



Amineborane-Based Chemical Hydrogen Storage

Department of Chemistry
University of Pennsylvania

DOE Chemical Hydrogen
Storage Center of Excellence

2009 DOE Hydrogen Program Review

May 19, 2009 Project ID: st_16_sneddon

This presentation does not contain any proprietary or confidential information

Project Overview

Timeline

Project Start: FY 2005
Project End: March 2010
Percent complete: 80%

Budget

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

DOE Funding in 08: \$300,000
DOE Funding in 09: \$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 methods that can meet the DOE targets for hydrogen storage is key to enabling the use of hydrogen as an alternative energy carrier for transportation.

Project Objectives

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

In collaboration with Center Partners, the focus of this project is to develop new methods for H₂-release and regeneration that exploit the high hydrogen density and facile H₂-elimination of amineboranes for chemical hydrogen storage.

Ammonia-borane H₂-Release



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 regeneration methods that: (1) give high yields; (2) avoid formation of B-O bonded intermediates; (3) avoid formation of hazardous diborane; (4) recover all products. Penn method focuses 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



Penn Research Team

PI: Larry Sneddon
Postdoctoral: Laif Alden
Students:

Dan Himmelberger
Bill Ewing
Emily Berkeley

- Identify optimal temperature/composition conditions for AB H₂-release in ionic liquids
- Optimize and expand studies of base-promoted AB H₂-release.
- Find new metal catalysts for promoting AB H₂-release in ionic liquids.
- Refine boron halide based regeneration processes.

Summary of Important Penn Accomplishments/ Milestones Since 2008 AMR

- Significant rate enhancements along with high mat-wt% H₂-release (up to 11.4%) were demonstrated with 20 wt% ionic-liquid/AB mixtures at 110 °C.
- Base-induced H₂-release in ionic liquids was extended to new bases and shown to increase the release rate of the second AB H₂-equivalent
- A variety of metals were found to catalyze AB H₂-release in ionic liquids with significant increases for the rate of loss of the first AB H₂-equivalent.
- The boron halide reduction step in the regeneration scheme was demonstrated to be simple, quantitative and allow the separation and recovery of all products. Initial Rohm and Haas analysis indicates a scalable separation process.

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

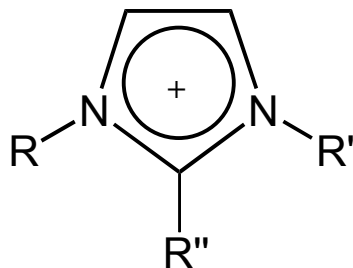
- 1. Ionic Liquids**
- 2. Chemical Promotors**
- 3. Metal Catalysts/Ionic-Liquids**



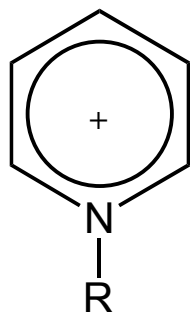
Why Ionic Liquids for Amineborane H₂-Release?

Ionic Liquids

Cations:



N,N'-imidazolium



N-pyridinium

Anions:

