Chemical Hydrogen Storage using Ultra-High Surface Area Main Group Elements
(part of the DOE Chemical Hydrogen Storage Center of Excellence)

Philip P. Power (pppower@ucdavis.edu) and Susan M. Kauzlarich (smkauzlarich@ucdavis.edu)
University of California
May 16, 2006

This presentation does not contain any proprietary or confidential information

Project ID #
STP 26
Overview--Innovation Beyond Boron

**Timeline**
- Project Start Date: FY05
- Project End Date: FY09
- 20% complete

**Budget**
- Total project funding
  - DOE share
  - Contractor share $0.5 M
- Funding for FY05
  - $100K (DOE) $20K (cost share)
- Funding for FY06
  - $193K (DOE) $40K (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
Objectives – Innovation Beyond Boron

Overall

• To identify hydrogen storage material enabling DOE targets and increase the understanding of synthetic approaches and physical properties of main group element clusters, such as Si, B, Al, and alloys thereof, BP and BN compounds.

2005-2006

• To design simple routes to such compounds using mild conditions to provide commercially viable materials.

• To investigate the viability of the synthesized materials for commercial application by studying weight and volume as well as the reversibility of hydrogen uptake.

2007-2009

• To analyze measurements to identify compounds that offer relatively lightweight, easily handled solid materials capable of hydrogen storage that are synthesized, activated and regenerated in a simple manner.
## Approach

<table>
<thead>
<tr>
<th>Methods</th>
<th>Synthesis</th>
<th>Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Utilize standard laboratory equipment to produce materials. Synthesis will ideally not require specialist equipment</td>
<td>Design mild routes to Si, B, Al alloys, BP and BN compounds otherwise produced under harsh conditions</td>
<td>Characterize the materials using common spectroscopic methods and investigate the production of hydrogen</td>
</tr>
</tbody>
</table>
Results

1) Room temperature synthesis of amide-capped silicon nanoparticles (Task 1)

2) Solution and solid-state synthesis of nanocrystalline silicon with hydrogen (Task 1)

3) First synthesis of organo-capped boron nanoparticles (Task 1)

4) Synthesis of molecular compounds by addition of hydrogen across a multiply-bonded system (Task 2)
$\text{Si}_x(\text{NH}_2)_n \rightarrow \text{Si}_x\text{N}_n + n\text{H}_2$

$\text{SiCl}_4 + \text{Na.naphthalenide} \xrightarrow{\text{glyme}} (\text{Cl})_n + \text{NaCl}$

$\text{(Cl)}_n \xrightarrow{\text{NH}_3 (g)} (\text{NH}_2)_n + \text{NH}_4\text{Cl}$
Results - 2

SiHₙ → Si + n/2 H₂

Solution Route

Solid State Route

CP $^{29}$Si NMR
Boron Nanoparticles

\[ \text{BBr}_3 + \text{Na.naphthalide} \xrightarrow{\text{glyme}} \quad \rightarrow \quad (\text{Br}_n) + \text{NaBr} \]

\[ (\text{Br}_n) \xrightarrow{\text{octanol(t)}} \quad \rightarrow \quad (\text{octaoxy})_n + \text{HBr} \]

Facile Activation of Dihydrogen by an Unsaturated Heavier Main Group Compound  
G.H. Spikes, J.C. Fettinger, P.P. Power JACS, 2005

\[
\begin{align*}
\text{Ar’GeGeAr’ (1) + 1H}_2 & \rightarrow 60\% \text{ Ar’GeGeAr’ (1)} & (1) \\
& + 21\% \text{ Ar’HGeGeHAr’ (2)} \\
& + 10\% \text{ Ar’H}_2\text{GeGeH}_2\text{Ar’ (3)} \\
& + 9\% \text{ Ar’GeH}_3 \quad (4)
\end{align*}
\]

\[
\begin{align*}
\text{Ar’GeGeAr’ (1) + 2H}_2 & \rightarrow 2\% \text{ Ar’HGeGeHAr’ (2)} & (2) \\
& + 85\% \text{ Ar’H}_2\text{GeGeH}_2\text{Ar’ (3)} \\
& + 13\% \text{ Ar’GeH}_3 \quad (4)
\end{align*}
\]

\[
\begin{align*}
\text{Ar’GeGeAr’ (1) + 3H}_2 & \rightarrow 65\% \text{ Ar’H}_2\text{GeGeH}_2\text{Ar’ (3)} & (3)
\end{align*}
\]

Crystal structure determined
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.
## Timeline

<table>
<thead>
<tr>
<th>Task</th>
<th>Year 1</th>
<th>Year 2</th>
<th>Year 3</th>
<th>Year 4</th>
<th>Year 5</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Task 1: Nanoparticle Synthesis</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Synthesis of SiH and Si(NH₂)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Characterization of SiH and Si(NH₂)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Synthesis of Si₁₋ₓMₓH and Si₁₋ₓMNH₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Characterization of Si₁₋ₓMₓH and Si₁₋ₓMNH₂ composition and reactivity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Optimization of reaction to provide material to partners</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Task 2: Main group Compound Synthesis</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Synthesis of (H₂BXH₂)ₙ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Characterization of composition and reactivity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>explore main group analogs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Task 3: Characterization and Testing</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Test reactivity and thermolysis of various alloys and main group compounds</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Summary

• Amide capped and hydrogen capped Si nanoparticles have been synthesized by two different low temperature routes.
• These nanoparticles have been shown to evolve substantial amounts of gas when heated.
• Boron nanoparticles capped with -OR groups have been synthesized by a low temperature route.
• H₂ has been shown to react with a “digermyne”, RGeGeR at room temperature and pressure.
Publication List

1. **Facile Activation of Dihydrogen by an Unsaturated Heavier Main Group Compound**  

2. **Nanocrystalline Silicon for Hydrogen Storage**  

3. **Room Temperature Synthesis of Surface-Functionalised Boron Nanoparticles**  