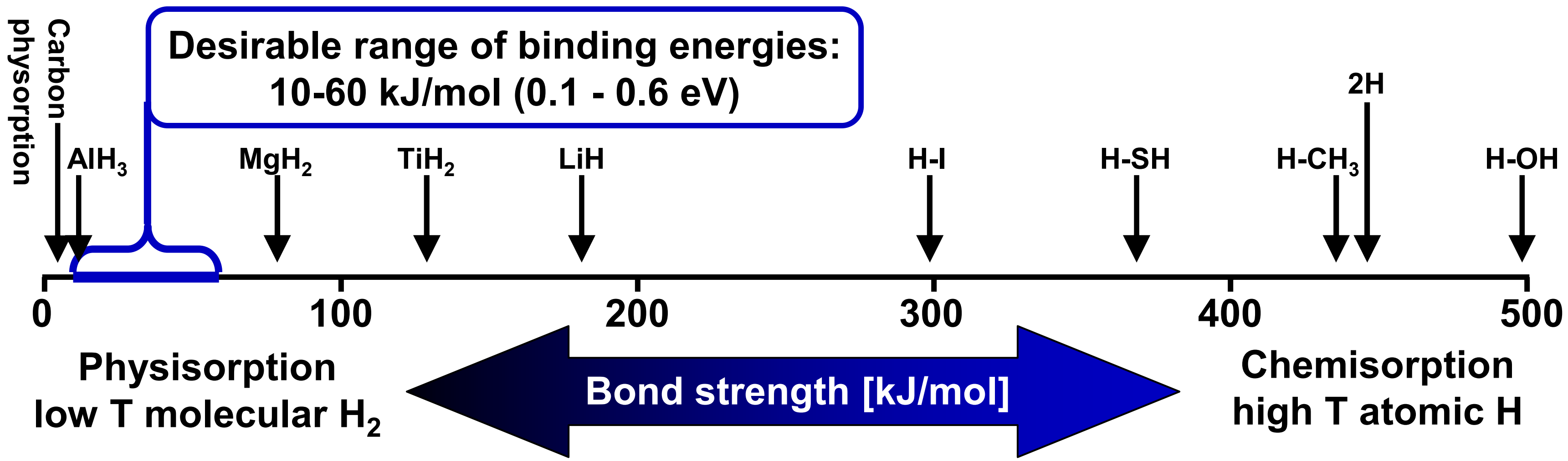
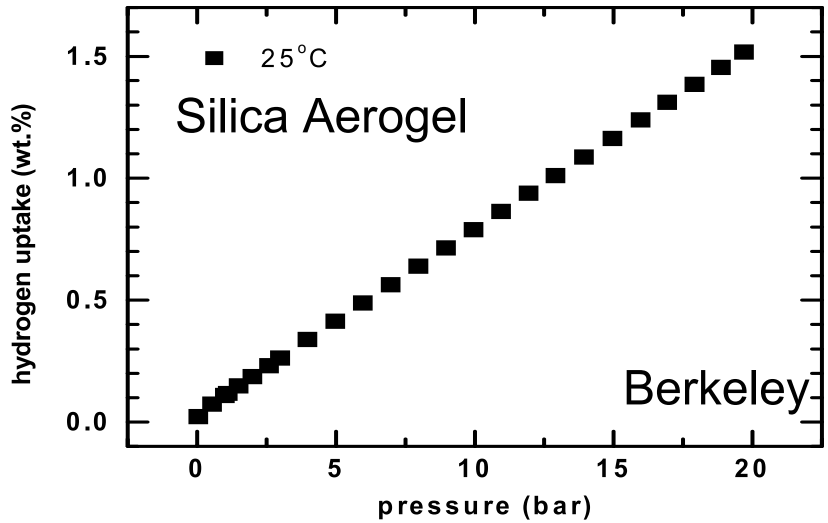
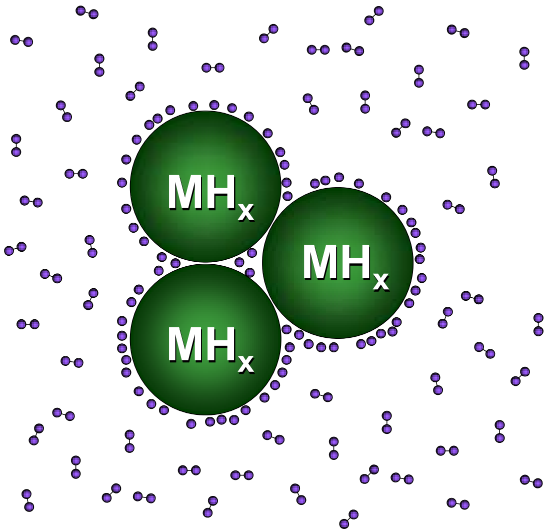
Binding Energy Range







Chemi+Physi Sorption

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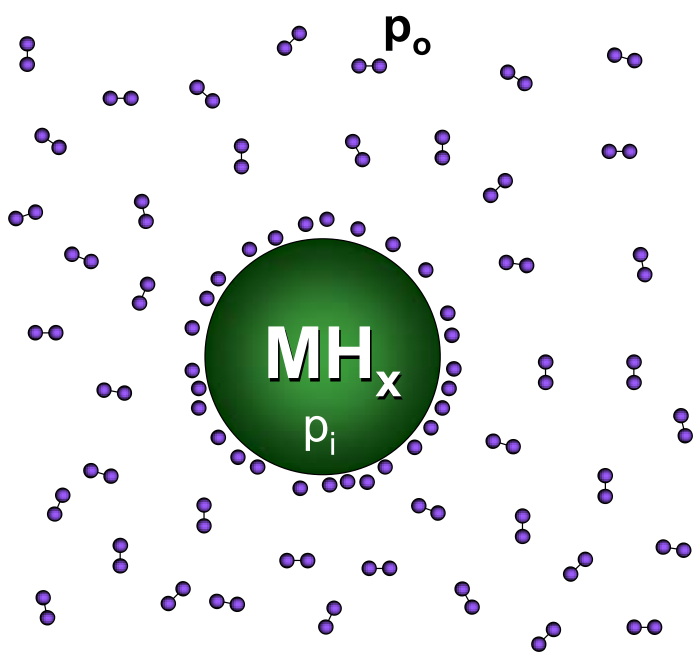
Benefits of Nanostructures

- Increase kinetics: diffusion time ~ radius square/diffusivity
- Possibility of co-existence of chemi- and physi-sorption
- Possibility of changing thermodynamic properties



