

Amineborane Hydrogen Storage

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This presentation does not contain any proprietary or confidential information

Project ID: ST 3



Project Overview

Timeline

Project Start: FY 2005
Project End: FY 2009
Percent complete: 30%

Budget

Total Project Funding: \$1,727,356
DOE: \$1,381,886
Penn: \$345,470

DOE Funding in 05: \$197,000
DOE Funding in 06: \$250,000

Barriers Addressed

Barriers

- A. System Weight and Volume
- B. System Cost
- C. Durability/Operability
- R. Regeneration Processes

Targets

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

Partners on Amineborane Project



Overall Objectives

- Develop Methods for On-Demand, Low Temperature Hydrogen Release from Chemical Hydrides that Can Achieve DOE Targets
- Develop High Conversion Off-Board Methods for Chemical Hydride Regeneration

Approach

In collaboration with Center Partners we are developing new methods for **Amineborane Hydrogen-Release and Regeneration Reactions** that will enable their use for chemical hydrogen storage.

Penn Work Complements Partner Studies

Penn: new dehydrogenation and hydrolysis catalysts; and characterization and regeneration reactivity of a-BN products

LANL: homogeneous and acid dehydrogenation catalysts and regeneration methods

PNNL: supported dehydrogenation catalysts and studies of key dehydrogenation steps

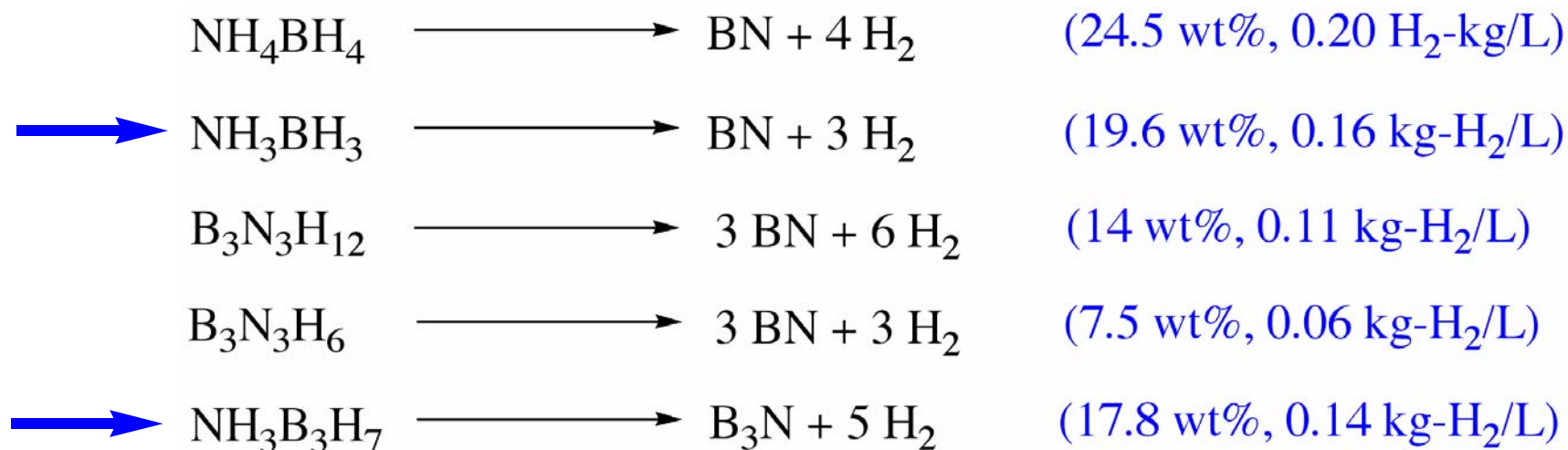
U. of Washington: studies of fundamental amineborane coordination chemistry and mechanisms of homogeneously catalyzed dehydrogenation

U. of Alabama: computational studies of amineborane reaction pathways and stabilities

Northern Arizona U.: amineborane syntheses and properties

Intematix: High throughput catalyst screening

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



DOE Targets

2007: 4.5 wt%, 0.036 kg-H₂/L; **2010:** 6.0 wt%, 0.045 kg-H₂/L;

2015: 9.0 wt%, 0.081 kg-H₂/L

Initial Objectives:

- Improve synthetic routes to key amineboranes
- Determine if ammonia triborohydride (AT) is a candidate for hydrogen storage
- Improve the extent, rate and control of hydrogen release from amineboranes by both hydrolytic and thermolytic reactions
- Characterize the dehydrogenation products and develop new methods for amineborane regeneration

Summary of Initial Discoveries/Achievements:

- A new synthetic route to ammonia triborohydride (AT) and the demonstration that AT is soluble and stable in water
- Acids and metal catalysts induce hydrolytic hydrogen release from AT under mild conditions. The metal catalysts have extended lifetimes in buffered solutions
- Chemical additives, ionic liquids and metal catalysts increase the extent and rate of thermolytic hydrogen release from ammonia borane (AB) and ammonia triborohydride (AT) and several systems have been identified that have potential to meet DOE targets
- A key step needed for amineborane regeneration, digestion of the polyaminoborane polymer, has been achieved.



