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)

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Overview

Timeline

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

Barriers

- Cost
- System weight and volume
- Regeneration Processes

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)

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 $Si_{1-x}M_xH$ 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, $E\text{-}NH_2$, 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

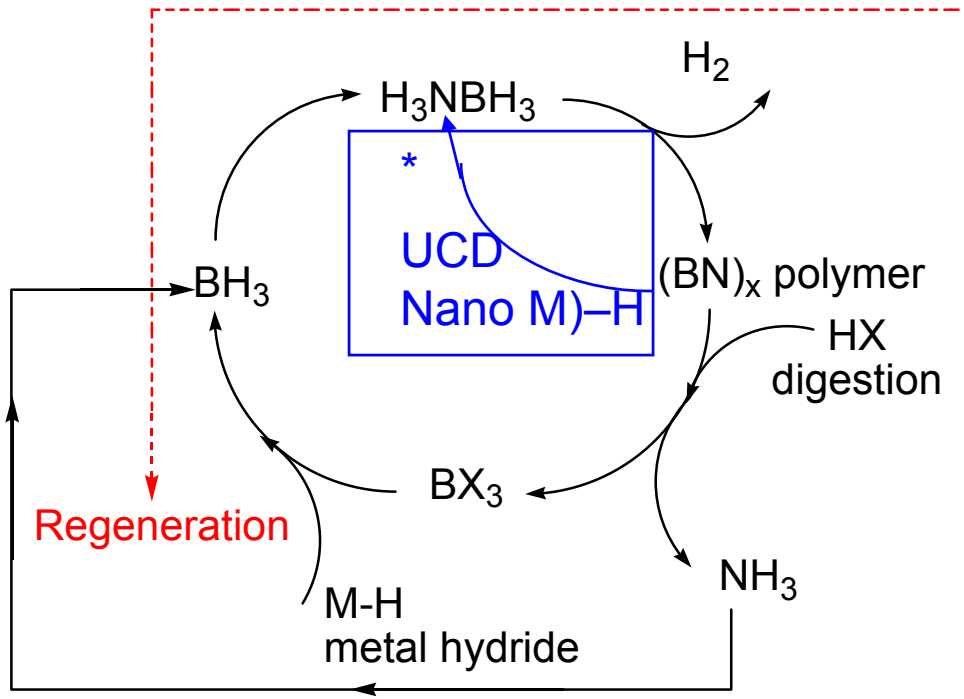
- Synthesize light element hydride nanomaterials and react with $B(OR)_3$ and BX_3 and follow reaction by NMR.

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

Reduce heat released from AB during dehydrogenation

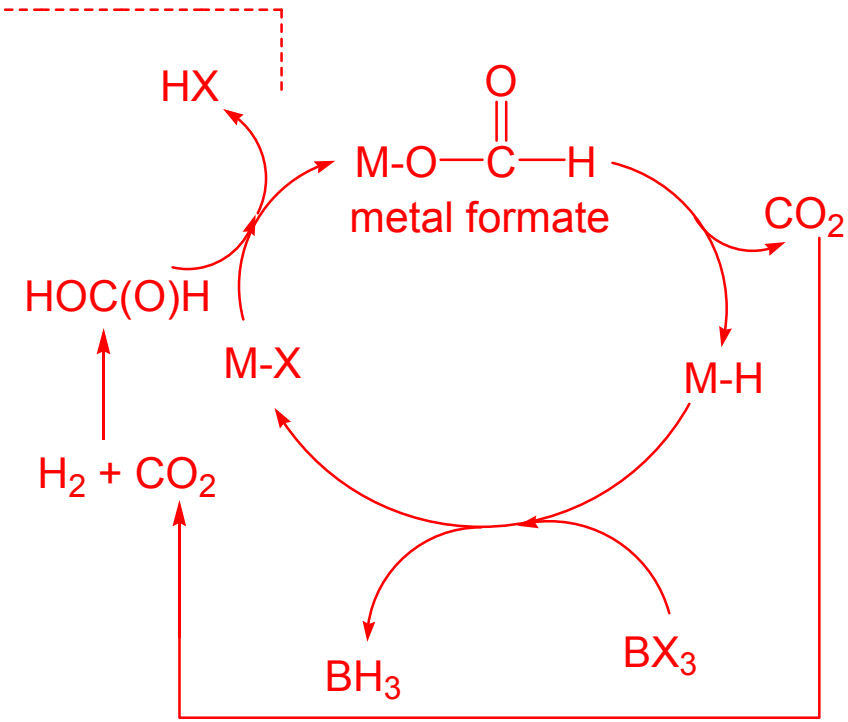
–Reduce/eliminate byproducts (ammonia and borazine) from the dehydrogenation reaction of ammonia borane.
–Eliminate/reduce foaming of ammonia borane.
–Use a nanomaterial that can be easily regenerated and doesn't add contamination or complications to the regeneration of AB.