- **Yang's Equation:**

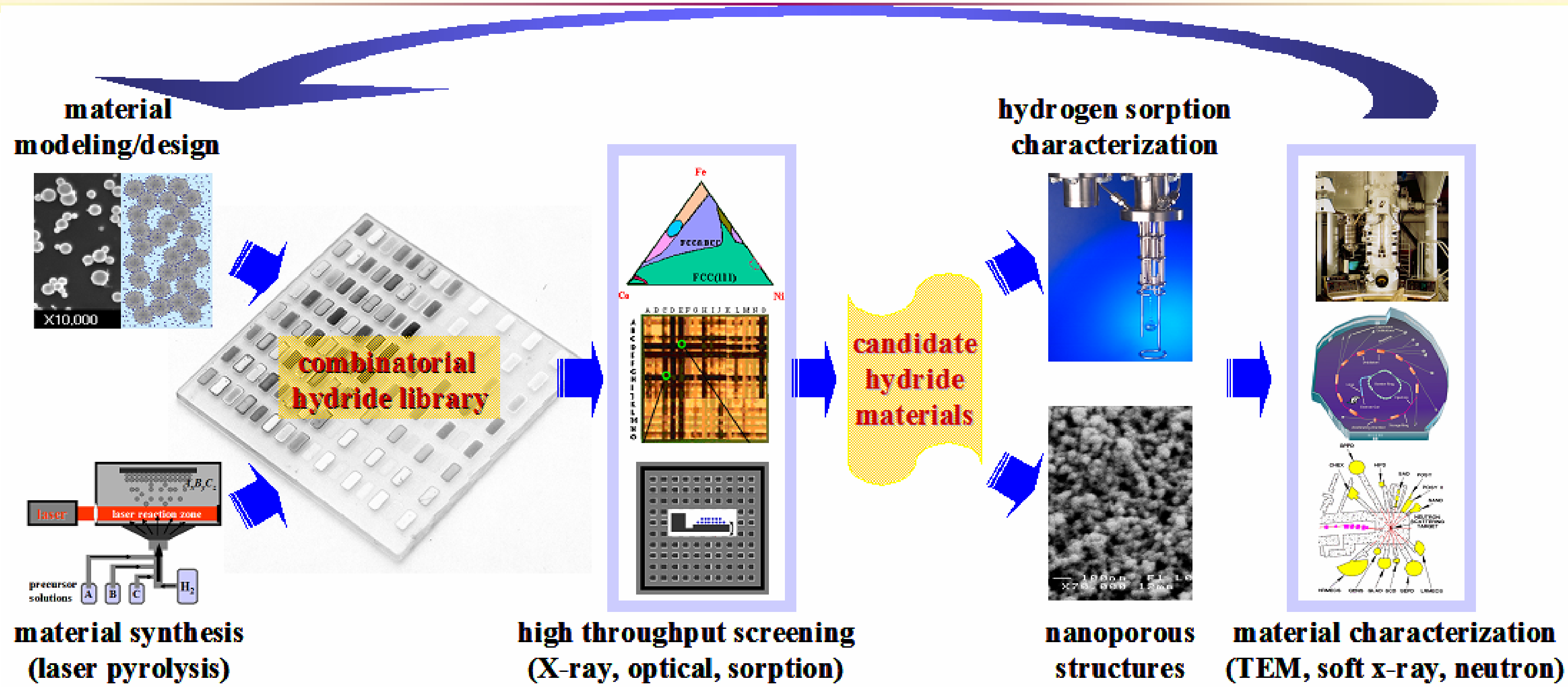
$$p_i - p_o = \frac{2\sigma}{r}$$

2σ ← Surface Tension

r ← Radius

- **Kelvin Theory:**
  - For multiphase system, transition temperature, equilibrium pressure and enthalpy of reaction change with radius.
  - For hydride, we can expect similar dependence in release temperature, equilibrium pressure and enthalpy of formation.

Proposed Approaches



Key Strategies:

- Destabilize materials: nanostructures synthesized by laser pyrolysis
- Combinatorial synthesis: search large phase space
- Nanostructures for both chemi- and physi- sorption coexistence
- Size effects: to modify thermodynamics and transport
- Address thermal conductivity reduction at nanoscale

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Teaming and Interactions

Team Members:

- G. Chen, mass and heat transport, thermodynamics
- M.S. Dresselhaus, electronic structure, physisorption
- C. Grigoropoulos, characterization, fabrication
- S. Mao, characterization
- X.D. Xiang, combinatorial synthesis
- T.F. Zeng, nanoporous structures

Collaboration

- Group meetings, Weekly at MIT and Berkeley
- Team meetings: physical (2) and teleconference (4)
- Individual visits, students exchanges
- Exchange of reports, meeting notes and research advances occurring elsewhere
- Daily email communication

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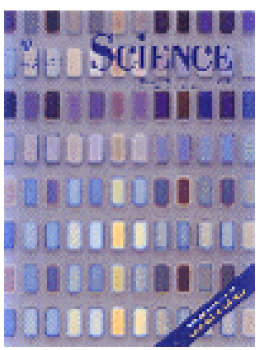
Combinatorial Material Screening

Materials Fabrication

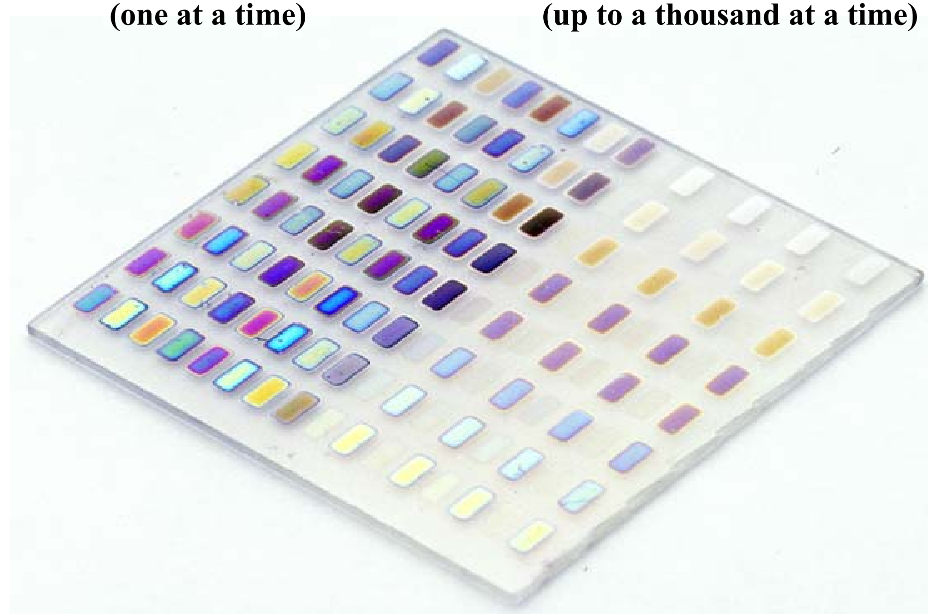
Proof of concept



***Science* 268**, 1738 (1995).

Series Process vs. **Parallel Process**

(one at a time) **(up to a thousand at a time)**



Metal and complex hydride materials

Combinatorial Nano-particle Discovery Engine™ (CNP)

- Capable of synthesizing nano-particles of metals, metal alloys and hydrides
- Reproducible high crystalline quality nanoparticles synthesized with narrow size distribution (< ±30%)
- Controllable process for combinatorial synthesis of nano-particle libraries with adjustable parameters:
  - particle size
  - material composition
  - synthesis conditions

Equipment at Intematix

Library of Nanoparticles with Narrow Size Distribution

Injection Rate (Frequency/Pulse Duration)