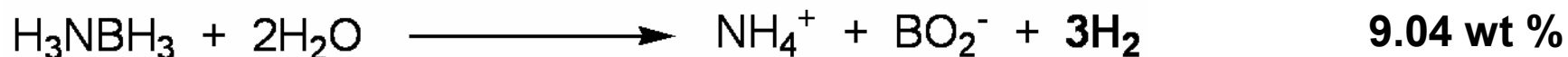
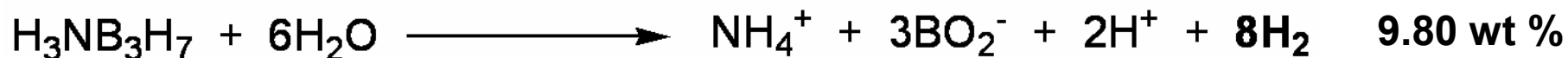
Penn Research Team

PI: Larry Sneddon

Postdoctorals: Martin Bluhm
Mark Bradley

Students: Chang Yoon
Bill Ewing

H₃NB₃H₇ Hydrolysis Compares Favorable with H₃NBH₃ and NaBH₄ Processes



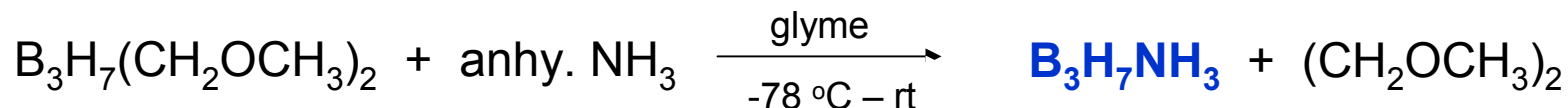
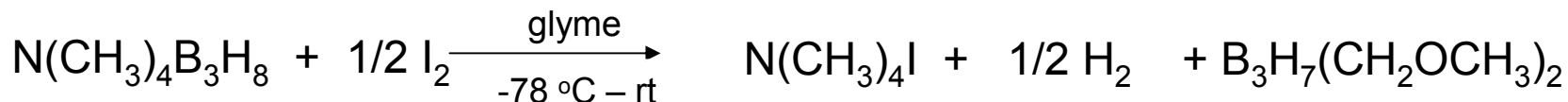
Manish Chandra, Qiang Xu *J. Power Sources* **2005**, in press



Int J Hydrogen Energy **2003**, 28, 1095

Key initial questions that we addressed to determine if AT hydrolysis is a candidate hydrogen storage process:

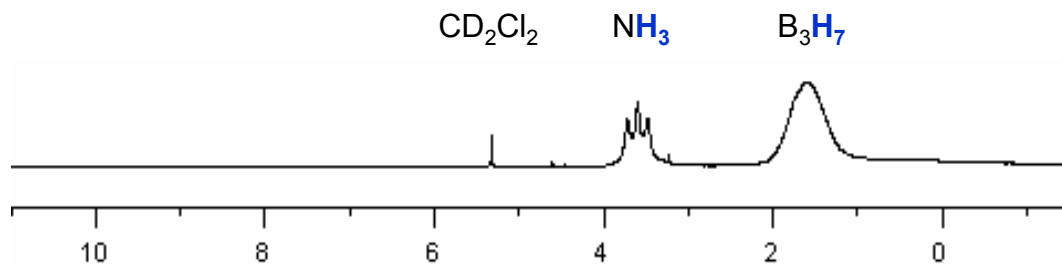
- Can a new more efficient and safe method for AT synthesis be developed?
- Is AT stable and soluble in water?
- Can hydrogen release be achieved under mild conditions?



