

Chemical Hydrogen Storage using Ultra-High Surface Area Main Group Materials & The Development of Efficient Amine-Borane Regeneration Cycles

(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

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This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Project Start Date: FY05
- Project End Date: FY09
- Percent complete: 80%

Budget

- Total project funding (05-09)
 - DOE Total \$ 1,348,229
 - Contractor share \$ 337,059
- Funding for FY08
 - \$ 400,000 (DOE) \$ 100,000 (cost share)
- Funding for FY09
 - \$ 250,000 (DOE) \$ 50,000 (cost share)

Barriers

- Cost
- System weight and volume
- Regeneration Processes

Direct Collaborators

- Participant in the DOE Chemical Hydrogen Storage Center of Excellence
- LANL, PNNL, U. Alabama, and SiGNa

Objectives

Regeneration of Ammonia Borane

- 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 from spent fuel with use of a metal formate/hydride cyclable system.
- To develop light element hydride nanomaterials
 - test light element hydride nanomaterials ability to transfer hydrogen using different spent fuel forms.
 - Test light element hydride nanomaterials for spent chemical hydride regeneration such as “AB” regeneration.

Release

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

Timeline

Task	Year 1	Year 2	Year 3	Year 4	Year 5
Task 1& 2: Nanoparticle and Main Group Compounds Synthesis Synthesis of SiH and Si(NH ₂), SiH and Si(NH ₂). Characterization of Si _{1-x} M _x H and Si _{1-x} M _x NH ₂ composition and reactivity .	→		⛔ No Go		
New 06/07: Task 2: Regeneration of E–H Materials (E = B, Al, Si, Zn, Ge, or Sn) Synthesis of compounds with E–H, E–NH ₂ , E–OC(O)H groups. Characterization of compounds and regeneration under mild conditions.		→			
		→			
Task 3: Characterization and Testing Test reactivity, thermolysis, and regeneration of various alloys and main group compounds.	→				
Task 4: Demonstrate the potential for hydride terminated nanoparticles to egenerate spent chemical hydrides such as ammonia borane.			→		
Task 5: Demonstrate the effect of nanoparticle addition to the kinetics of of hydrogen release.			→		
Task 6: Investigation of other main group element formates for ejection of carbon dioxide with formation of element hydrides.			→		
Task 7: Evaluate stability, cyclability, and reaction chemistry of main group hydride species.			→		

 New/revised

Plan & Approach

Regeneration: Use 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.

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 Ammonia-Borane.

Light element hydride nanomaterials

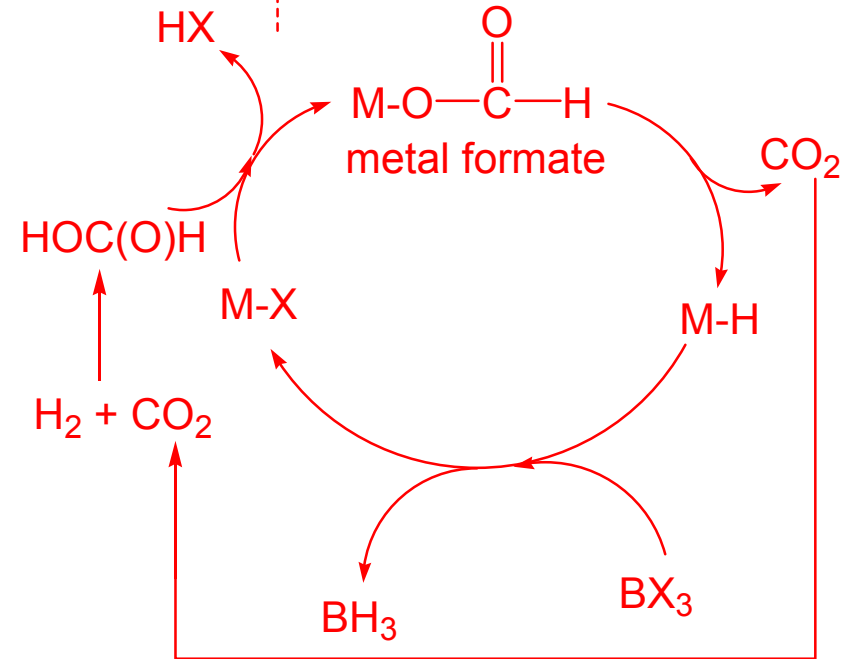
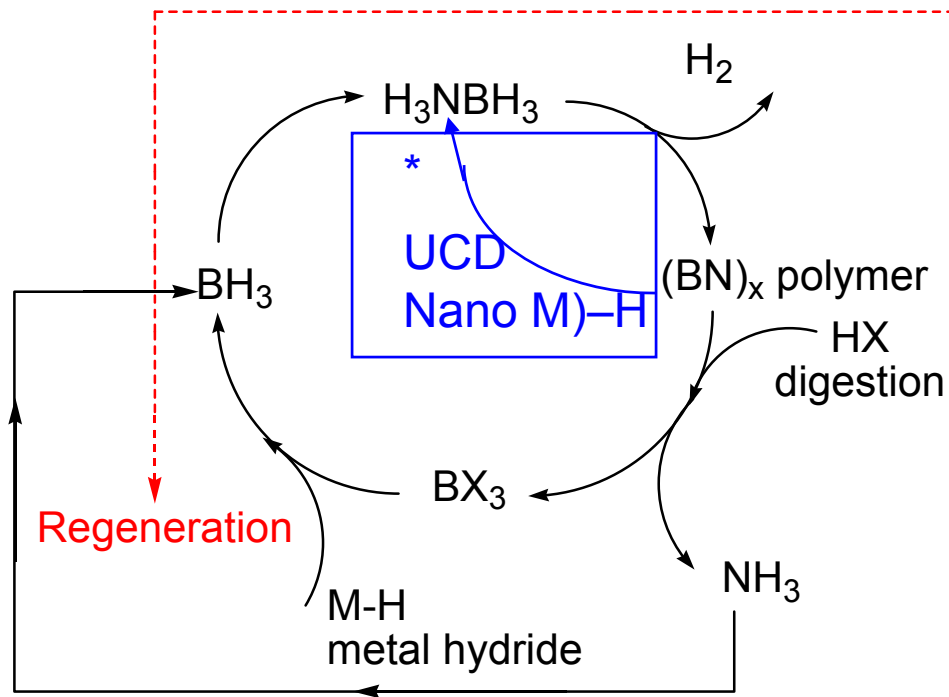
- Synthesize light element hydride nanomaterials and react with $B(OR)_3$ and BX_3 and follow reaction by NMR.