Reactive: AlCl_4^- , Al_2Cl_7^-

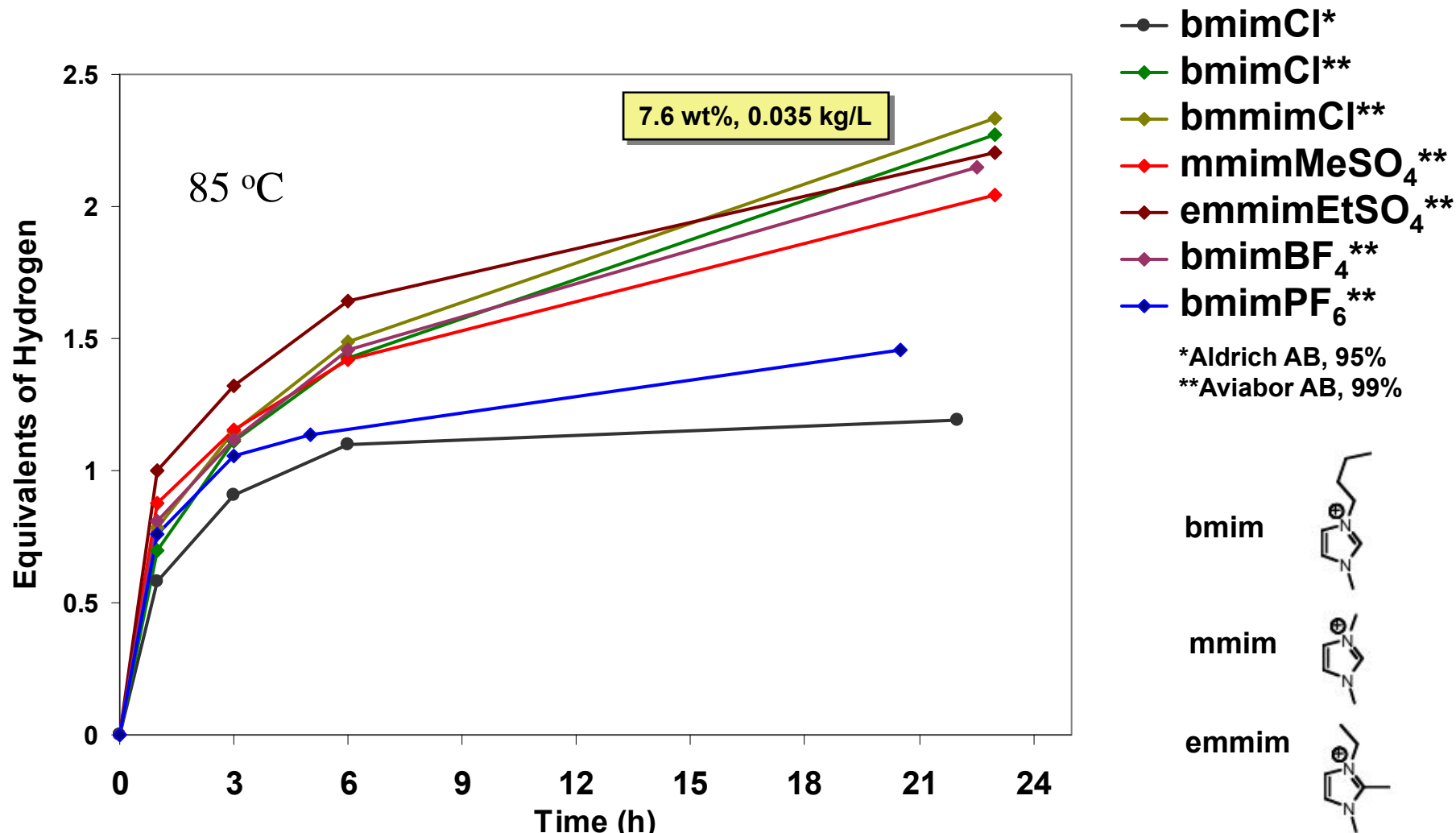
Inert: PF_6^- , BF_4^- , Cl^-

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**

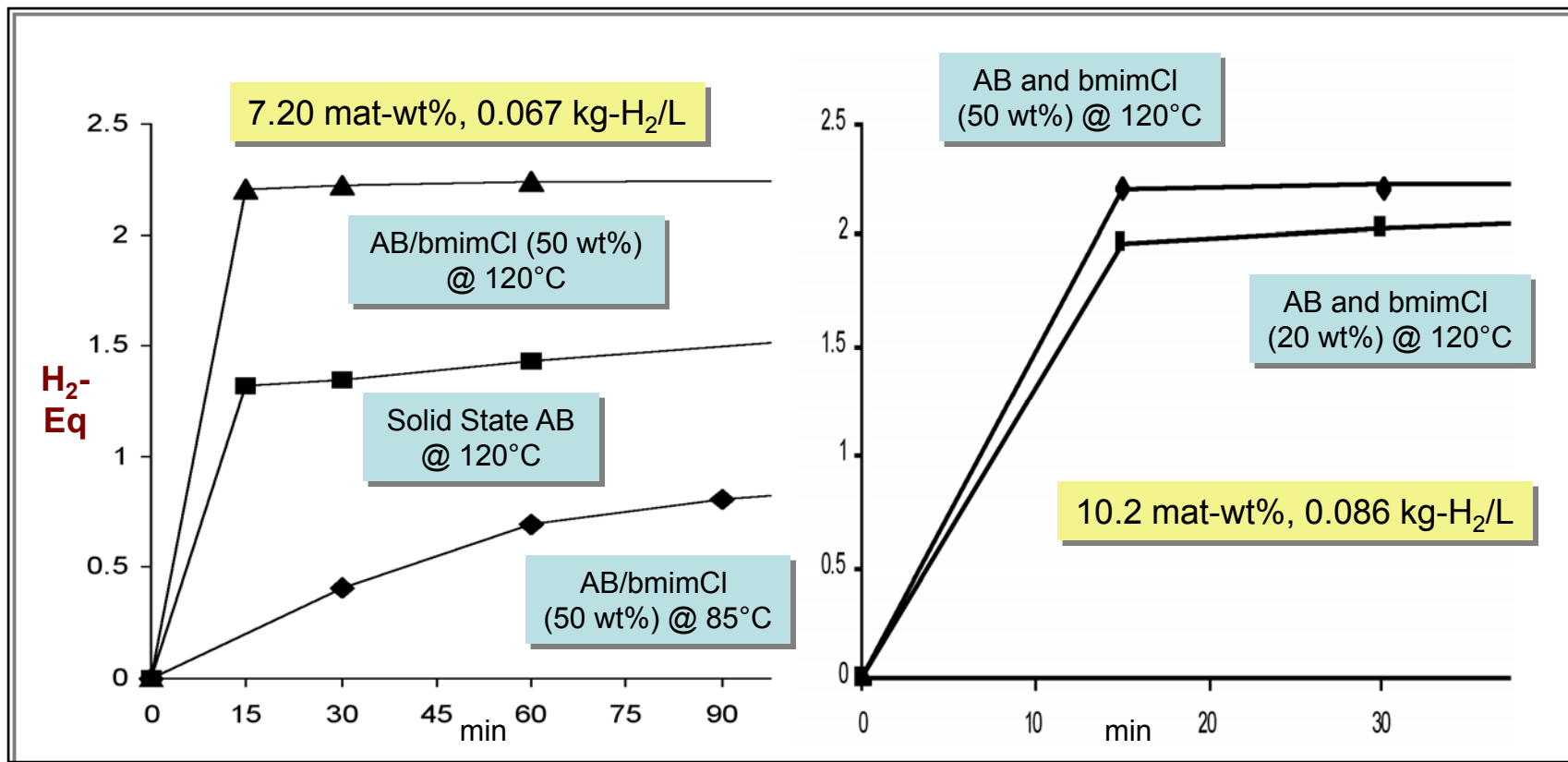
Technical Accomplishments

2006-7: Ionic Liquids Increase the Rate and Extent of AB H₂-Release and Eliminates Induction Period



Technical Accomplishments

2008: Initial Studies Show AB H₂-Release Rates in Ionic Liquids Are Greatly Increased at 120 °C

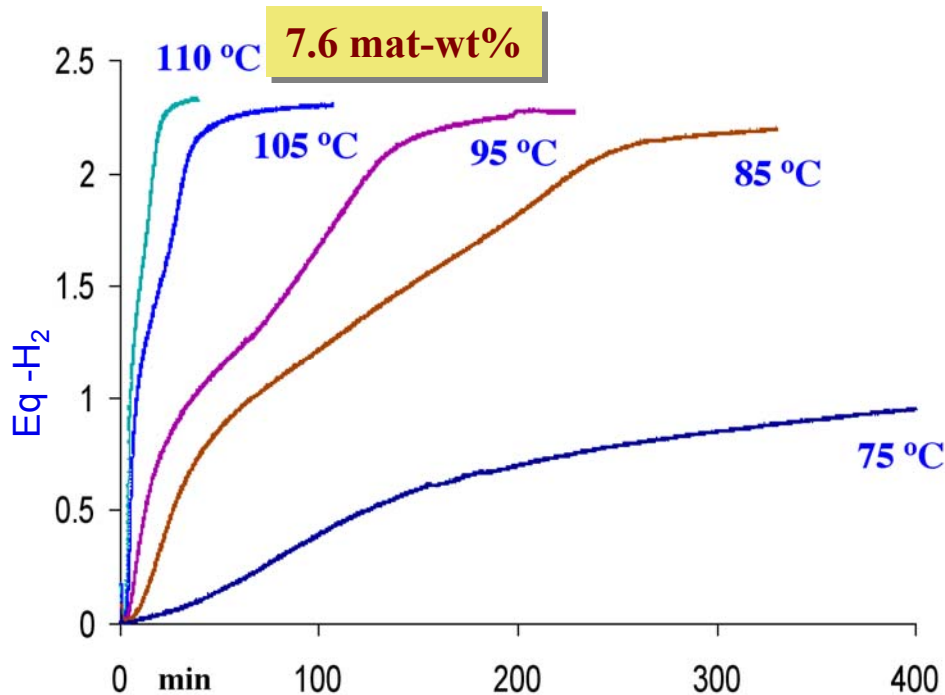


2009 Goal: Identify Optimal Temperature/Weight Conditions for AB H₂-Release in Ionic Liquids

Technical Accomplishments

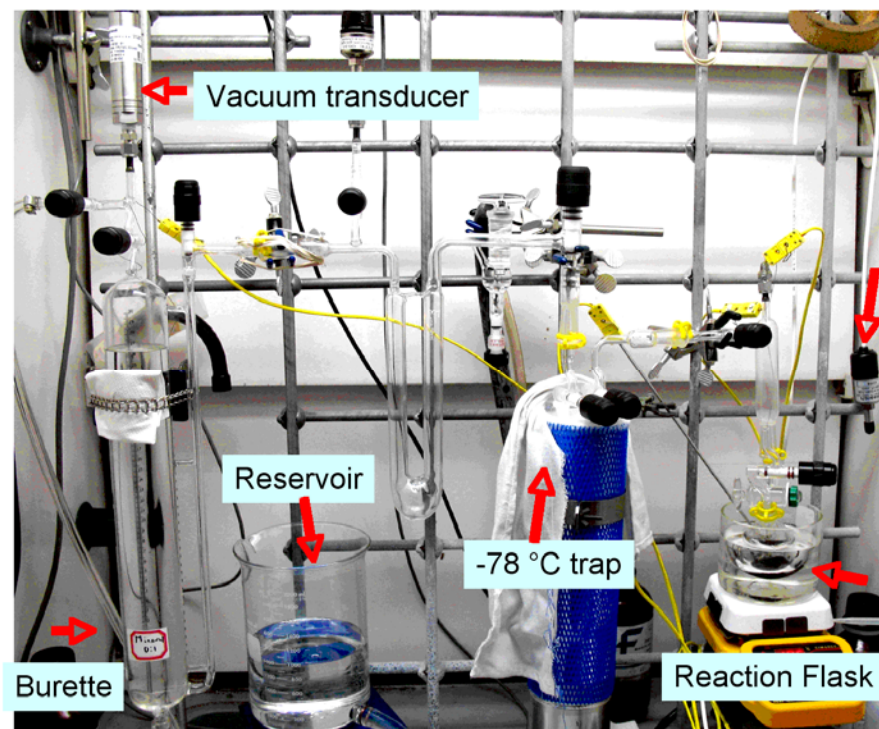
2009: Significantly Faster Rates for AB H₂-Release In Ionic Liquids with Only Small Temperature Increases