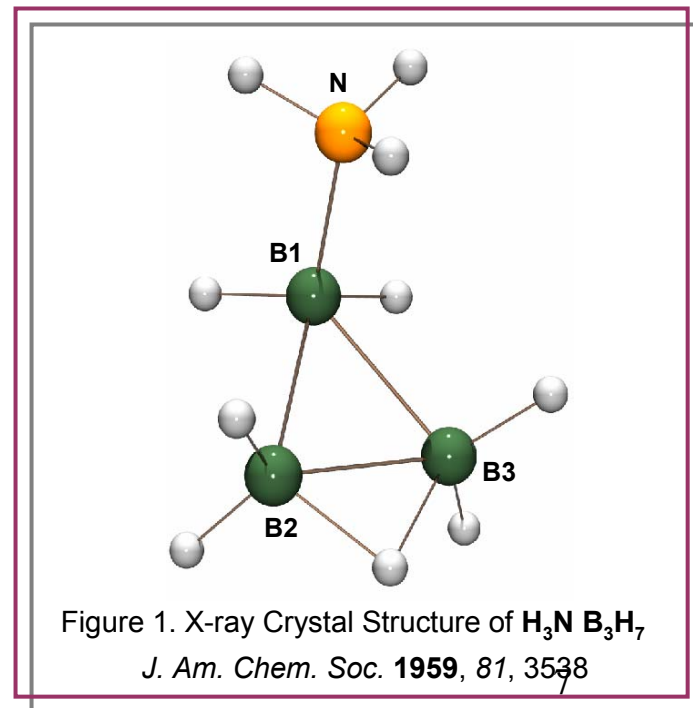
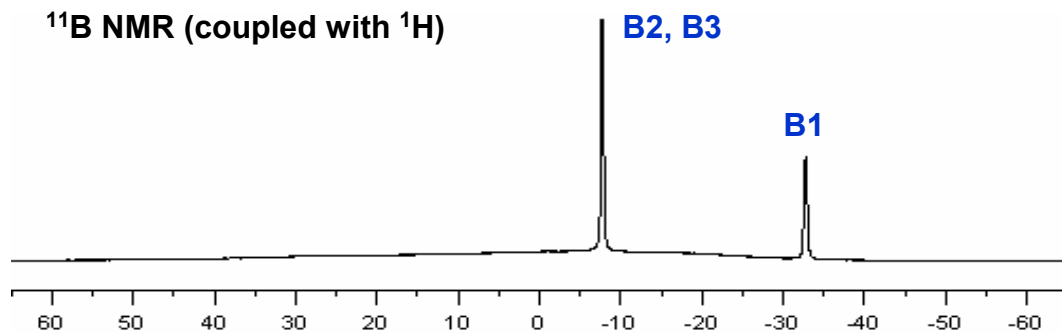
**White Crystalline
Powder, Yield >80%
mp ~73 °C**

Characterizations

1H NMR



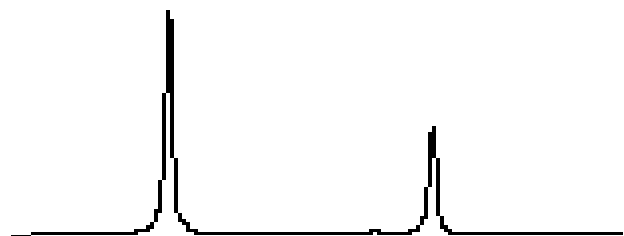
^{11}B NMR (coupled with 1H)



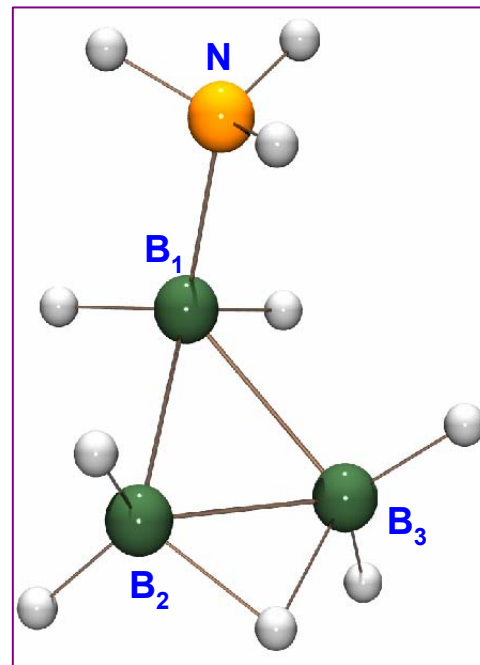
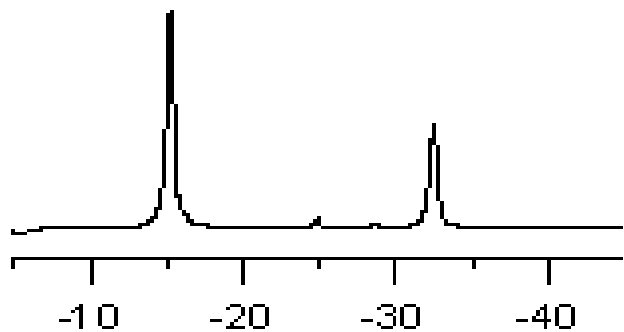
(a) ~ 25 wt % aqueous B₃H₇NH₃ solution