Release: Enhancement of hydrogen release for chemical hydrides such as ammonia-borane “AB” with light element nanoparticles.

Reduce heat released from AB during dehydrogenation

- Reduce/eliminate byproducts (ammonia and borazine) from the dehydrogenation reaction of ammonia borane.
- Eliminate/reduce foaming of ammonia borane.
- Use a nanomaterial that can be easily regenerated and doesn't add contamination or complications to the regeneration of AB.

Relevance to Overall Regeneration Cycle



X = halogen or oxo group

Simplified LANL Cycle for H₂ Storage

Formic acid: supplied via direct synthesis from methane

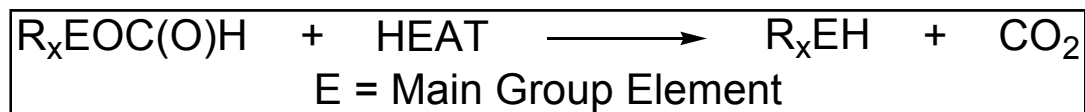
*Application of nano M)-H to regeneration of spent fuel

Simplified UC Davis Formate/Hydride Regeneration Cycle

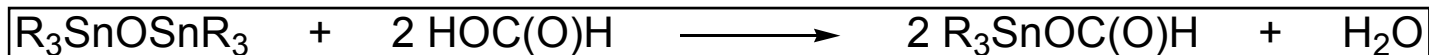
Cycle

Objective – Approach to Metal Hydrides

- Our approach to metal hydride synthesis is by the conversion of metal formates through loss of carbon dioxide under mild (< 200 °C) thermolysis conditions.



- There are a variety of synthetic strategies available for the generation of element-formate compounds. The choice of reaction conditions depends on the main group element and the organic substituents and can be guided by computational investigations.
 - For tin, the oxide is a good choice of reagent for formate synthesis



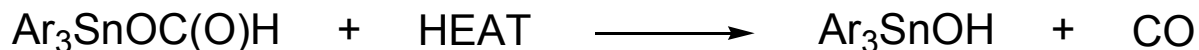
- The Center has chosen to start with commercially available, cheap hydrides and formic acid was deemed a reasonable starting point

