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: FY10
- Percent complete: 100%

Barriers

- Cost
- System weight and volume
- Regeneration Processes

Budget

- Total project funding (05-10)
  - DOE Total $ 1,348,229
  - Contractor share $ 337,059
- Funding for FY08
  - $ 400,000 (DOE) $ 100,000 (cost share)
- Funding for FY09
  - $ 329,281(DOE) (fully funded)
  - FY10 Funding =$ 0

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.
  - Use light element hydride nanomaterials like Si–H, for regeneration of the dehydrogenated material to AB. Make the Si)H NP and transfer a hydride to BX_3 (X= Cl, Br, OR).

- To research the literature and determine the feasability of mechanical activation for chemical regeneration of amine-boranes. Provide a written plan.

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.

Mechanically activated regeneration (collaboration with PNNL)

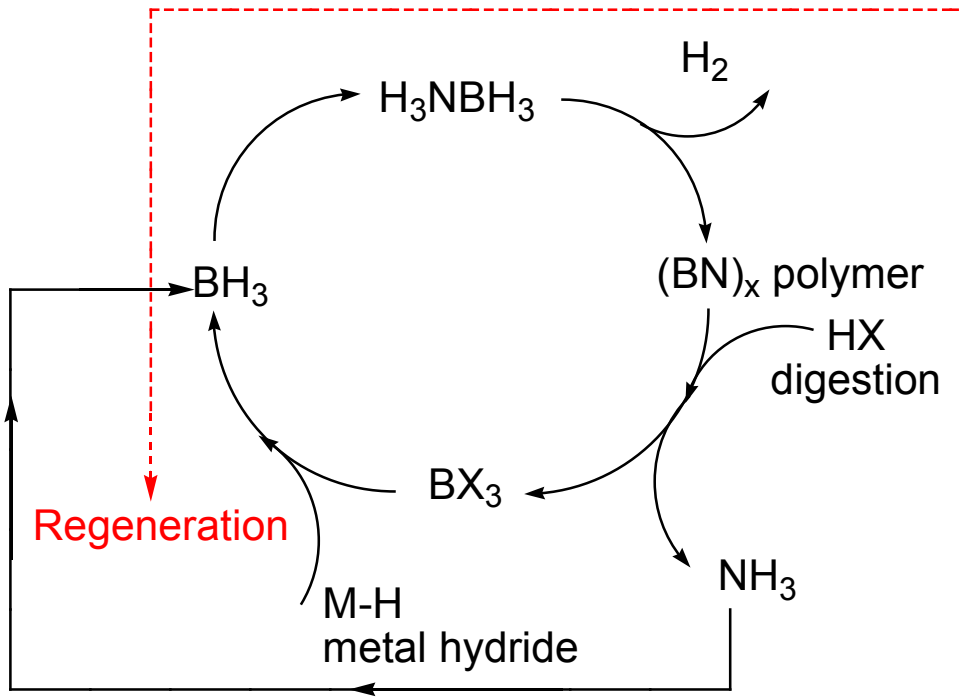
- Literature mining to develop a feasible plan for the chemical regeneration of ammonia-borane.

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

Reduce heat released from AB during dehydrogenation

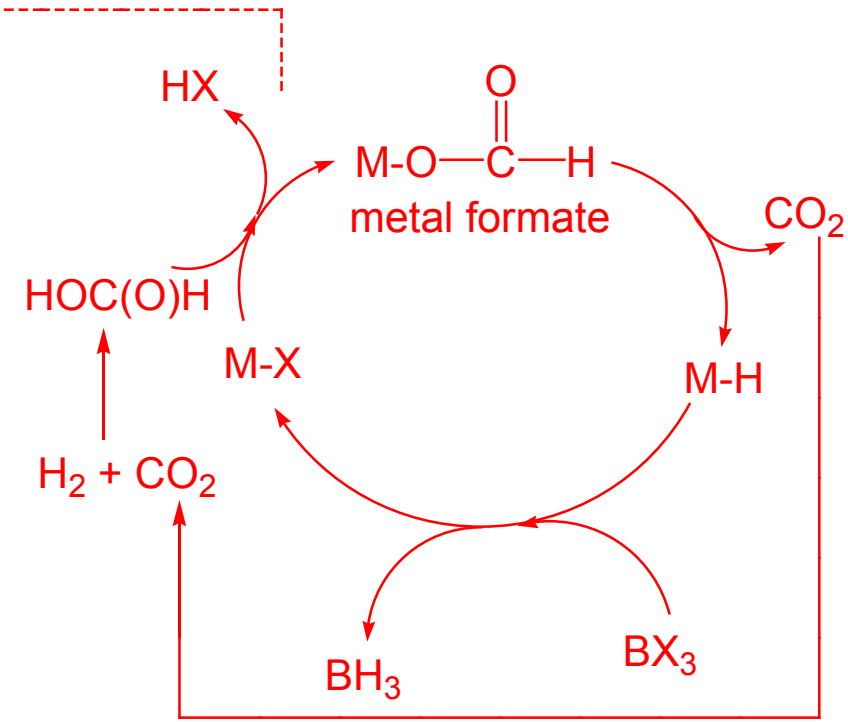
–Reduce/eliminate byproducts (ammonia and borazine) from the dehydrogenation reaction of ammonia borane.
–Eliminate/reduce foaming of ammonia borane.
–Use a nanomaterial that can be easily regenerated and doesn't add contamination or complications to the regeneration of AB.

BN Regeneration with Use of Metal Formates



X = halogen or oxo group

Simplified LANL Cycle for H_2 Storage



Simplified UC Davis Formate/Hydride Regeneration Cycle

Formic acid: supplied via direct synthesis from methane

Search for Metal Formates that Can be Converted to Metal Hydrides Under Mild Conditions

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

$$R_xEOC(O)H \quad + \quad HEAT \quad \text{———} \quad R_xEH \quad + \quad CO_2$$

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

$$R_3SnOSnR_3 \quad + \quad 2\ HOC(O)H \quad \text{———} \quad 2\ R_3SnOC(O)H \quad + \quad H_2O$$

- 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, which can have different srtuctures in the solid state, 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*

- Dibutyltin diformate did not eliminate CO or CO_2 under mild conditions. Instead sublimation of the diformate was observed.

