Amineborane Hydrogen Storage

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Project ID#: STP8

PENN
UNIVERSITY of PENNSYLVANIA

Project Overview

Timeline

Project Start: FY 2005
Project End: FY 2009
Percent complete: New Start

Budget

Total Project Funding:
$1,727,356 expected
DOE: $1,381,886 expected
DOE Funding in 05: $197,000

Barriers for Chemical Hydrogen Storage with Amineboranes

On-demand hydrogen release from amineboranes has not yet been achieved

Low cost methods for amine-borane regeneration have not been developed

Partners on Amineborane Project

LANL, PNNL, U. of W, NAU

Amineborane Hydrogen Storage Materials

Because of their protonic N-H and hydridic B-H hydrogens, amineboranes are unique in their ability to store and release hydrogen

Potential Hydrogen Storage Capacities of Common Amineboranes

$$NH_4BH_4 \longrightarrow BN + 4\,H_2 \quad (24.5\text{ wt\%, }0.20\text{ kg/L }H_2)$$

$$NH_3BH_3 \longrightarrow BN + 3\,H_2 \quad (19.6\text{ wt\%, }0.16\text{ kg/L }H_2)$$

$$B_3N_3H_{12} \longrightarrow 3\,BN + 6\,H_2 \quad (14\text{ wt\%, }0.11\text{ kg/L }H_2)$$

$$B_3N_3H_6 \longrightarrow 3\,BN + 3\,H_2 \quad (7.5\text{ wt\%, }0.06\text{ kg/L }H_2)$$

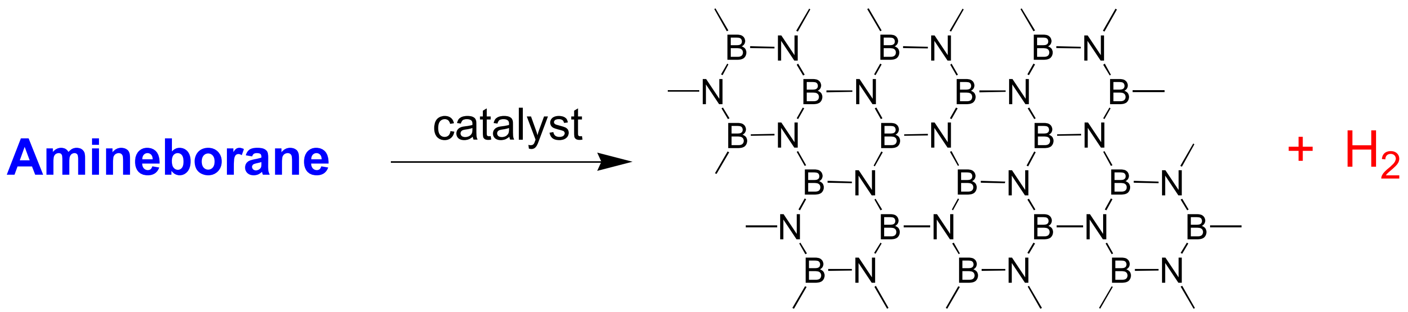
$$NH_3B_3H_7 \longrightarrow B_3N + 5\,H_2 \quad (17.8\text{ wt\%, }0.14\text{ kg/L }H_2)$$

DOE Targets:

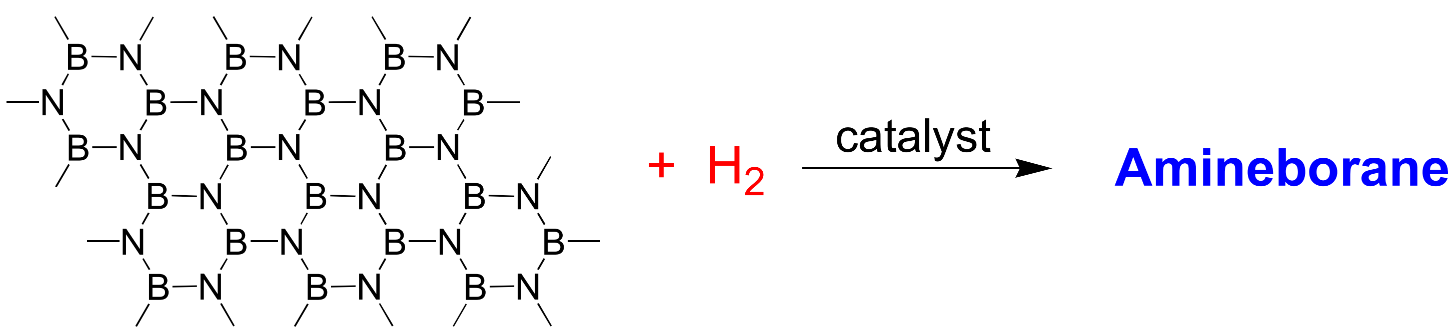
2005: 4.5 wt%, 0.036 kg/L H_2; 2010: 6.0 wt%, 0.045 kg/L H_2; 2015: 9.0 wt%, 0.081 kg/L H_2