Relevance to Overall Regeneration Cycle



X = halogen or oxo group

Simplified LANL Cycle for H_2 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

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.

$$R_xEOC(O)H + HEAT \longrightarrow R_xEH + CO_2$$

E = Main Group Element

- 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

$$R_3SnOSnR_3 + 2\ HOC(O)H \longrightarrow 2\ R_3SnOC(O)H + H_2O$$

- 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 oligiomeric tin monoformates that we tested did not release either CO_2 or CO at temperatures up to 200 °C. *Approach abandoned*

✓ Demonstrated recycle of tin hydride. Reaction of BCl_3 with formate generates tri-n-butyltin formate and subsequently eliminates CO_2 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.

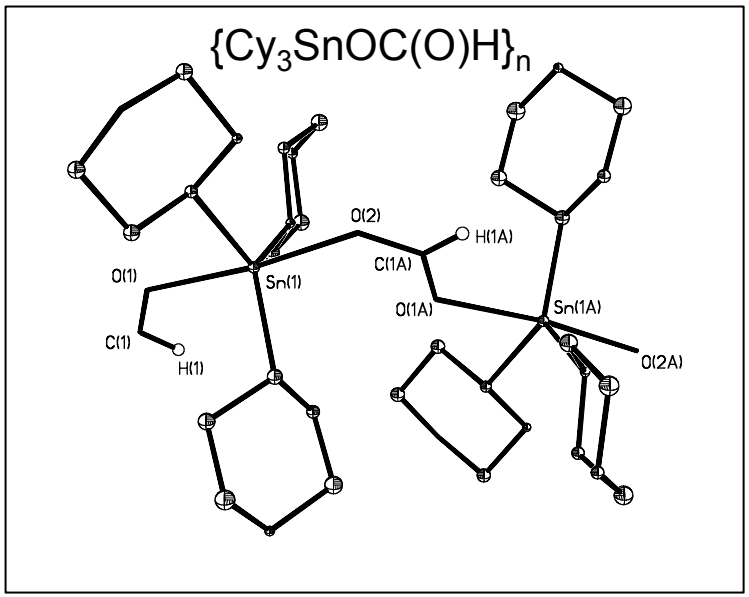
Switch to Tri-n-butyl Tin Monoformate

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

$$Ar_3SnOC(O)H \quad + \quad HEAT \longrightarrow Ar_3SnOH \quad + \quad CO$$

Ar = 2,4,6-$Me_3C_6H_2$ (Mes), 2,6-$Me_2C_6H_3$ (Dmp)

- 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.

$$R_3SnOC(O)H \quad + \quad HEAT \not\longrightarrow R_3SnH \quad \text{or} \quad R_3SnOH$$

R = C_6H_{11} (Cy), $CH_2C_6H_5$ (Bn)

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.

$$Bu_3SnOSnBu_3 + 2\ HOC(O)H \longrightarrow 2\ Bu_3SnOC(O)H + H_2O$$

- 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.