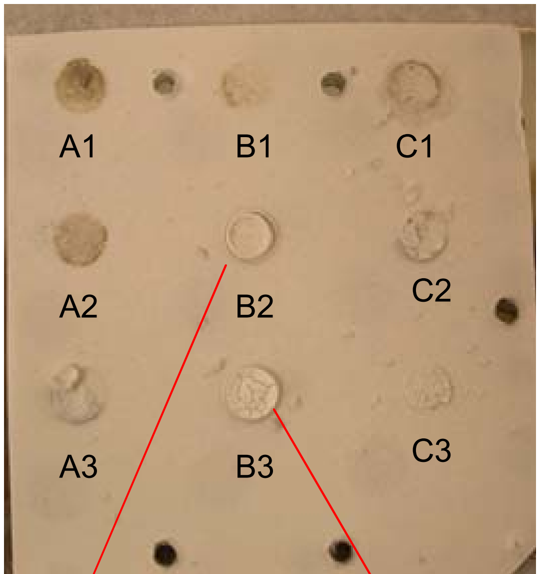
1Hz/0.5ms 2Hz/0.5ms 3Hz/0.5ms

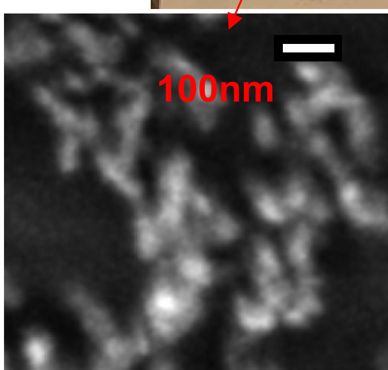
Laser Power

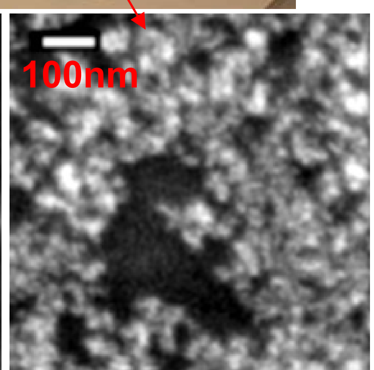
130W

190W

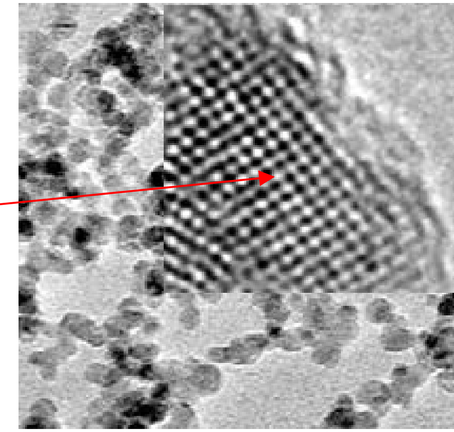
230W

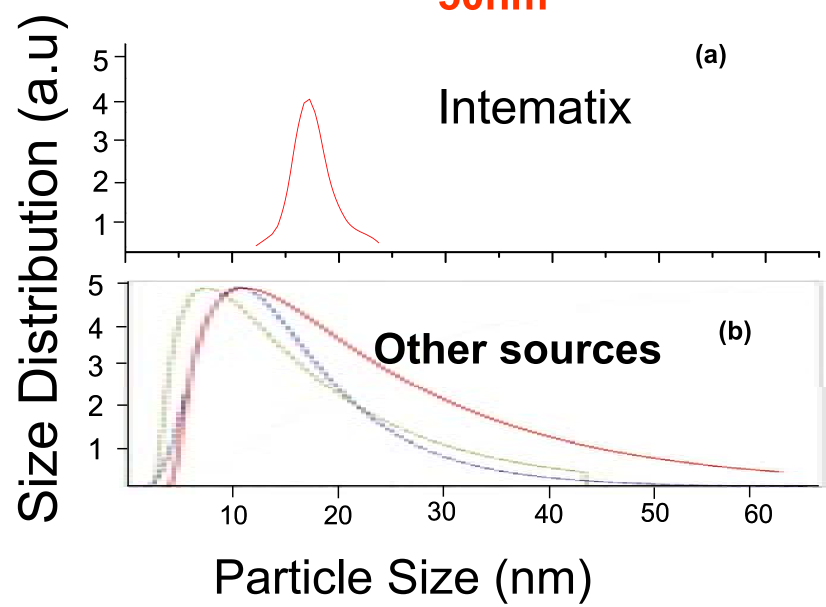






Atomic imaging





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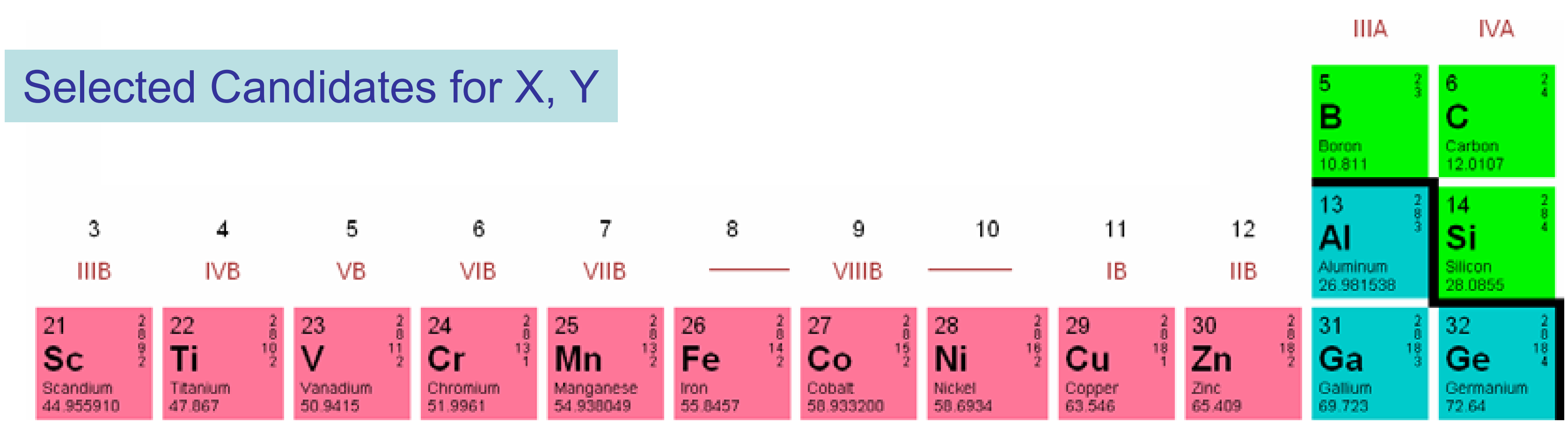
Start: Mg-X-Y System

- High hydrogen storage capacity (MgH_2, 7.7 wt% H_2)
- Hydrogen release temperature (T_r) (1 atm H_2 at 300°C) provides enough range in T_r for destabilization while T_r is not too high for direct dehydrogenation
- Example: Literature shows some improvement by Ni destabilization (Mg_2Ni, 2.5-3.2 atm H_2 at 300°C)