Project Objectives

1. Develop Catalytic Methods for On-Demand, Low Temperature (<200°C) Hydrogen Release from **Amineboranes**

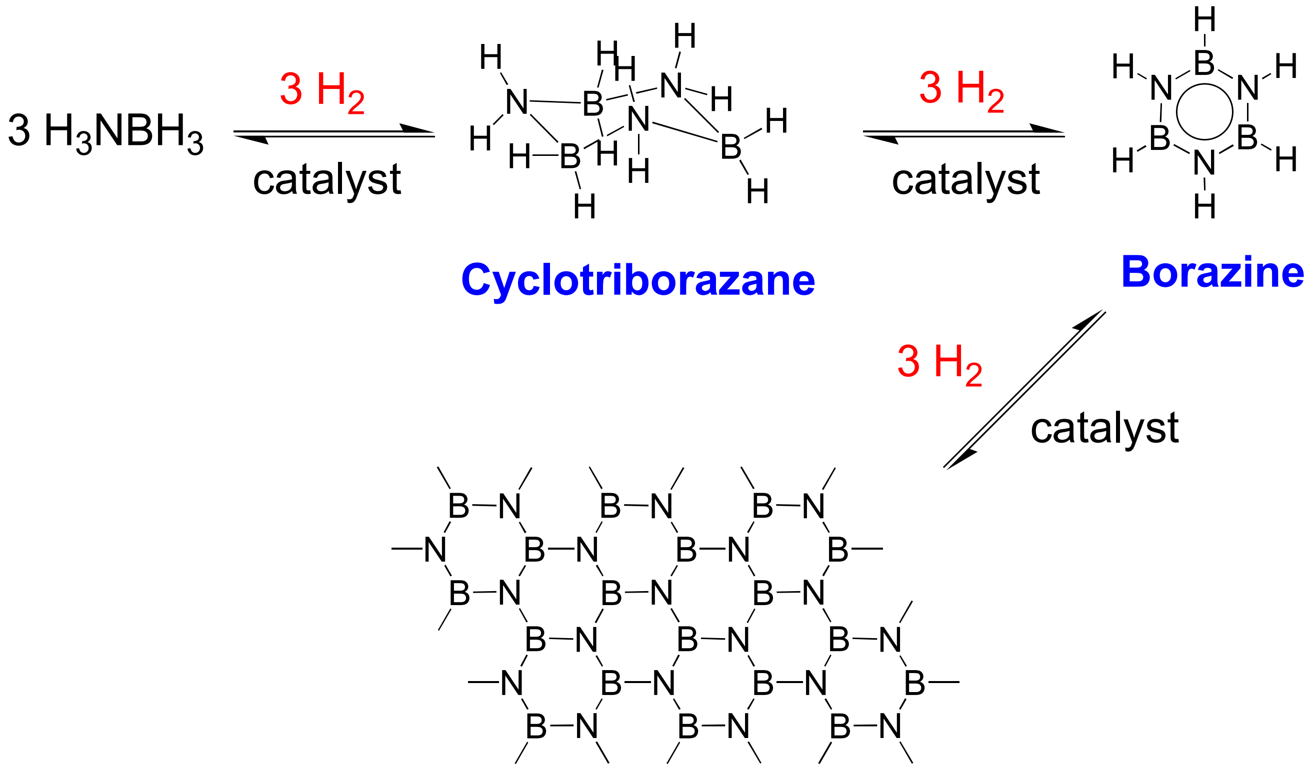


2. Develop High Conversion Off-Board Methods for **Amineborane** Regeneration



Approach

In collaboration with Center Partners LANL, PNNL, U of Washington and Northern Arizona U., we will develop catalyzed pathways for key **Amineborane Hydrogenation/Regeneration Reactions** that increase control and efficiency



Cyclotriborazane

Borazine

Boron Nitride

Go/No-Go Decision Points

3 Q of Year 2, decide:

1. What are the most promising classes of catalysts for amineborane dehydrogenation?
2. What is the most promising catalytic or stoichiometric method for amineborane regeneration?
3. What is the most promising amineborane for hydrogen storage?

