

IV.B.5f Chemical Hydrogen Storage using Ultra-High Surface Area Main Group Materials and The Development of Efficient Amine-Borane Regeneration Cycles

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- To synthesize and characterize compounds with E-H, E-NH₂, E-X (X= halogen or O) and E-C(O)H moieties (E=B, Al, Si, Zn) and investigate their interconversion.
- To use the synthetic and interconversion information to design a simple and efficient means of regenerating amine-boranes with use of element hydrides.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost
- (R) Regeneration Processes

Technical Targets

This project is conducting fundamental studies of light element nanoparticles and molecular compounds. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

- Cost: \$4/kWh net
- Specific energy: 2 kWh/kg
- Energy density: 1.5 kWh/L

The progress toward meeting these technical targets for hydrogen storage can be found in Table 1.

Objectives

- To identify light element nanomaterials and molecular compounds as storage materials enabling DOE targets to be met.
- To design and test simple routes to such materials and compounds using mild conditions.
- Optimize the synthesis and hydrogen capacity of these materials, while providing detailed physical characterization.
- Demonstrate the viability of the synthesized materials for commercial application by studying their weight and volume as well as mechanism of hydrogen release.

TABLE 1. Progress Toward Meeting Technical Targets for Hydrogen Storage

	4 nm Si/H	8 nm Si/H	10 nm Si/H	60 nm Si/H	2010 Center Goal
2010 System Gravimetric Capacity (6.0 wt%)	4.5 g H ₂ released/100 g	3.7 g H ₂ released/100 g	3 g H ₂ released/100 g	–	>6.0 wt% Phase I: Material Phase II: System-2010 Phase II: 9% Material-2015
2010 System Volumetric Capacity 0.045 kg/L	0.1 kg H ₂ /L laboratory vessel contents (4.5 g X 2.3 g/cm ³)/100 g	0.08 kg H ₂ /L laboratory vessel contents (4.5 g X 2.3 g/cm ³)/100 g	0.06 kg H ₂ /L laboratory vessel contents (3 g X 2.3 g/cm ³)/100 g	–	>0.045 kg/L Phase I: Material Phase II: System-2010 Phase II: 0.060 Material-2015

Accomplishments

- Identified low temperature synthetic route to different size hydrogen terminated silicon nanoparticles.
- Demonstrated hydrogen desorption upon heating with preliminary thermal gravimetric and mass spectrometry measurements.
- Prepared B and C doped alkali metal silicides as precursors to produce B and C doped Si nanoparticles.
- Provided samples to Rohm and Haas for testing their potential for sodium borohydride regeneration.
- Synthesized and spectroscopically characterized amide, hydride and formate derivatives of the Me_2B -ligand platform.
- Demonstrated conversion of both the hydride and amide to formate and quantitative yield.
- Synthesized and spectroscopically characterized a zinc hydride (X-ray structure) and amide. Their conversion to formate has been spectroscopically verified.



Introduction

This project is focused on the design and synthesis of light element compounds and nanomaterials that will reversibly store hydrogen. The large surface area of nanoparticles should facilitate a favorable weight to volume ratio, and low molecular weight elements such as boron, nitrogen and silicon exist in a variety of inexpensive and readily available precursors. During this phase, we concentrated primarily on the synthesis and characterization of hydrogen capped silicon nanoparticles. In addition, the scope of the work was realigned to include regeneration processes. The new scope includes providing new materials, compounds, and support for chemical regeneration of amine-boranes or boron amides from B-X (X= halide or oxide) compounds.