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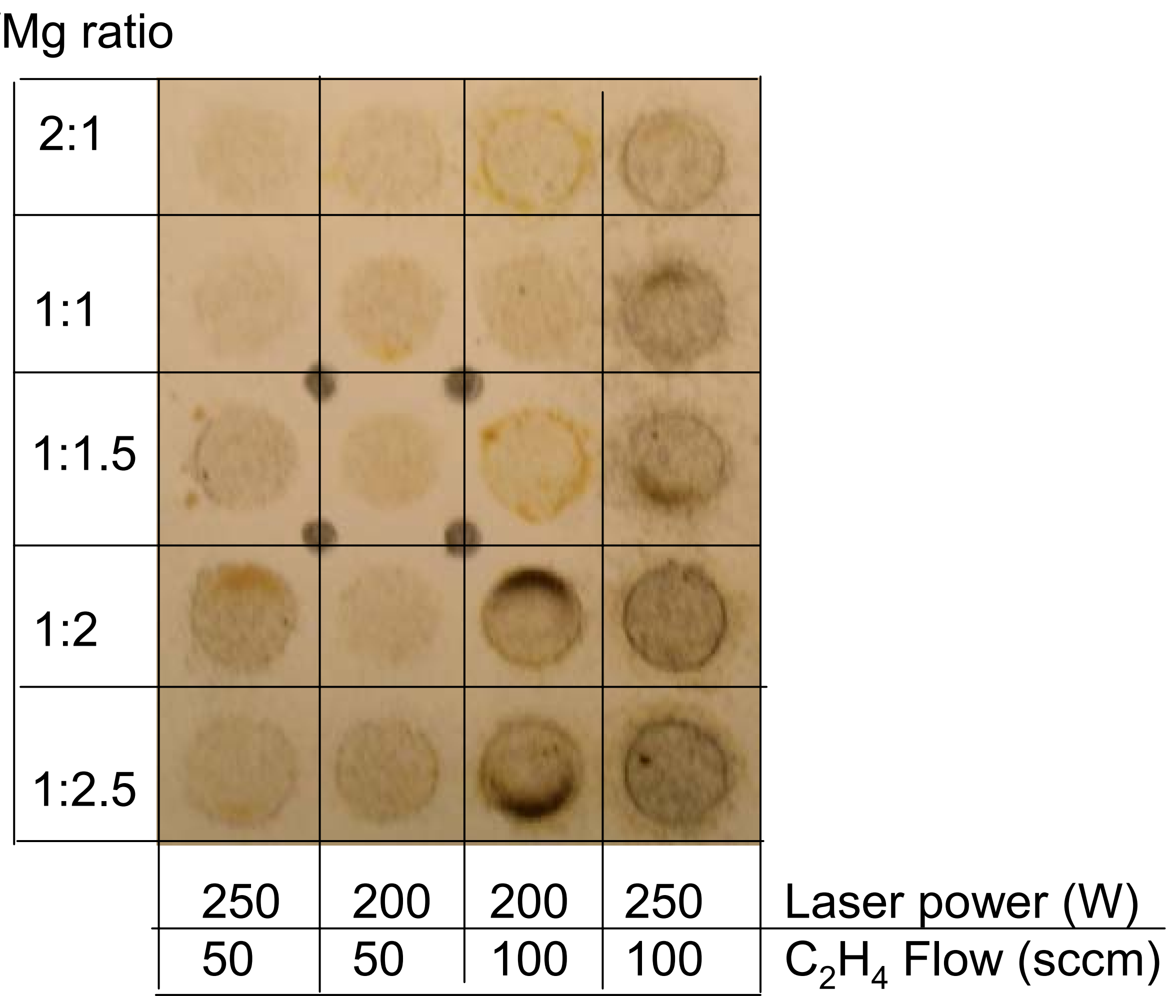
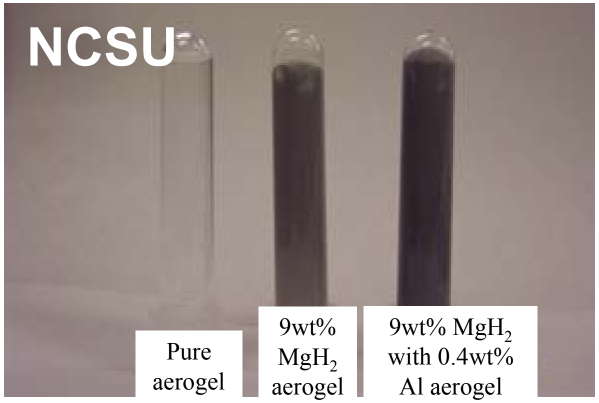
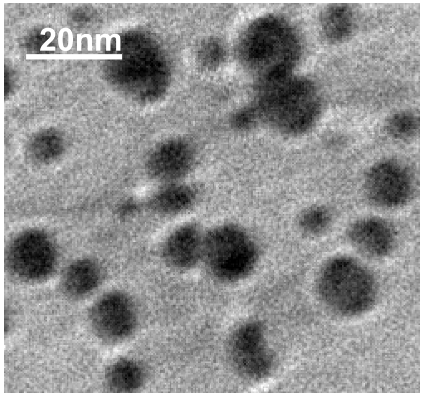
Mg-Ni Metal Hydride Library



MgH_2 in Aerogel Form

- Incorporation of MgH_2 into a nanoporous silica aerogel increases diffusion and prevents particle sintering
- Possibility of simultaneous chemi- and physi- sorption





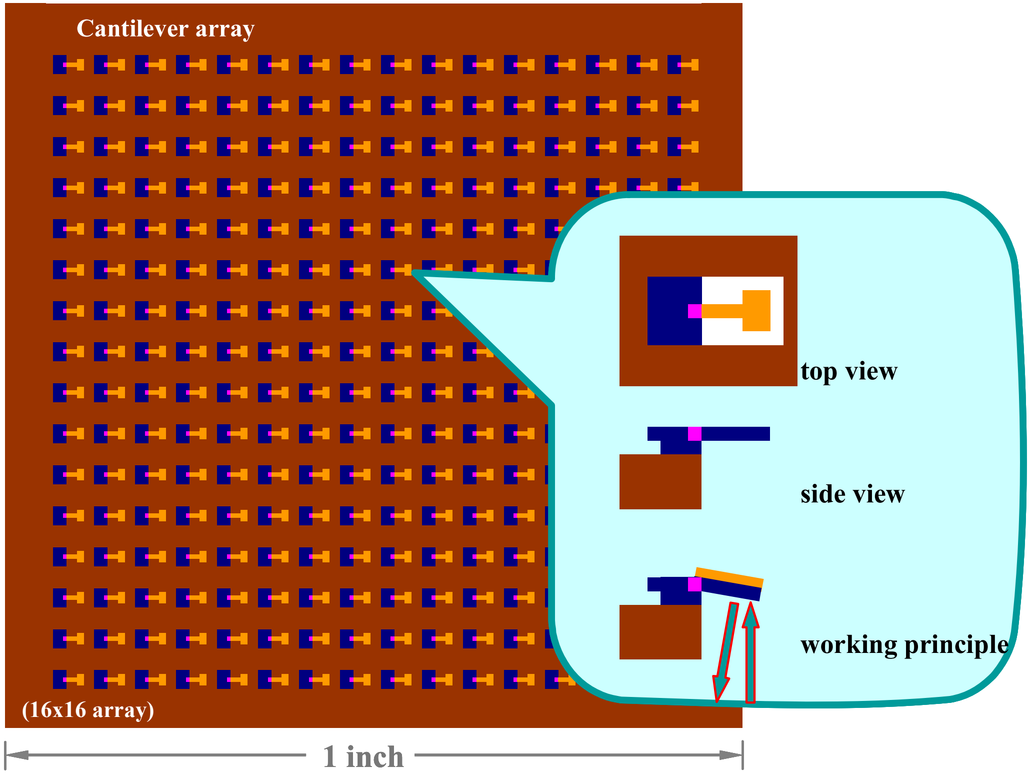
Ni nanoparticles

- Synthesized silica aerogel with surface area 1,100 m^2/g
- Modified a well established aerogel synthesis route to prevent MgH_2 decomposition
- Incorporate nanoscale catalyst into aerogel
- Also used laser to deposit MgNi into aerogel

Screening of Combinatorial Library

- X-ray analysis
- Infrared Imaging
- Pump-and-Probe
- Cantilever Arrays

Change in natural frequency of oscillation offers direct measurement of hydrogen intake.



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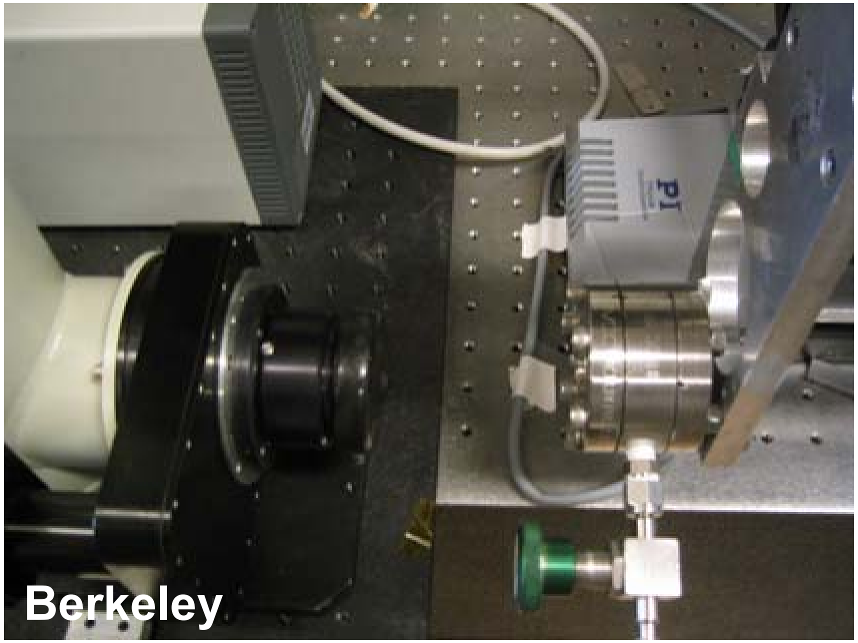
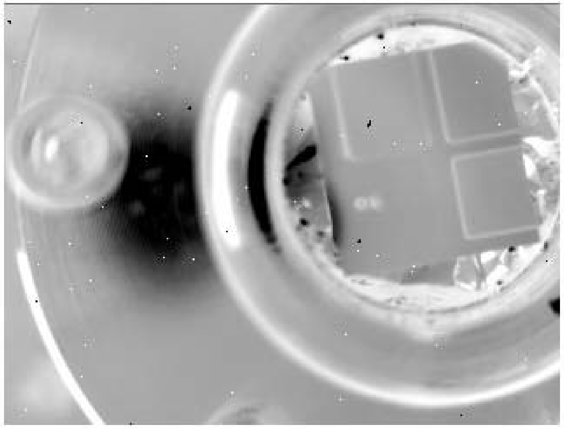
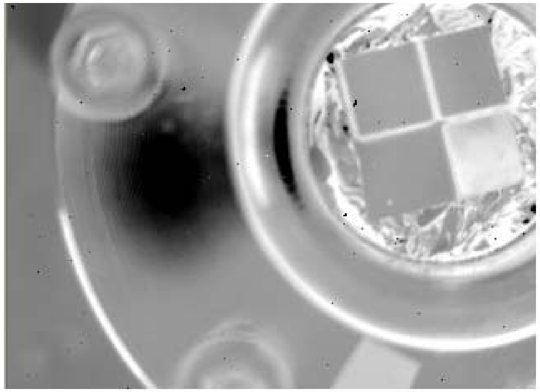
IR Imaging