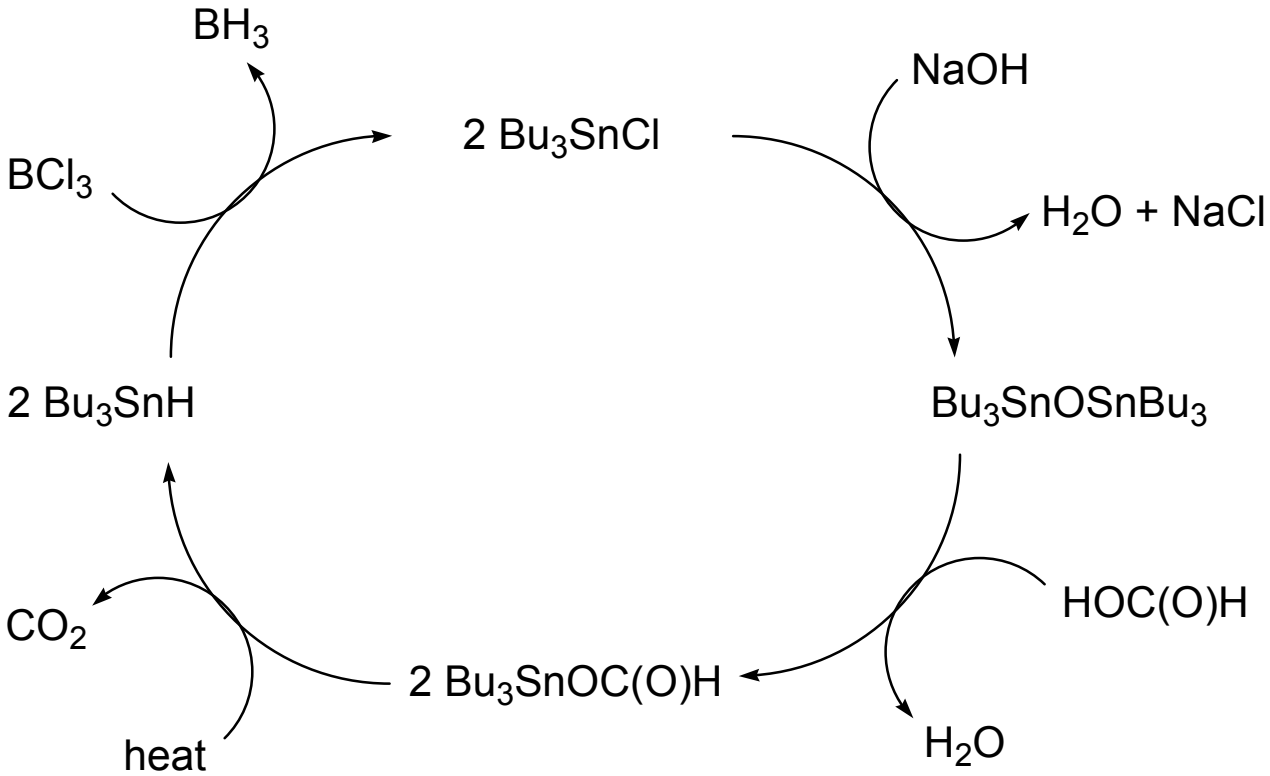
$$2\ Bu_3SnCl + xs\ NaOH \longrightarrow Bu_3SnOSnBu_3 + NaCl + H_2O$$