Summary of Accomplishments – Regeneration

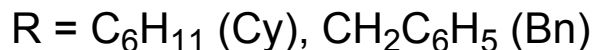
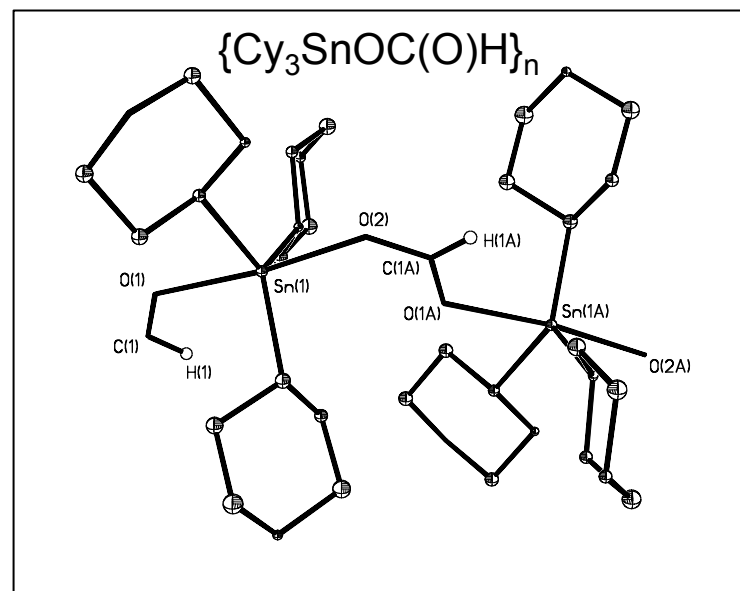
- ✗ Triaryl tin monoformates eliminate CO at elevated temperatures to yield tin hydroxides (instead of tin hydride. This is an undesirable reaction).
Discarded triaryl tin approach
- ✗ The oligomeric tin monoformates that we tested did not release either CO₂ or CO at temperatures up to 200 °C. *Approach abandoned*
- ✓ Demonstrated recycle of tin hydride. Reaction of BCl₃ with formate generates tri-n-butyltin formate and subsequently eliminates CO₂ to give tri-n-butyltin hydride – *useful approach continued.*
- ✓ Improved concept for the regeneration cycle of tin hydride from tin chloride via direct conversion of tin chloride to tin formate.
- ✓ Demonstrated regeneration of AB from B-Cl and B-O via reduction with Si)-H in simple one pot method.

Switch to Tri-n-butyl Tin Monoformate

- Thermolysis reactions of the triaryl tin monoformates (monomeric in the solid-state) resulted in CO elimination to yield the tin hydroxide.

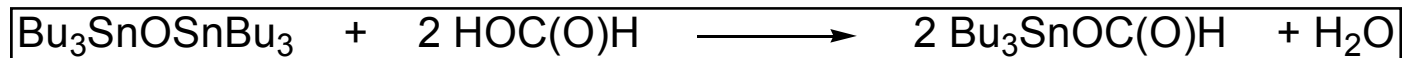


- Thermolysis reactions with alkyl-based substituents (which are extended chains in the solid-state) did not result in any products that could be identified as either the tin hydride or the tin hydroxide.
- Only tri-n-butyltin formate resulted in hydride formation under thermolysis.

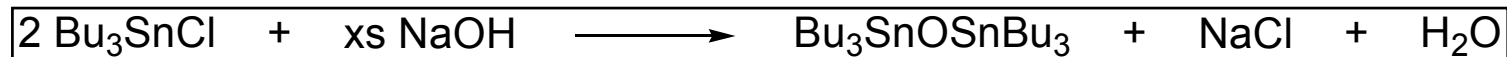


Synthesis of Tri-n-butyltin formate

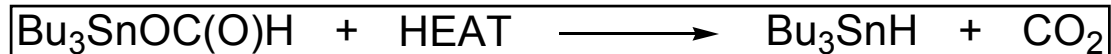
- Tri-n-butyltin formate is readily accessible by treatment of tin oxide with formic acid, which may be carried out without solvent.
 - The reaction is quantitative by ^{119}Sn NMR spectroscopy.



- Tri-n-butyltin oxide can be synthesized by heating a solution of the tin chloride with excess sodium hydroxide.
 - The reaction needs further study to minimize by-product formation and increase tin oxide yield.