- Demonstrated recycle of the tin hydride $Bu_2SnOC(O)H$. 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.

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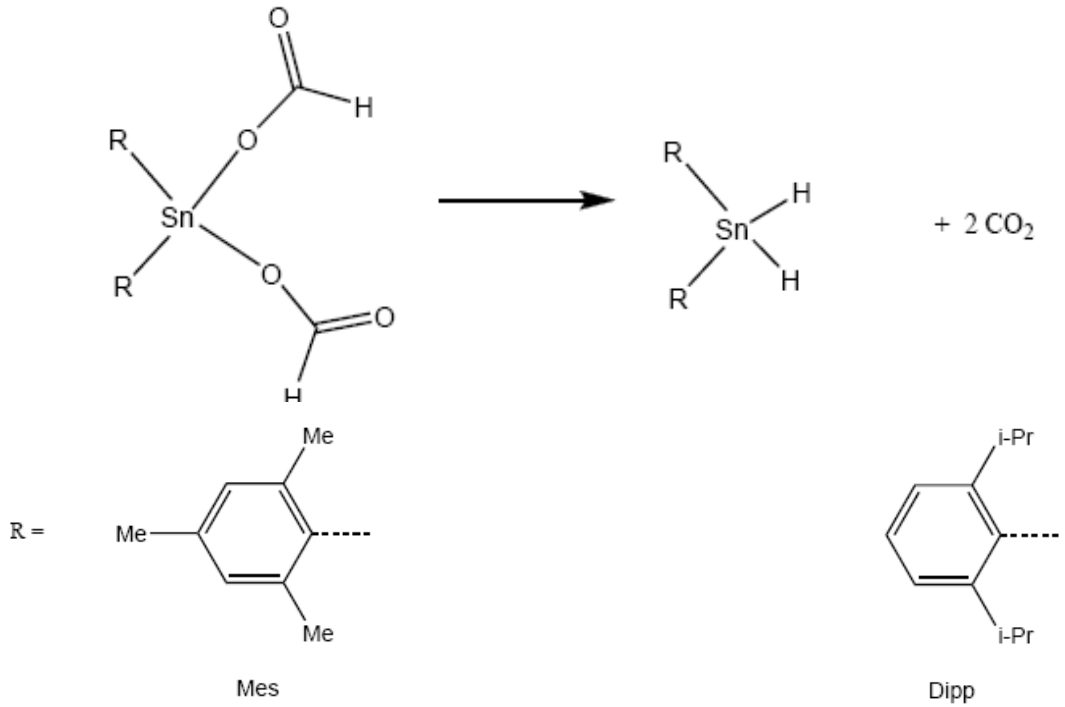
Calculations on Formates Showed that CO_2 Release is Energetically Favored with Hydride Regeneration