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

$$Bu_3SnOC(O)H + HEAT \longrightarrow Bu_3SnH + CO_2$$

Regeneration Cycle of Bu_3SnH

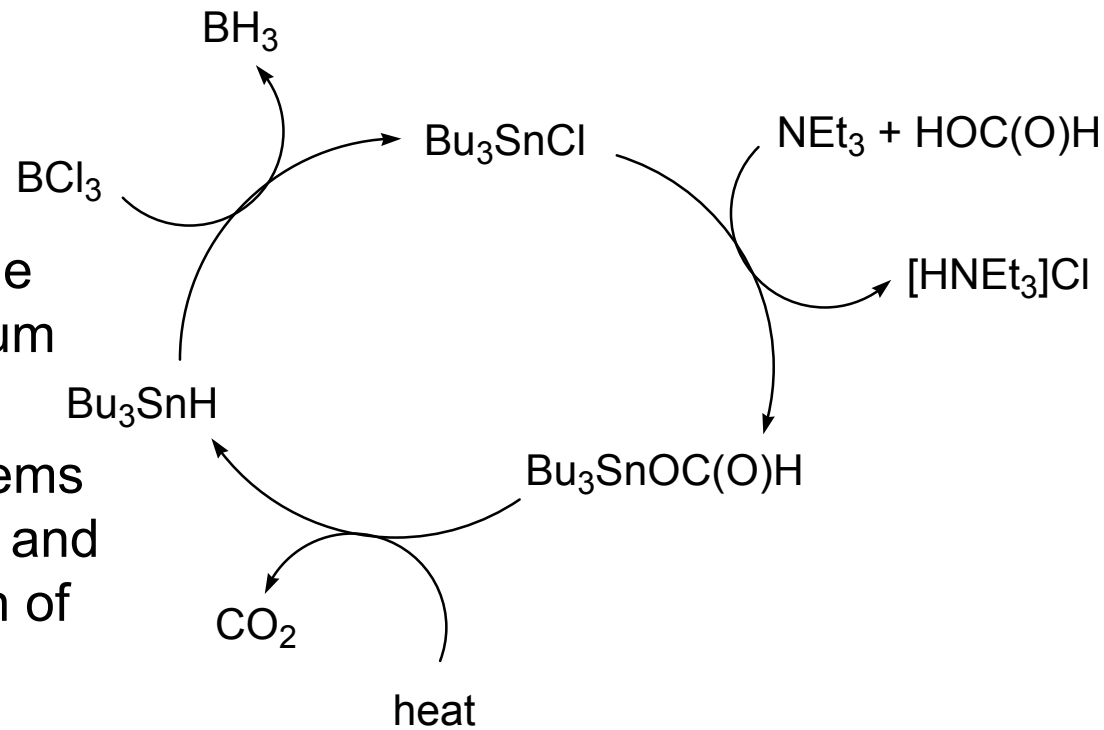
- The following cycle summarizes the regeneration of Bu_3SnH from Bu_3SnCl:



- 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

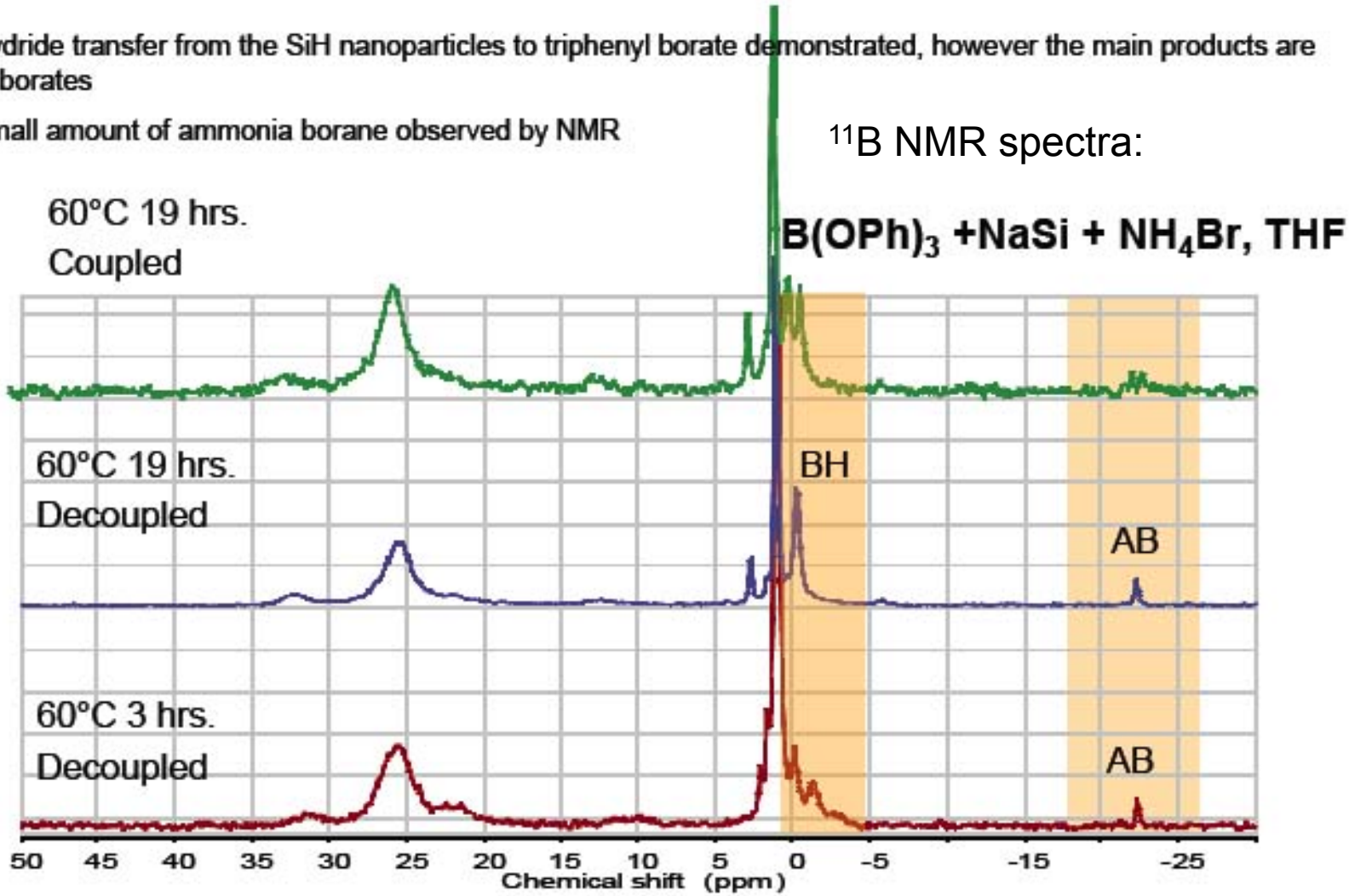


- Initial work employed NEt_3. We are currently investigating other weak bases, in addition to the recovery of NEt_3 and HCl from $[HNEt_3]Cl$.
  - Note: NH_3 and HCl are recoverable from $[NH_4]Cl$
- We are also optimizing the reaction conditions at each step.

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

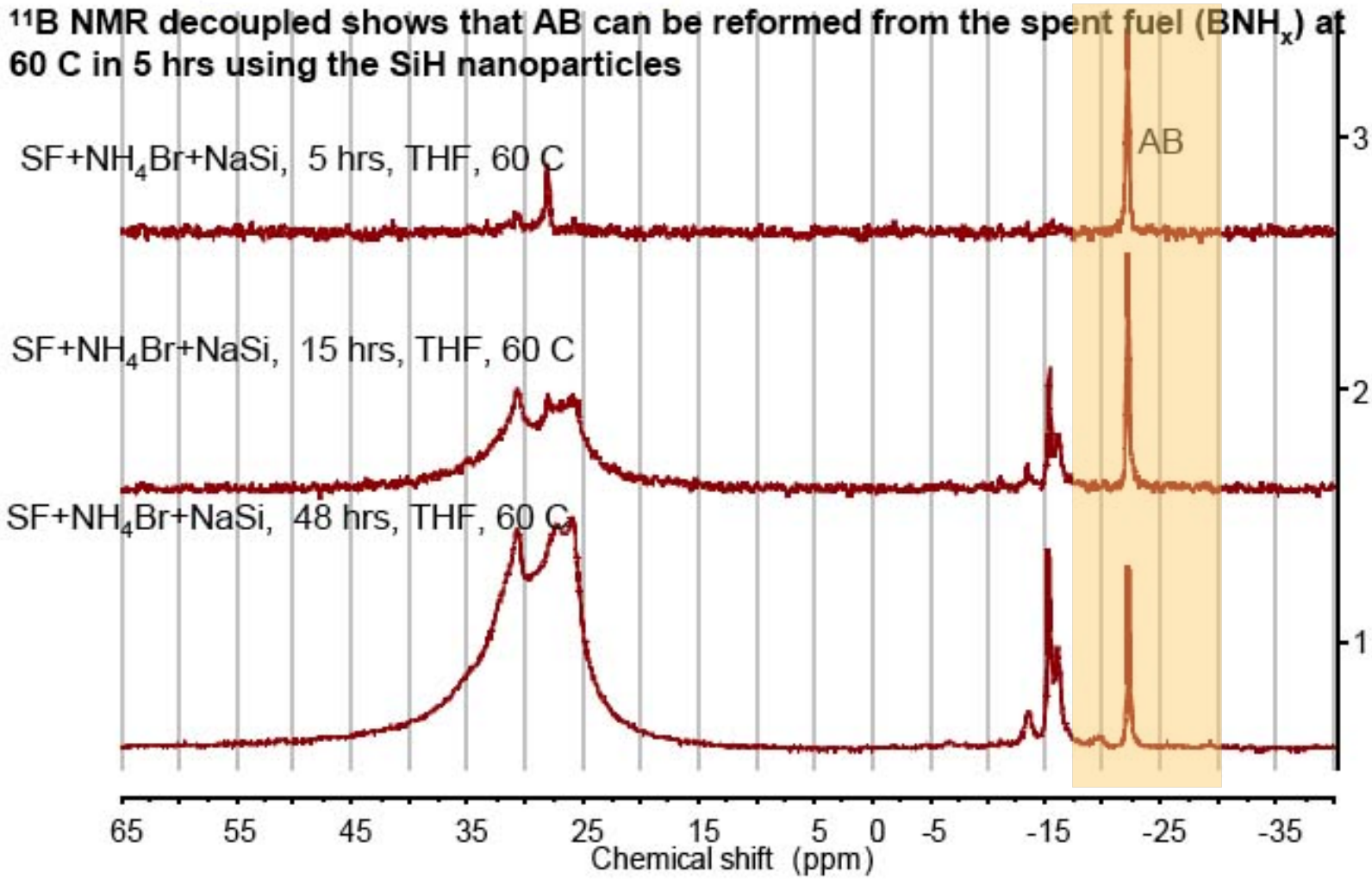
- Hydride transfer from the SiH nanoparticles to triphenyl borate demonstrated, however the main products are still borates
- Small amount of ammonia borane observed by NMR