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

PNNL-Designed Automatic Gas-Burette Used for Continuous H₂-Release Measurements

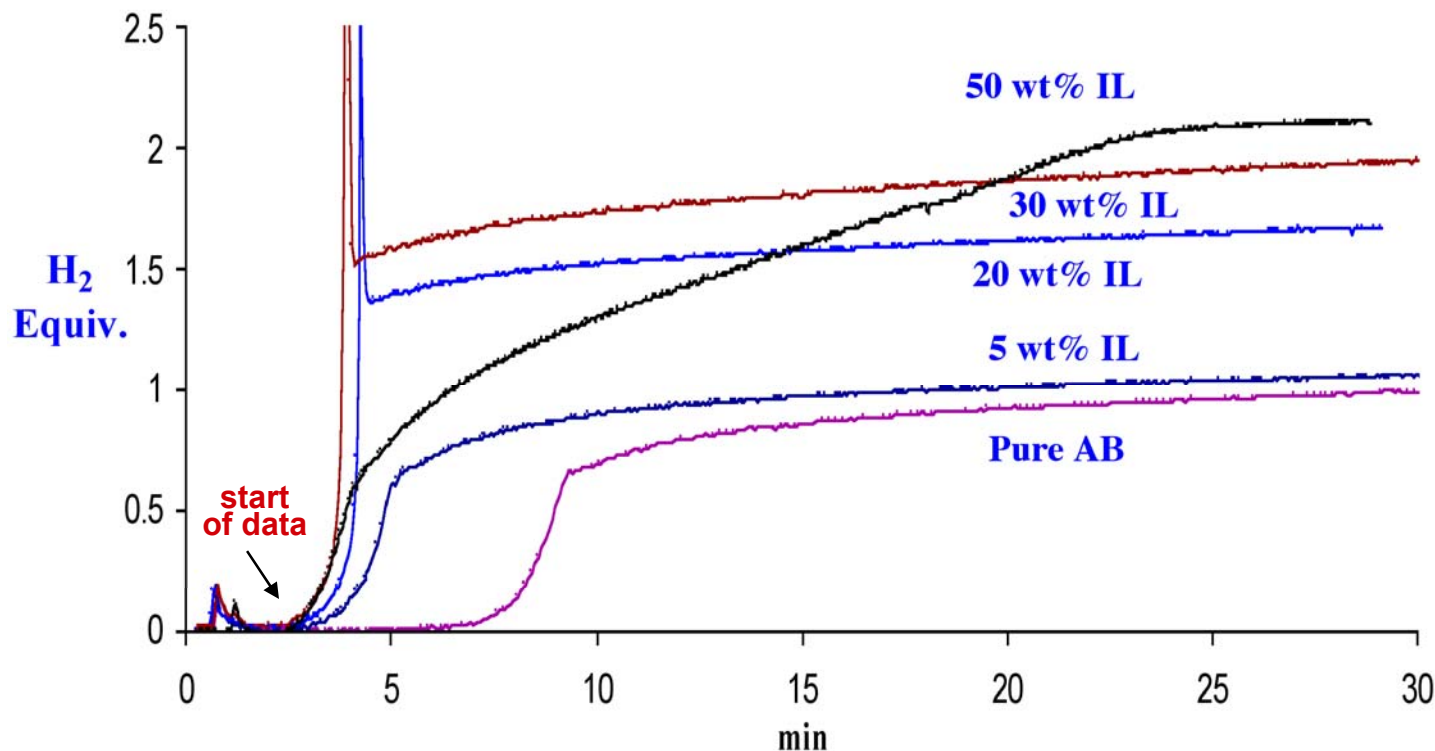


Zheng et. al. *Rev. Sci. Instrum.* **2008**, 79, 084103

Technical Accomplishments

2009: Reactions at 110 °C with Only 20 wt% Ionic Liquid Still Have Fast H₂-Release Rates

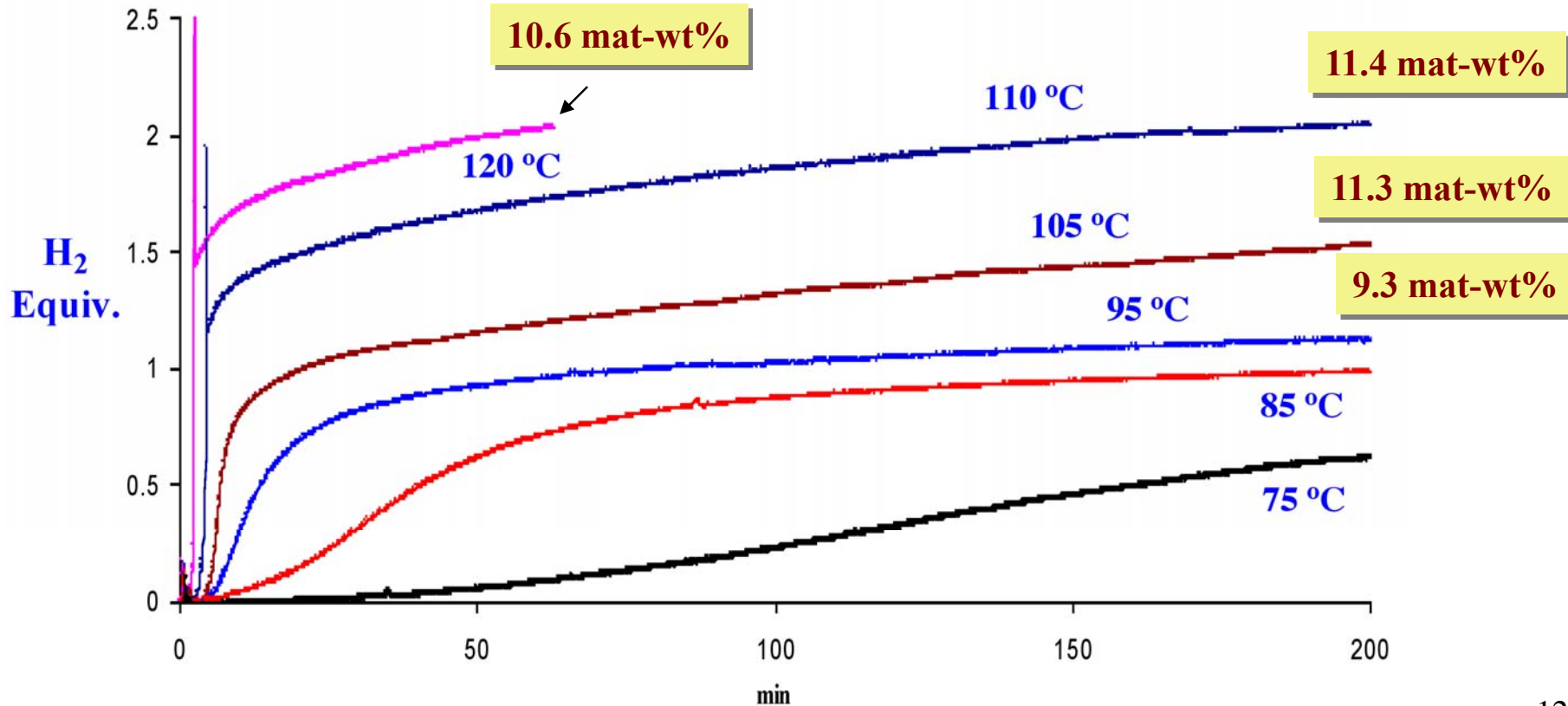
Initial AB H₂-Release versus bmimCl wt% at 110 °C