R	Δ*H* (0 K)	Δ*H* (298 K)	Δ*G* (298 K)
Mes	17.9	18.2	-2.4
Dipp	16.8	17.2	-5.7

B3LYP/DZVP2 and cc-pVDZ-PP (ECP) for Sn

B. L. Davis, A. D. Sutton, K. X. Bhattacharyya, B. D. Ellis, J. C. Gordon, P. P. Power, unpublished work

Several Tin Formates Were Synthesized and Characterized

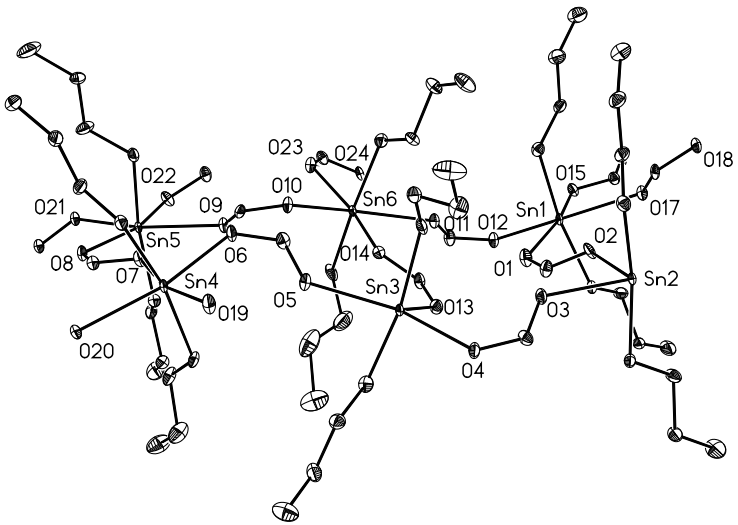


Figure 1. Structure of $\{^{n}Bu_2Sn\{OC(O)H\}_2\}_n$

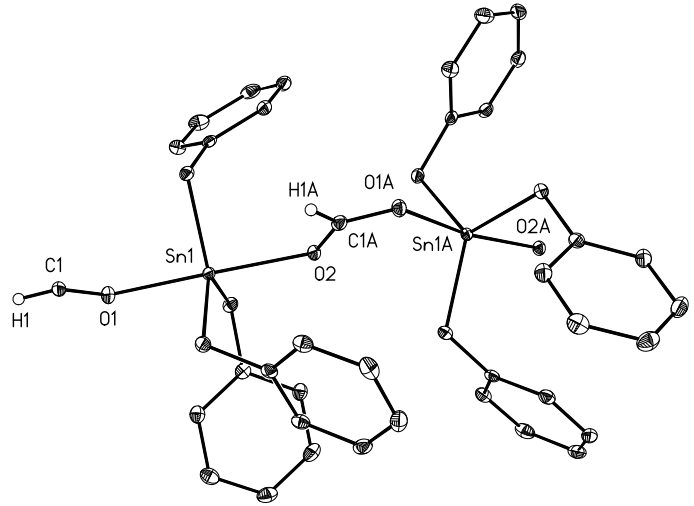


Figure 2. Structure of $\{(PhCH_2)_3SnOC(O)H\}_n$

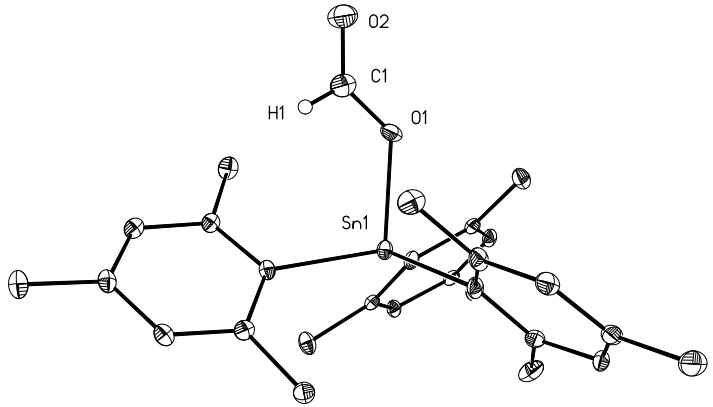


Figure 3. Structure of $Mes_3SnOC(O)H$

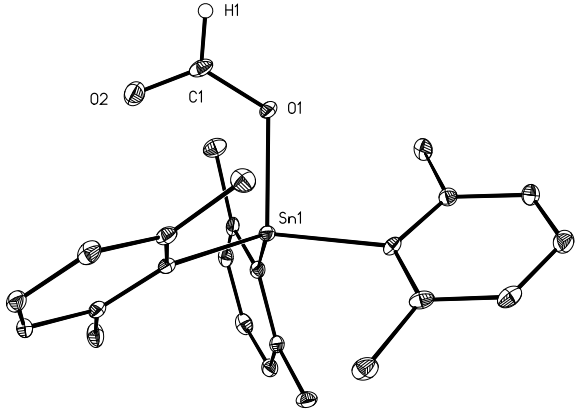


Figure 4. Structure of $\{2,6\text{-}Me_2H_4C_6\}_3SnOC(O)H)$

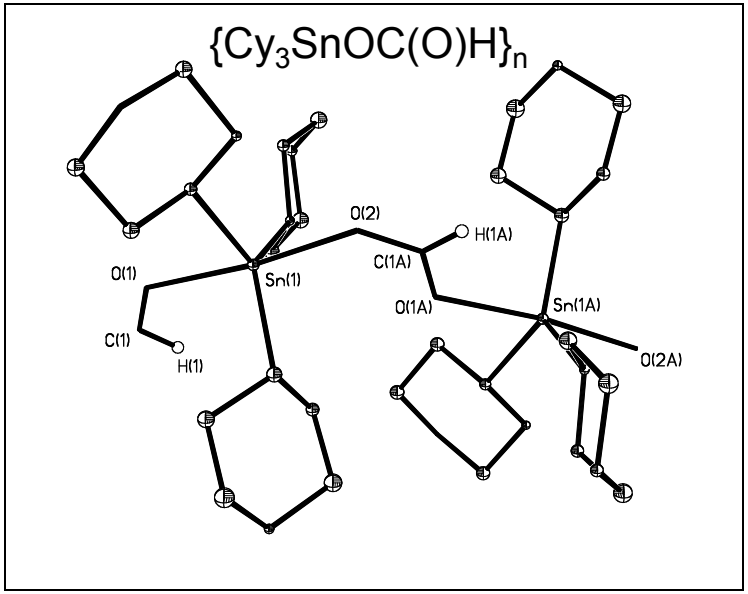
We found that Tri-n-butyl Tin Monoformate was the Only Monoformate Examined that Released CO_2 to Afford a Tin Hydride

- 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.

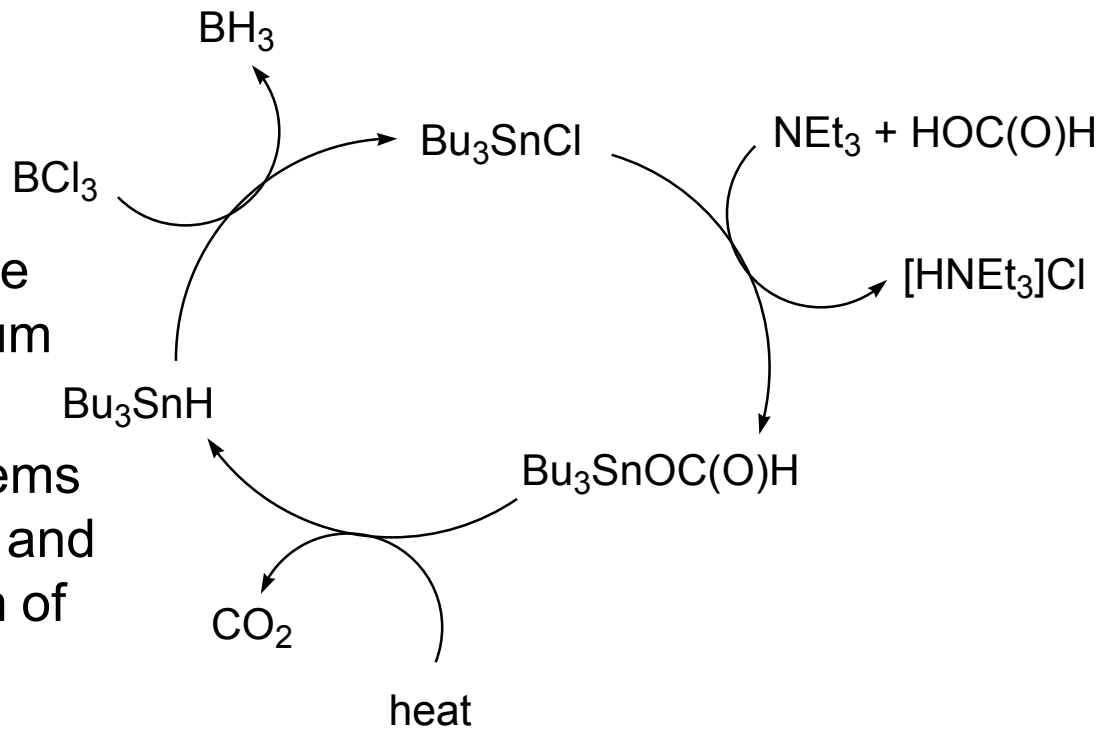
$$2\ Bu_3SnCl + \text{xs NaOH} \text{ ——— } Bu_3SnOSnBu_3 + NaCl + H_2O$$