^{11}B NMR spectra:



Partners: PNNL, Alabama

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



SF = spent fuel

Partners: PNNL, Alabama

Future Directions – Regeneration

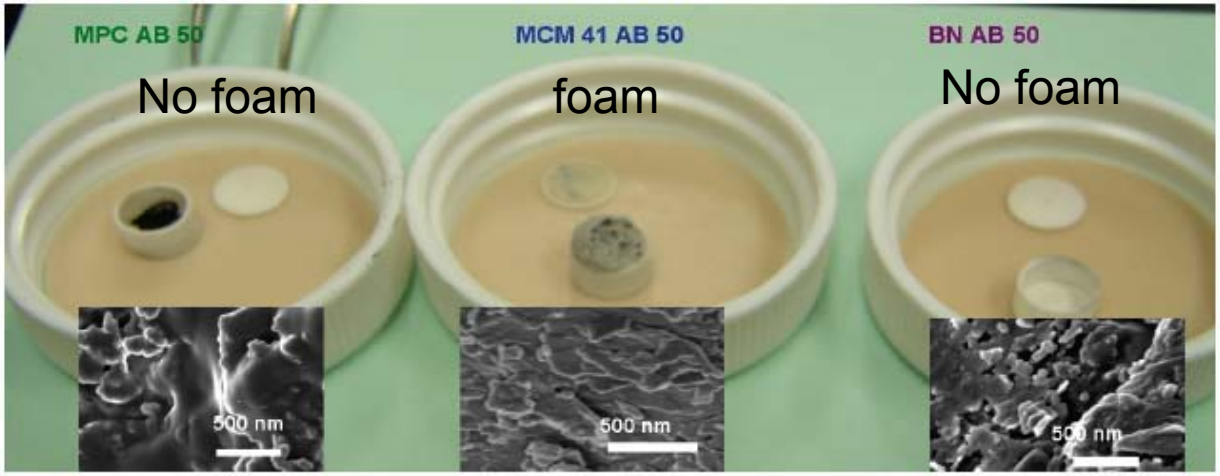
- Optimization of reaction conditions in the regeneration cycle of Bu_3SnH.
  - Test NH_3 as a potential weak base in the generation of $Bu_3SnOC(O)H$
- Evaluate the lifetime of Bu_3SnH through multiple regeneration cycles.
- Investigation of other routes to Main Group formates that do not involve formic 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 H_2 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