Technical Accomplishments

2009: 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

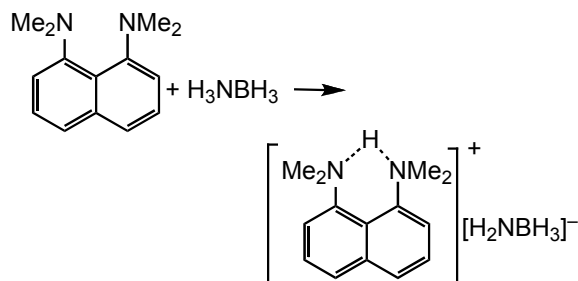


Approach and Technical Accomplishments

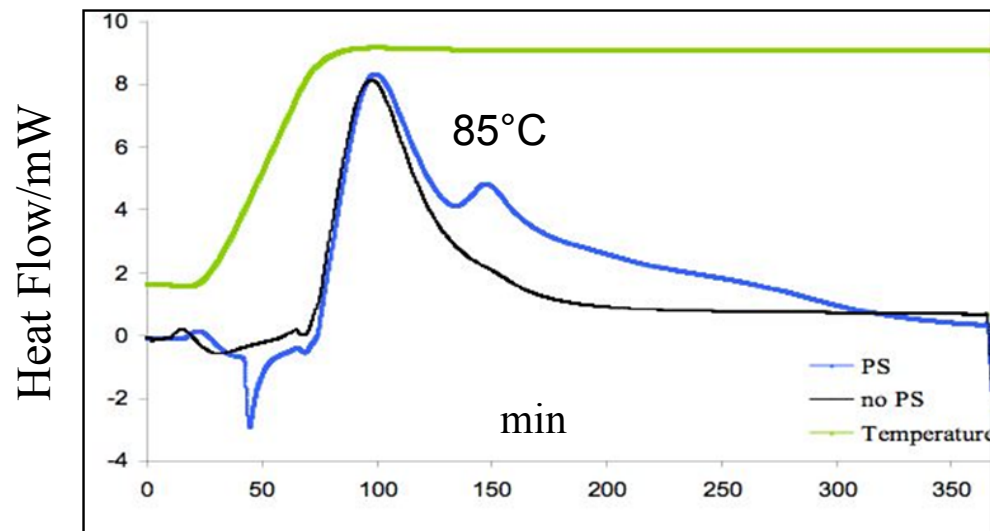
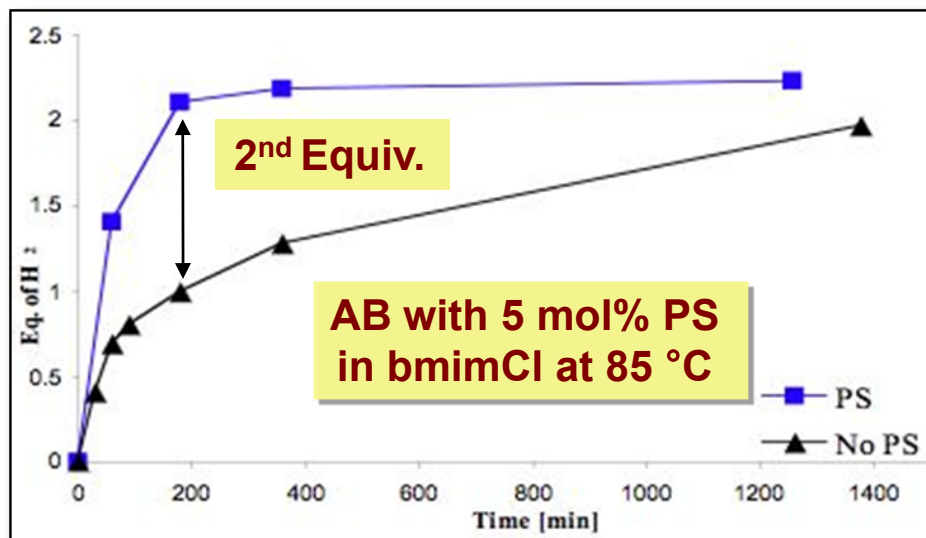
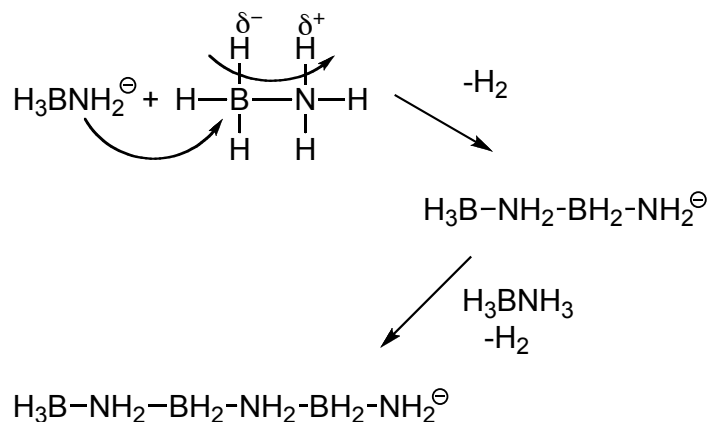
2008: Proton Sponge Increases the Release Rate of the Second H₂-Equivalent from AB and Reduces Foaming