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

$$Bu_3SnOC(O)H + \text{HEAT} \text{ ——— } Bu_3SnH + CO_2$$

Optimization of the Bu_3SnH Regeneration Cycle

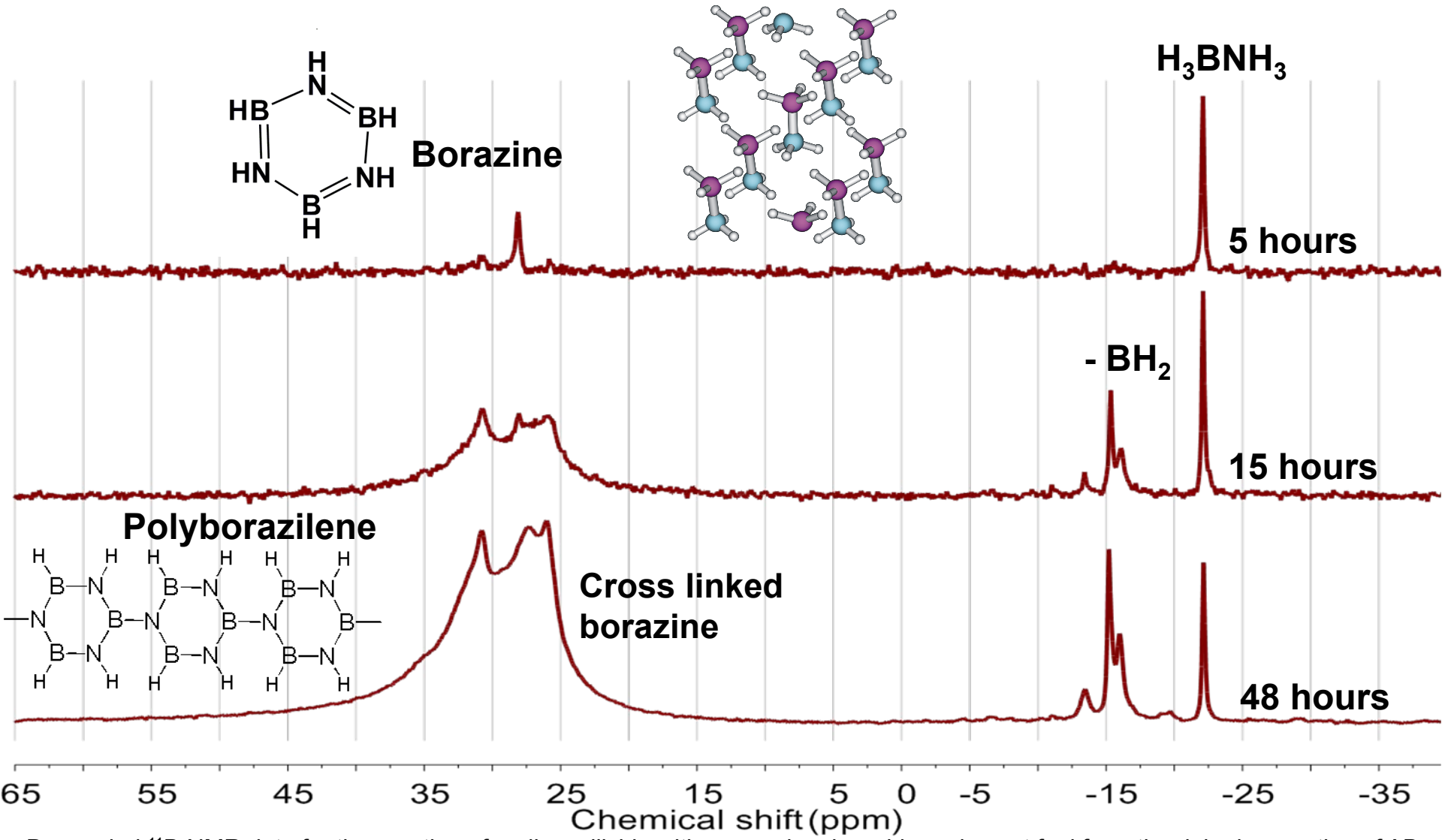
- We have determined that the problematic tin oxide step can be eliminated by direct conversion tin chloride to tin formate with ammonium formates
  - This removes the problems with low tin oxide yields and consumption/generation of NaOH/NaCl



- 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 Bonds

NaSi + NH_4Br + (spent fuel) BNH_x



Decoupled ^{11}B NMR data for the reaction of sodium silicide with ammonium bromide and spent fuel from the dehydrogenation of AB

Regeneration of AB from Mechanical Alloying

The temperature in the materials during ball milling is lower than 60 C (prevents decomposition of AB).