3 Q of Year 3, decide:

4. What final processes, catalysts and amineborane materials will be optimized?

4 Q of Year 4, decide:

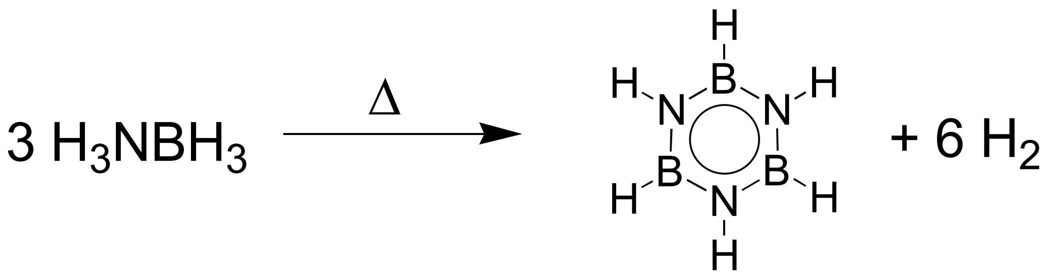
5. Does the optimized process meet the DOE targets?

2 Q of Year 5, decide:

6. Is any redesign of scaled up process necessary?

Previous Penn Studies of Ammonia Borane Dehydrogenations

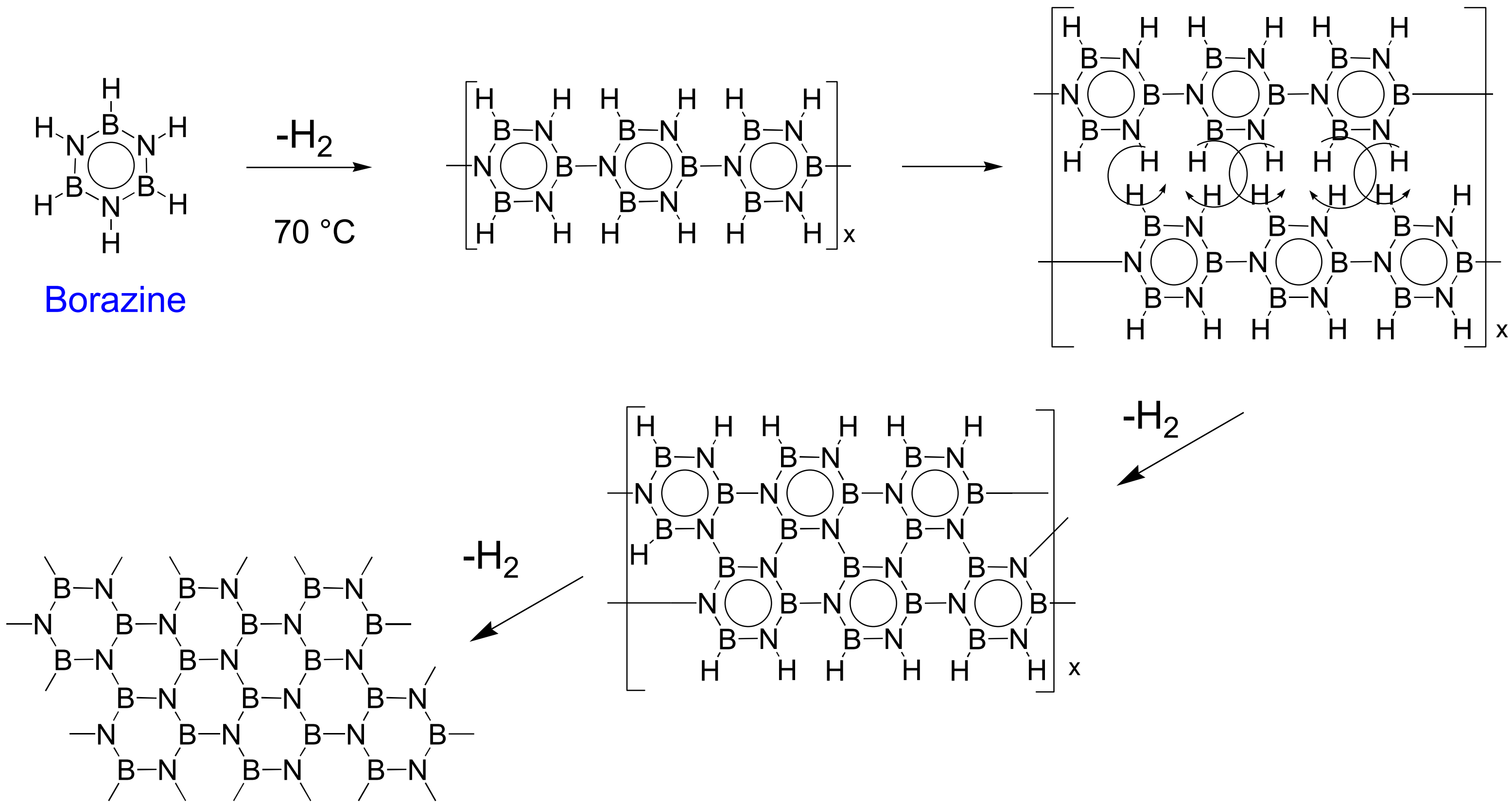
1. Ammonia Borane dehydrogenation to Borazine has been achieved at Penn