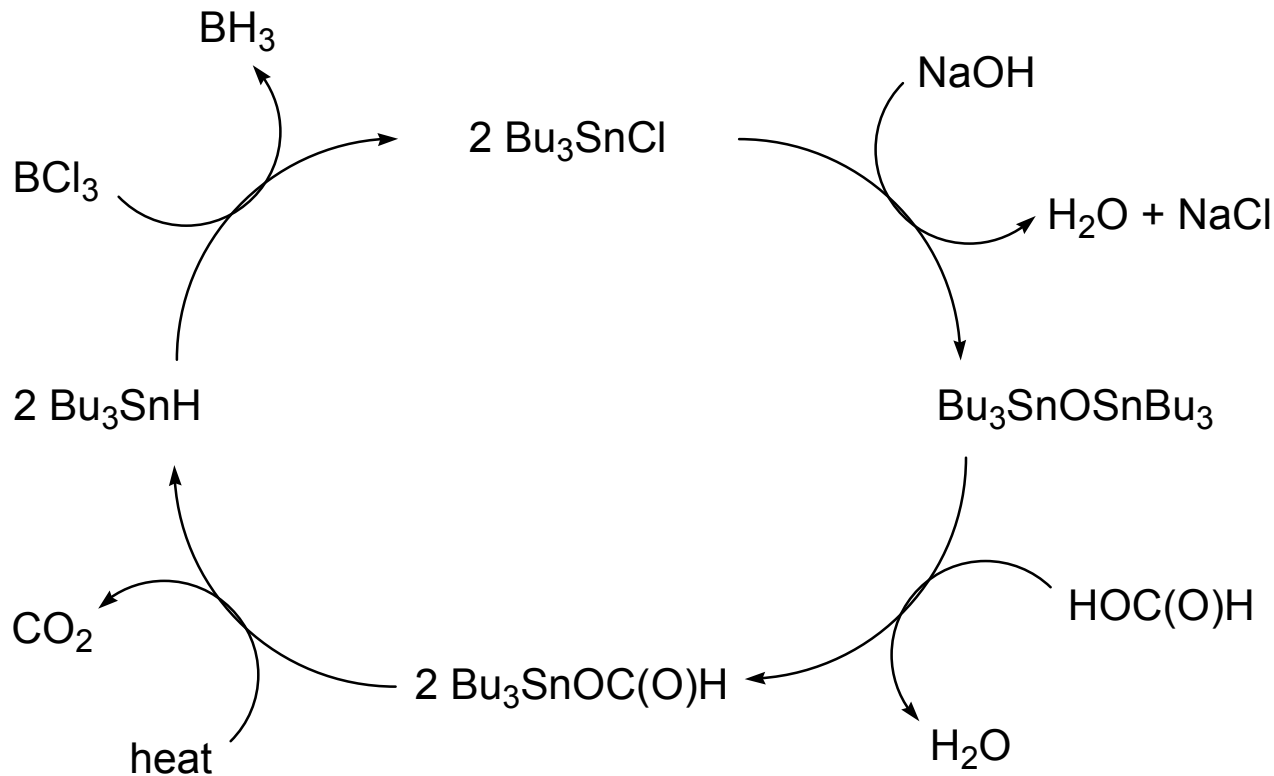


- The tin hydride is accessible by vacuum distillation (with a Vigreux column of sufficient length) of the tin formate



Regeneration Cycle of Bu_3SnH

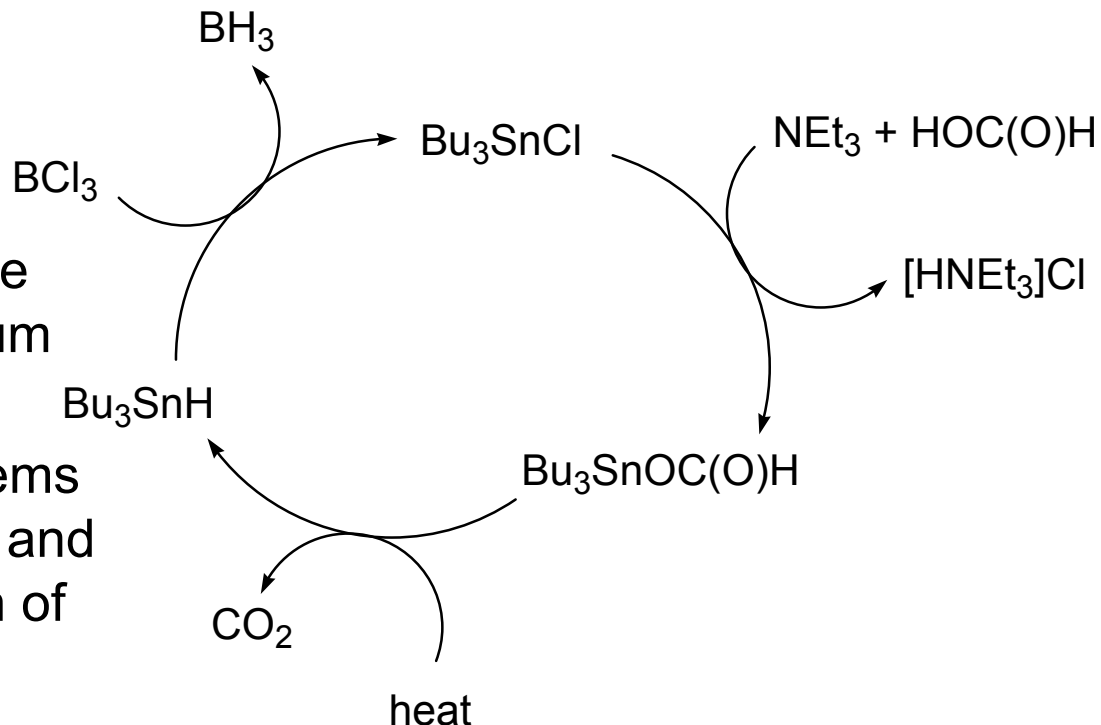
- The following cycle summarizes the regeneration of Bu_3SnH from Bu_3SnCl :