Possible Reactions to pursue:

BNH_x + NaSi + NH_4Br ball mill mull of THF or glyme

$B(OPh)_3$ + NaSi + NH_4Br ball milled mull of THF or glyme

$(C_2H_5)_3N$ HCl + NaSi + NH_4Br + $B(OPh)_3$

Other reagents:

R_3NHBr

Remaining Issues and Proposed Future Work

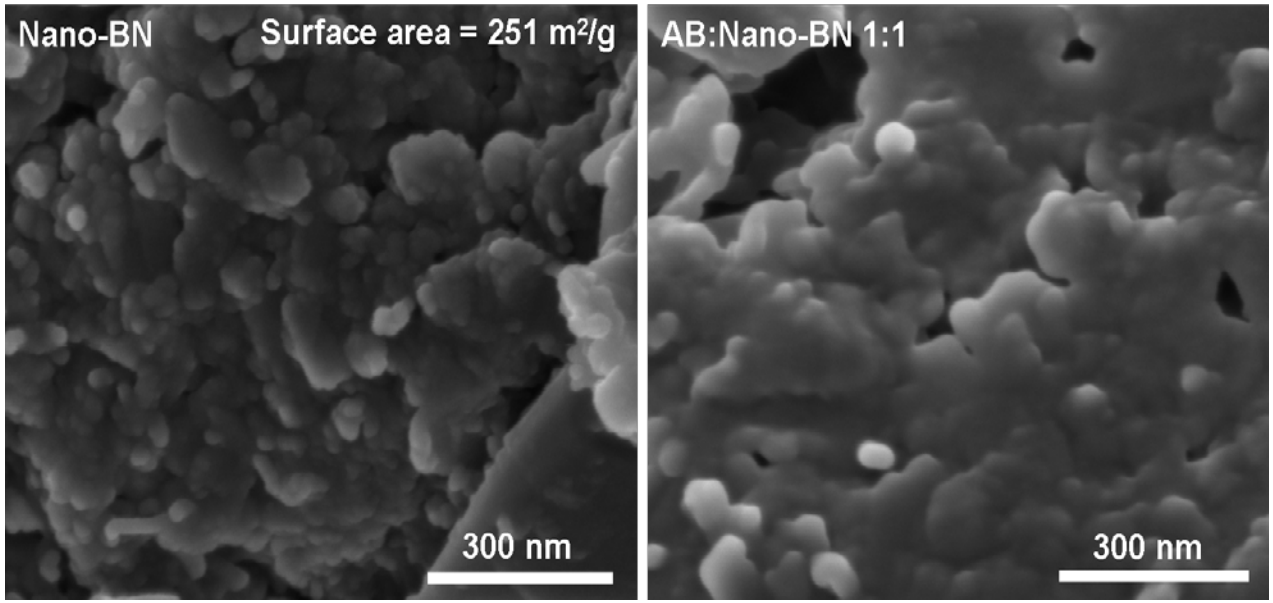
- Optimization of reaction conditions in the regeneration cycle of Bu_3SnH.
  - Test NH_3 as a potential weak base in the generation of $Bu_3SnOC(O)H$
- Evaluate the lifetime of Bu_3SnH through multiple regeneration cycles.
- Investigation of other routes to Main Group formates that do not involve formic acid:
  - Hydrogenolysis of singlet diradical compounds
  - Hydrogen addition to unsaturated Main Group compounds (eg. aluminum)
  - Direct addition of hydrogen to E-X bonds
- Experimentally investigate the possibility of mechanical alloying as a low cost method to regeneration AB from spent fuel.

Summary of Accomplishments – Release

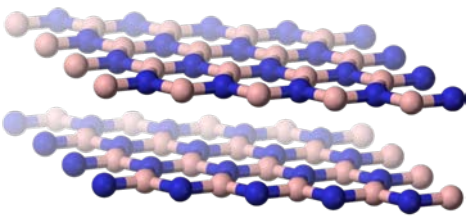
- Studied the possibility of using nanomaterials obtained via BM to affect the hydrogen release from AB (MCM, MPC, graphite, BN neat and doped with Ti, Co, TiO_2)
- Down selected to nano-BN from all of the above due to its composition (B and N) and properties (lower temperature of release) and understand the mechanism of hydrogen release from AB:nano-BN to help develop better additives
- The effect of nano-BN studied via high field NMR, high resolution TEM, TG/DSC/MS, and Raman spectroscopy.
  - Elimination of foam problem associated with hydrogen release from AB
  - Lowering of the release temperature as compared to AB
  - Smaller enthalpy for the first equivalent of H_2 released from AB
  - Eliminates the induction period as compared to AB
  - Reduces ammonia release as compared to AB
  - Increases borazine released as compared to AB
- Quantify borazine via NMR for AB and AB:nano-BN mixtures
- Partnered with PNNL