Approach

The UC Davis group divides its efforts between the synthesis of light element nanomaterials as hydrogen storage materials and synthesis of such materials for possible regeneration of boron containing chemical hydrides such as sodium borohydride. As Tier III, beyond boron, we are synthesizing and

characterizing new materials. We are working with other Chemical Hydrogen Storage Center of Excellence (CHSCoE) partners such as Pacific Northwest National Laboratory, Los Alamos National Laboratory, and Rohm and Haas to test the materials. We have recently revised our scope to reduce the amount of effort on nanomaterials and realign towards new compounds capable of recycling ammonia borane in an efficient manner. The new scope adds the synthesis and characterization of compounds with E-H, E-NH₂, E-X (E = halogen or O), and E-C(O)OH moieties (E = B, Al, Si, or Zn containing groups). Their interconversion under mild reaction conditions will be investigated with the object of creating a simple chemical cycle to regenerate E-N bonds that will facilitate the storage of hydrogen.

Results

We have prepared silicon nanoparticles by a low temperature high yield method. We have been able to show that reaction conditions, such as temperature, time and composition, can be controlled to produce various sizes of hydrogen capped Si nanoparticles as either crystalline, amorphous, or mixtures of both. Figure 1 shows powder X-ray diffraction data for four different samples, along with the corresponding scanning electron microscopy (SEM) or transmission electron microscopy (TEM) images. The particle size for Figure 1a based on the powder X-ray pattern full width at half maximum of the 28.7° 2θ peak is 60 nm. The

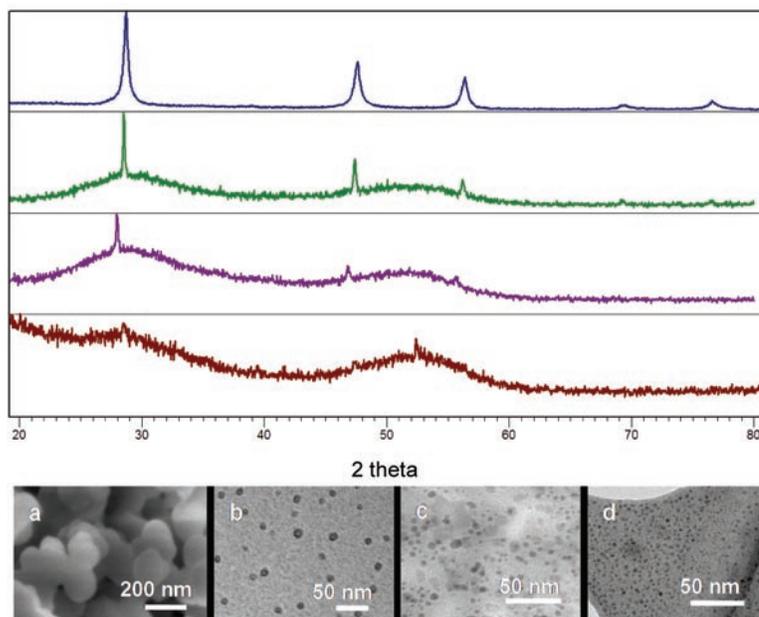


FIGURE 1. Power X-Ray Diffraction and Particle Images for Materials Prepared with Different Parameters: (a) 60 nm (SEM) (b) 11 nm (TEM) (c) 8 nm (TEM) and (d) 4 nm (TEM) Diameter Nanoparticles

SEM image, Figure 2a, is consistent with such a particle size and the particles are spherical. The powder X-ray diffraction data for the Figure 1b sample show that this material is a mixture of amorphous and crystalline silicon. The amorphous silicon peaks are broad and can be seen at 28° and 49° 2θ , and the crystalline silicon diffraction peaks are at 28.7° , 47.5° , 56.5° , 69.3° and 76.6° corresponding to [111], [220], [311], [400], and [331] Miller indices. The X-ray powder pattern data show that the sample (Figure 1c) prepared in solution is a mixture of amorphous with crystalline silicon and the sample (Figure 1d) is amorphous. The average particle size of these nanoparticles was measured from TEM data and found to be 8 and 4 nm, respectively. Solid state ^1H and ^{29}Si nuclear magnetic resonance (NMR) data were obtained and are consistent with hydrogen capped silicon nanoparticles. Fourier transform infrared (FTIR) spectroscopy data confirm the presence of hydrogen on the surface of these particles. The broad peak at $1,100\text{ cm}^{-1}$ is the asymmetric stretching mode of Si-O-Si in the case of the 60 nm and 11 nm particles. These results show that the samples are very oxygen sensitive and,

