

Chemical Hydrogen Storage using Ultra-High Surface Area Main Group Elements

(part of the DOE Chemical Hydrogen Storage
Center of Excellence)



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Project ID #
STP 6

Overview--Innovation Beyond Boron

Timeline

Project Start Date: FY05

Project End Date: FY09

New Start

Budget

- Total project funding
 - DOE share
 - Contractor share \$0.5 M
- Funding received in FY04 \$0.0
- Funding for FY05
\$100K (DOE) \$ \$20K (cost share)

Barriers

- Cost
- Weight and volume
- Hydrogen capacity

Targets

- Gravimetric capacity: >8%

Direct Collaborators

- Participant in the DOE Chemical Hydrogen Storage Center of Excellence
- LANL, PNNL, Penn, Alabama

Innovation Beyond Boron

To develop low cost synthetic routes to light element nanoparticles and compounds that meet or exceed the DOE goals for hydrogen capacity.

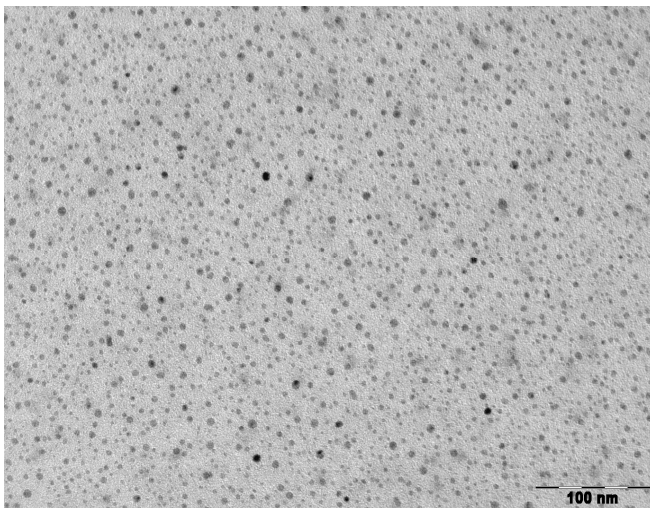
- We propose to develop a simple syntheses of small (less than 4 nm) light element nanoparticles (Si, B, Al, and alloys thereof) with hydrogen and amine capped surfaces.
 - Synthesize nanoparticles of the composition $\text{Si}_{1-x}\text{M}_x$ (M = B, Al) and terminate them with hydrogen or amine surface groups.
- We propose to synthesize light element main group hydrides.
 - Synthesize novel main group boron nitride and phosphide compounds.

Objectives--Innovation Beyond Boron

- To develop the synthesis of small nanoparticles of light elements, $\text{Si}_{1-x}\text{M}_x\text{H}$ and $\text{Si}_{1-x}\text{M}_x(\text{NH}_2)$, ($\text{M} = \text{B}, \text{Al}$) and explore their use for reversible hydrogen storage. (collaborative with LANL)
- To develop the synthesis of hydrogen substituted H_xBN and H_xBP species for polymerization studies in collaboration with other Center members (collaborative with LANL, Penn, Alabama).

Premise--Innovation Beyond Boron

- Chemical hydrogen storage using small light element nanoparticles.
 - Low cost
 - High hydrogen capacity

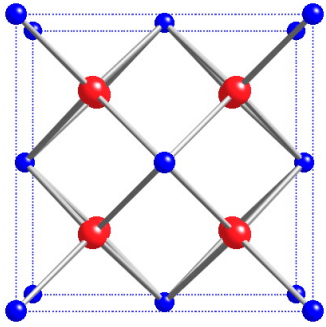


Bright field TEM image of Si nanoparticles.*

1 nm particle has the approximate relative stoichiometry of SiH (hydrogen weight % 3.4). With increasing x , $\text{Si}_{1-x}\text{B}_x\text{H}$, hydrogen weight % increases to 8.5%

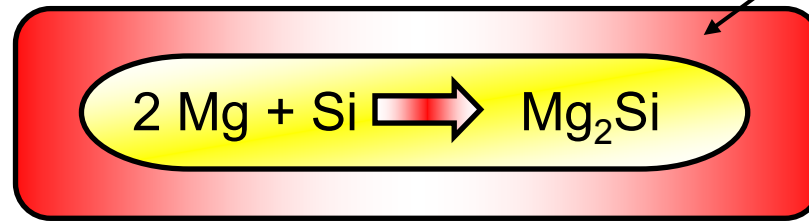
*Zou, J., Baldwin, R. K., Pettigrew, K. A., and Kauzlarich, S. M. *Nano Letters*, 4:1181-1186 (2004).