Before



After

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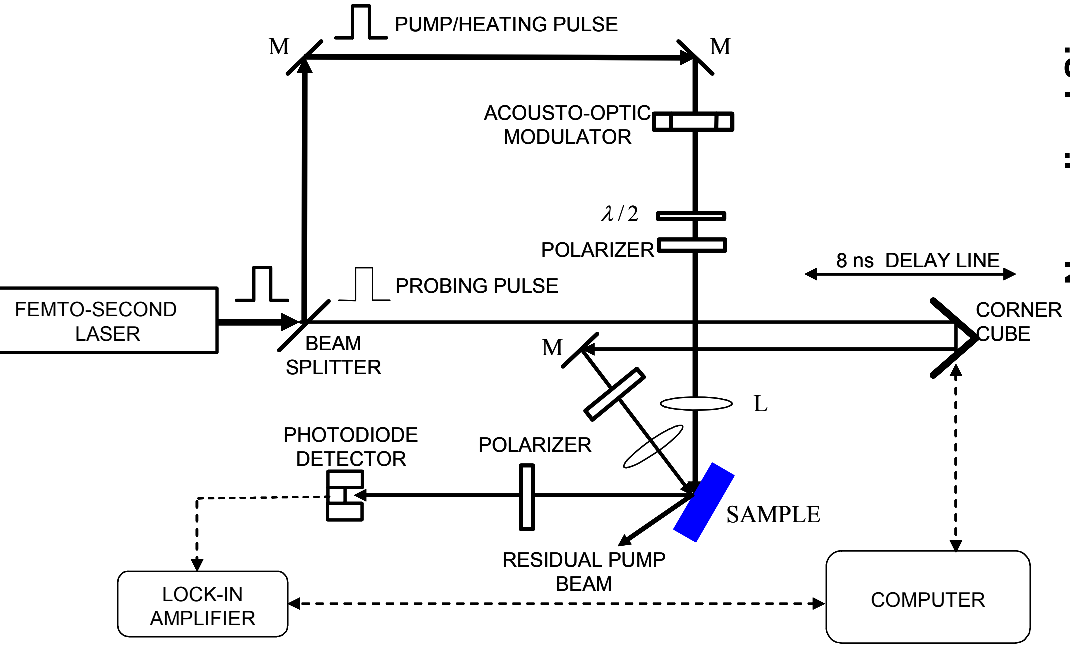
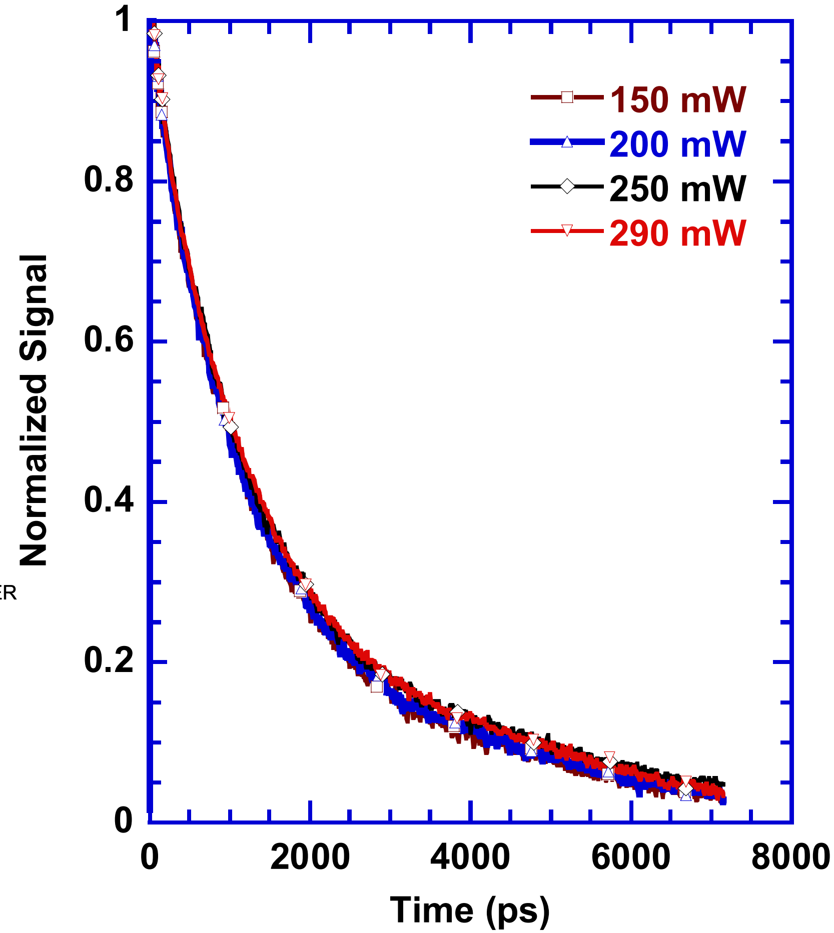
Pump-and-Probe Technique