while careful handling can reduce the amount of oxide on the surface, all samples showed some oxidation. The solvent systems do not show the same sensitivity to oxygen, presumably because they are protected from further oxidation through some Si-OR linkages also seen in the ^1H and ^{29}Si cross polarization magic angle spinning NMR data. Thermogravimetry/mass spectroscopy (TG/MS) under flowing He data confirm the desorption of hydrogen upon heating (Figure 2). The data show initial weight loss with a rise in the hydrogen MS signal. The data shown here support our surface area-hydrogen content correlation in that the smaller particles have the biggest weight loss. These results are in the process of being written up for publication.

We have investigated the synthesis and characterization hydrocarbon soluble formate derivatives of boron and zinc. The most straightforward synthetic routes to these involve the use of previously known aryl element halides as starting materials. Early attempts to convert the halides directly to the formate yielded multiple products and incomplete conversion. However the halides can be converted in high yield to their

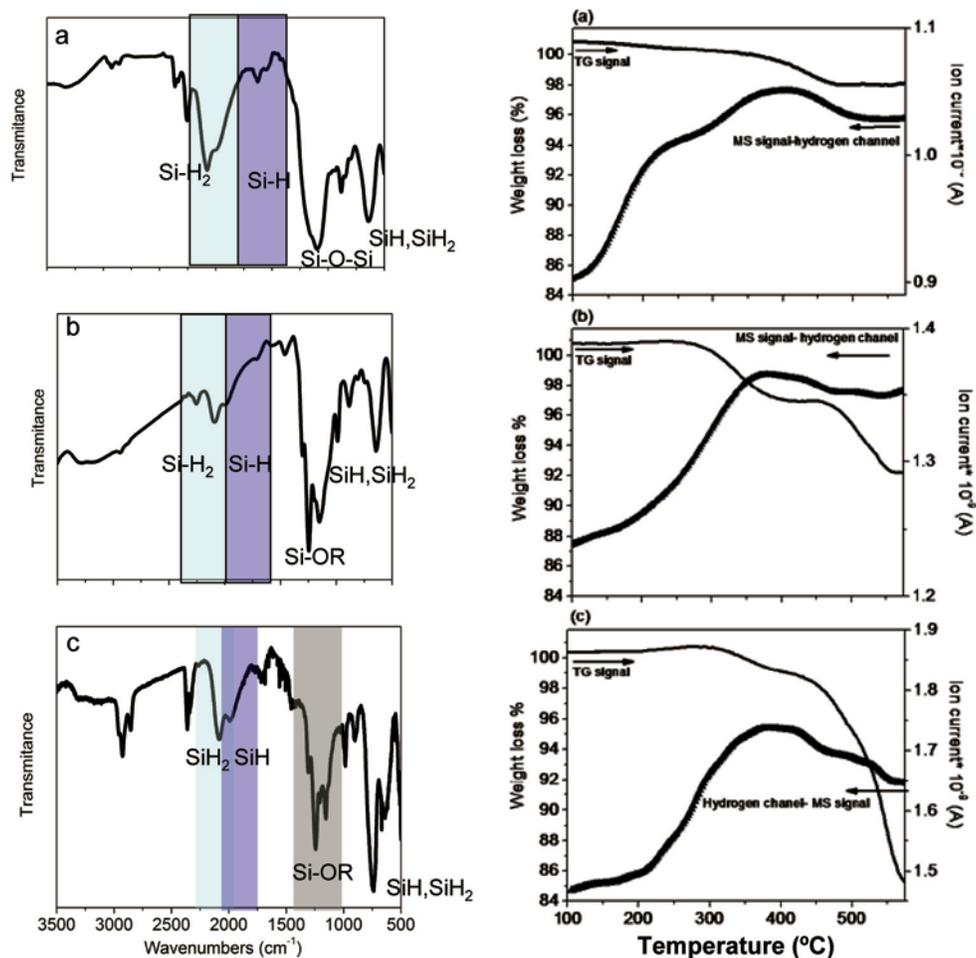


FIGURE 2. FTIR Spectra and TG/MS for (a) 11 nm (b) 8 nm and (c) 4 nm Diameter Nanoparticles

