

IV.B.1b Chemical Hydrogen Storage using Ultra-High Surface Area Main Group Materials and The Development of Efficient Amine-Borane Regeneration Cycles

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Objectives

Regeneration

- Provide new materials, compounds and support for chemical regeneration of amine-boranes or boron amides from B-X (X= halide or oxide) compounds.
- To develop a method of regenerating amine-boranes or other chemical hydrides from spent fuel with use of a metal formate/hydride cyclable system.
- To develop light element hydride nanomaterials for spent chemical hydride regeneration such as ammonia-borane "AB" regeneration.

Release

- Enhancement of hydrogen release for chemical hydrides such as AB with light element hydride nanoparticles.
 - Produce light element hydride nanoparticles in a low-cost, high-yield method.

Technical Barriers

This project addresses the following technical barriers from the 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
- (C) Efficiency
- (R) Regeneration Processes

Technical Targets

This project is conducting 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

Accomplishments

Regeneration

- Experimental validation that boron formates, proposed for the metal formate/hydride cyclable system for regeneration, confirmed that boron formates eject CO rather than CO₂ (as predicted by calculations – Camaioni, Pacific Northwest National Laboratory, PNNL), thus reducing the number of possible formate complexes to investigate.
- In agreement with the hypothesis that a monomeric tin formate is the most likely candidate for the formate/hydride cycle, experimental validation that a dialkyltin diformate, gave neither CO nor CO₂ ejection (resulting from polymeric solid-state structure), further focused the research efforts.
- Developed and demonstrated a generic route to tin monoformate synthesis; tin monoformates were identified as the most promising compounds for the metal formate/hydride cycle for regeneration.
- Synthesis and characterization of monomeric and one-dimensional tin formates to test the metal formate/hydride cycle.
- Si-H nanoparticles for regeneration of B-H from B-Cl and B-O: preliminary results (nuclear magnetic resonance, NMR) show the production of AB by simple one pot method.

Release

- Light element hydride nanomaterials to affect hydrogen release kinetics: preliminary results show elimination of foam problem associated with release, lowering of the release temperature and providing a smaller enthalpy for the first release of H₂ from AB.
- No-go for further development of Si and Si alloy nanoparticles as hydrogen storage materials (wt% ~4, release temperature at 250°C).
- No-go for further investigation of light element framework structures (clathrates) as current wt% is too low and not enough promise for significant hydrogen uptake. (If one assumes that at least 4 H₂ molecules fill the large cages and 2 H₂ molecules in the small cages, the expected composition would be H₁₂₈Si₁₃₆ or approximately 3.5 wt% hydrogen.)



Introduction

UC Davis has two efforts in support of the Center on Chemical Hydrogen Storage Materials: nanomaterials and light molecule development for regeneration of molecular-based chemical hydrogen materials and enhancement of hydrogen release. These are new objectives that were introduced in January 2008 after the Center's no-go decisions on several nanomaterials under investigation: light element nanoparticles such as boron and silicon and clathrate framework compounds for hydrogen storage. A detailed decision tree can be found in the Center's report. In order to help support the Center, the UC Davis group is providing two approaches to the regeneration cycle, working closely with Los Alamos National Laboratory (LANL) and PNNL on strategies. For regeneration the UC Davis group investigated main group formate small molecules or hydride nanomaterials as low-cost reagents to convert B–O or B–X in one step to B–H, as is proposed for the metal formate/hydride cycle as part of the overall LANL regeneration scheme. One postdoc from UC Davis is currently working at PNNL to enable more effective collaboration on the use of nanomaterials for regeneration. We are exploring the potential of nanoparticles of metal hydrides (silicon and other light elements) for regeneration of B–H from B–O, using a model system of B(OPh)₃, where Ph = phenyl. For release: nanoparticles provide an inexpensive additive that can affect the release of hydrogen from AB by providing a weakly coordinating Lewis acid platform. Preliminary results from these efforts suggest that main group formates may be viable precursors to hydride reagents for B–H regeneration and that nanomaterials may have applications towards both regeneration of AB and release of hydrogen from AB.

Approach

Regeneration

Main Group Formate Compounds

- Synthesize main group formates.
- Investigate their interconversion under mild reaction conditions with the object of creating a simple chemical cycle to regenerate B–H bonds in AB.

Light Element Hydride Nanomaterials

- Synthesize light element hydride nanomaterials such as Si–H, Si_{1-x}C_x–H, Si_{1-x}Al_x–H, and react with B(OR)₃ and BX₃ and follow reaction by NMR.

Release

- Enhancement of release kinetics with additional of light element metal hydride nanomaterials. (Elimination of foaming problem related to hydrogen release of AB.)