Properties of interest: (a) thermal conductivity, (b) specific heat

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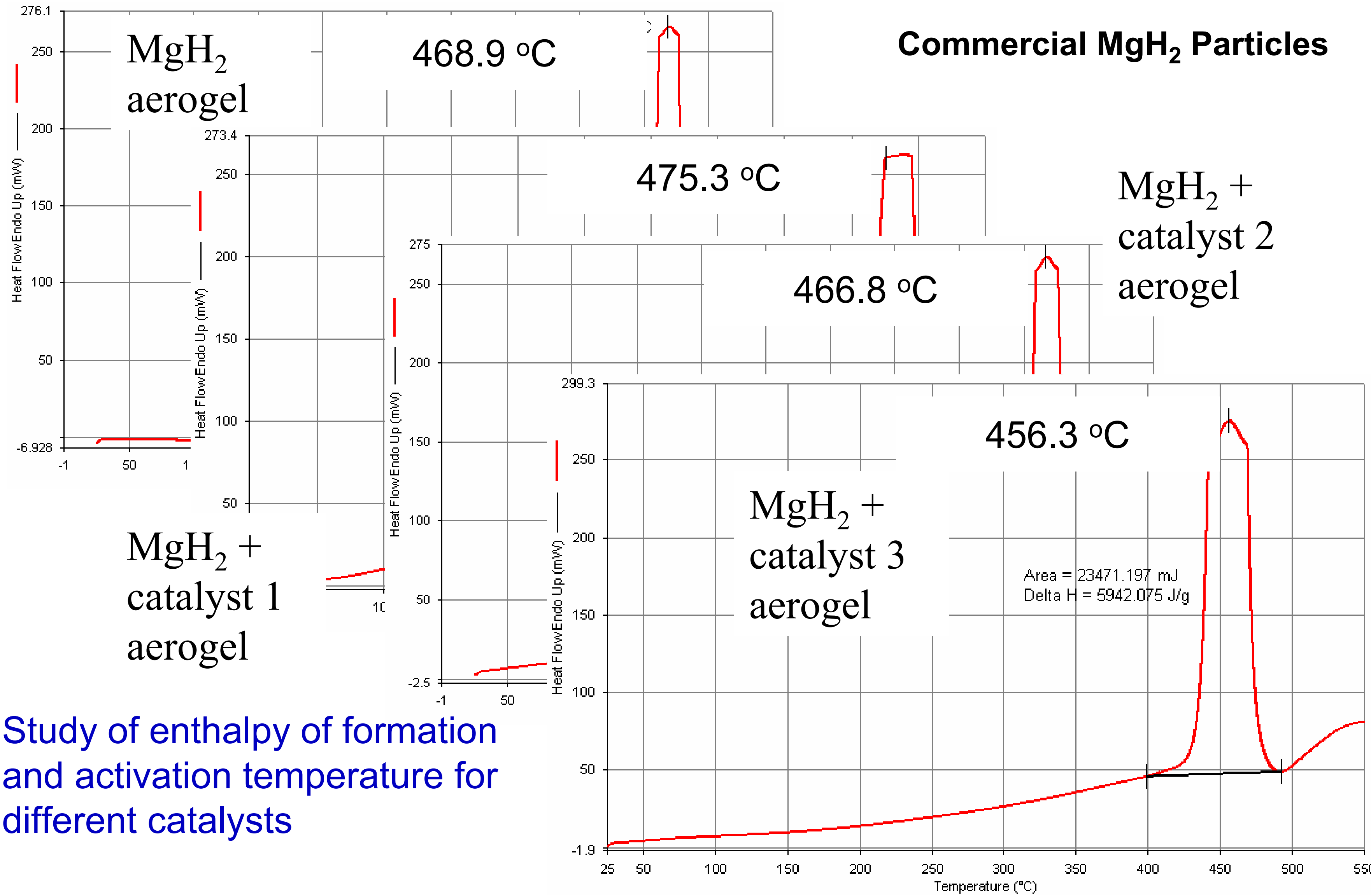
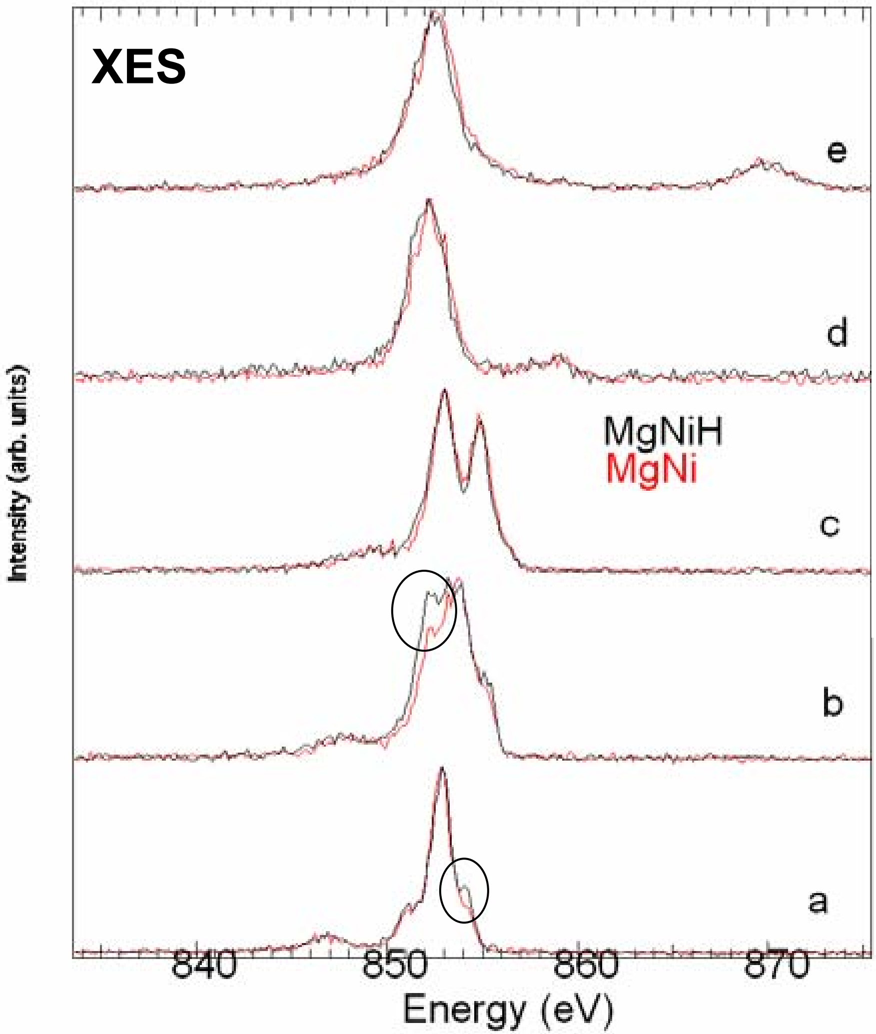
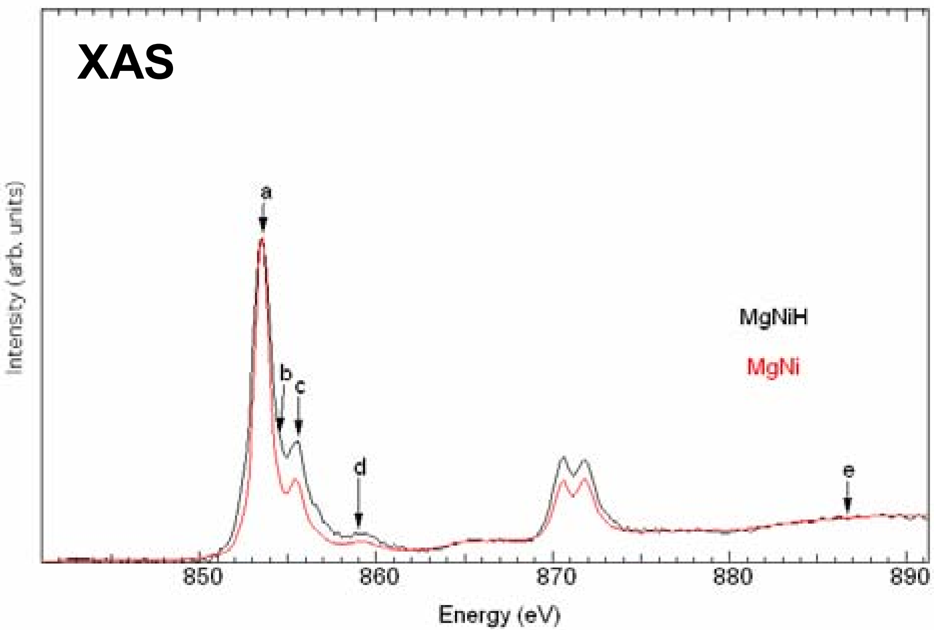
Differential Scanning Calorimetry



Study of enthalpy of formation and activation temperature for different catalysts