hydride or amide derivatives. These, upon treatment with formic acid, afford the corresponding formate derivatives. In the case of boron they have been spectroscopically characterized (Figure 3). Crystals of formate derivatives suitable for X-ray crystallography have not yet been obtained (although the structures of several amide or hydride precursors [e.g., Figure 4] have been determined) but the aryl ligands used in these

Boron Formates can be generated by 2 efficient routes

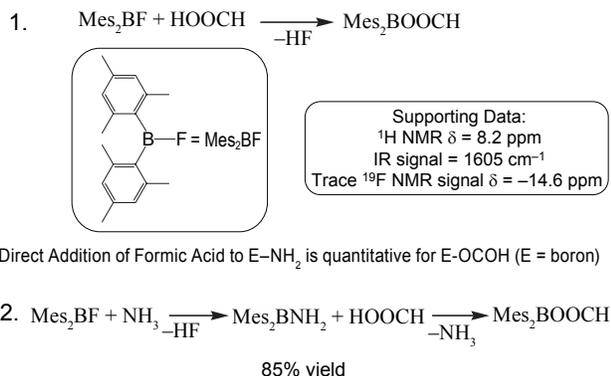
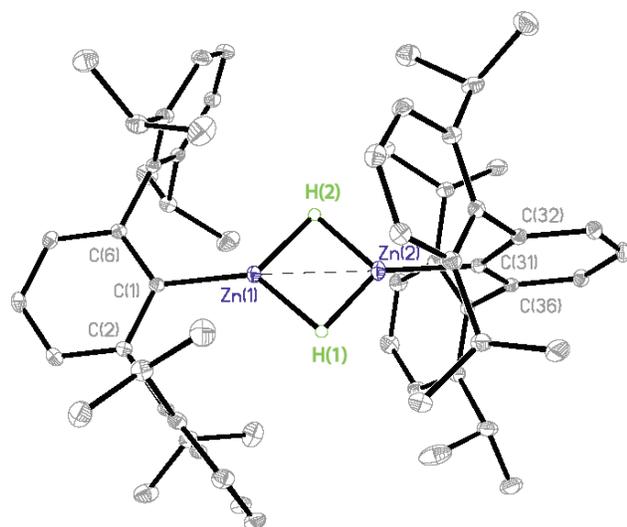


FIGURE 3. Two Simple Routes for the Efficient Generation of Boron Formate



^1H NMR (C_6D_6 , 300 MHz, 25°C): δ 4.84 (s, 1H, ZnH)

Zn(1)-Zn(2) 2.4084(3)
 Zn(1)-H(1) 1.67(2)
 C(1)-Zn(1)-Zn(2) 175.14(5)
 C(1)-Zn(1)-H(1) 138.3(9)
 Zn(2)-Zn(1)-H(1) 45.2(8)

FIGURE 4. Thermal ellipsoid plot of the zinc hydride $\text{Ar}'\text{Zn}(\mu\text{-H})_2\text{ZnAr}'$ ($\text{Ar}' = \text{C}_6\text{H}_3\text{-2,6}(\text{C}_6\text{H}_3\text{-2,6-Pr}_2)_2$). (H atoms are not shown.)

experiments can be readily modified by changing the ring substituents. In addition to the boron and zinc aryl derivatives, several promising aluminum and gallium aryl hydrido derivatives developed previously by us are now available for conversion to their formate derivatives. The gallium species are of particular interest to us because recent theoretical data (D. Camaoni, May 2007) have predicted that relatively mild heating of its formate derivative should regenerate the hydride.

