



Amineborane-Based Chemical Hydrogen Storage

Department of Chemistry
University of Pennsylvania

DOE Chemical Hydrogen
Storage Center of Excellence

2010 DOE Hydrogen Program Review

June 10, 2010

Project ID: ST039

This presentation does not contain any proprietary or confidential information

Project Overview

Timeline

Project Start: FY 2005
Project End: March 2010
Percent complete: 95%

Budget

Total Project Funding: \$1,783,787
DOE: \$1,417,353
Penn: \$366,434

DOE Funding in 09: \$300,000
DOE Funding in 10: \$300,000

Barriers Addressed

Barriers

- A. System Weight and Volume
- B. System Cost
- E. Charging/Discharging Rates
- R. Regeneration Processes

Targets

DOE storage targets for kg-H₂/kg, kWh/L and \$/kWh

Collaborators on Amineborane Project



Relevance and Overall Objectives

Project Relevance

The development of efficient hydrogen storage systems that can meet the DOE targets is key to enabling the use of hydrogen as an alternative energy carrier for transportation.

Project Objectives

- *Develop new chemical hydride based systems for on-demand, low temperature H₂-release that can achieve the DOE targets for hydrogen storage*
- *Develop high conversion off-board methods for chemical hydride regeneration*

In collaboration with Center Partners, this project focused on new methods for H₂-release and spent-fuel regeneration that exploited the high hydrogen density and facile H₂-elimination reactions of amineboranes.

Ammonia Borane H₂-Release



Approach and Specific Objectives

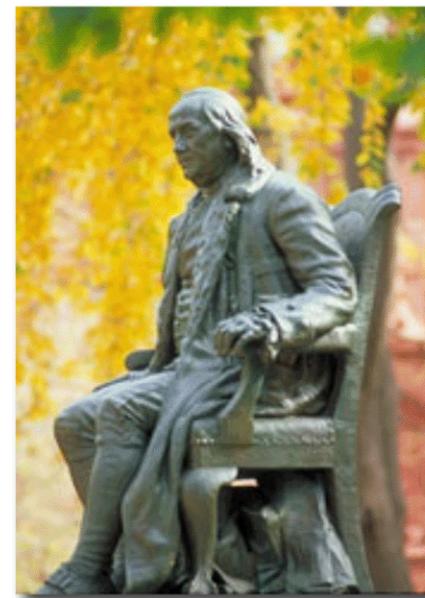
Penn Project Approach

Hydrogen-Release: Enhance the rate and extent of H₂-release from amineboranes using the activating effects of (1) **ionic liquids**, (2) **chemical promoters** and (3) **metal-catalysts**.

Regeneration: Develop spent fuel regeneration methods based on digestion of BNH_x to boron trihalides, then conversion to AB via sequential coordination, reduction and displacement reactions.

Specific Objectives for the Past Year

- Develop an understanding of the activating effects and reaction mechanisms of ionic-liquid and base promoted AB H₂-release.
- Identify optimal temperature/composition conditions for AB H₂-release in ionic liquids and provide high quality kinetic data for system analyses at Argonne.
- Optimize base-promoted AB H₂-release.
- Find new metal catalysts for promoting AB H₂-release in ionic liquids.
- Make final Go/No-Go Decision on boron halide based spent-fuel regeneration processes.



Penn Research Team

PI: Larry Sneddon

Students:

Dan Himmelberger
Bill Ewing
Emily Berkeley

Approach

Penn Approach to H₂-Release. Increase the Rate and Extent of AB H₂-Release by Activation with:

1. Ionic Liquids

2. Chemical Promoters

3. Metal-Catalysts/Ionic-Liquids

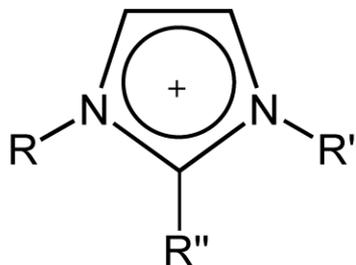


Approach

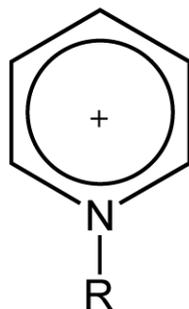
1. Why Ionic Liquids for Amineborane H₂-Release?

Ionic Liquids

Cations:



N,N'-imidazolium



N-pyridinium

Anions:

Reactive: AlCl₄⁻, Al₂Cl₇⁻

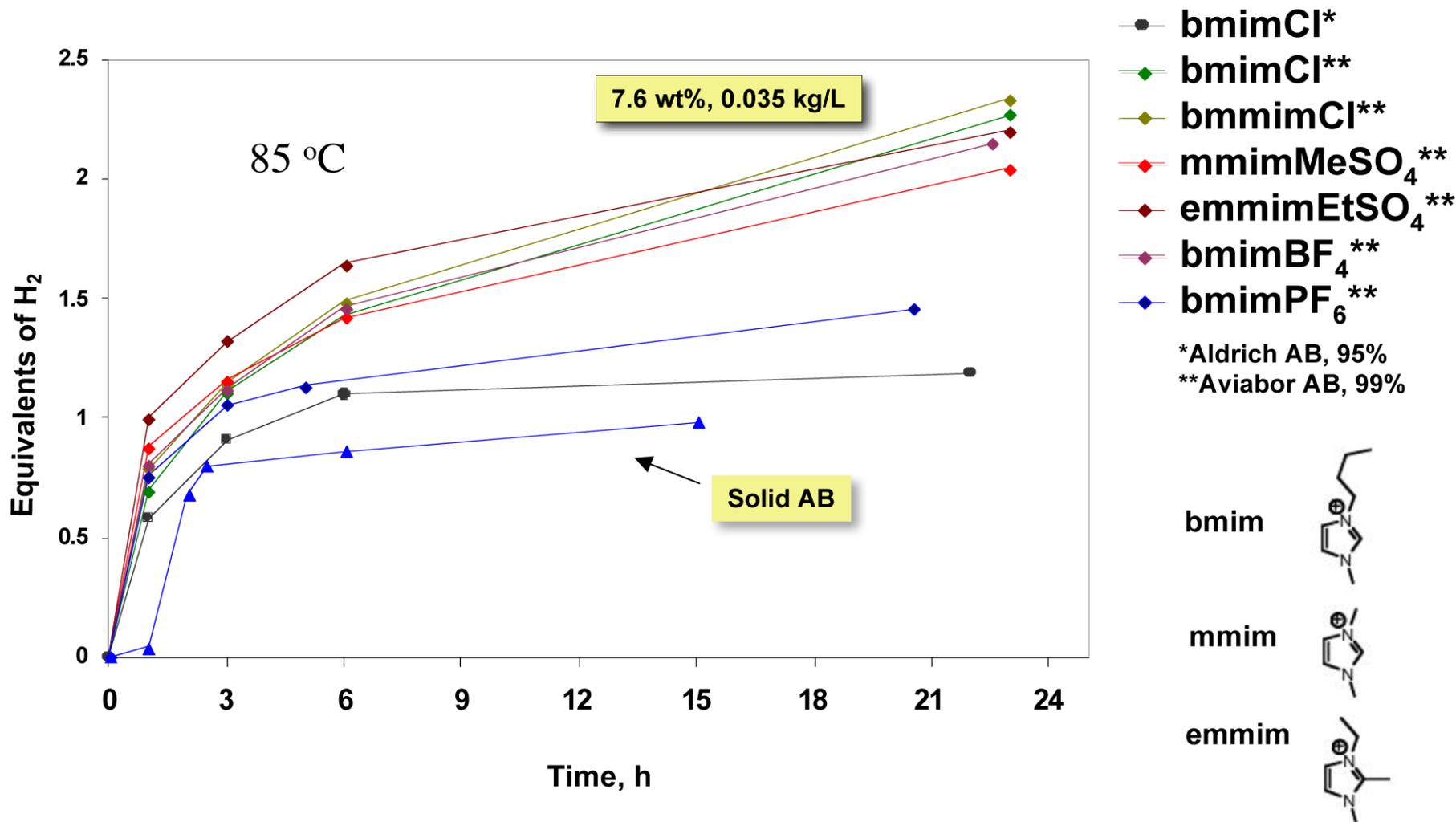
Inert: PF₆⁻, BF₄⁻, Cl⁻

Advantages

- Negligible vapor pressures
- Dissolve both neutral and ionic species
- Thermally stable to elevated temperatures
- Non-coordinating anions and cations provide an inert, polar reaction medium
- **Promote the formation of ionic or polar intermediates and transition states**