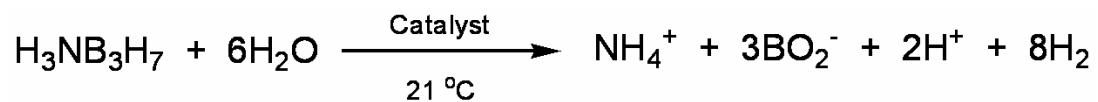
(b) After 24h



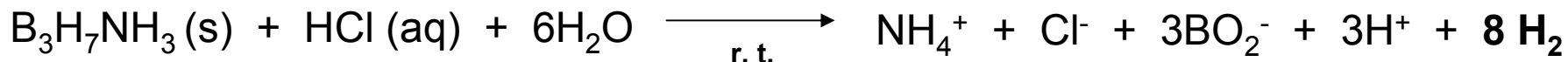
(c) After 96h



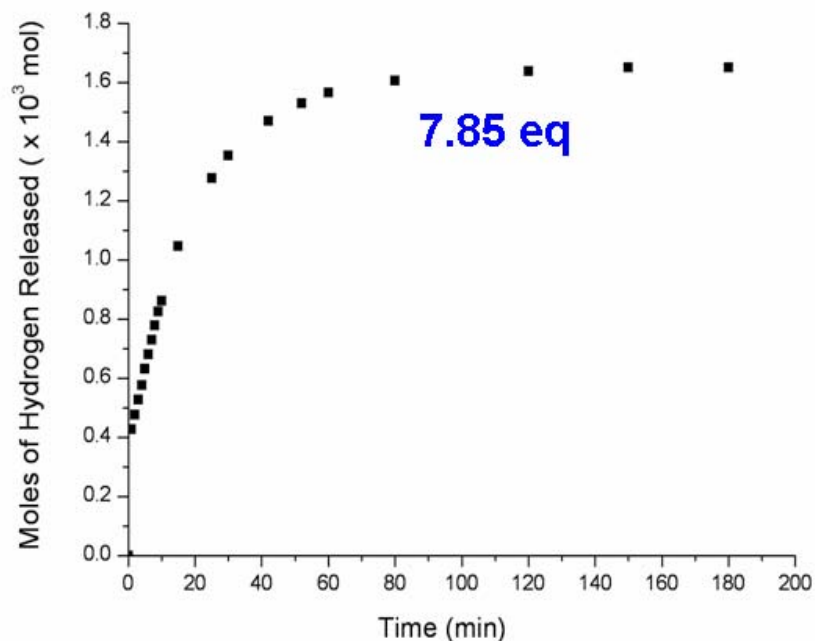
At least **33 wt%** B₃H₇NH₃ dissolves in H₂O