- One significant problem was the consumption of NaOH and the generation of NaCl

Improving the Bu_3SnH Regeneration Cycle

- We have determined that the problematic tin oxide step can be eliminated by direct conversion tin chloride to tin formate with ammonium formates
 - This removes the problems with low tin oxide yields and consumption/generation of NaOH/NaCl

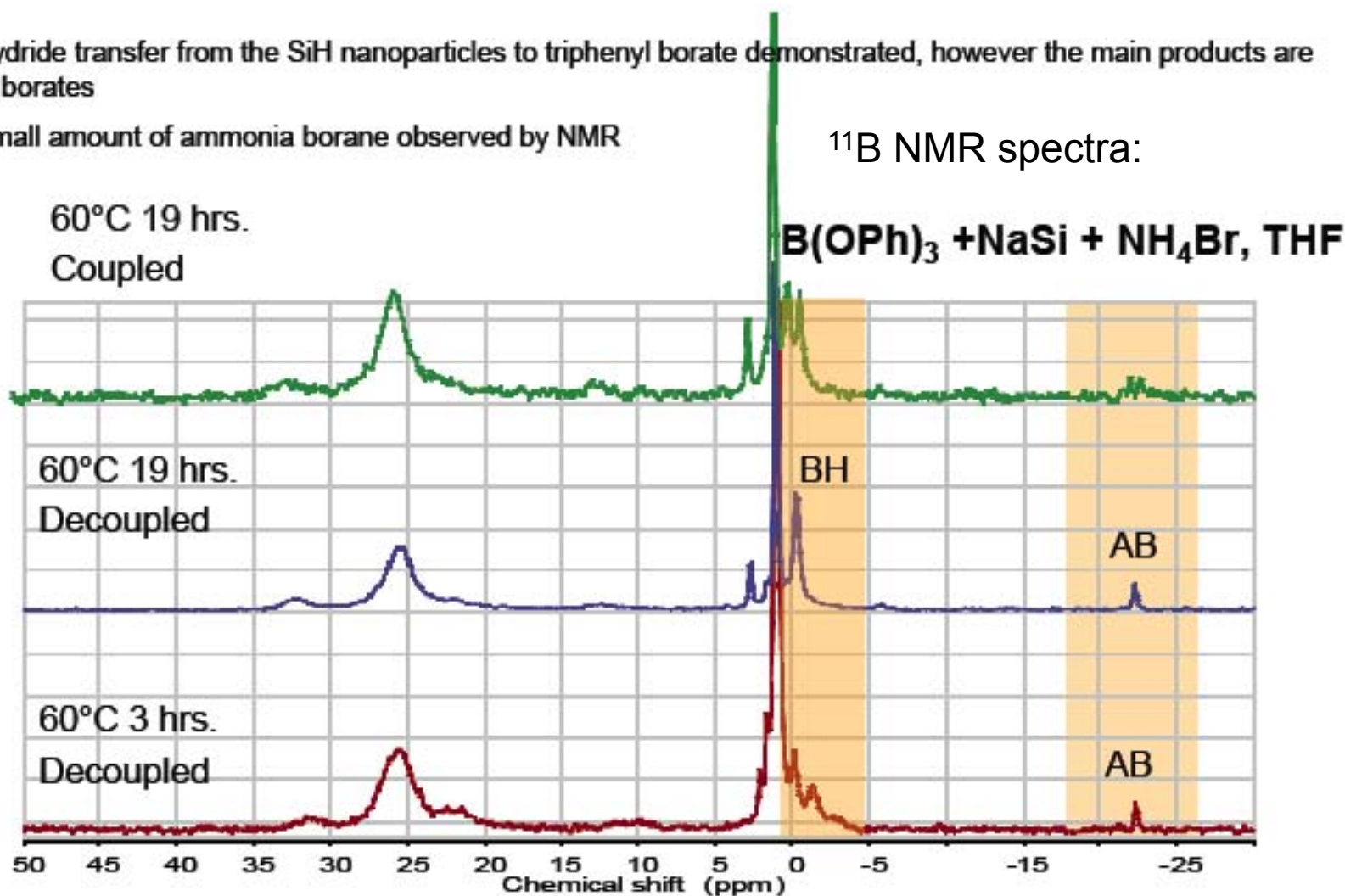


- Initial work employed NEt_3 . We are currently investigating other weak bases, in addition to the recovery of NEt_3 and HCl from $[\text{HNEt}_3]\text{Cl}$.
 - Note: NH_3 and HCl are recoverable from $[\text{NH}_4]\text{Cl}$
- We are also optimizing the reaction conditions at each step.