Technical Accomplishments

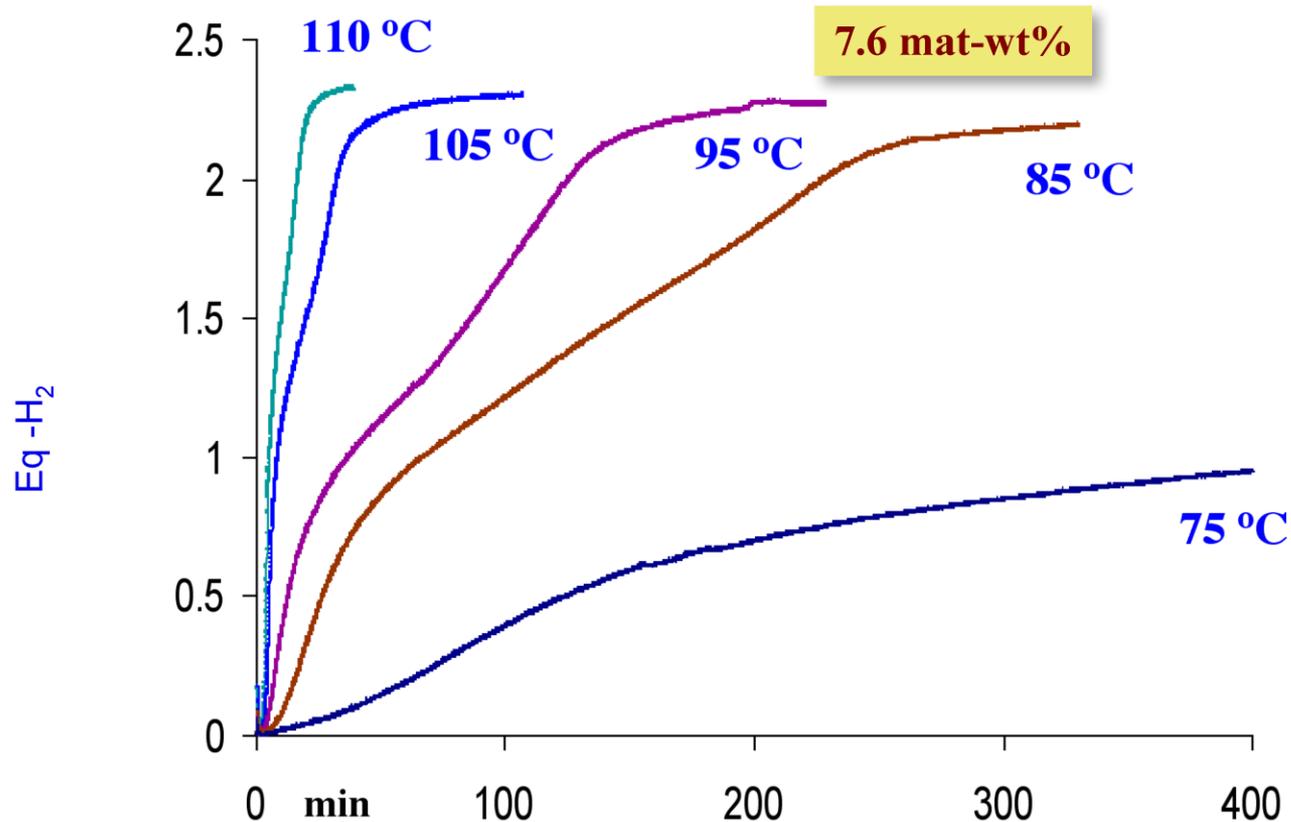
Ionic Liquids Increase the Rate and Extent of AB H₂-Release and Eliminate Induction Period



Technical Accomplishments

Significantly Faster Rates for AB H₂-Release In Ionic Liquids with Only Small Temperature Increases

AB H₂-Release versus Temperature for 50 wt% bmimCl/AB

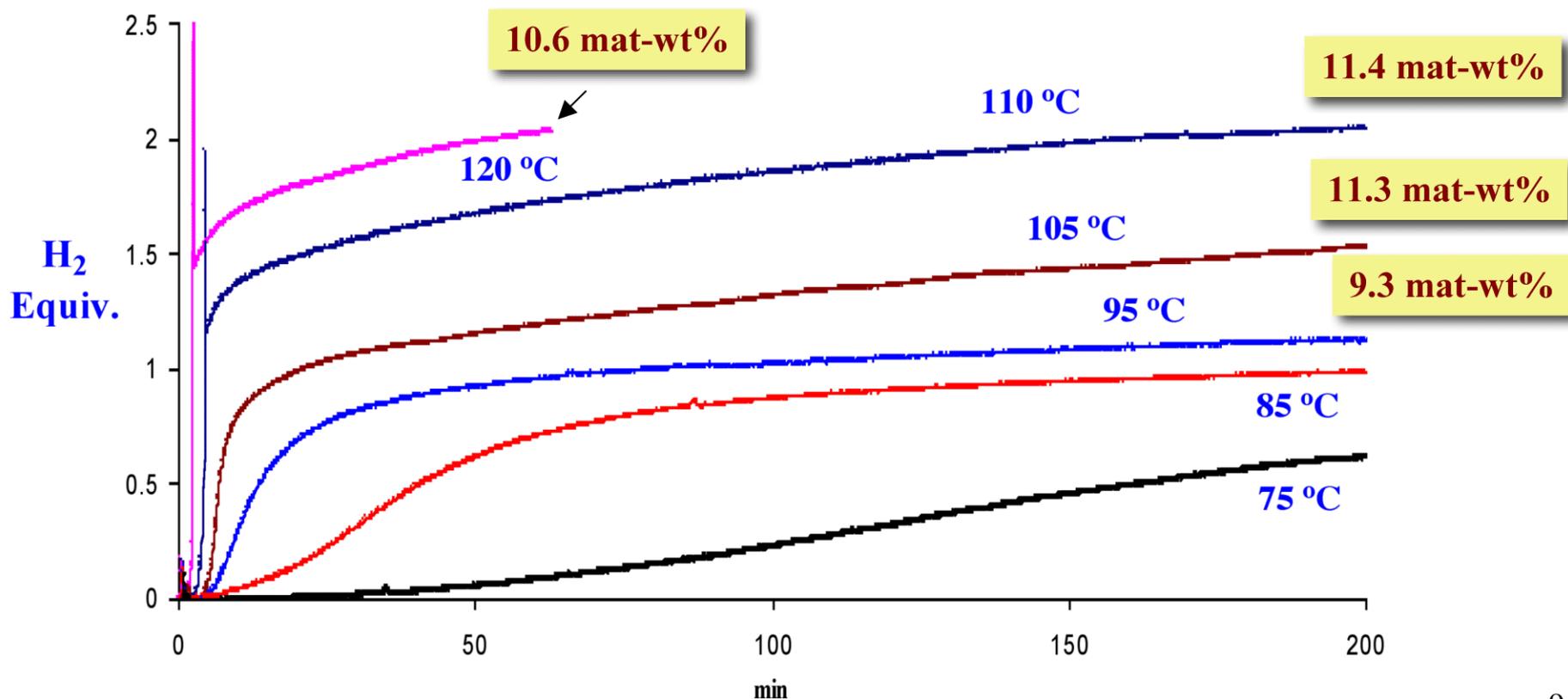


Conclusion: Fast H₂-Release at higher temperatures, but need to increase mat-wt% by decreasing % ionic liquid