➡ **~9.5 wt %** H₂ can be stored



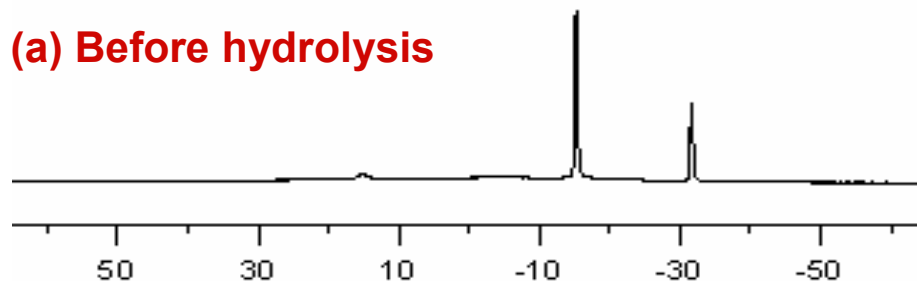
¹¹B NMR of the Resulting Solution



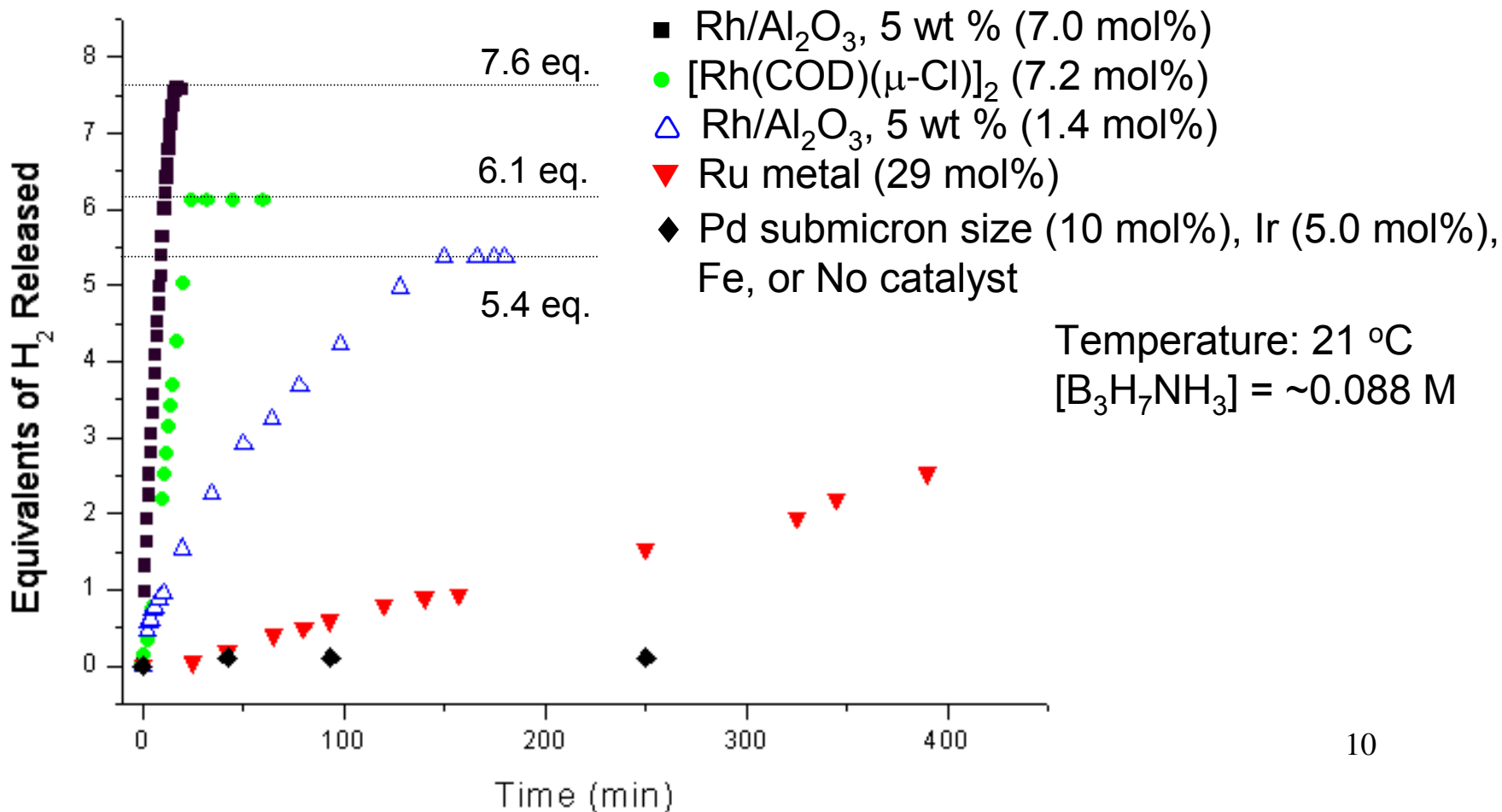
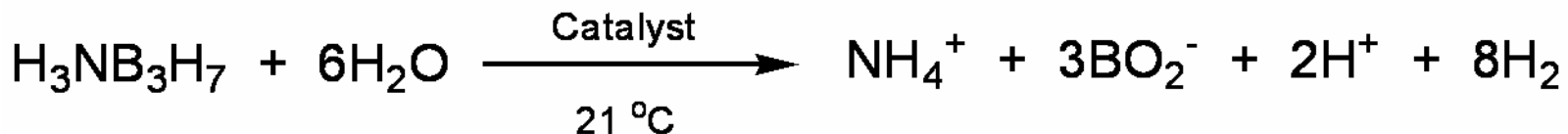
(b) After hydrolysis