Borazine

Wideman, T.; Sneddon, L. G. *Inorg. Chem.* **1995**, *34*, 1002.

2. Borazine dehydrogenation to Boron Nitride has been demonstrated at Penn



Boron Nitride

Fazen, P. J.; Remsen, E. E., Beck, J. S.; Sneddon, L. G. *Chem. Mater.* **1995**, *7*, 1942.

Previous Studies of Metal Catalyzed Borane Dehydrogenations

1. Penn Studies have shown that metals can catalyze polyborane dehydrogenation reactions

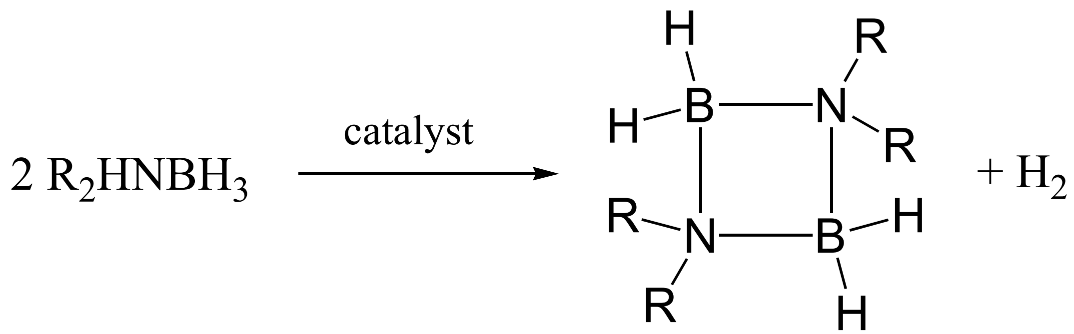
$$2\,B_5H_9 \xrightarrow{PtBr_2} (B_5H_8)_2 + H_2$$

$$2\,B_4H_{10} \xrightarrow{PtBr_2} (B_4H_9)_2 + H_2$$

$$2\,B_2H_6 \xrightarrow{PtBr_2} B_4H_{10} + H_2$$

Corcoran, Jr. E. W.; Sneddon, L. G. *J. Am. Chem. Soc.* **1984**, *106*, 7793

2. Manners has shown that metals catalyze Amineborane dehydrogenation reactions, but complete dehydrogenation was not achieved



Jaska, C. A.; Temple, K; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2003**, *125*, 9424

Both the Penn and Manners studies strongly suggest that new metal catalyzed reactions can be developed for efficient and exhaustive amineborane dehydrogenation

Proposed Research: Develop Nanoparticle Catalysts for Amineborane Hydrogenation/Dehydrogenations

Heterogeneous nanoparticle transition metal catalysts with narrow size distributions will be generated by either chemical or electrochemical reduction of metal salts or controlled decomposition of organometallic compounds.