Technical Accomplishments

Fast Rate and a 11.4 mat-wt% H₂-Release was Demonstrated for 20 wt% ionic-liquid/AB at 110 °C

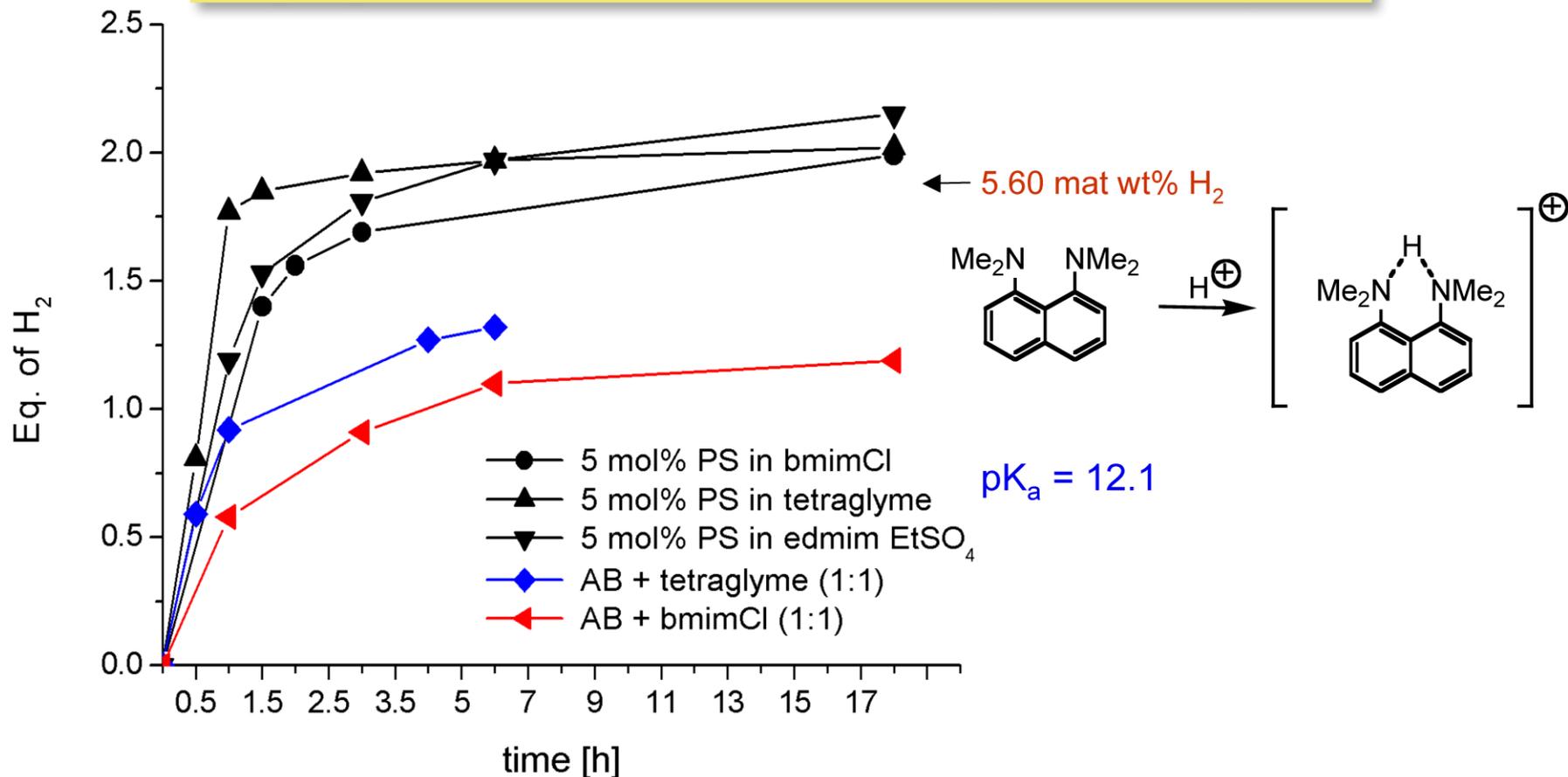
AB H₂-Release versus Temperature in 20 wt% bmimCl