Results

Regeneration

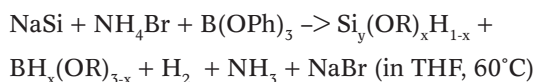
Main Group Formate Compounds

UC Davis is collaborating with LANL on the regeneration of B–X to B–H. The proposed cycle starts with a metal formate with the ejection of CO₂ to give the metal hydride. This is part of the overall regeneration scheme for AB, proposed by LANL. The goal of this research is to find a molecular compound that can be used in this cycle and then optimize the process. Following the confirmation that boron formates preferentially eject CO over CO₂ to give hydroxides instead of the desired hydrides, we have focused on the synthesis of tin formates, R_xSn(OC(O)H)_{4-x}. Tin diformates, R₂Sn(OC(O)H)₂, adopt 2-dimensional polymeric structures that prevent either CO or CO₂ elimination. Our focus then shifted to tin monoformates, R₃SnOC(O)H, which are readily accessible by treatment of either tin hydroxides (R₃SnOH) or tin oxides (R₃SnOSnR₃) with formic acid following the elimination of water. We have prepared tin formates with aryl substituents of varied steric bulk in order to determine which ligands are large enough to allow for the isolation monomeric formates and that are not too sterically crowded to still allow for CO₂ ejection. The bulkiest ligand we used, C₆H₂-2,4,6-Me₃ (Mes), yielded the first structurally characterized monomeric tin formate in the solid-state, but did not eliminate CO₂ even at 165°C under reflux conditions. A smaller ligand, CH₂C₆H₅ (Bn), resulted in a 1-dimensional polymer that also does not show any indication of hydride formation under

thermolysis conditions. We are currently investigating ligands on the tin formates of intermediate steric bulk with emphasis on alkyl groups as tin substituents to find the optimal conditions for CO₂ elimination and tin hydride formation.

Light Element Hydride Nanomaterials

We have started exploring the regeneration of B-H bonds from a B-O model system, by reacting nanoparticles of hydrogen terminated Si with B(OPh)₃ in solution. Several approaches were taken to react the nanoparticles directly and a solution of nanoparticles with B(OPh)₃: large sized (≥10 nm) and small sized (≤10 nm) nanoparticles were employed. Both solid phase and solution synthetic procedures were employed. Neither of these synthetic approaches provided positive evidence for the replacement of B-O with B-H. A possible hypothesis for why these nanoparticles were unreactive was that this may be due to oxidation of the silicon nanoparticles, making them less reactive. Therefore, we prepared the nanoparticles in situ according to the reaction:



This reaction provided new resonances in the ¹¹B solution NMR consistent with the products indicated above, along with a small amount of AB. We are systematically investigating this reaction in order to determine the optimal conditions.

Release

We have also been systematically exploring the application of nanomaterials as possible “scaffolds” for AB. Preliminary results suggested that nanomaterials provide enhancement of hydrogen release, along with lowering of the heat of reaction. In addition, the presence of the nanomaterials reduces “foaming” of AB upon hydrogen release. This work is being verified with a goal of understanding the mechanism for hydrogen release and reduction of the heat released.

Conclusions and Future Directions

This project is relevant to the Centers goals of recycling spent chemical hydride and AB regeneration. The approach provides novel nanomaterials and the synthesis of metal hydrides for efficient AB regeneration. We have made progress on two major areas that are part of the overall Center goals, collaborating with LANL and PNNL. (Regeneration): We were able to experimentally verify the elimination of boron formates as a potential hydride precursor, and systematically explore the syntheses of tin monoformates for conversion to the hydride. We have obtained preliminary results for nanoparticles showing the regeneration of B-H bonds from a B(OR)₃ model system. (Release): Preliminary

results show that nanoparticle additives reduce the temperature and release of H₂ from AB while eliminating the foam problem. In terms of technology transfer/collaborations, we have active partnerships with LANL, PNNL, Rohm & Hass, and the University of Alabama and have provided the results to the wider scientific public by means of presentations, publications, and patent applications. We initiated a collaboration with a start-up company, SigNa, a start-up company that was developed an inexpensive route to NaSi, which is a starting material for the hydrogen capped silicon nanoparticles during this time period.

Future directions include testing nanoparticles for possible regeneration ability and effect on hydrogen release effects of AB. Testing of tin monoformates especially with alkyl substituents at tin for CO₂ release and investigation of other synthetic routes to suitable metal hydrides.

Regeneration

Main Group Formate Compounds

Develop a method of M-H recycling via hydrogenolysis as an alternative to the metal formate/hydride approach.

Light Element Hydride Nanomaterials

Systematically optimize the reaction to regenerate AB in a low-cost, one-pot procedure.

Release

Further optimization of light element nanoparticles (such as BN) to reduce foam and to affect the hydrogen release kinetics without adding contamination, additional weight, and regeneration issues.

Investigate the rate of H₂ release with addition of nanoparticles.

Investigate the number of equivalence that can be obtained with addition of light element nanoparticles.

Regenerate the Si_xE_{1-x}-X (X = Cl, O) nanoparticles to Si_xE_{1-x}-H.

FY 2008 Publications/Presentations

- Boron-Pnictogen Multiple Bonds: Donor-Stabilized P=B and P=As Double Bonds and a Hindered Imino Borane with a BN Triple Bond*, E. Rivard, W.A. Merrill, J.C. Fettinger, R. Wolf, G.H. Spikes and P.P. Power, *Inorg. Chem.*, **2007**, 46, 2971. (cover illustration)
- Hydrogen Encapsulation in a Silicon Clathrate Type I Structure: Na_{5.5}(H₂)_{2.15}Si₄₆: Synthesis and Characterization*, D. Neiner, N. L. Okamoto, C.L. Condron, Q. M. Ramasse, P. Yu, N.D. Browning, S.M. Kauzlarich, *J. Am. Chem. Soc.*, **2007**, 129, 13857.