Regeneration of B–H from Triarylborates. Supports PNNL Regen Scheme

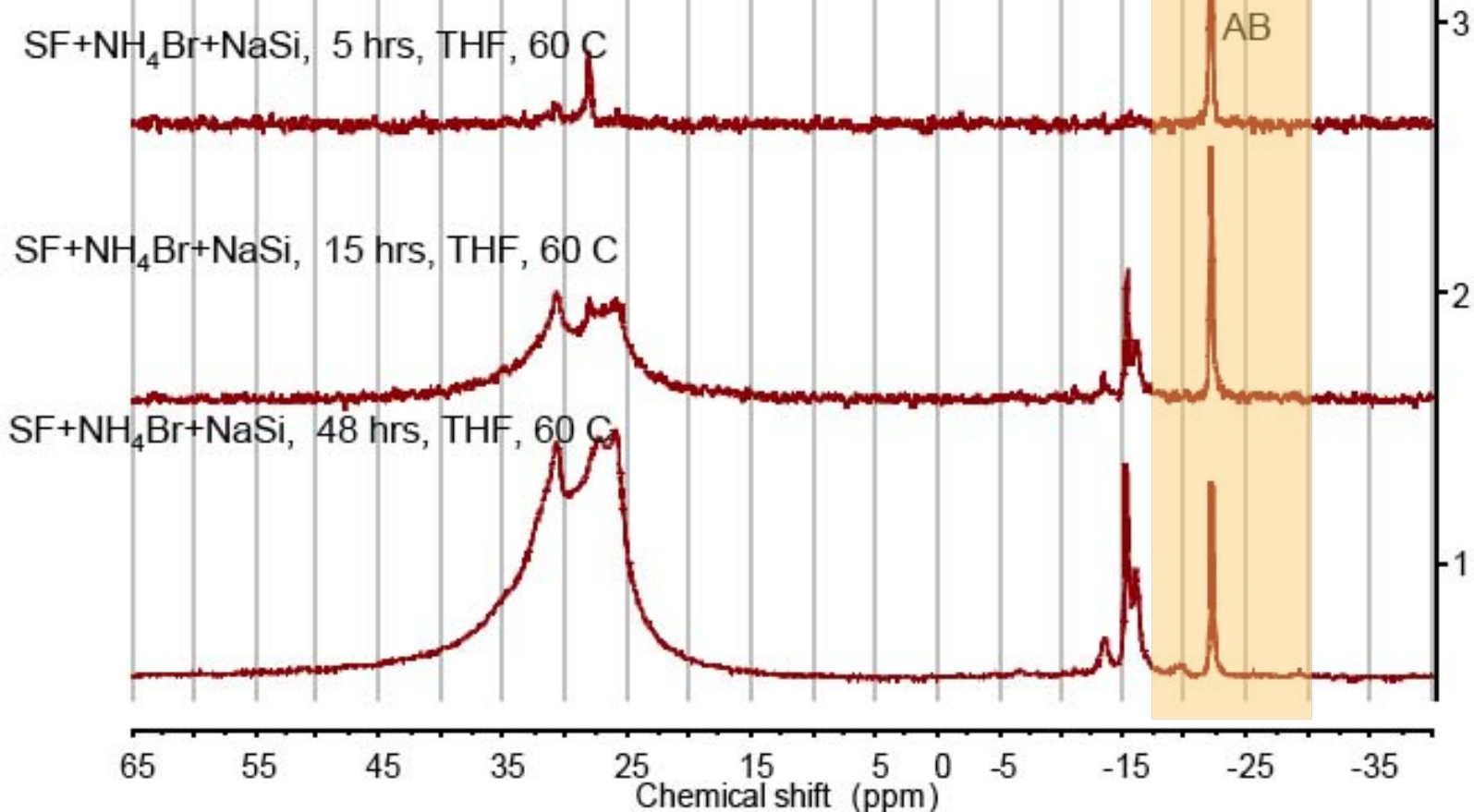
- Hydride transfer from the SiH nanoparticles to triphenyl borate demonstrated, however the main products are still borates
- Small amount of ammonia borane observed by NMR

^{11}B NMR spectra:



Regeneration of AB Directly from Spent Fuel (SF) with Si)-H NPs

^{11}B NMR decoupled shows that AB can be reformed from the spent fuel (BNH_x) at 60 C in 5 hrs using the SiH nanoparticles



SF = spent fuel

Partners: PNNL, Alabama

Future Directions – Regeneration

- Optimization of reaction conditions in the regeneration cycle of Bu_3SnH .
 - Test NH_3 as a potential weak base in the generation of $\text{Bu}_3\text{SnOC(O)H}$
- Evaluate the lifetime of Bu_3SnH through multiple regeneration cycles.
- Investigation of other routes to Main Group formates that do not involve formic acid:
 - Hydrogenolysis of singlet diradical compounds
 - Hydrogen addition to unsaturated Main Group compounds (eg. aluminum)
 - Direct addition of hydrogen to E-X bonds
- Gain a better understanding through NMR and other spectroscopies as to why spent fuel can be almost fully regenerated, but B(OR)_3 cannot.
- Quantify the reaction of Spent Fuel (SF) for production of AB. Optimize reaction parameters.