Synthesis of Mg₂Si



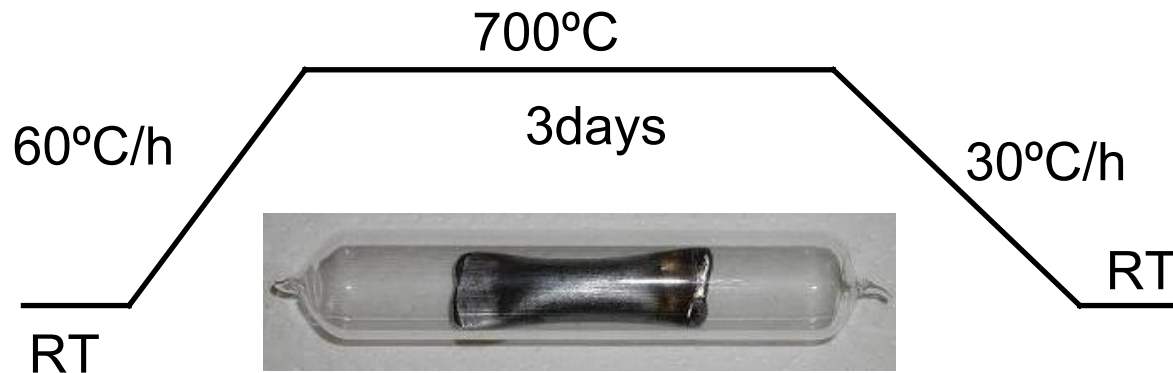
z
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Structure of Mg₂Si



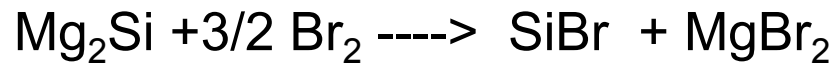
Etched Ta ampoule
Length ~70 mm

Fused Silica sealed
under 1/5 atm Ar



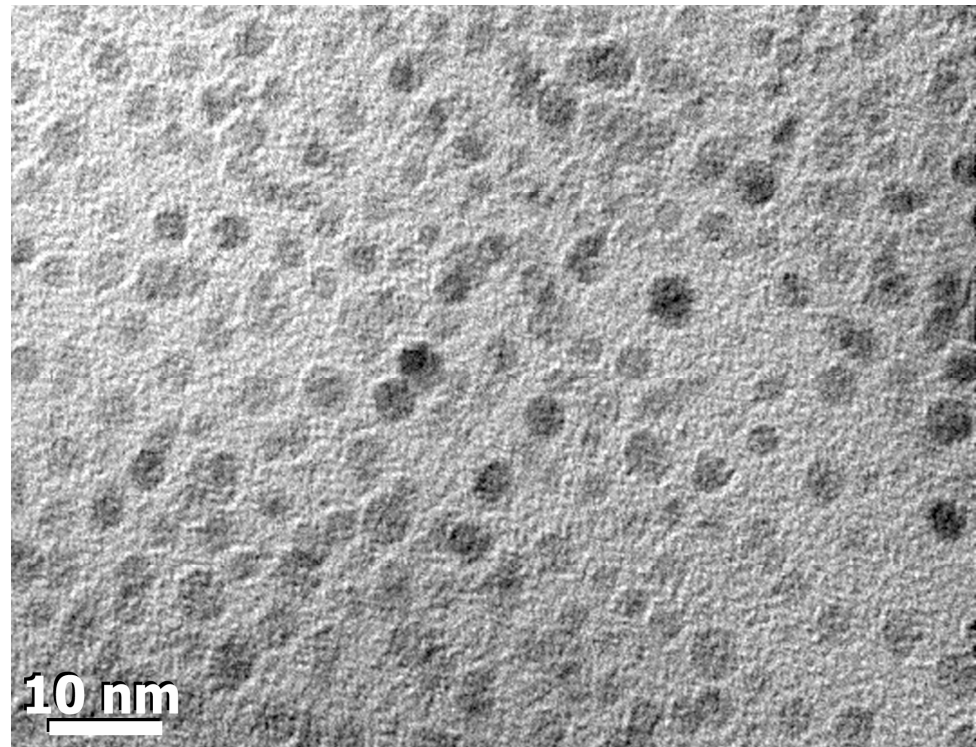
Synthesis of 4 nm SiH Nanoparticles

Proposed:

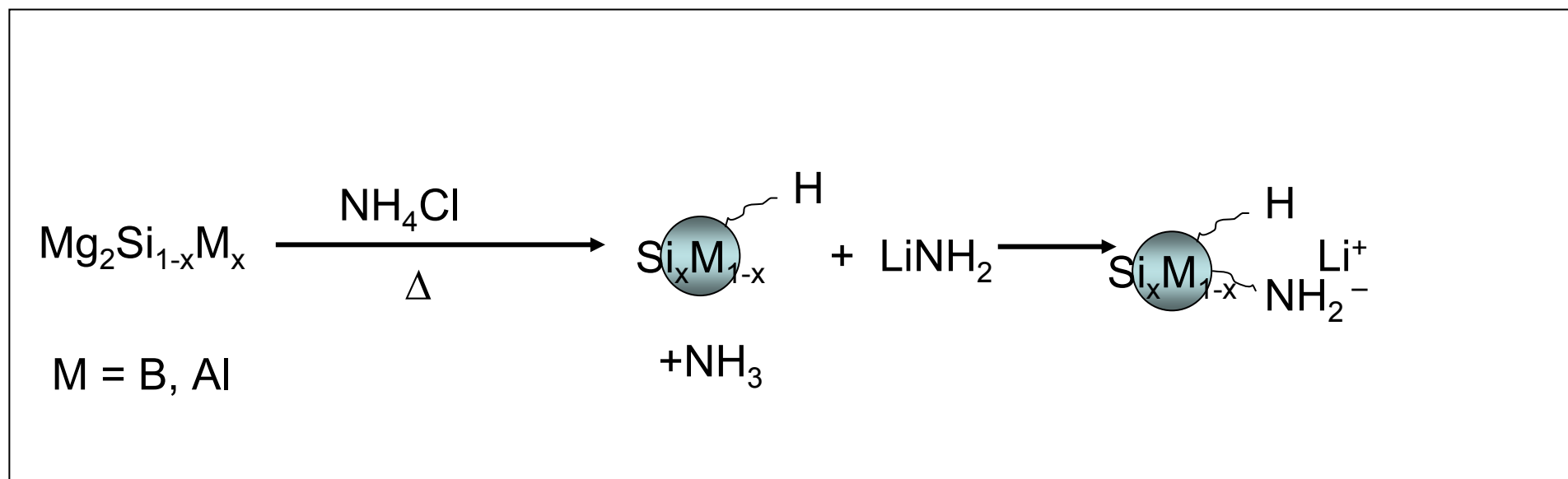


Based on:

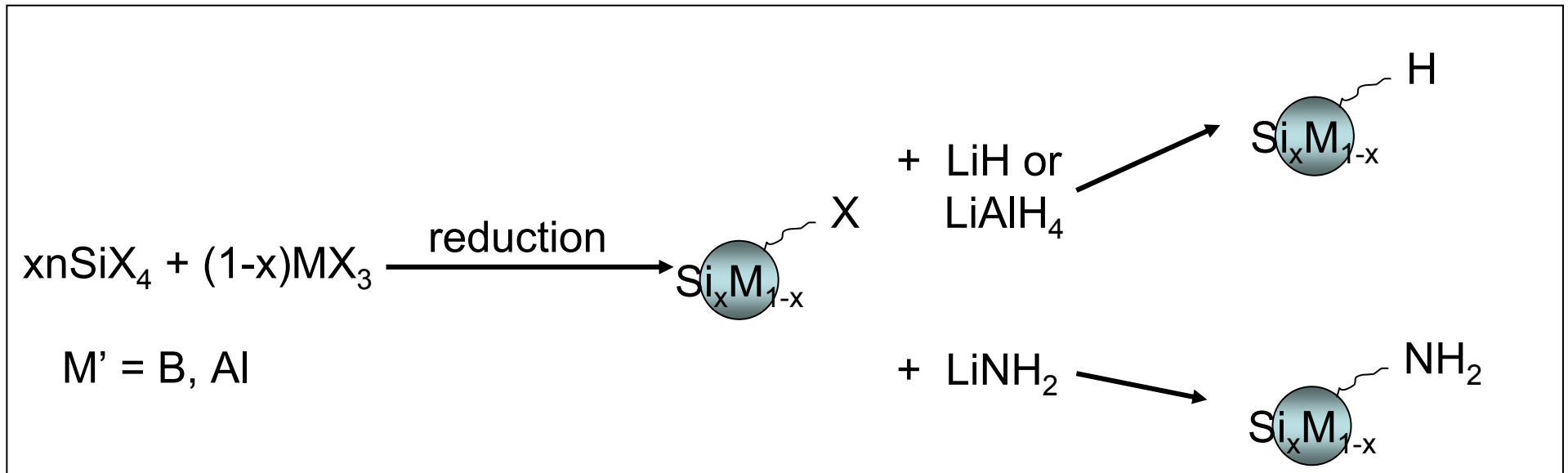
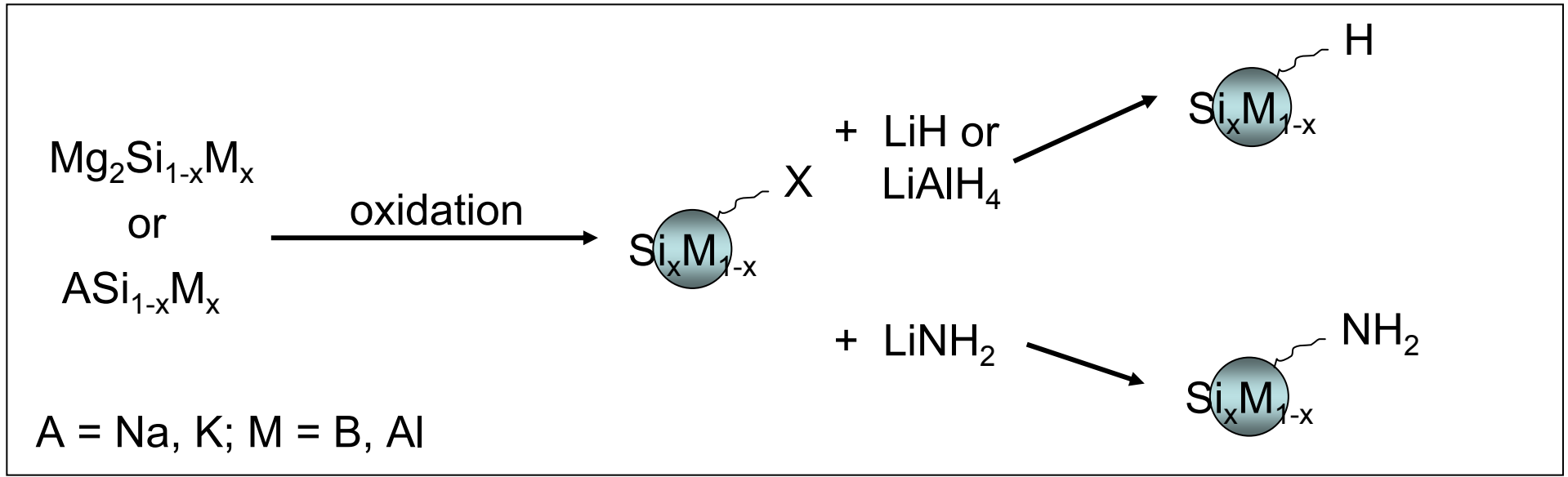
Pettigrew, K. A., Liu, Q., Power, P. P., and Kauzlarich, S. M. "Solution Synthesis of Alkyl- and Alkyl/Alkoxy-Capped Silicon Nanoparticles via Oxidation of Mg_2Si ", *Chemistry of Materials*, **15**:4005-4011 (2003).