Approach and Technical Accomplishments

2. Enhanced AB H₂-Release with Proton Sponge in Ionic Liquids or Tetraglyme with Reduced Foaming

NH₃BH₃ + 5 mol % PS at 85 °C in Ionic-Liquids or Tetraglyme

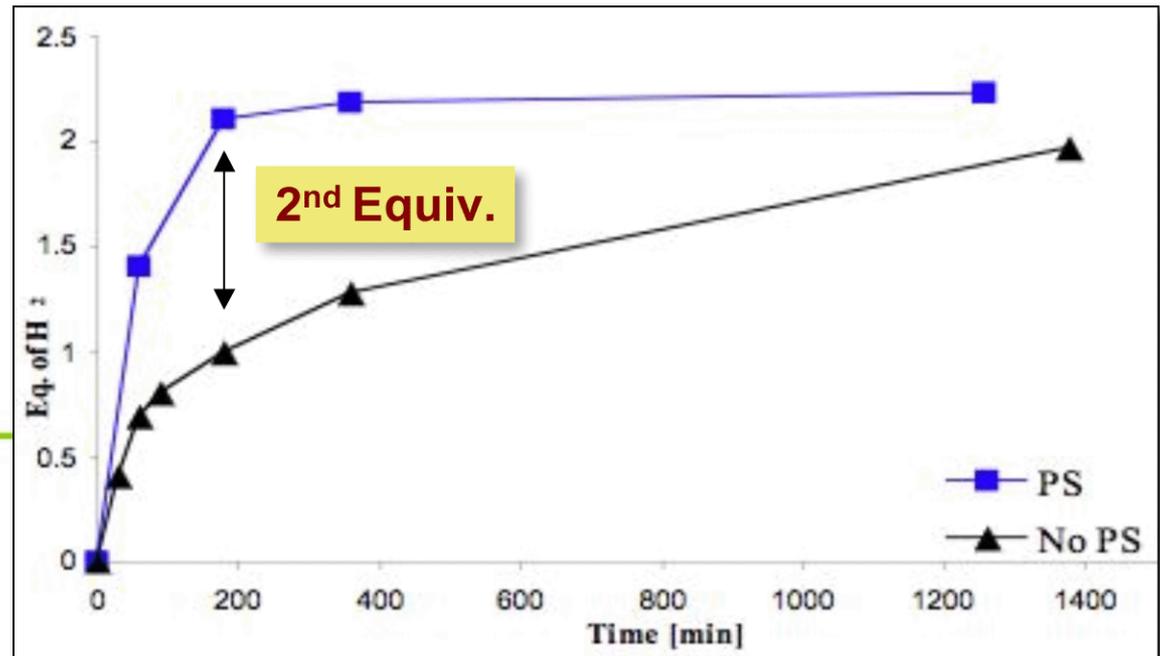
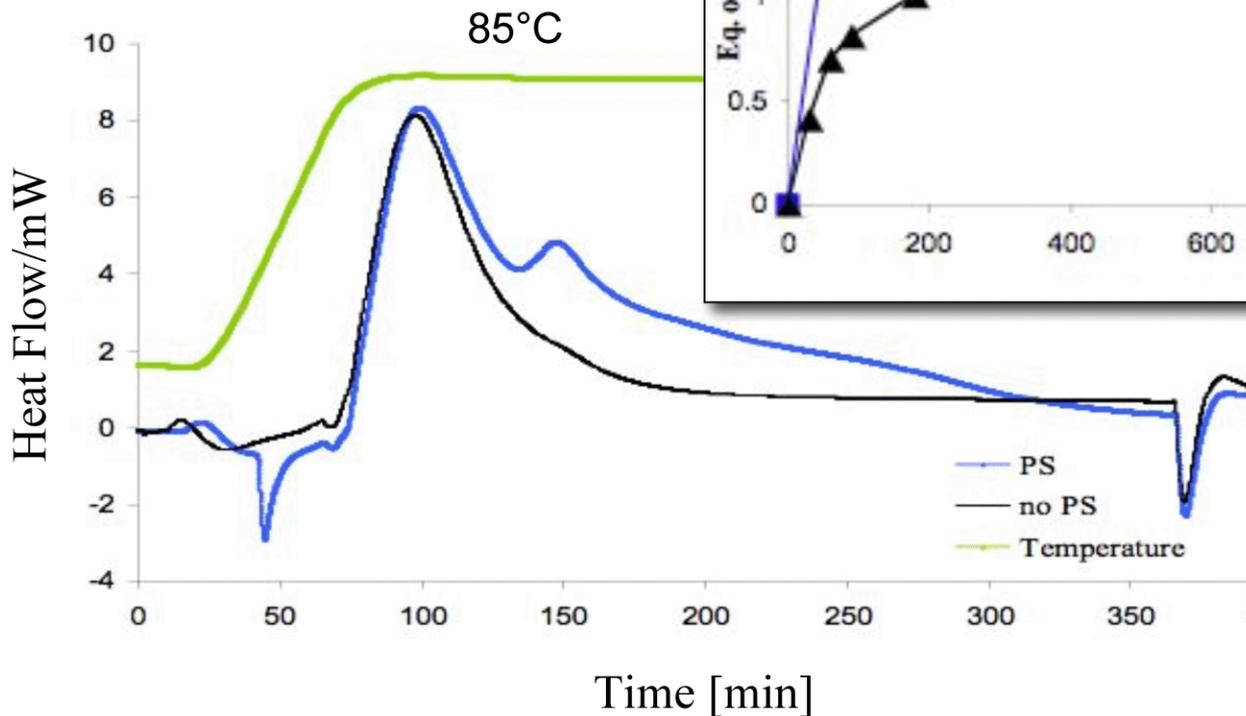


Himmelberger, D.; Yoon, C. W.; Bluhm, M. E.; Carroll, P. J.; Sneddon, L. G.
J. Am. Chem. Soc. **2009**, *131*, 14101-14110.

Technical Accomplishments

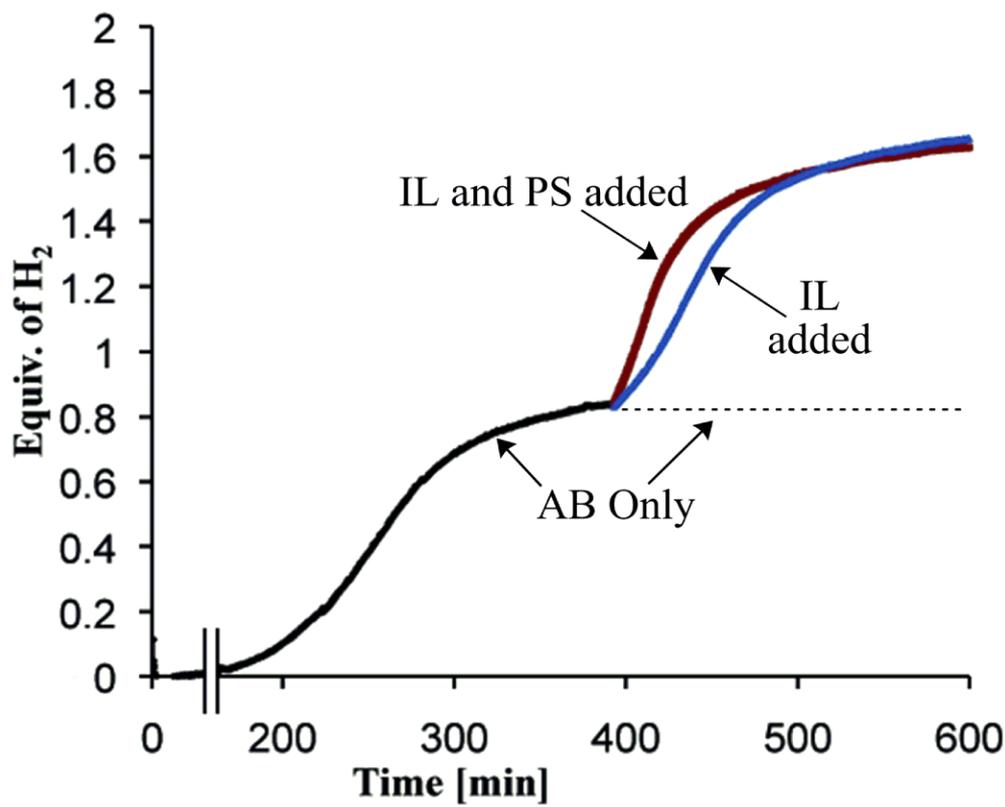
Proton Sponge Increases the Release Rate of the Second Equivalent of H₂ from AB