Our studies will be focused initially on nanoparticle catalysts for amineborane hydrogenations/dehydrogenations. Such catalysts have been shown to have high activity for arene hydrogenations, suggesting they should have comparable activities for boron-nitrogen species containing borazine type fragments.

Overview and Timelines of Primary Tasks for Amineborane Dehydrogenation Objective

1.1 prepare key amineboranes, aminepolyboranes and amineborane polymers and develop new routes where necessary (3Q, Y1)
1.2 screen activities of likely dehydrogenation catalysts (4Q, Y2)
1.3 quantify hydrogen production of most promising reactions (4Q, Y3)
1.4 establish effects of reaction conditions, including solvent, temperature on dehydrogenation of amineboranes (4Q, Y4)
1.5 optimize and scale-up lead dehydrogenation system (4Q, Y5)

Penn Work Complements Partner Studies on Amineborane Dehydrogenations

Penn: development of nanoparticle-based dehydrogenation catalysts: characterization and reactivity of a-BN products

LANL: development of homogeneous and/or acid dehydrogenation catalysts

PNNL: development of supported dehydrogenation catalysts

U. of Washington: studies of fundamental amineborane coordination chemistry and mechanistic studies of homogeneously catalyzed dehydrogenation

Northern Arizona U.: studies of the catalyzed dehydrogenation of alkylborazines

First Project Milestones for Amineborane Dehydrogenations

1. Initial screening of nanoparticle-based dehydrogenation catalysts for amineborane activity will be completed in first 18 months.

2. Initial screening of catalysts for a variety of key amineborane dehydrogenations will be completed in first 12 months.

$$NH_3BH_3 \xrightarrow{\text{catalyst}} BN + 3\ H_2$$

$$B_3N_3H_{12} \xrightarrow{\text{catalyst}} 3\ BN + 6\ H_2$$

$$B_3N_3H_6 \xrightarrow{\text{catalyst}} 3\ BN + 3\ H_2$$

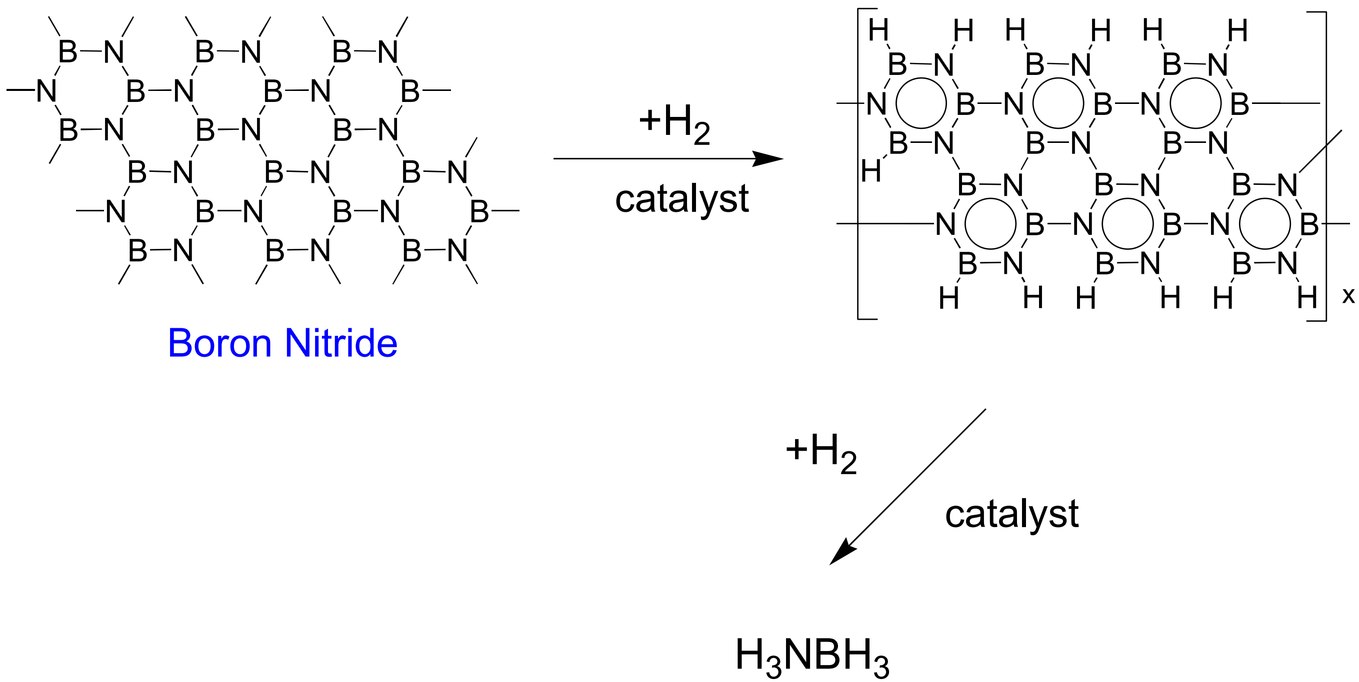
$$NH_3B_3H_7 \xrightarrow{\text{catalyst}} B_3N + 5\ H_2$$