Approach: H₂-Release by AB Anionic Polymerization

Initial Step



Chain-Growth/H₂-Release

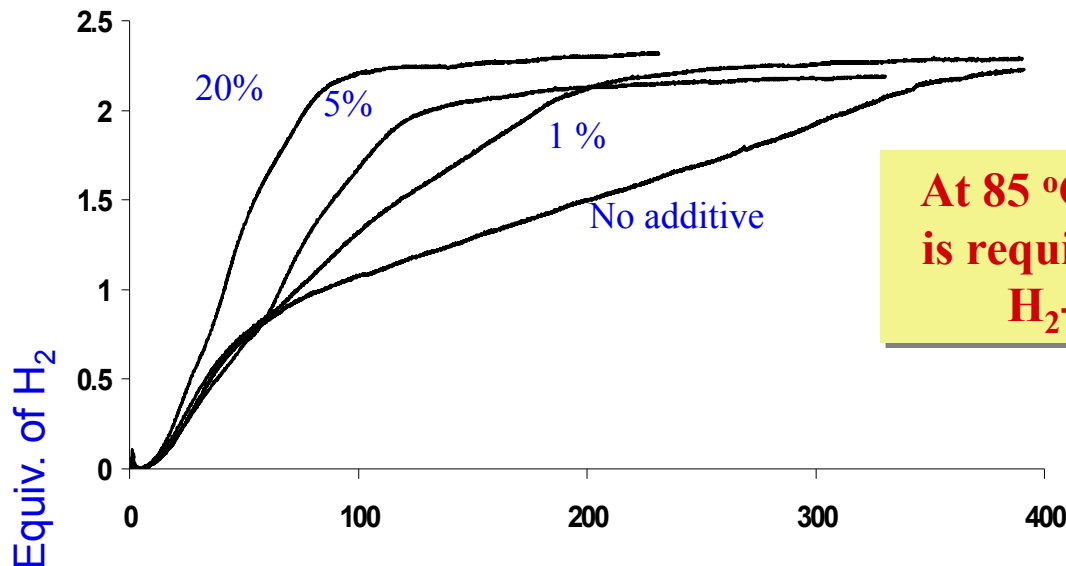


Technical Accomplishments

2009: Less Base is Required at Higher Temperatures

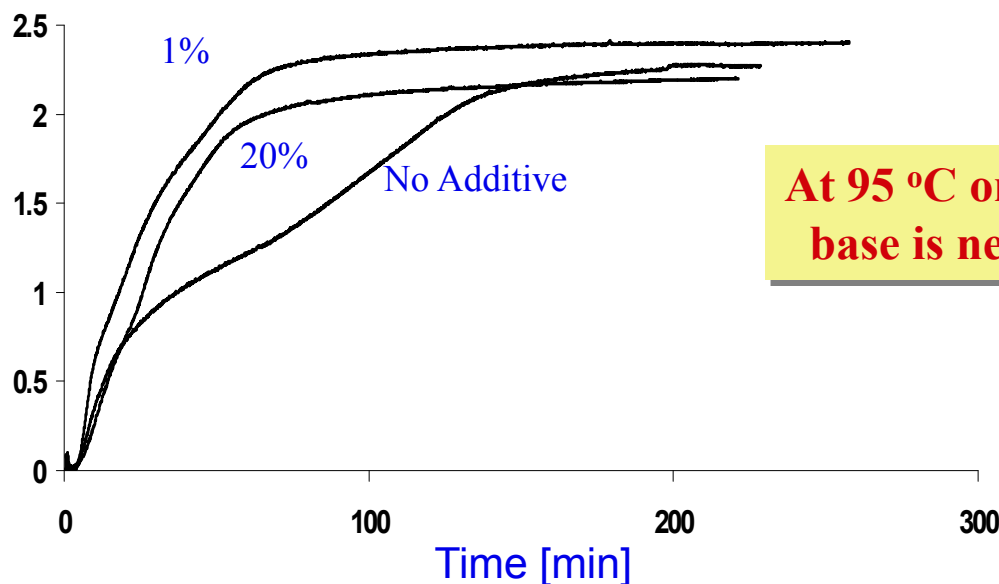
150 mg AB and
150 mg bmimCl

85 °C



At 85 °C 20% base
is required for fast
H₂-release

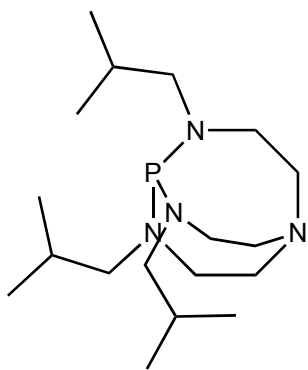
95 °C



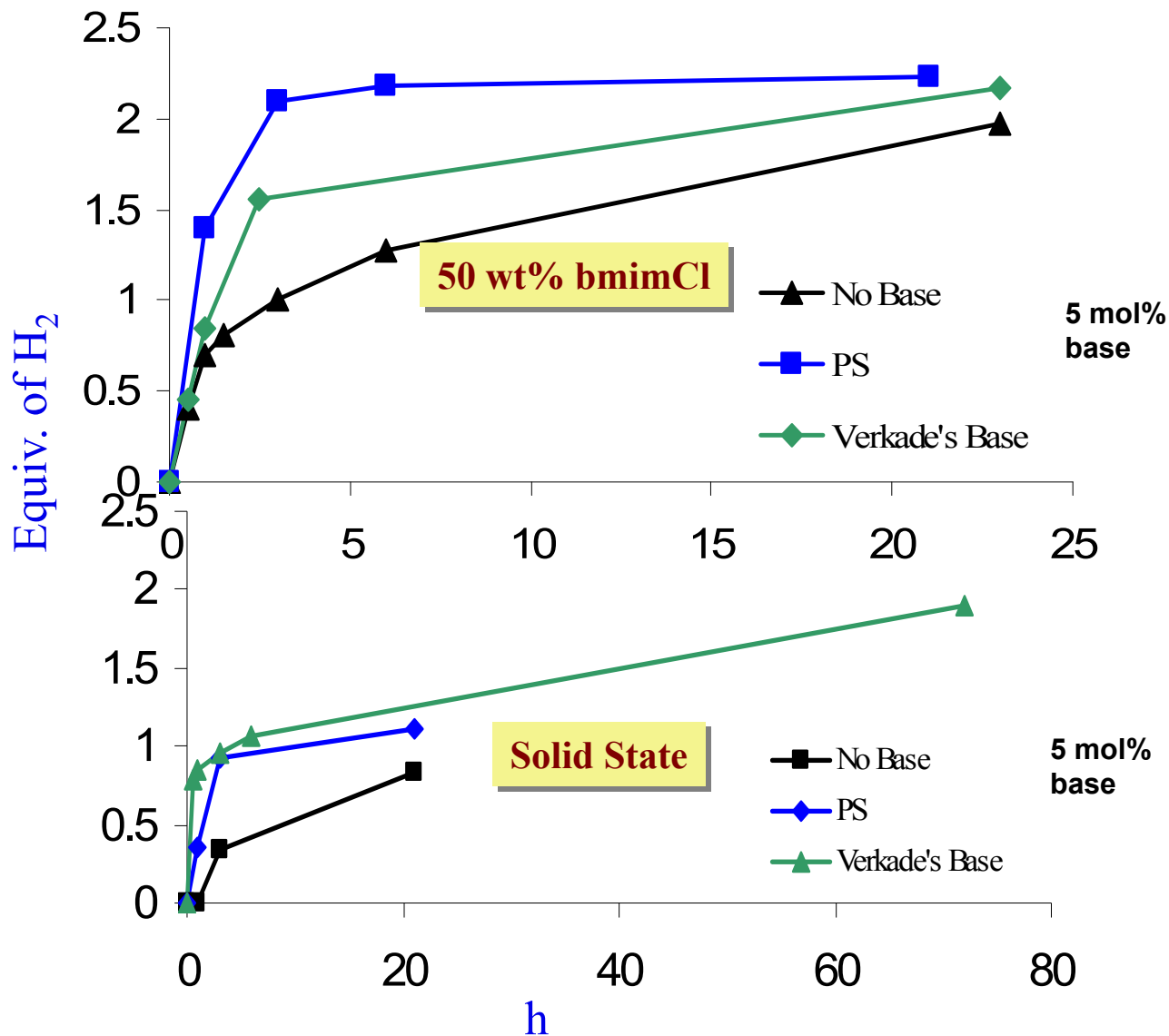
At 95 °C only 1%
base is needed!

Technical Accomplishments

2009: Other Strong Bases Also Activate AB H₂-Release



Verkade's Base



Technical Accomplishments

2009: 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)

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

Catalysts in Conjunction with Ionic Liquids Could Provide:

- (1) **Faster H₂-Release**
- (2) **Better Control of H₂-Release Rates**
- (3) **Lower Temperature Reactions**
- (4) **Synergistic Release Mechanisms**