AB with 5 mol% PS
in bmimCl at 85 °C

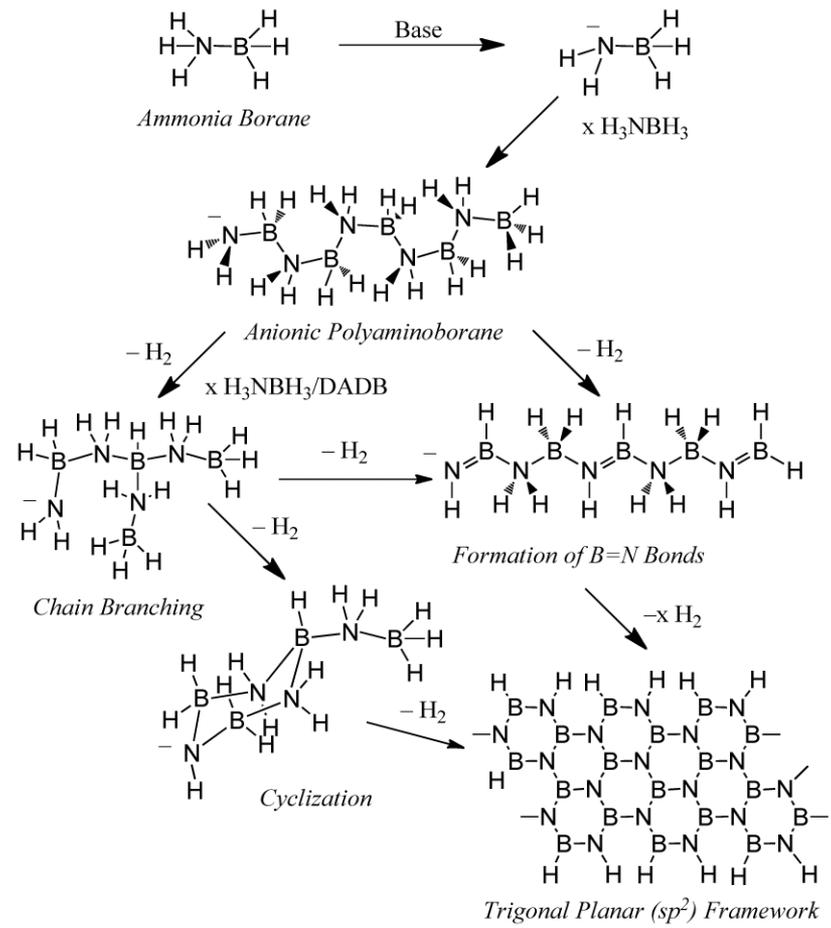


Technical Accomplishments

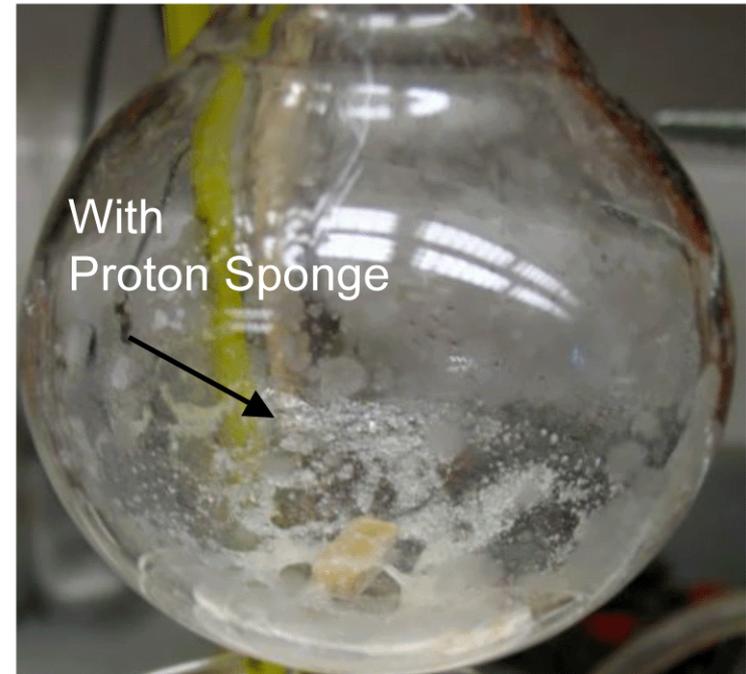
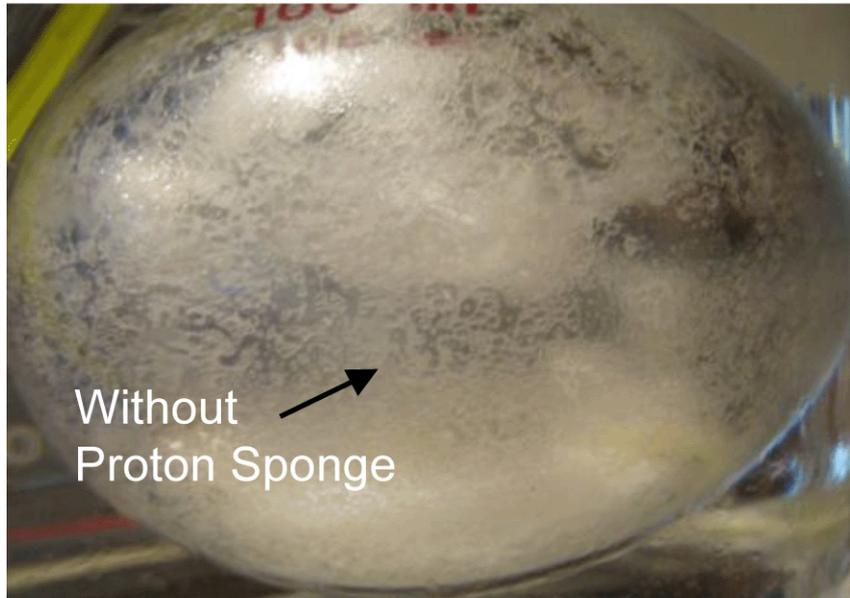
Proton Sponge Induces Loss of a Second H₂-Equivalent from Thermally Dehydrogenated AB



Possible Mechanistic Steps



Foaming Suppressed with Proton Sponge



3. Why Use Metal Catalysts for Amineborane Dehydrogenations in Ionic Liquids?

Catalysts in Conjunction with Ionic Liquids Could Provide:

- **Faster H₂-Release**
- **Better Control of H₂-Release Rates**
- **Lower Temperature Reactions**
- **Synergistic Release Mechanisms**