X-Ray (Synchrotron) Spectroscopy

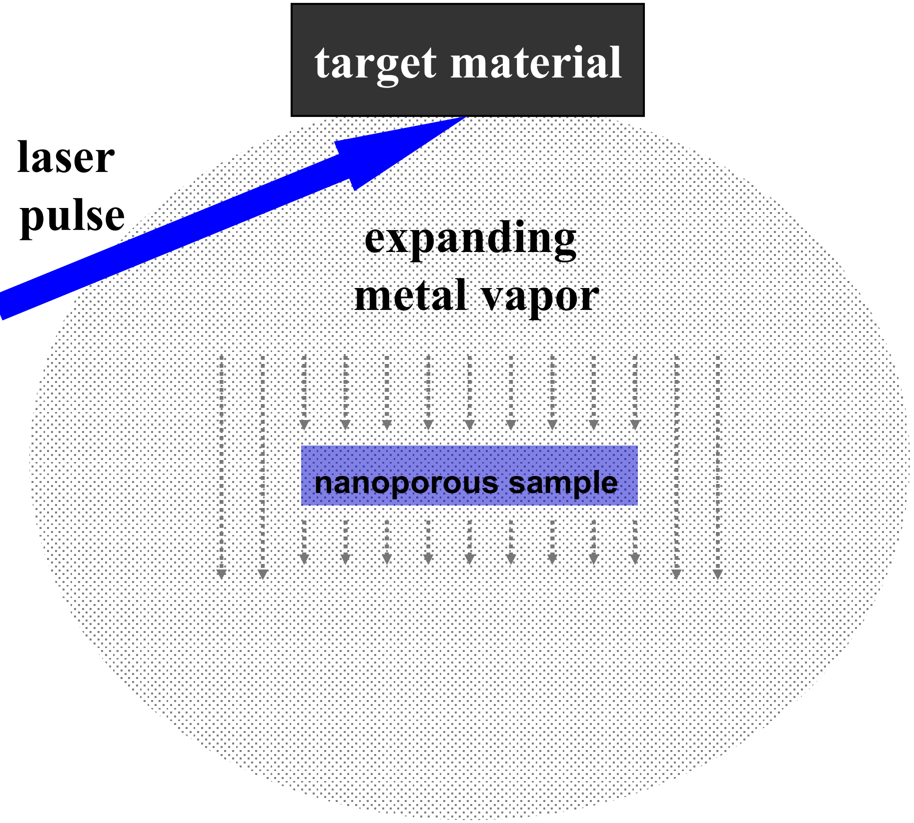


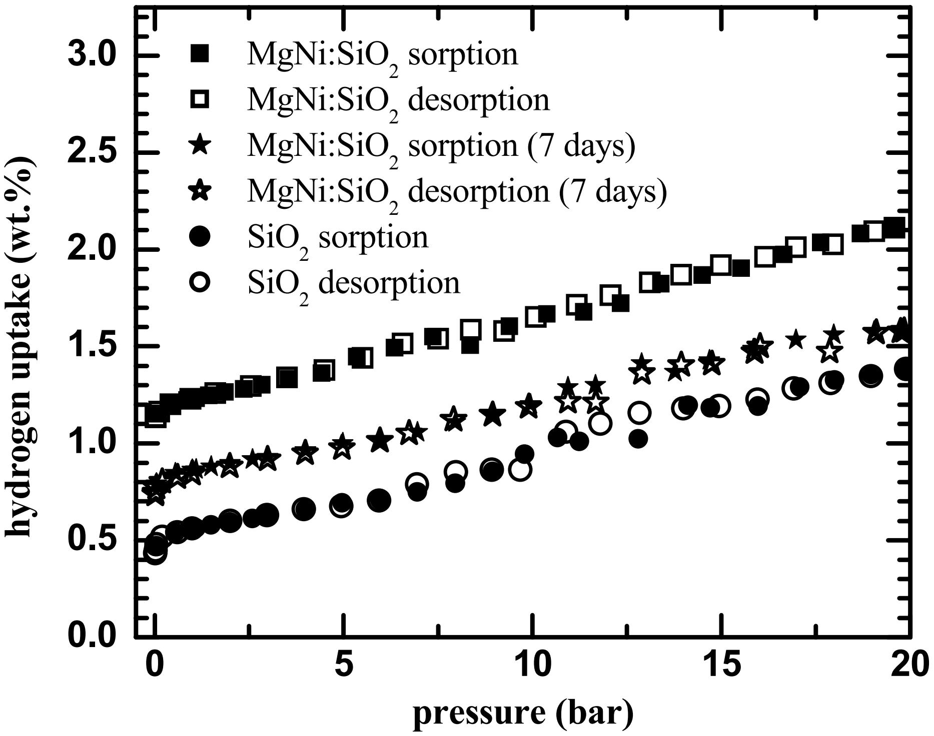


- Resonant Inelastic X-ray Spectroscopy (RIXS) used to excite specific core electrons (a, b, c, etc. from XAS plot).
- Some small differences were noted after hydride formation, but spectra strongly resemble NiO (J. Phy. Soc. Japan, 70, 1813)
- Need to repeat experiment with pure samples for more accurate results

DOE User Facility, ALS at LBNL

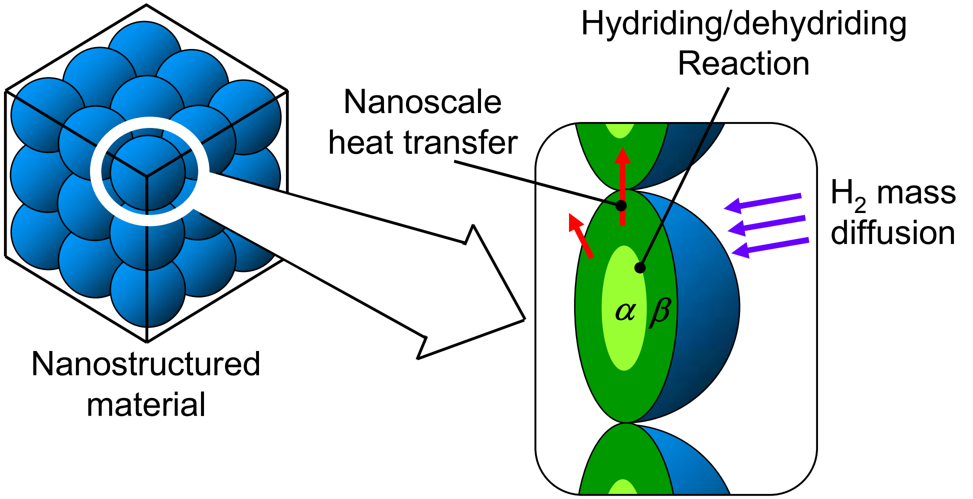
In-Situ Deposited MgNi

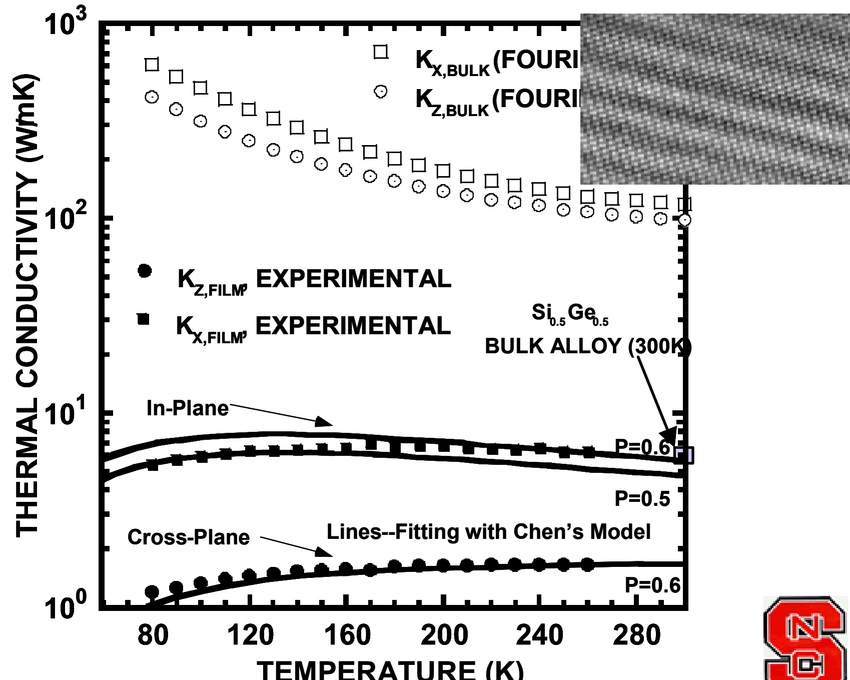




Mass and Heat Transfer

- Diffusion limited hydride reaction.
- Optimal pore and particle sizes: balance pore diffusion and diffusion in the solid particle to control kinetics.
- The strongly exothermic hydriding reaction increases the sample's temperature which reduces the reaction rate or even stops the reaction altogether.
- Rapid hydriding reaction thus requires effective heat removal solution.
- Nanostructures usually have poor heat transfer characteristics. Therefore, we need to balance mass diffusion kinetics with heat transfer.