Nano-BN and AB:nano-BN, SEM Images

Simple mixture of AB and nano-BN



Hexagonal-BN



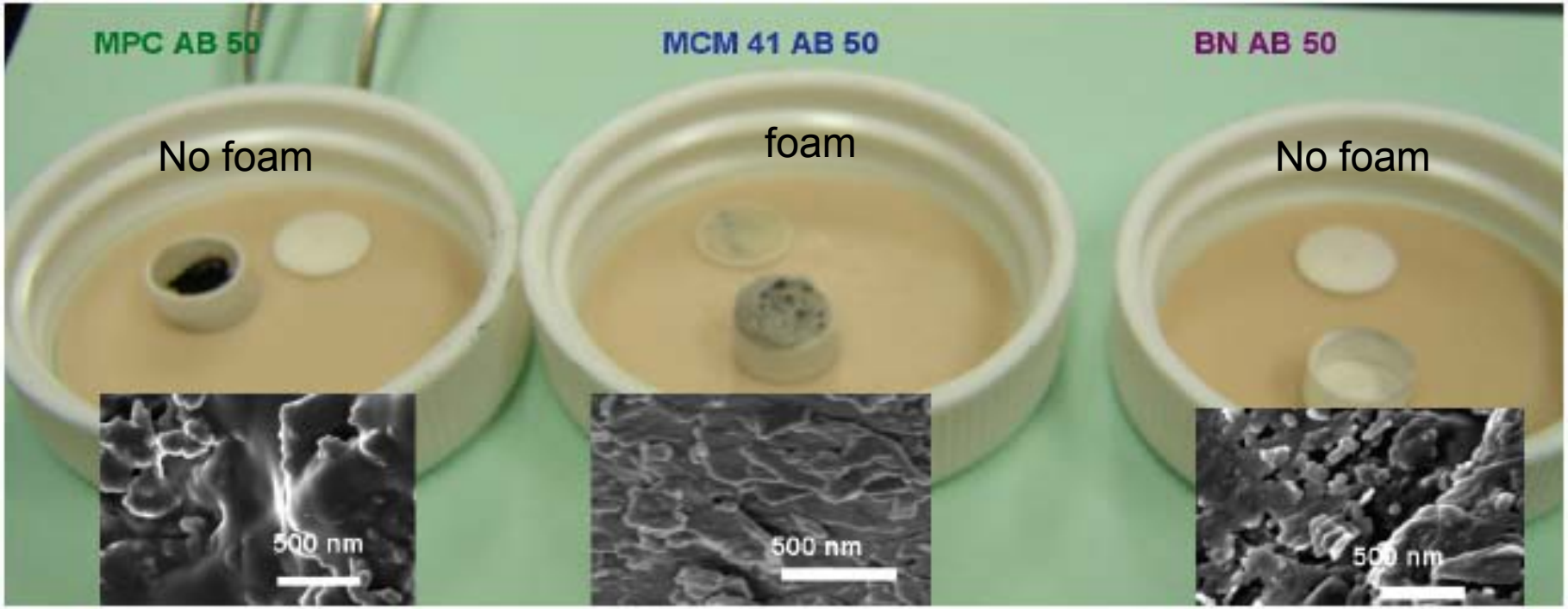
+ AB

- Light-weight additive
- Inert support
- High surface area
- No contamination that might complicate AB regeneration

Partner: PNNL

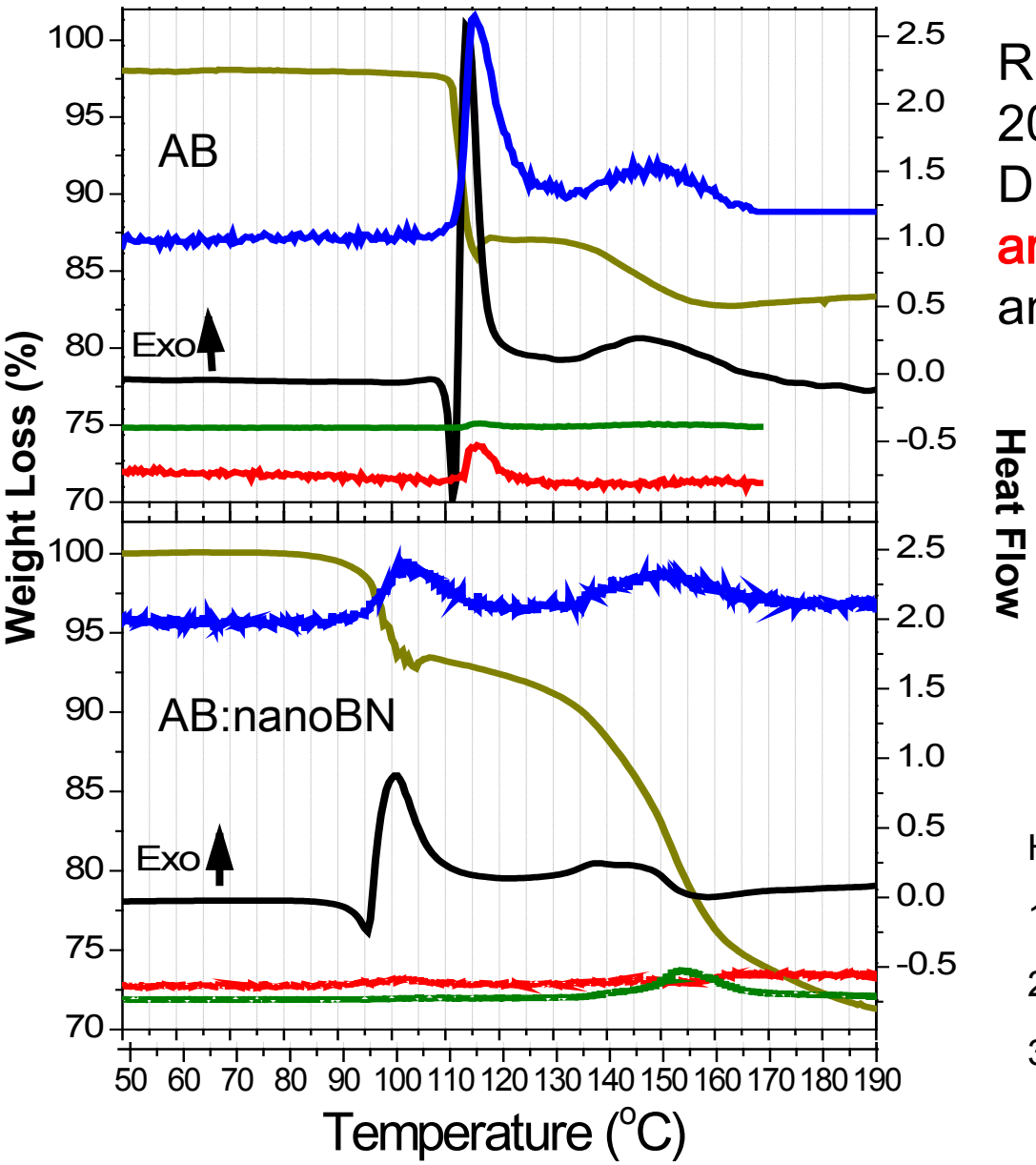
Effect of Nanomaterial for Hydrogen Release from Ammonia Borane (AB)

Compared mesoporous carbon (MPS), zeolite (MCM 41) and nano-BN. Only MPC and nano-BN show an absence of foaming after hydrogen release.