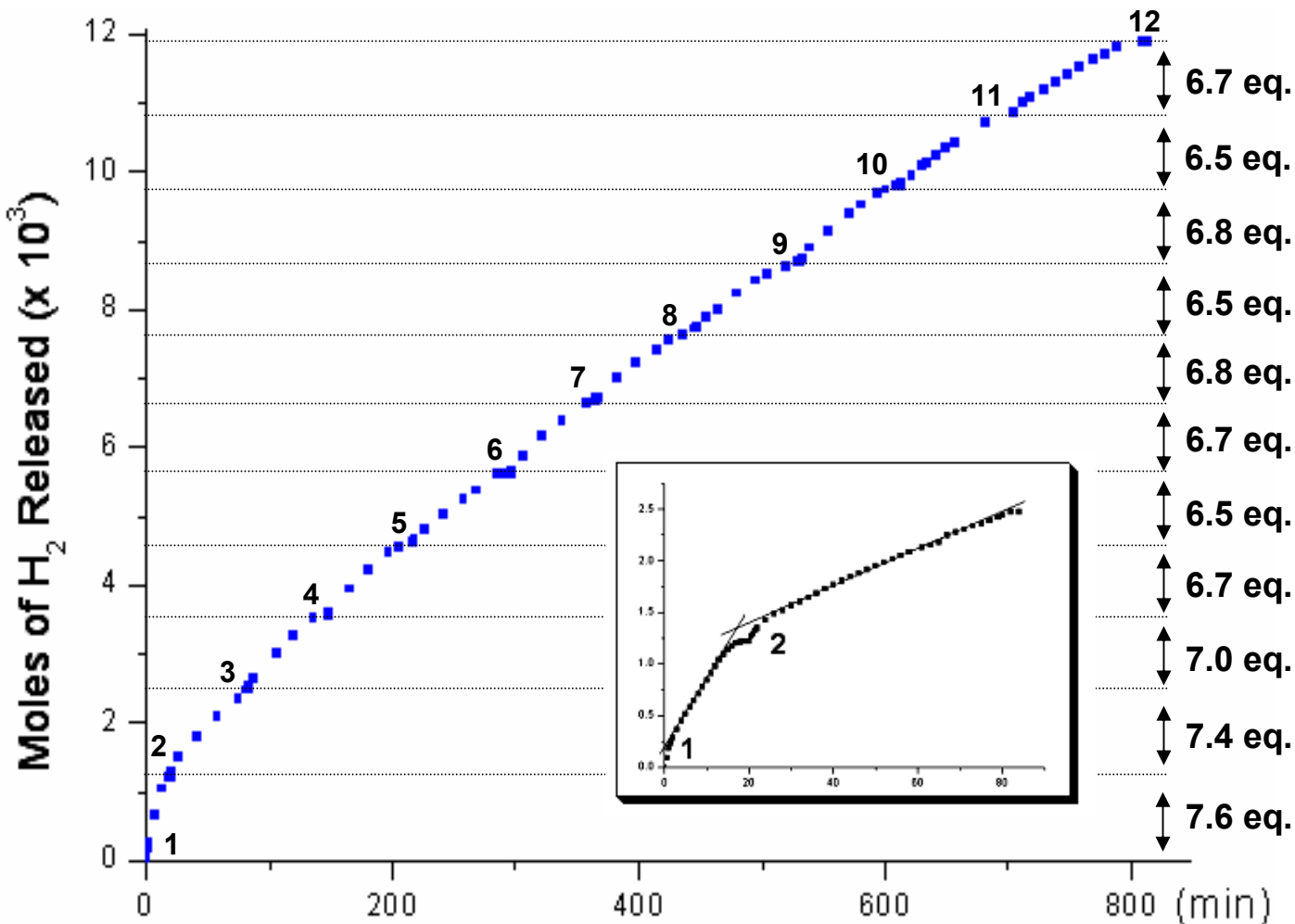
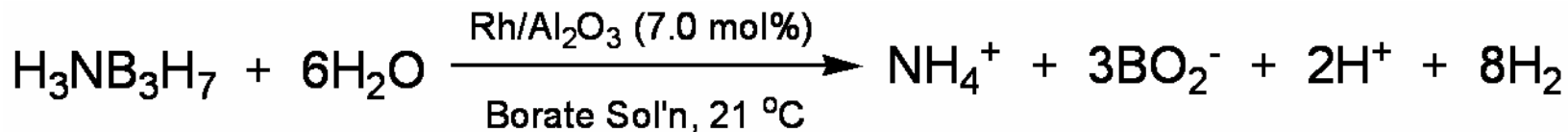
(a) Before hydrolysis