Synthesis of $\text{Si}_{1-x}\text{M}_x\text{H}$ and $\text{Si}_{1-x}\text{M}_x(\text{NH}_2)$ ($\text{M} = \text{B}, \text{Al}$) Alloy Nanoparticles

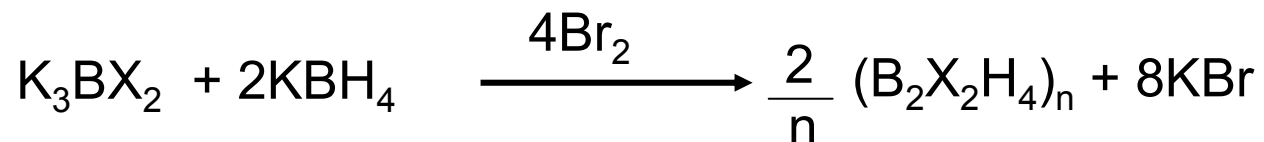
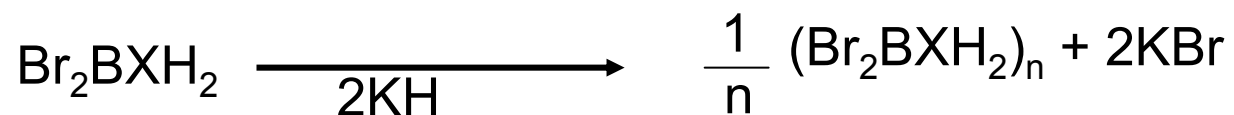
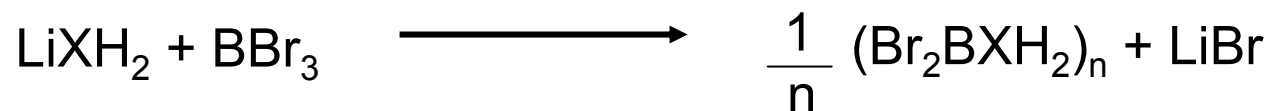


Synthesis of $\text{Si}_{1-x}\text{M}_x\text{H}$ and $\text{Si}_{1-x}\text{M}_x(\text{NH}_2)$ ($M = \text{B, Al}$) Alloy Nanoparticles



By varying M and x , H wt percents of 8% may be obtained (no H_2O)

H₂BXH₂ (X = N, P) Synthetic Strategies



Year 1

- H and NH₂ capped Si nanoparticle synthesis and characterization. Surface reactivity as a function of particle size will be explored along with thermal analysis. The synthesis of alloy nanoparticles will be initiated.
- Main-group compound synthesis and characterization.

Safety Plan

- **Scope of Work**

- The first portion of the program is heavily focused on development and characterization of chemical compounds that have high gravimetric and volumetric storage densities for hydrogen. These compounds will in general be constructed of light elements such as B, Al, P, N, Li, Mg, and Si. In many cases, the compounds will be air sensitive and require handling as such. Initial efforts will involve very small amounts of material and relatively low degree of safety concern. At UC Davis in the research groups of Professors Power and Kauzlarich, handling of small amounts of material is routine practice and already covered in existing protocols at UC Davis.








- **Risk Mitigation Plan**

- The UC Davis Chemical Laboratory Safety Manual and Chemical Hygiene Plan template can be found at the UC Davis Environmental Health and Safety website:
http://ehs.ucdavis.edu/chem/chem_mnl/index.cfm.

Future Work

- FY05-06
 - Prepare hydrogen and amine terminated Si nanoparticles and characterize. Investigate alloy nanoparticle synthesis and characterize.
 - Prepare main group compounds and characterize.
- FY07
 - Determine the most promising composition with highest hydrogen gravimetric amount. Explore reaction mechanism and prepare materials in high yield.
- FY08
 - Provide materials to partners for testing.
- FY09
 - Optimize synthesis for further testing.

Future Work

Task	Year 1	Year 2	Year 3	Year 4	Year 5		
<p>Task 1: Nanoparticle Synthesis</p> <p>Synthesis of SiH and Si(NH₂) characterization of SiH and Si(NH₂) Synthesis of Si_{1-x}M_xH and Si_{1-x}MNH₂ Characterization of Si_{1-x}M_xH and Si_{1-x}MNH₂ composition and reactivity Optimization of reaction to provide material to partners</p>							
<p>Task 1: Main group Compound Synthesis</p> <p>Synthesis of (H₂BXH₂)_n characterization of composition and reactivity explore main group analogs</p>							
<p>Task 3: characterization and testing</p> <p>test reactivity and thermolysis of various alloys and main group compounds</p>	