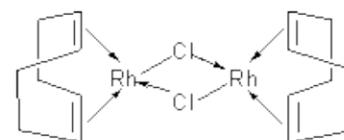
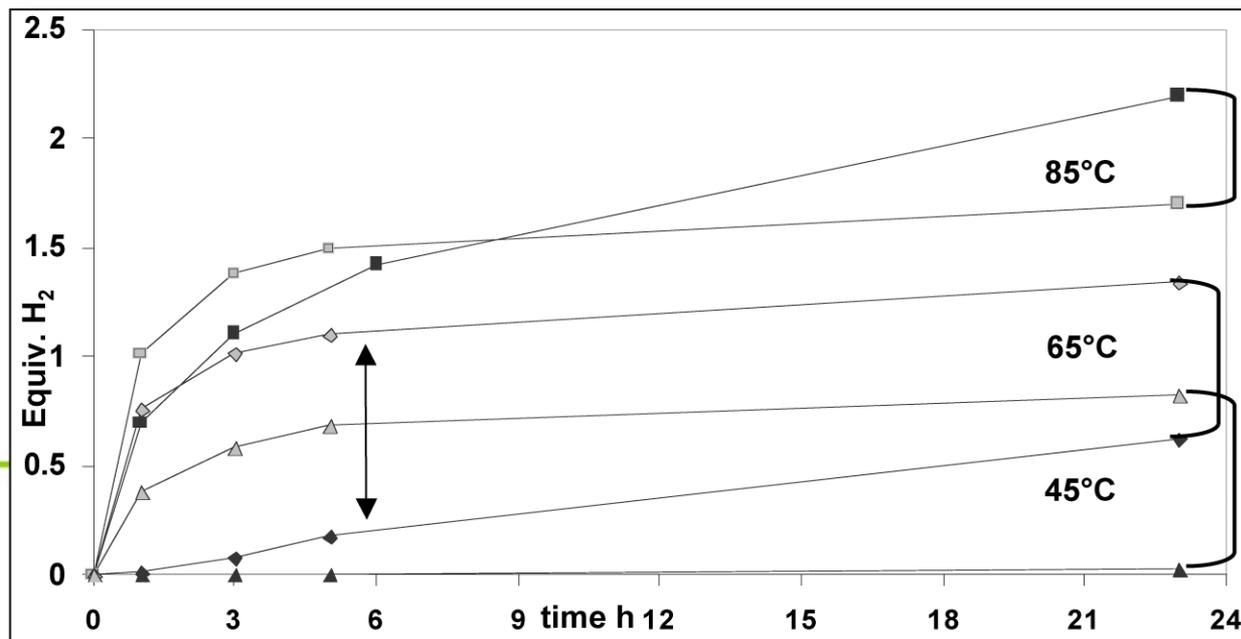
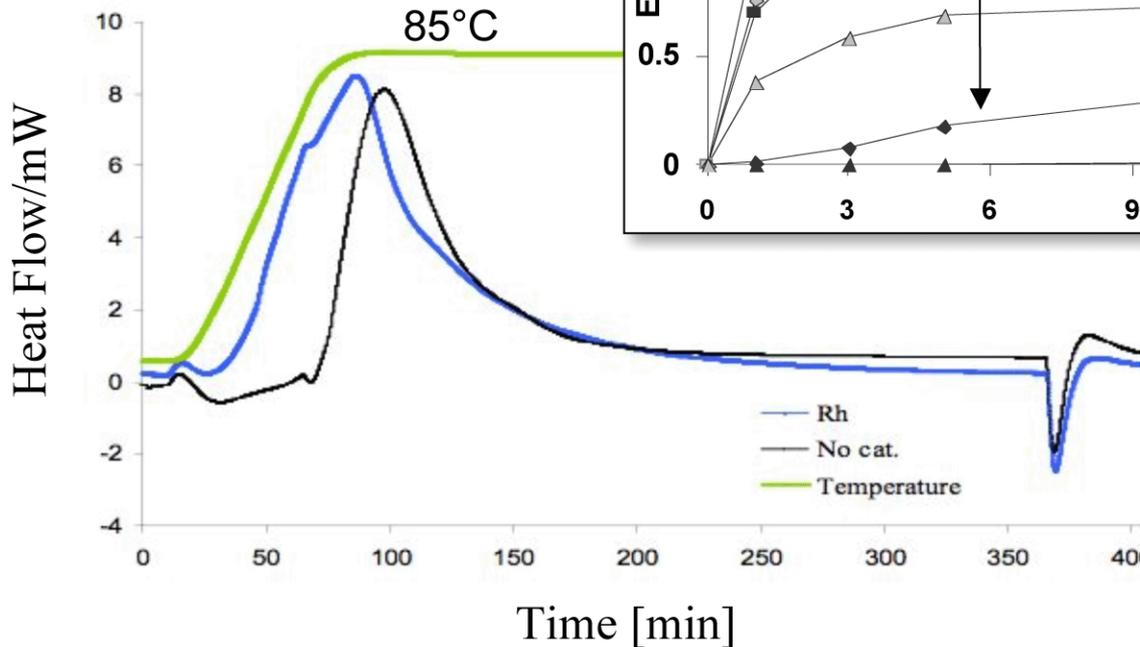
Center Partners (LANL and U Washington) have previously demonstrated metal catalyzed AB H₂-release in organic solvents.

Technical Accomplishments

Rh Catalyst Increases Release Rate of the First Equivalent of H₂ from AB in Ionic Liquids

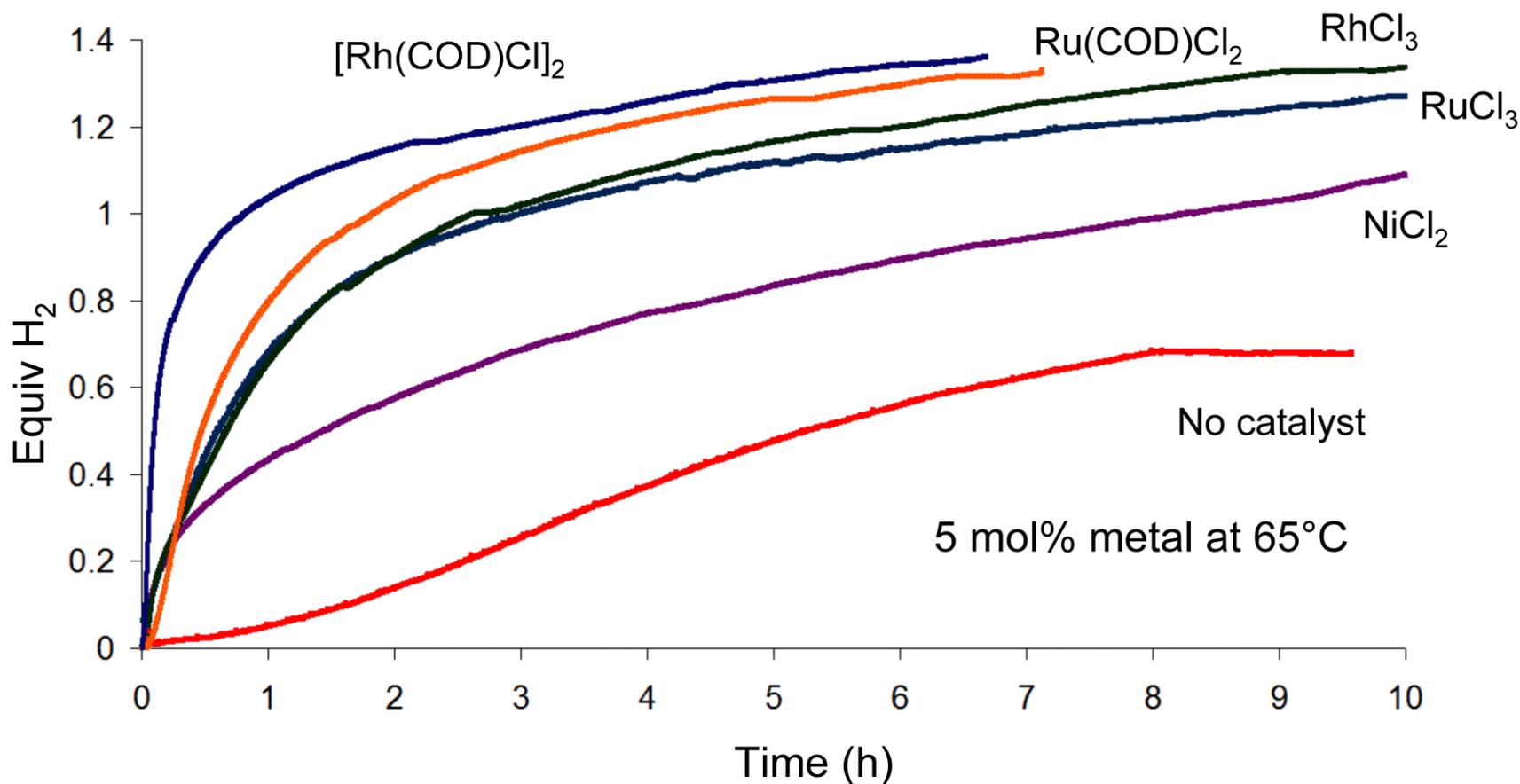
50 wt% AB
in bmimCl
5 mol% Rh

DSC



- 85°C
- ◆ 65°C
- ▲ 45°C
- 85°C w/ Rh
- ◇ 65°C w/ Rh
- ▲ 45°C w/ Rh

Other Metal Catalysts Increase the Rate of AB H₂-Release in Ionic Liquids



Technical Accomplishments

H₂-Release Systems Show Significant Increases in the Mat-Wt% and Rate of H₂-Release