3. The characterization of the solid-state boron-nitrogen products of amineborane dehydrogenations will be complete in 18 months.

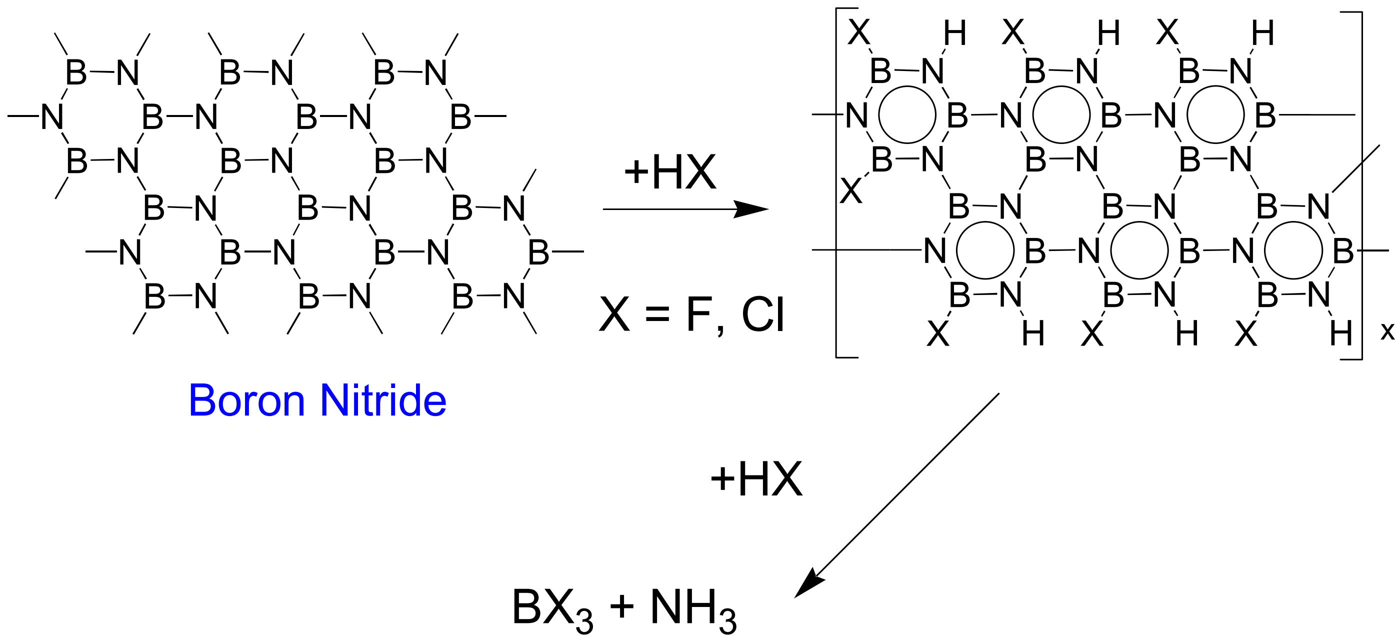
4. There will be continuous comparison of Penn results with complementary studies of homogeneous and heterogeneous animeborane dehydrogenation catalysts at LANL, PNNL, U. of Washington and Northern Arizona University.