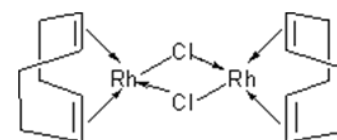
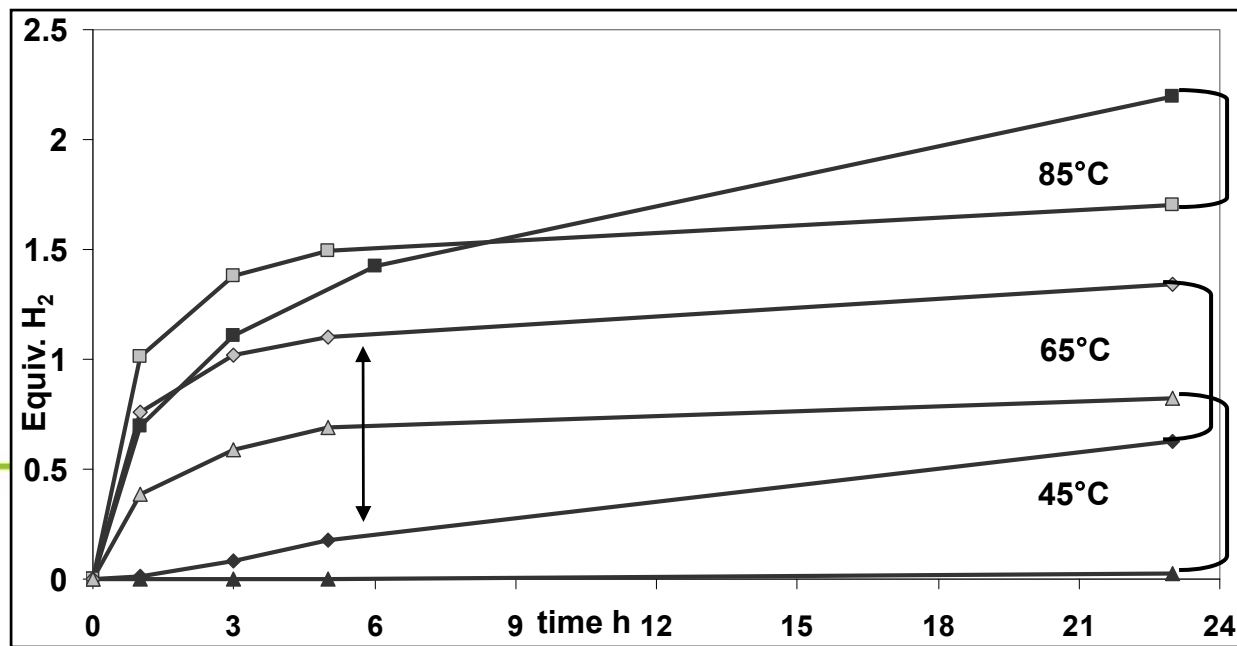
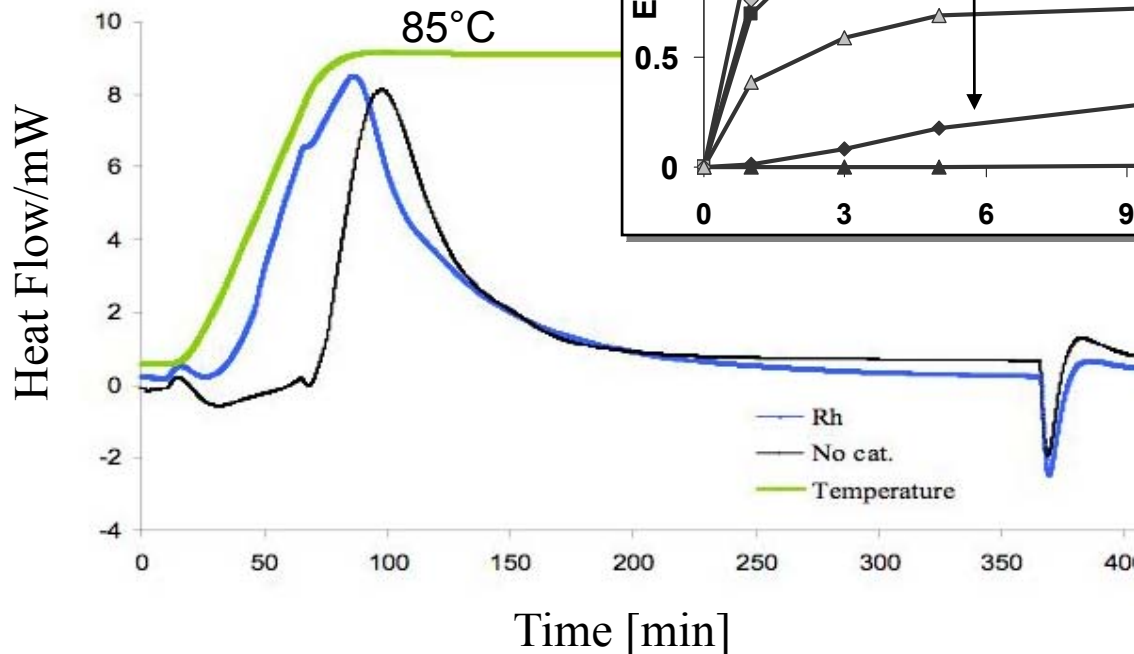
Center Partners (LANL and U Washington) have previously demonstrated metal catalyzed AB H₂-release in organic solvents.

Technical Accomplishments

2008: Rh Catalyst Increases Release Rate of the First Equivalent of H₂ from AB in Ionic Liquids