Under acidic conditions, H₃NB₃H₇ produces ~ 8 equivalent of hydrogen



Rh/Al₂O₃ Catalysts Show Extended Activities in Buffered Solutions



[B ₃ H ₇ NH ₃] = ~ 0.08 M		
	B ₃ H ₇ NH ₃ (mg)	pH
1:	9.0	7.2
2:	9.6	7.6
3:	8.9	8.0
4:	8.7	8.0
5:	8.8	8.0
6:	8.8	8.0
7:	8.8	8.0
8:	8.5	8.0
9:	9.2	8.0
10:	9.1	8.0
Add HCl to adjust pH ~7.2		
11:	8.7	~7.2
12:		~7.5

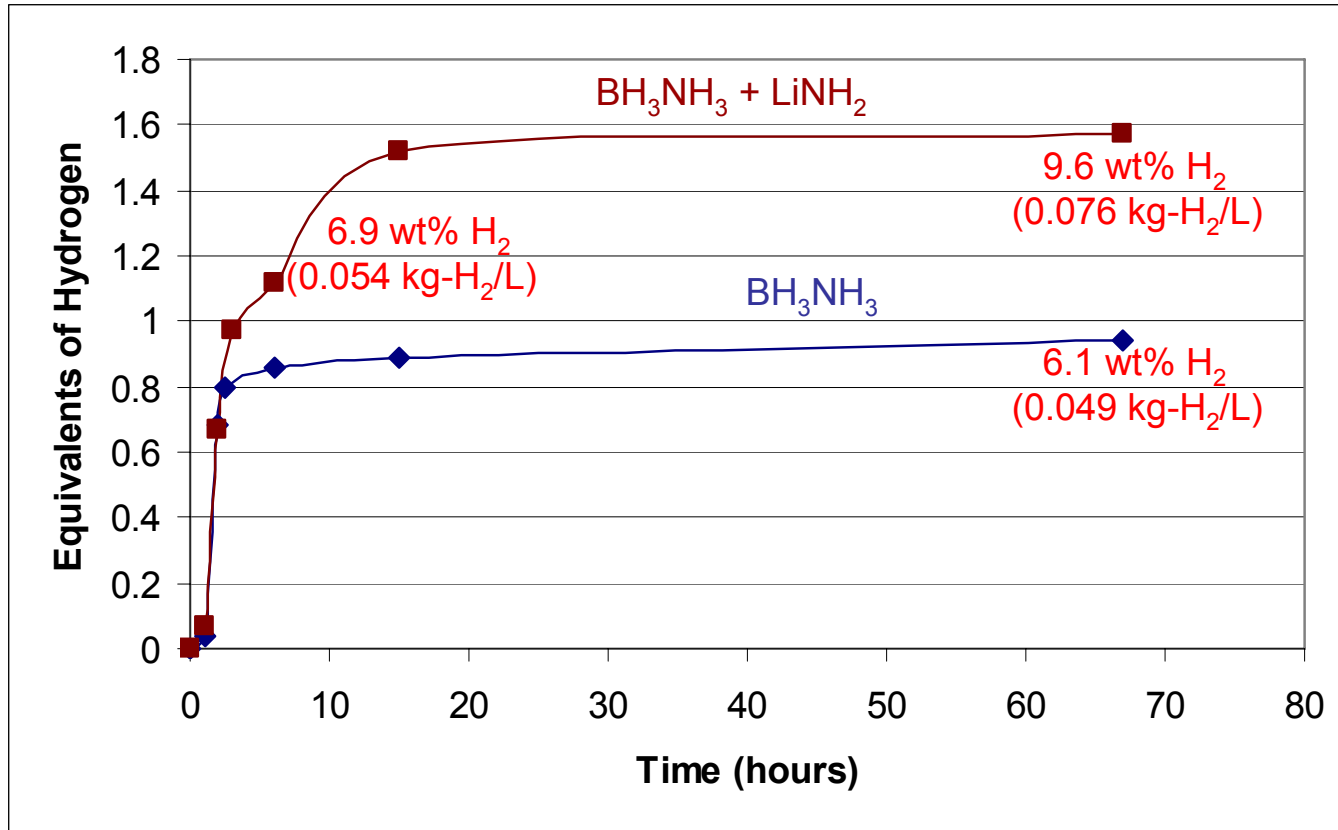
Both AB and AT Have High Thermolytic H₂ Storage Capacities



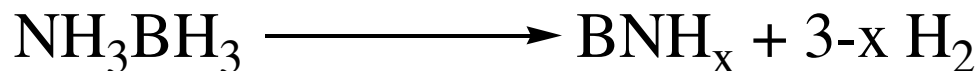
Key questions that we addressed:

- Can chemical additives, ionic liquids and/or metal catalysts be used to increase the extent and rate of hydrogen production from ammonia borane and ammonia triborohydride?
- What are the products of the dehydrogenations and which are the most suitable for regeneration?
- What methods can be used for regeneration of spent [BNH]_x materials?