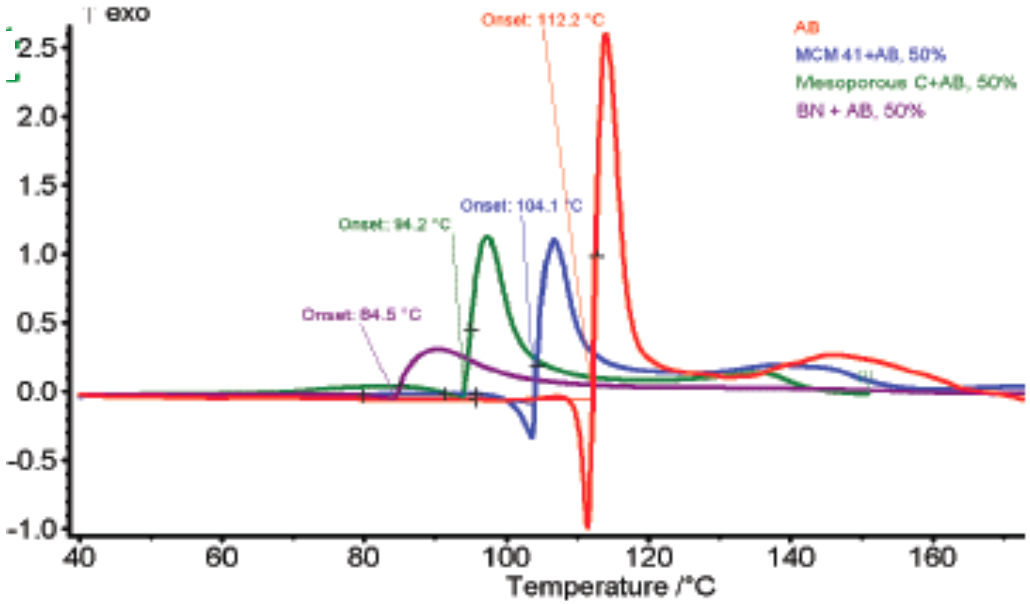
Nanomaterial Supports for Hydrogen Release from Ammonia Borane (AB)

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



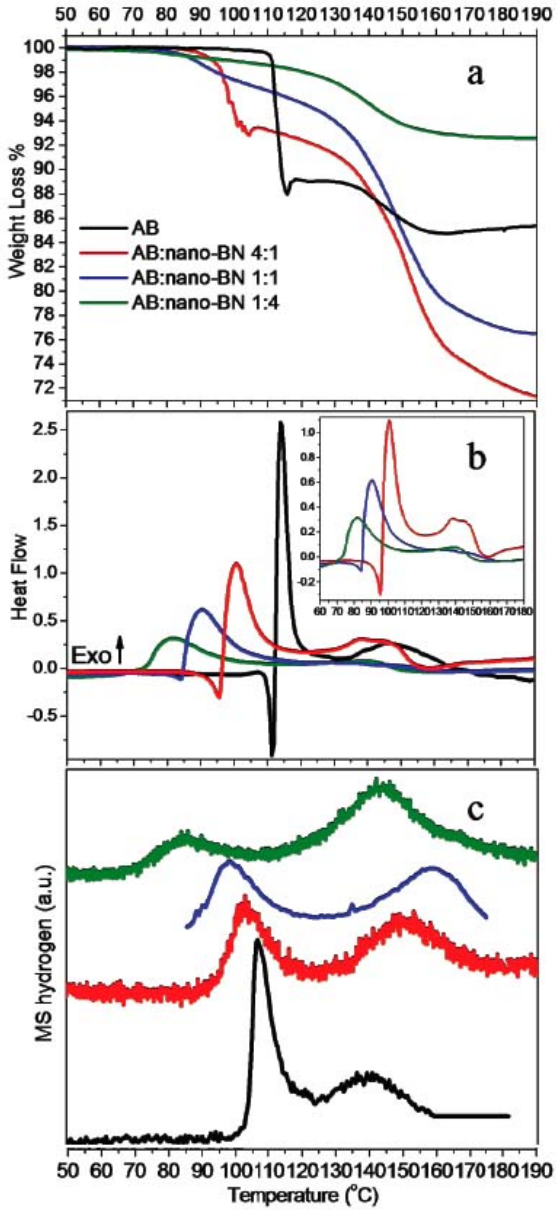
DSC trace of the various combinations normalized for AB.

Nano-BN shows the best results.



Partner: PNNL

Hydrogen Release from nano-BN:AB



1) $H_3NBH_3 \rightarrow (H_2NBH_2)_x + H_2$, 90-120 °C,

2) $(H_2NBH_2)_x \rightarrow (HNBH)_x + xH_2$, 120-160 °C

3) $(HNBH)_x \rightarrow BN + xH_2$, 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

Partner: PNNL

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 H_2 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 CO_2 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.

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