	AB and 20 wt% bmimCl		AB and 50 wt% bmimCl		AB and 50 wt% bmimCl 5 mol % PS
	120 °C Two equiv. in 52 min	110 °C Two equiv. in 157 min	120 °C Two equiv. in 7 min	110 °C Two equiv. in 22 min	110 °C Two equiv. in 9 min
Initial Rate (mol/sec)	4.4x10 ⁻⁵	1.8x10 ⁻⁵	2.3x10 ⁻⁵	8.3x10 ⁻⁶	2.1x10 ⁻⁵
Grav. density (Mat. wt%)	11.4 2.2 Equiv.	11.4 2.16 Equiv.	7.2 2.06 Equiv.	6.9 2.11 Equiv.	6.1 2.21 Equiv.
Vol. density (Kg-H ₂ /L Mat.)	0.089	0.095	0.067	0.063	0.057
H ₂ Flow Rate (g/s) per kg Material	0.47	0.193	0.08	0.056	0.119
Kg of Mat. for 0.8 mol/sec	3.4	8.4	10	29	13

DOE Total System Targets for Hydrogen Storage Systems

Gravimetric Density (wt%)

4.5 (2007), 6.0 (2010), 9.0 (2015)

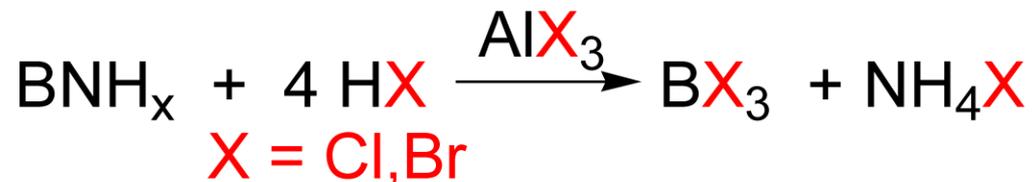
Volumetric Density (Kg-H₂/L)

0.036 (2007), 0.045 (2010), 0.081 (2015)

Approach

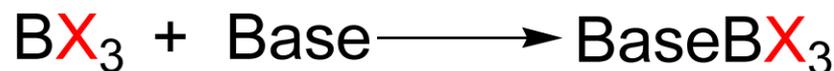
Penn Approach to Regeneration: Super-Acid/Halide-Reduction Process

First Step: Digestion of Spent Fuel by Super Acidic Halo-Acids



Second Step: One-Pot Conversion of BX_3 to AB

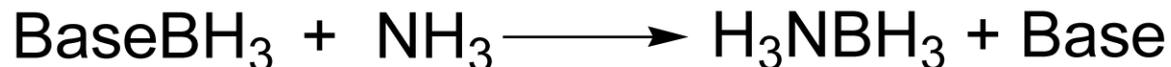
Coordination of BX_3



BX Reduction



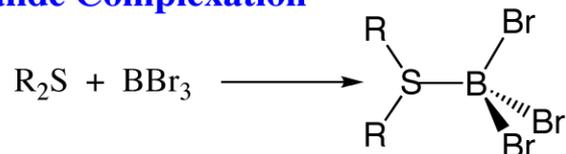
Base Displacement by NH_3 Yields AB



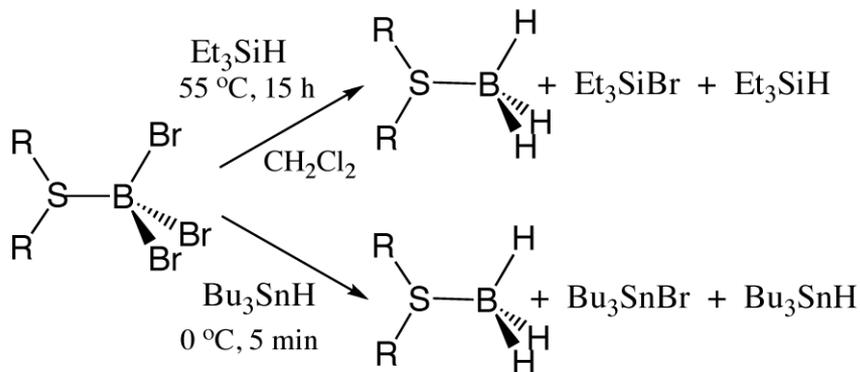
Technical Accomplishments

Step 2: Boron Halide Reduction Processes are Simple, Quantitative and Allow Separation and Recovery of All Products

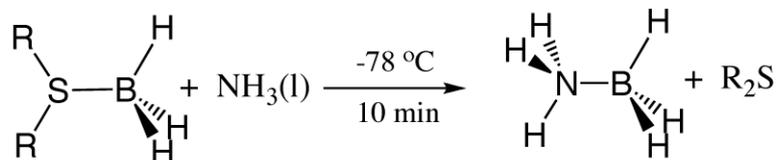
Boron Halide Complexation



Complex Reduction with Silanes or Stannanes

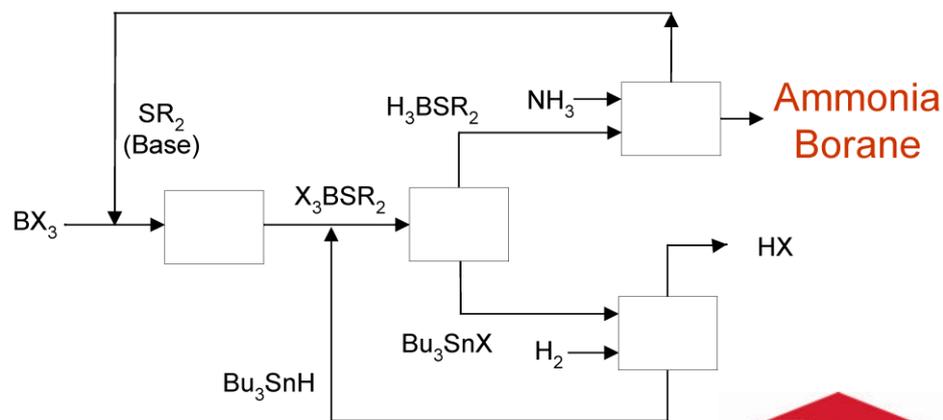


Displacement with Ammonia



Demonstrated Advantages:

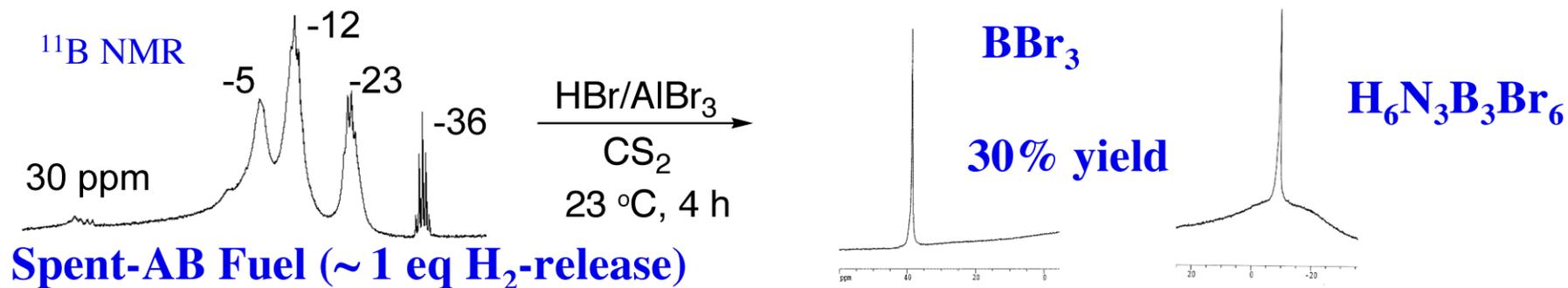
- (1) high, 96-100%, yields on multi-gram laboratory scale-ups
- (2) avoids the formation of B-O bonds
- (3) avoids the formation of B_2H_6
- (4) simple product isolation based on volatility with separation/recovery of all materials
- (5) 2008-9 Rohm and Haas analysis indicates a scalable process