Conclusions and Future Directions

Hydrogen terminated silicon nanoparticles of different sizes have been prepared and characterized. The weight loss increases with decreasing particle size; further characterization by TG/MS needs to be done, however. Problems with oxidation occur upon washing the solid-state prepared materials, while no oxidation is observed with the solvent prepared particles. Oxidation of the surface is an undesired effect since it replaces potential hydrogen sites with oxygen. The presence of solvent seems to be protecting the surface from oxygen; the solvent, however, binds to the particles.

Our future investigations will include:

- Further optimization of this reaction to reduce oxygen on the surface and to better understand the reaction mechanism;
- Preparation of hydrogen capped silicon with B, C, Al, or P alloy nanomaterials;
- Analysis of the effect of doping upon hydrogen content as well as desorption temperature;
- Synthesis of aluminum and gallium formate from their hydride or amide derivatives already prepared in this laboratory;
- Employing a range of aryl substituents to allow a library of boron, aluminum gallium or zinc derivatives to be synthesized;
- Investigating the thermolysis of the formate for CO or CO₂ elimination to afford hydroxide or hydride products; and
- Investigating the reaction of the hydride derivatives with CO₂ for formate regeneration.

FY 2007 Publications/Presentations

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2. D. Neiner, H.W. Chiu, and S.M. Kauzlarich, "Low-Temperature Solution Route to Macroscopic Amounts of Hydrogen Terminated Silicon Nanoparticles", *J.A.C.S.*, 2006; 128(34); 11016-11017.

3. A.L. Pickering, C. Mitterbauer, N.D. Browning, S.M.Kauzlarich, P.P. Philip, "Room Temperature Synthesis of Surface-Functionalised Boron Nanoparticles," *Chemical Communications*, 2007, 580.
3. A.L. Pickering, C. Mitterbauer, Christoph, N.D. Browning, S.M.Kauzlarich, P.P. Philip, "Room Temperature Synthesis of Surface-Functionalised Boron Nanoparticles," *Organic Biomolecular Chemistry*, 2007, 580.
4. E. Rivard, W. A. Merrill, J.C. Fettinger, R. Wolf, Geoffrey H. Spikes and Philip P. Power, "Boron-Pnictogen Multiple Bonds: Donor-Stabilized P=B and P=As Double Bonds and a Hindered Amino Borane with a BN Triple Bond," 2007.
5. D. Neiner, C.L. Condrón, S.M. Kauzlarich, "Hydrogen in Silicon Clathrates," poster presentation at the International Symposium on Metal- Hydrogen System Fundamentals and Applications, October 1–6th, 2006, Lahaina, Maui, Hawaii.
6. D. Neiner, C. Chervin, H. W. Chiu, M. Blessent, S. M. Kauzlarich, "Nanocrystalline Silicon for Hydrogen Storage," poster presentation at the International Symposium on Metal- Hydrogen System Fundamentals and Applications, October 1–6th, 2006, Lahaina, Maui, Hawaii.
7. D. Neiner, C. L. Condrón, S. M. Kauzlarich, "Type I Silicon Clathrates: Synthesis and NMR Characterization," poster presentation at The 232nd ACS National Meeting, San Francisco, CA, September 10–14, 2006.
8. D. Neiner, H. W. Chiu, M. Blessent, S. M. Kauzlarich, "Investigation of Nanocrystalline Silicon as a Possible Hydrogen Storage Material," poster presentation at The 232nd ACS National Meeting, San Francisco, CA, September 10–14, 2006.
9. D. Neiner and S. M. Kauzlarich, "Nanocrystalline Silicon for Hydrogen Storage," poster presentation at International Symposium on Materials Issues on Hydrogen Production and Storage, August 20–25th, 2006, Santa Barbara, CA, USA.
10. D. Neiner, C. Chervin, H. W. Chiu, M. Blessent, S. M. Kauzlarich, "Nanocrystalline Silicon for Hydrogen Storage," poster presentation at the Materials Research Society Meeting, April 17–21st, 2006, Moscone West, San Francisco, CA, USA.