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Size Effects on Thermodynamic Properties

Assuming the following reaction

$$M + H_2 \rightarrow MH_2$$

- At nanoscale, surface and size affect reaction enthalpy.
  - Increase the surface to volume ratio.
  - Increase adsorption sites due to low coordination surface atoms.
  - Lower binding energy in small metallic clusters.

Bulk molar free energy of formation

$$\Delta G = \Delta G_o + RT \ln\left(\frac{a_{MH}}{a_M P_{H_2}}\right)$$

Van't Hoff relation

$$\ln P_{H_2}^{eq} = \frac{\Delta H_o}{RT} - \frac{\Delta S_o}{R}$$

Nanoparticle molar free energy of formation

$$\Delta G(r) = \Delta G_o(r) + RT \ln\left(\frac{a_{MH}}{a_M P_{H_2}}\right) + \frac{3\overline{V_M}\Delta_{M\rightarrow MH}(\gamma, r)}{r}$$

$$\Delta_{M\rightarrow MH}(\gamma, r) = (\gamma_{MH}(r)\left(\frac{\overline{V_{MH}}}{\overline{V_M}}\right)^{2/3} - \gamma_M(r)) + E_{adsorption}$$

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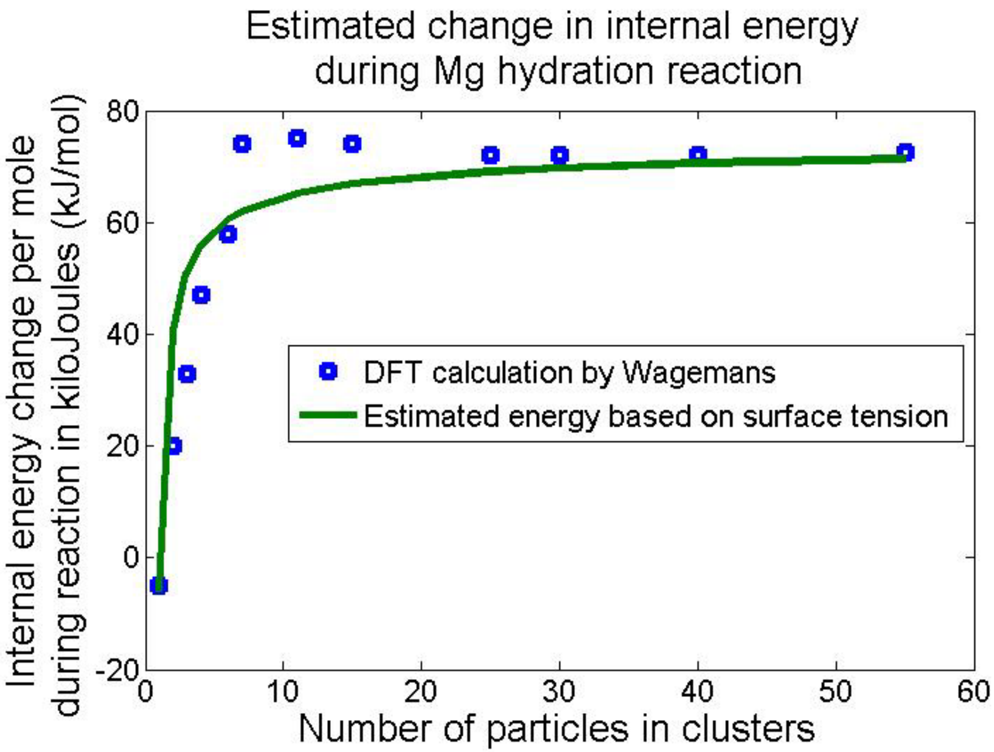
Modeling DFT Results

- If internal energy dependence on radius is all contained in the surface energy term

$$\Delta E(r) \approx \Delta E_{Bulk} + \frac{3\overline{V_M}\Delta_{M\rightarrow MH}(\gamma, r)}{r}$$

- Following Tolman's work, surface tension is allowed to vary with radius

$$\Delta = \frac{\Delta_o}{1 + \frac{a}{r}}$$

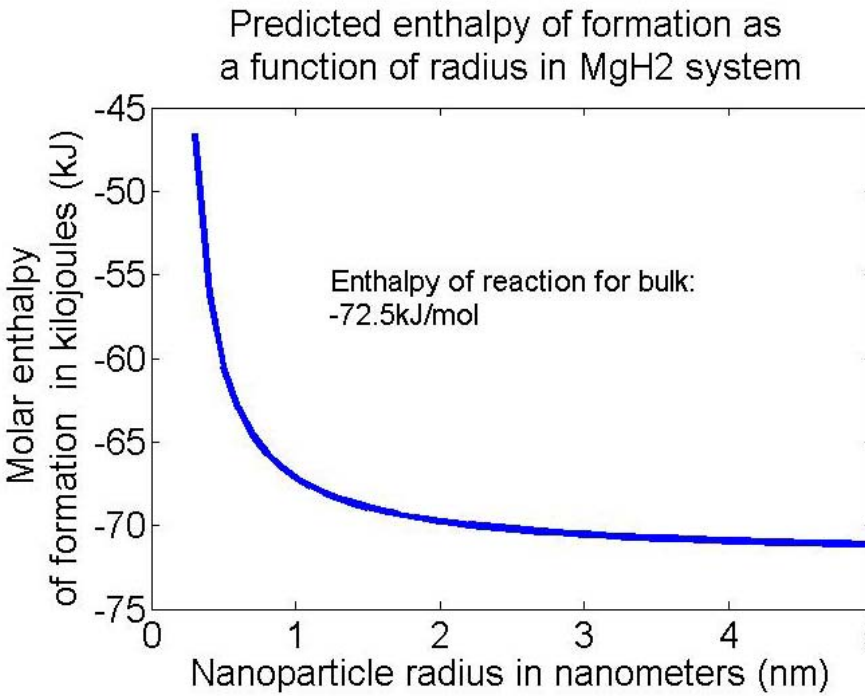


DFT values of internal energy calculated by Wagemans et al. J.Am. Chem. Soc. 2005, 127

Enthalpy of Reaction

$$\ln P_{H_2}^{eq} = \frac{\Delta H_o}{RT} + \frac{3\overline{V}_M \Delta_{M\rightarrow MH}}{rRT} - \frac{\Delta S_o}{R}$$

$$\Delta H_{eff} = \Delta H_o + \frac{3\overline{V}_M \Delta_{M\rightarrow MH}}{r}$$



- **Nanoparticles with positive Δ will have**

Lower equilibrium temperature
Less heat release during hydrogenation

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Summary

Major Work Carried Out Since 09/05

1. **Synthesis**
   - Synthesized Mg-Ni libraries
   - Incorporated metal hydrides into aerogel
2. **Characterization**
   - Developing fast characterization tools
   - Aerogel + MgNi sorption and desorption data suggests simultaneous physi- and chemi-sorption
   - Synchrotron XAS and XES analysis of samples
3. **Modeling**
   - Theoretical studies of size effects on transport and thermodynamics

Future Plan

1. Synthesis
   - Improve laser based synthesis method
   - Continue synthesis of Mg-X-Y library and other libraries
   - Incorporate hydride nanoparticles in aerogel
   - Developing nanoporous composites of nano-catalysts along with hydride nanoparticles
2. Characterization
   - Continue developing characterization tools (IR, XAS, XES, pump and probe, cantilever analysis)
   - Continue characterizing samples
3. Modeling
   - Continue developing transport and thermodynamics models, and incorporate heat transfer considerations
   - Carry out first principles calculations to study the effect of size on key parameters