Partner: PNNL

TG/DSC/MS of AB and AB:nano-BN (4:1)



Ramping 1K/min to 200 C under 20 ml/min Ar flow, showing TG, DSC, MS for hydrogen, ammonia, and borazine for AB and B:nano-BN (4:1)

Results of BN addition

- Lower temperature of release
- Lower heat released
- Lower ammonia
- Higher Borazine

Hydrogen Release from AB:

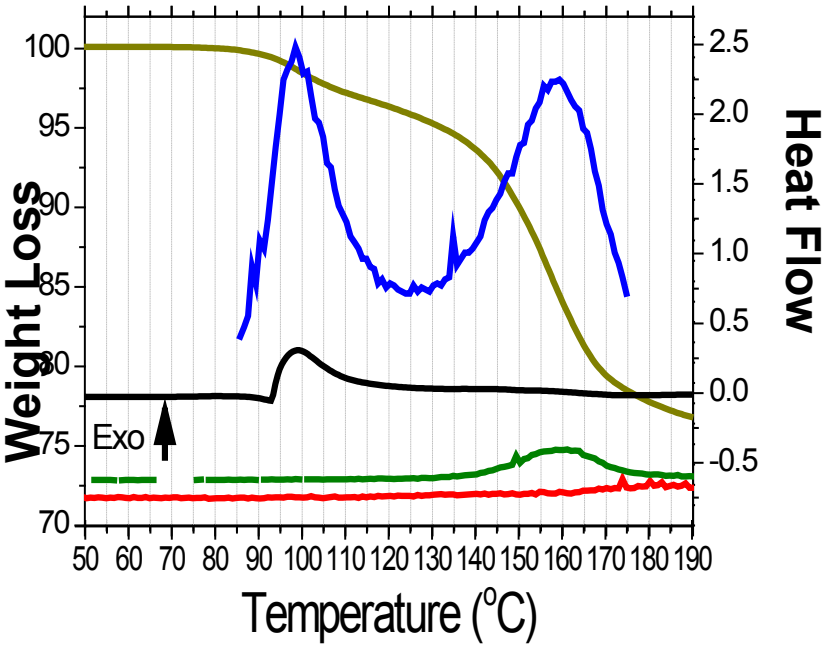
1) H_3NBH_3 --> $(H_2NBH_2)_x + H_2$, 90-120 °C

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

3) $(HNBH)_x$ --> $BN + xH_2$, 500 °C

Partner: PNNL

TG/DSC/MS of AB:nano-BN (1:1)



Ramping with 1K/min to 200 C under 20 ml/min Ar flow, showing TG, DSC, MS for hydrogen, ammonia, and borazine.

AB:nano-BN 1:1 system (to compare with MCM-41 results)[1]

Results of BN addition

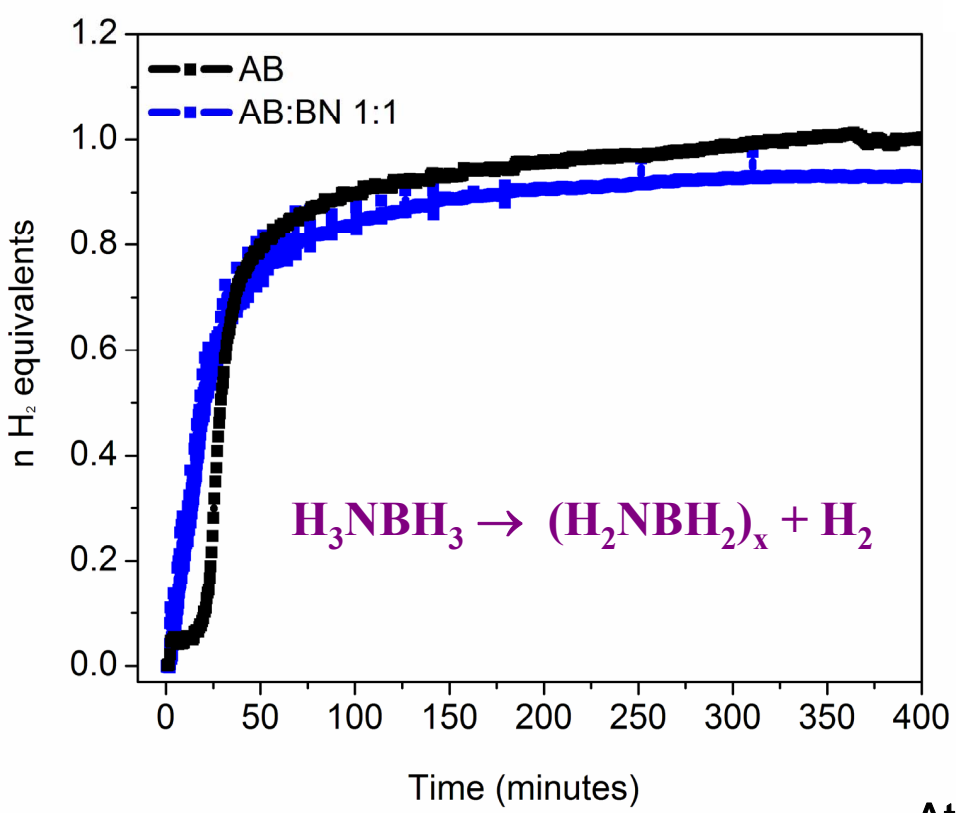
- Lower temperature of release
- Lower heat release
- Lower ammonia
  - -(200 ppm vs 2000 ppm from AB neat)
- Higher Borazine
  - -2.4 0.02 mol % from AB:nano-BN 1:1
  - -1.8 0.7 mol% from AB