Summary of Accomplishments – Release

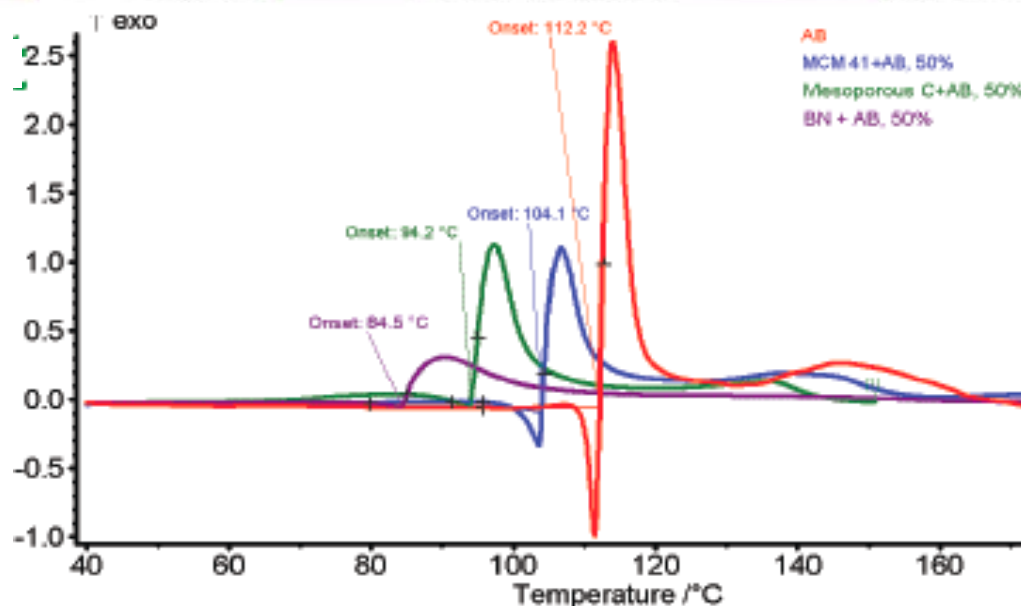
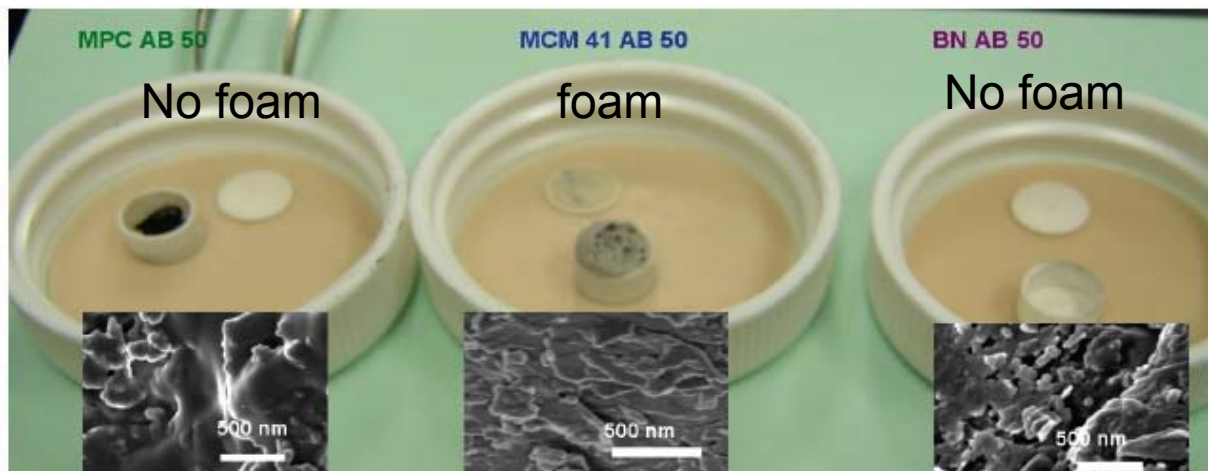
- Light element hydride nanomaterials to affect hydrogen release kinetics: Preliminary results show elimination of foam problem associated with release, lowering of the release temperature, smaller enthalpy for the first release of H₂ from AB.
- The ratio of nano-BN:AB has been optimized.
- Delay in hydrogen release at temperature is eliminated.
- Preliminary understanding of the effect of nano-BN accomplished through high field NMR, high resolution TEM, TG/DSC/MS, FTIR, and Raman spectroscopy.
- Collaboration with PNNL

Nanomaterial Supports for Hydrogen Release from Ammonia Borane (AB)