50 wt% AB
in bmimCl
5 mol% Rh

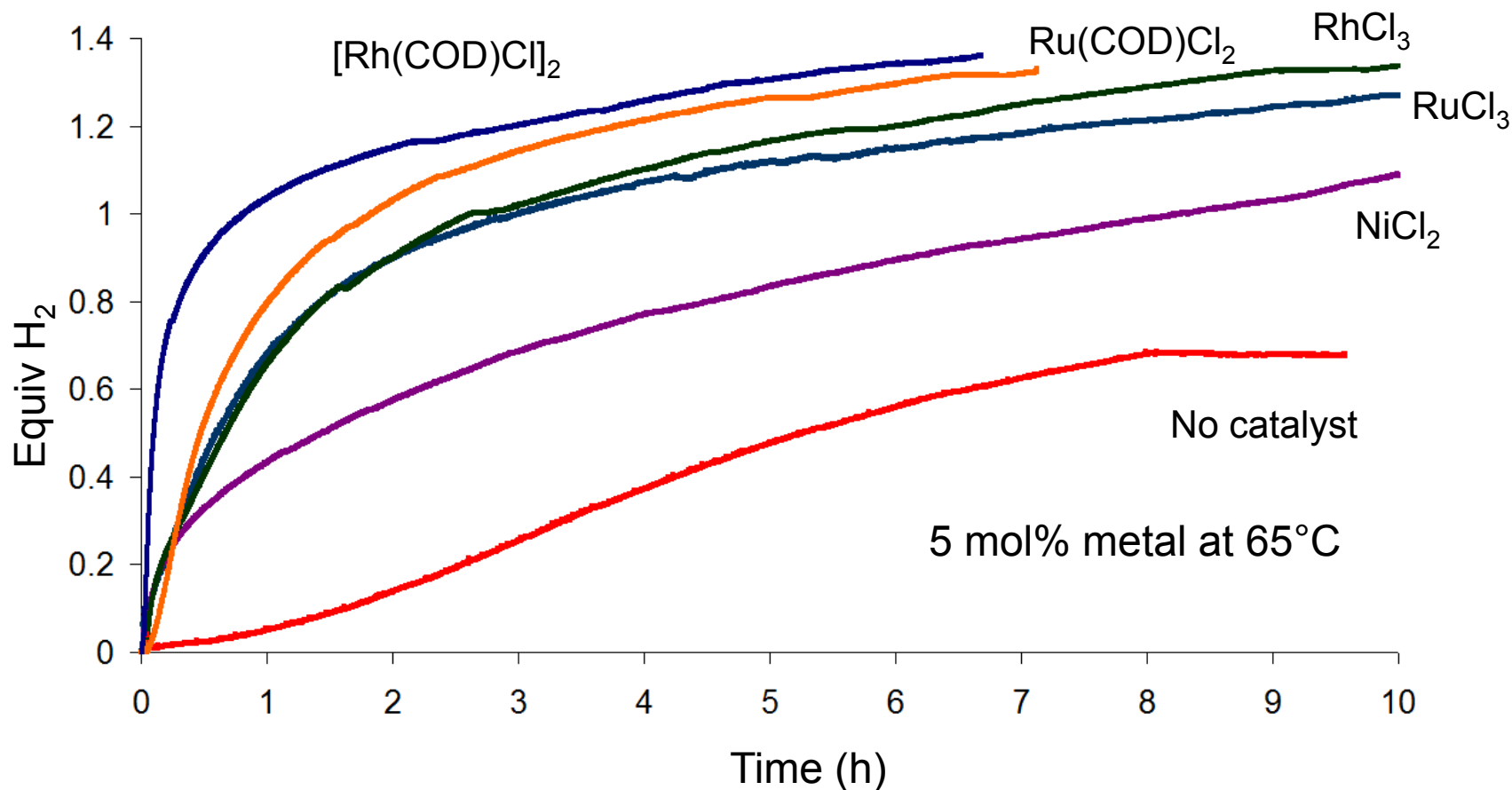
DSC



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

Technical Accomplishments

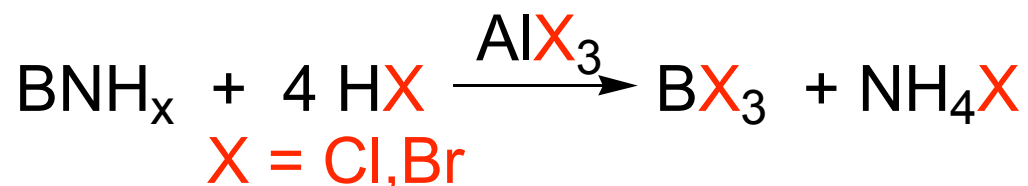
2009: Other Metal Catalysts have been found to Increase the Rate of AB H₂-Release in Ionic Liquids



Approach

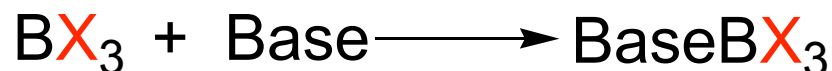
Penn Approach to Regeneration: Super-Acid/Halide-Reduction Process

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

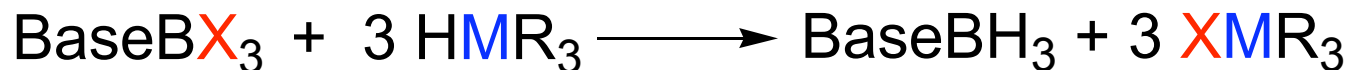


Second Step: One-Pot Conversion of BX_3 to AB

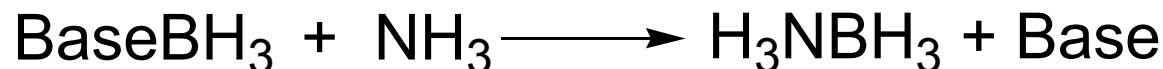
Coordination of BX_3



BX Reduction



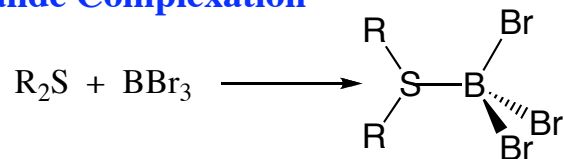
Base Displacement by NH_3 Yields AB



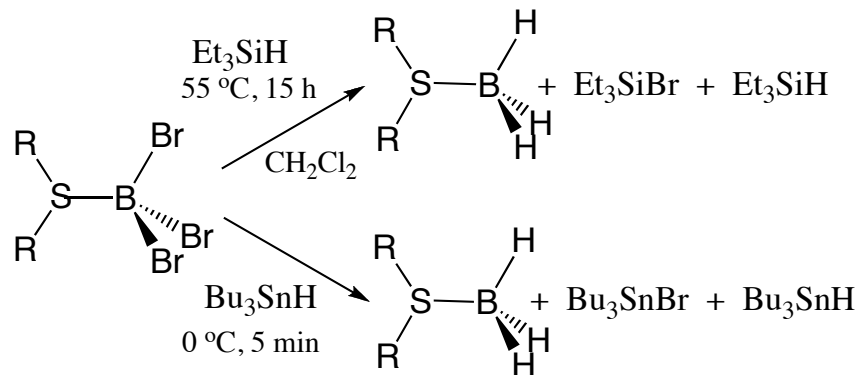
Technical Accomplishments

2008-2009: Step 2: Boron Halide Reduction Processes are Simple, Quantitative and Allow Separation and Recovery of All Products

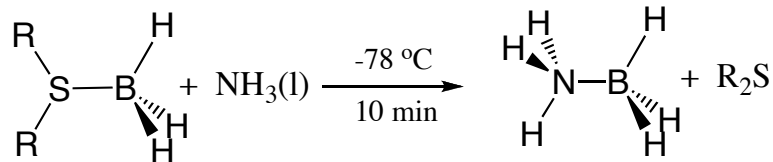
Boron Halide Complexation



Complex Reduction with Silanes or Stannanes

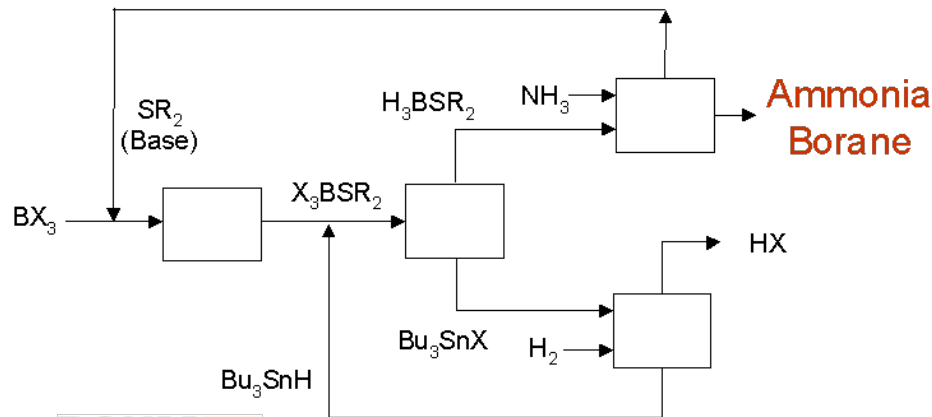


Displacement with Ammonia



Demonstrated Advantages:

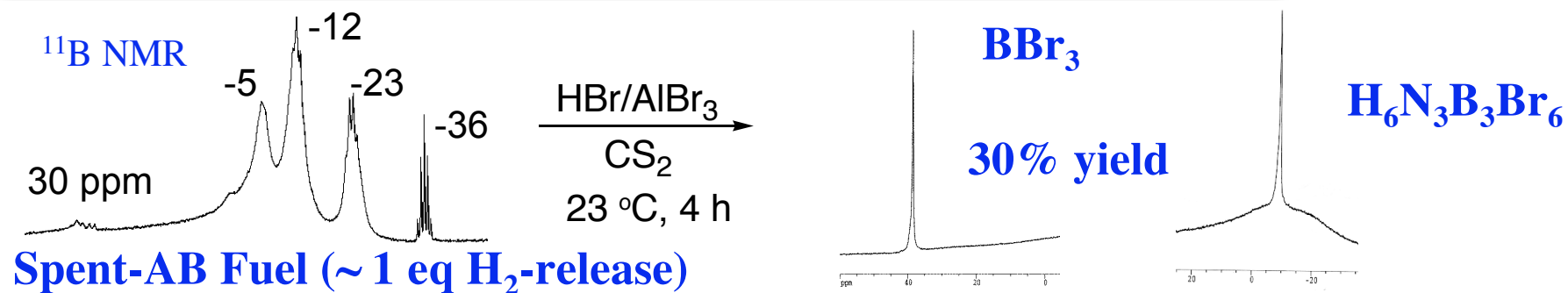
- (1) high, 96-100%, yields on multi-gram laboratory scale-ups
- (2) avoids the formation of B-O bonds
- (3) avoids the formation of B_2H_6
- (4) simple product isolation based on volatility with separation/recovery of all materials
- (5) 2008-9 Rohm and Haas analysis indicates a scalable process