Partner: PNNL

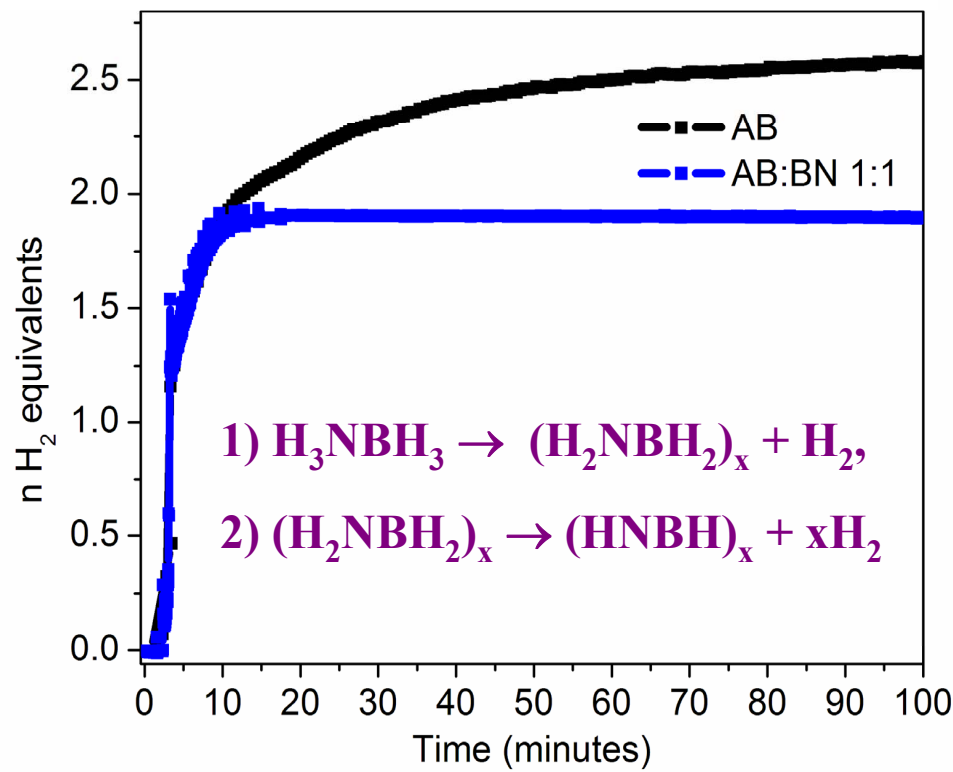
[1] Gutowska, et al. *Angew. Chem.-Int. Ed.* **2005**, *44*, 3578.

Volumetric Gas Burette Measurements

T= 90 °C



T= 150 °C



1 equivalent of hydrogen released from neat AB as compared to 0.96 released from 1:1 AB:nano-BN

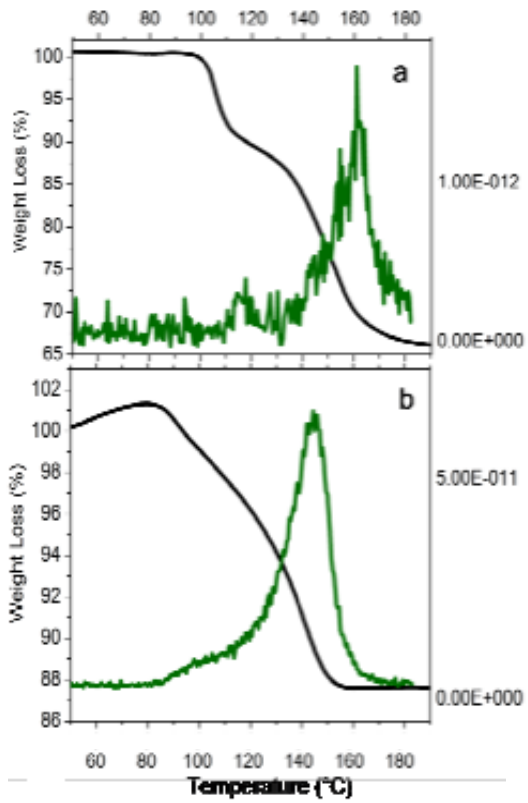
At 150°C under isothermal conditions

AB releases 2.6 eq. H_2 and 0.5±0.26 mol% borazine

AB:nano-BN releases 1.9 eq. H_2 and 1.6±0.4 mol% borazine

Partner: PNNL

New Hydrogen Release Pathway with nano-BN



TG/MS data obtained by heating the samples under Ar flow with 1 K/min to 200□C for a) ^{15}N labeled AB and b) ^{15}N labeled 1:1 AB: nano-BN. TG axis is on the left and MS axis is on the right.

TG/MS experiments on ^{15}N labeled AB indicate that BZ is produced from AB and not by reaction with nano-BN. These results suggest that the mechanism of hydrogen release and BZ production is affected by interaction of AB with nano-BN surface: the ring structure of BZ is favored by slow heating rates and interaction with the nano-BN surface. These interactions lead to lower temperatures and exothermicity of hydrogen release suggesting that a high surface area material like nano-BN may provide an optimal support for AB dehydrogenation.

Partner: PNNL

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) Nanocrystallite 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. Informal interactions with SiGNa.
- Proposed Future Research: Optimization of nanocrystallite phases for regeneration and for hydrogen release from AB, explore the addition of catalyst to change the pathway and eliminate BZ release. 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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Avery Luedtke (PNNL)

Alex Navrotsky (UCD): XRD
Ping Yu (UCD): MAS NMR

Michael Lefenfeld SiGNa

Small Molecules:

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Zhongliang Zhu

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John Gordon (LANL)
Ben Davis (LANL)
Jerry Potter (PNNL)
Michael Mock (PNNL)