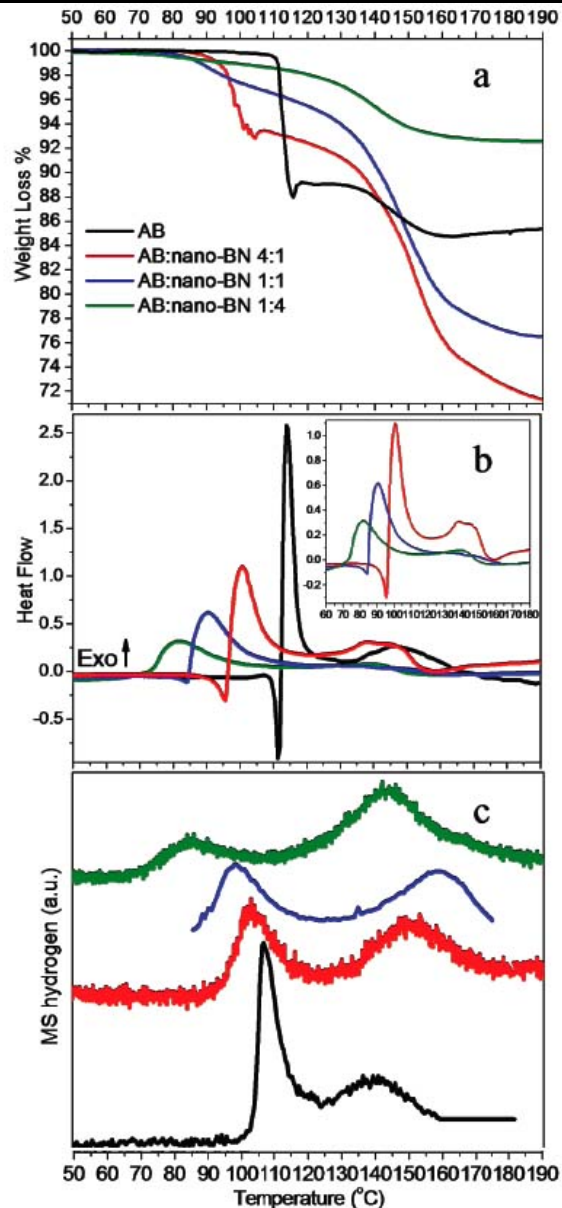
Only MPC and nano-BN show an absence of foaming after hydrogen release.

DSC trace of the various combinations normalized for AB.

Nano-BN shows the best results.



Hydrogen Release from nano-BN:AB



- 1) $\text{H}_3\text{NBH}_3 \rightarrow (\text{H}_2\text{NBH}_2)_x + \text{H}_2$, 90-120 °C,
- 2) $(\text{H}_2\text{NBH}_2)_x \rightarrow (\text{HNBH})_x + x\text{H}_2$, 120-160 °C
- 3) $(\text{HNBH})_x \rightarrow \text{BN} + x\text{H}_2$, well above 500 °C

- TG shows that weight loss starts at lower temperatures with increasing nano-BN concentration
- DSC indicates that the onset temperature for reaction 1 shifts to lower temperatures with increasing nano-BN concentration
- The heat release for reaction 1 and 2 seem to decrease with nano-BN concentration

Future Directions - Release

- Develop a method of M-H recycling via hydrogenolysis as an alternative to the metal formate/hydride approach.
- 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.
- Addition of catalyst for AB release to the nano-BN.
- Preparation of meso-BN in order to further optimize the effect of nano-BN upon hydrogen release from AB. This will take advantage of higher surface area.

Project Summary

- Relevance: Spent chemical hydride and ammonia borane (AB) regeneration. Nanomaterials enhance hydrogen release properties and regeneration routes.
- Approach: Synthesis and characterization of novel nanomaterials and the synthesis of metal hydrides for efficient ammonia borane (AB) regeneration.
- Technical Accomplishments and Progress: (**Regeneration**) Tributyltin formate can be synthesized in one step and yields tin hydride under thermolysis. Metal hydride nanoparticles show the regeneration of AB from spent fuel. (**Release**) Nanoparticle additives reduce the temperature and release of H₂ from AB while eliminating the foam problem.
- Technology Transfer/Collaborations: Active partnership with LANL, PNNL, U. Alabama, presentations, and publications.
- Proposed Future Research: Optimization of nanoparticles for regeneration and for hydrogen release from AB. Testing of tin monoformates for CO₂ release and investigation of other synthetic routes to suitable metal hydrides.

Collaborations

- **LANL:** Synthesis of metal hydrides for cost effective regeneration. Provide support for metal hydride recycle to overall regeneration scheme.
- **PNNL:** Characterization of nanomaterials, theoretical calculations of regeneration cycle energetics. Support for kinetics and release of ammonia borane (AB).
- **U. Alabama:** theoretical calculations of hydrogen storage cycles, application of nanomaterials to regeneration and release.
- **SiGNa:** scale-up and commercial source of NaSi.

Acknowledgements

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Ping Yu (UCD): MAS NMR

Michael Lefenfeld SiGNa

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