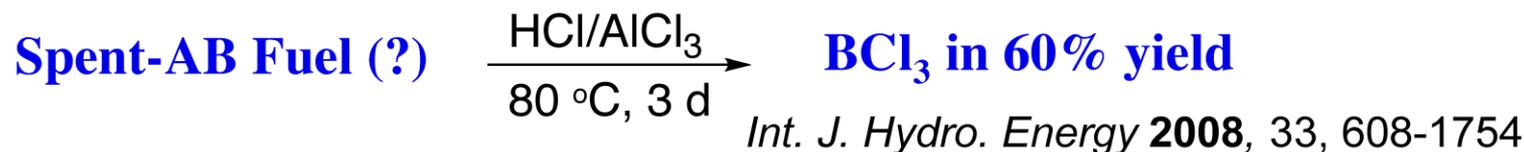
Technical Accomplishments

Step 1: Progress on Spent Fuel Digestion to BX_3

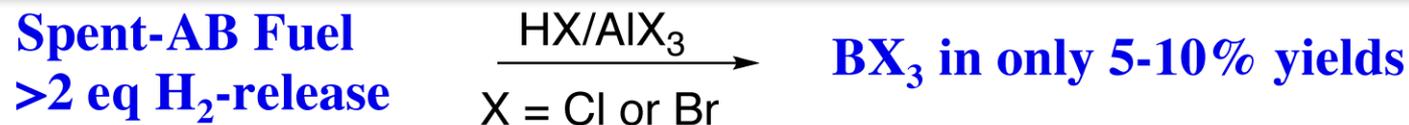
2007 Penn: Superacidic HX/AlX_3 Solutions Digest Spent-Fuels



2008: Mertens et. al. Report Digestion with Superacidic $HCl/AlCl_3$



2009-10 Penn: Superacidic Conditions Do Not Give Good Yields of BX_3 from Highly Dehydrogenated Fuels



Conclusion: Super-Acid Approach is No-Go Owing to Unsatisfactory Spent Fuel Digestion

Summary of Project Accomplishments/Conclusions



- Significant rate enhancements with reduced borazine formation and a high mat-wt% H₂-release (up to 11.4%) were achieved with 20 wt% ionic-liquid/AB mixtures at 110 °C.
- Base-induced H₂-release in ionic liquids increases the release rate of the second AB H₂-equivalent and reduces foaming.
- Metals catalyze AB H₂-release in ionic liquids with significant increases in the rate of loss of the first AB H₂-equivalent.
- Generated quality kinetic data for Argonne zero-order onboard system analysis.
- A simple, quantitative boron halide reduction process was developed that allowed the separation and recovery of all products, but a No-Go decision was made on the overall Penn regeneration process owing to incomplete spent fuel digestion.



Collaborations and Technology Transfer

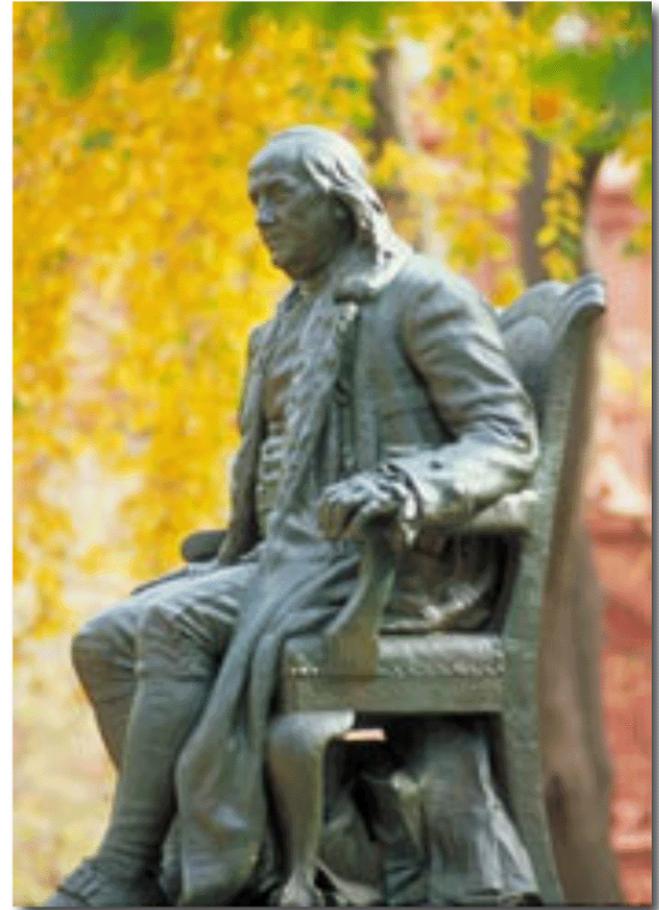
Penn work on H₂-Release/Regeneration was Highly Coordinated with Partners by Frequent “Brainstorming” Discussions, Laboratory Visits, and Sample and Measurement-Sharing.

Some Examples of Collaborations and Technology Transfer

- Provided Penn kinetic data on AB/ionic-liquid H₂-release to Argonne for their zero-order onboard system analysis.
- PNNL postdoctoral visited Penn to learn how to perform the borazine synthesis at PNNL.
- Penn students and postdoctoral carried out research at PNNL on several extended visits to use the unique capabilities at PNNL in DSC, solid-state NMR and H₂ measurements to study H₂-release from the Penn ionic liquid based systems.
- PNNL provided essential help in constructing two PNNL-designed gas burette systems at Penn. These systems have enabled much of the key H₂-release measurements on Penn systems.
- Penn and Dow (Chen and Lipiecki) evaluated the scale up feasibility of the of the boron halide reduction/separation step for regeneration.
- U. of Ottawa (Baker) and Penn carried out joint investigations of the mechanisms of AB H₂-release.

Some Important Future Questions

- Can new fuels or fuel/mixtures be developed that will generate liquid spent fuel products in ionic liquids?
AB/alkyl-boranes/additives?
AB/ammonia-triboranes?
- Can new ionic liquids be developed that will extend the liquid range of the spent fuels?
- What is the most effective metal catalyst that can be used in conjunction with ionic liquids to promote H₂-release?
- Can other efficient synergistic methods be developed to activate H₂-release?
- Borazine formation is reduced in ionic liquids, but can it be completely eliminated?
- Can spent fuels be directly regenerated in ionic liquids?



Project Summary

Relevance: *The development of efficient hydrogen storage systems are essential to the success of the DOE Hydrogen Initiative for transportation.*

Approach: *Enhance the rate and extent of H₂-release from amineboranes using the activating effects of (1) ionic liquids, (2) chemical promoters, and (3) metal-catalysts and develop high yield halide-based regenerations.*

Technical Accomplishments and Progress: *Significant increases in both the rate and extent of AB H₂-release were attained.*

Technology-Transfer/Collaborations: *Active partnerships and collaborations across the Chemical Hydride Center.*

Future Research: *Some key issues for future research have been identified.*

Larry Sneddon
215-898-8632
Lsneddon@sas.upenn.edu