Approaches for Off-Board Amineborane Regeneration

1. Transition metals should catalyze hydrogenation of boron nitride materials to regenerate amineboranes



2. Stoichiometric hydrohalogenation of boron nitride followed by hydrogenation will be explored as an alternative pathway for regeneration



$$2\,BX_3 + 6\,H_2 \longrightarrow B_2H_6 + 6\,HX$$

$$B_2H_6 + 2\,NH_3 \longrightarrow 2\,NH_3BH_3$$

Overview and Timelines of Primary Tasks for Amineborane Regeneration Objective

2.1 characterize the amorphous boron nitride (a-BN) products resulting from amineborane dehydrogenation under different conditions (4Q, Y1)
2.2 screen the activity of a-BN for hydrogenation by known hydrogenation catalysts and determine the activity of a-BN towards chemical reagents such a HX and NH_3 that could aid in amineborane regeneration (4Q, Y2)
2.3 determine the most reactive a-BN product towards both hydrogenation and hydrohalogenation reactions (4Q, Y3)
2.4 establish effects of reaction conditions, including solvent, temperature on both hydrogenation and hydrohalogenation reactions of a-BN (4Q, Y4)
2.5 optimize and scale-up lead regeneration system (4Q, Y5)

First Project Milestones for Amineborane Regeneration

1. Complete initial screening of nanoparticle-based metal catalysts for boron nitride hydrogenation activity (18 months)
2. Complete initial screening of known arene-hydrogenation catalysts for boron nitride and borazine hydrogenation activity (18 months)
3. Complete initial screening of reactions of haloacids with amorphous boron nitride and borazine-based polymers (12 months)
4. Determine if the boron nitride products from the dehydrogenation of different amineboranes have different reactivities (18 months)

Outline of Future Work

TASKS	FY 05	FY 06	FY 07	FY 08	FY 09
TASK 1.1 Prepare amineboranes and develop improved syntheses where necessary	■	■			
TASK 1.2 Screen dehydrogenation catalysts	■	■	■		
TASK 1.3 Quantify hydrogen production of most promising reactions		■	■	■	
TASK 1.4 Optimize dehydrogenation reaction conditions			■	■	
TASK 1.5 Scale-up lead dehydrogenation system				■	■
TASK 2.1 Characterize amphorous BN products from amineborane dehydrogenations	■	■			
TASK 2.2 Screen activity of amphorous BN for hydrogenation and chemical regeneration	■	■	■		
TASK 2.3 Identify the most active amphorous BN materials for regeneration		■	■		
TASK 2.4 Optimize reactions conditions for regeneration			■	■	
TASK 2.5 Scale-up lead regeneration system				■	■

Penn Research Team

Principal Investigator:

Larry G. Sneddon

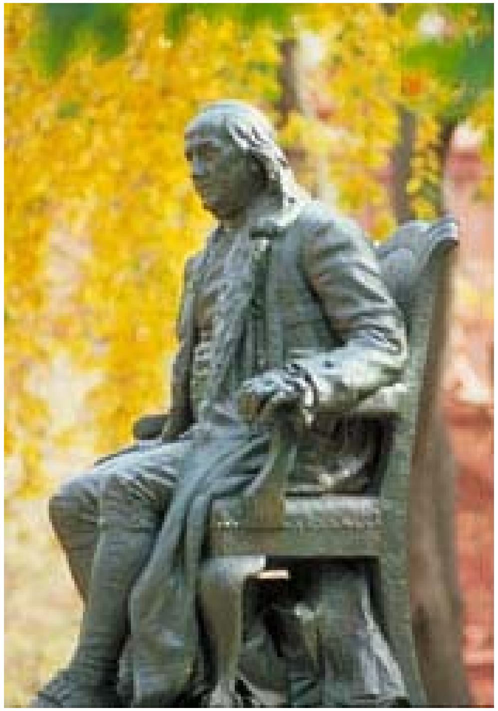
Postdoctorals:

Martin Bluhm

Mark Bradley

Graduate Student

William Ewing



Hydrogen Safety

As per the solicitation requirements, a detailed safety plan for project activities requiring handing hydrogen and reactive materials is under development.

The most significant hydrogen hazard associated with this project is:

an uncontrolled release of hydrogen gas from a compressed gas cylinder.

Hydrogen Safety

Our approach to deal with this hazard is:

Work will take place in a well ventilated (8-12 air changes per hour) laboratory

The cylinder will be appropriately secured and closed when not in use. A two stage regulator with a needle valve will be used to dispense the gas.

The gas will be dispensed using tubing which is chemically compatible with hydrogen and the burst pressure will be a minimum of four times the maximum discharge pressure of the regulator.

All fittings and connections will be a compression type. Friction connections, if present will be located in the fume hood or glove box filled with an inert atmosphere and secured with a clamp.