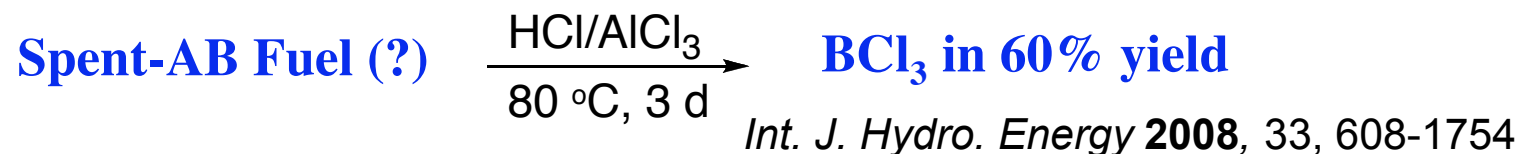
Technical Accomplishments

Step 1: Progress on Spent Fuel Digestion to BX_3

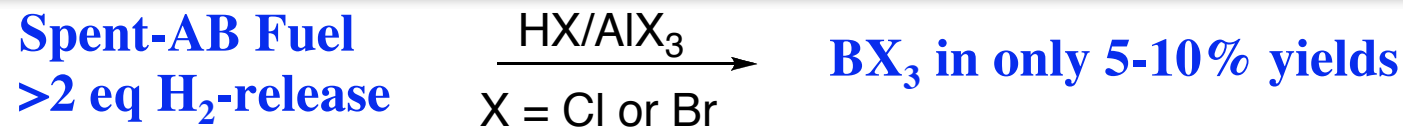
2007 Penn: Superacidic HX/AlX_3 Solutions Digest Spent-Fuels



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



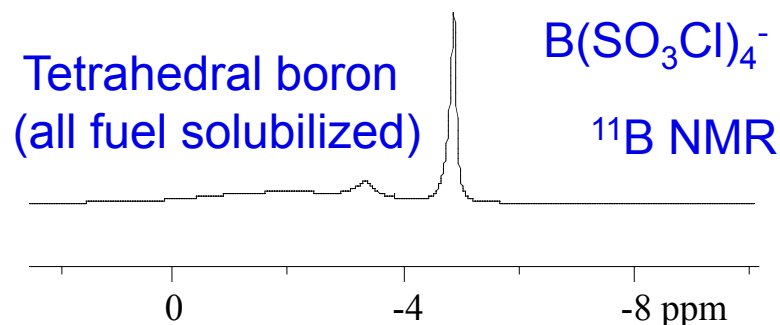
2008-9 Penn: Superacidic Conditions Do Not Give Good Yields of BX_3 from Highly Dehydrogenated Fuels



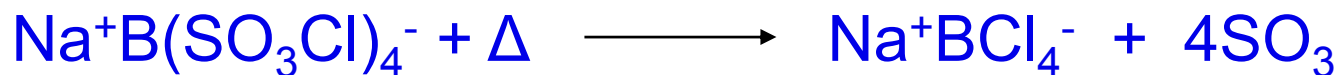
2009 Conclusion: Spent Fuel Digestion to BX_3 Must be Improved for a Halide-Based Regeneration to be “Go”

Examples of Alternative Methods Under Study for Spent Fuel Conversion to BX_3

1. Spent Fuel Digestion in Chlorosulfonic Acid

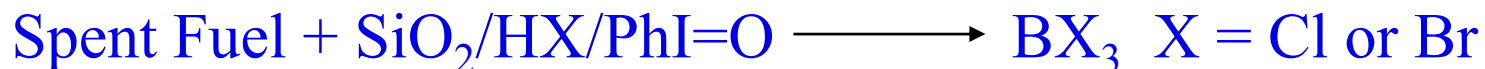


Conversion to Boron Halides?



Drache et. al. *Bull. Soc. Chim. Fr.* **1976**, 1749-1754

2. Reactions with Halogen/Oxidant Systems



Future Studies



- Complete H₂-release studies for: (1) ionic-liquid/AB mixtures at different temperatures, (2) base-initiated ionic-liquid/AB mixtures, and (3) metal-catalyzed ionic-liquid/AB.
- Complete the optimization of the temperature/weight-ratios for ionic liquid based H₂-release.
- Continue to develop and optimize new chemical-promoter systems with improved H₂-release rates
- Explore the activities of non-precious metal catalysts in ionic liquids for improving the rate of AB H₂-release.
- Take advantage of synergistic mechanisms to improve H₂-release rates.
- Explore alternative methods for the formation of boron trihalides
- Explore, with Center partners, the development of hybrid regeneration methods

Collaborations and Technology Transfer

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

Some Examples of 2008-9 Collaborations and Technology Transfer

- PNNL postdoctoral visited Penn to learn how to perform the borazine synthesis at PNNL.
- Penn students and postdoctoral carried out research at PNNL on two 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 PNNL (Linehan) began a collaboration on identifying the nature of the active catalyst in the rhodium catalyzed AB H₂-release in ionic liquids.
- Penn and Rohm and Haas (Chen and Lipiecki) began evaluating the scale up feasibility of the of the boron halide reduction/separation step for regeneration.
- U. of Ottawa (Baker) and Penn are carrying out joint investigations of the mechanisms of AB H₂-release.

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 and a key barrier to boron-halide based regeneration was identified.*

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

Proposed Future Research: *Broad based experimental studies on both H₂-release and regeneration that build on past discoveries.*

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Additional Slides

H₂-Release Systems Reported at 2007 Program Review

Metrics	Hydrolysis 22 °C	Thermolysis at 85 °C					
		Solid-State			Solution-State		
	22.7 wt% aq. AT (1.1 mol%Rh)	AB/LiNH ₂ (9 mol%)	AB/LiH (17 mol%)	AB/AT(5mol%) /PS(5mol%)	AB/PS(5mol%) /bmimCl	AB/edmimCl	AB/AT(5mol%) /PS(5mol%)/bmimCl
Grav. density (Mat. wt%)	6.1, 4h	5.9, 3h 9.3, 15h	5.7, 3h 9.4, 15h	5.1, 1h 6.9, 3h	5.1, 3h 5.8, 6h	3.1, 1h 4.2, 3h 5.3, 6h	5.3, 1h 6.5, 3h
Vol. density (Kg-H ₂ /L Mat.)	0.090, 4h	0.047, 3h 0.074, 15h	0.045, 3h 0.073, 15h	0.044, 1h 0.059, 3h	0.047, 3h 0.054, 6h	0.018, 1h 0.023, 3h 0.030, 6h	0.049, 1h 0.060, 3h
H ₂ Flow Rate (g/s) per kg Material	0.0042, 4h	0.0055, 3h 0.0017, 15h	0.0053, 3h 0.0017, 15h	0.014, 1h 0.0064, 3h	0.0047, 3h 0.0027, 6h	0.0086, 1h 0.0038, 3h 0.0024, 6h	0.015, 1h 0.0060, 3h
Kg of Mat. for 0.8 mol/sec	377, 4h	295, 3h 938, 15h	304, 3h 931, 15h	114, 1h 250, 3h	342, 3h 599, 6h	186, 1h 420, 3h 670, 6h	108, 1h 267, 3h

H₂-Release Systems Reported at 2008 Program Review

Metrics	AB Thermolysis at 120°C		
	Solution-State (15 min, ~2 Eq. H ₂)		
	50 wt% BmimCl	40 wt% BmimCl	20 wt% BmimCl
Grav. density (Mat. wt%)	7.2	8.7	10.2
Vol. density (Kg-H ₂ /L Mat.)	0.067	0.078	0.086
H ₂ Flow Rate (g/s) per kg Material	0.08	0.097	0.114
Kg of Mat. for 0.8 mol/sec	20	17	14