$\text{BH}_3\text{NH}_3 + 10 \text{ mol } \% \text{LiNH}_2$ at $85 \text{ }^\circ\text{C}$

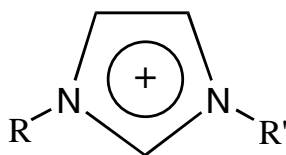


Why Use Ionic Liquid Solvents for Amineborane Dehydrogenations?

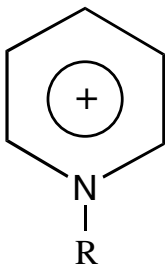


Ionic Liquid Solvents

Cations:



N,N'-imidazolium



N-pyridinium

Anions:

Reactive: AlCl_4^- , Al_2Cl_7^-

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

Advantages

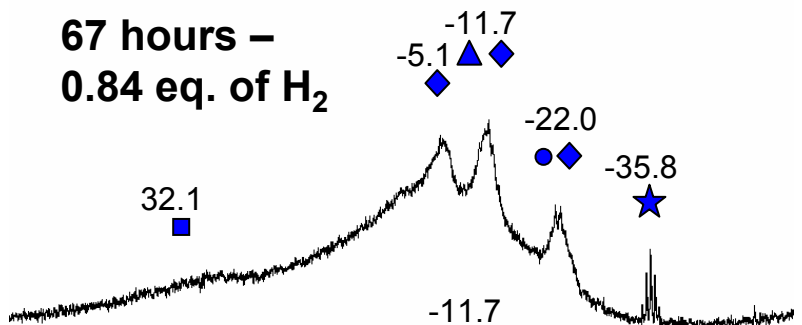
- Dissolve both neutral and ionic species, promote polar transition states
- Negligible vapor pressures
- Non-coordinating anions and cations provide polar, inert reaction medium for catalytic reactions.

Neat NH₃BH₃

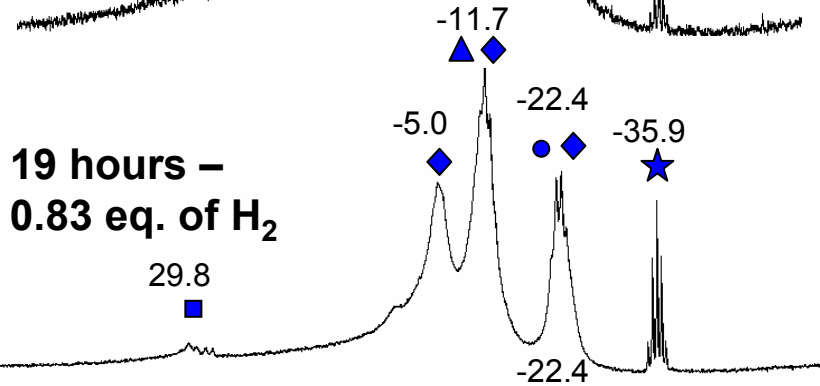
¹¹B NMR Spectra of Residues

NH₃BH₃ + Ionic Liquid[#]

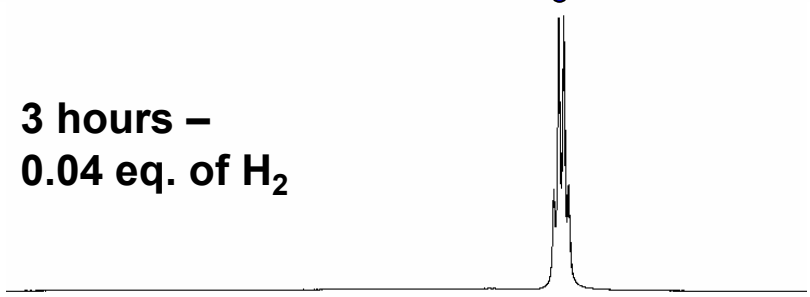
67 hours –
0.84 eq. of H₂



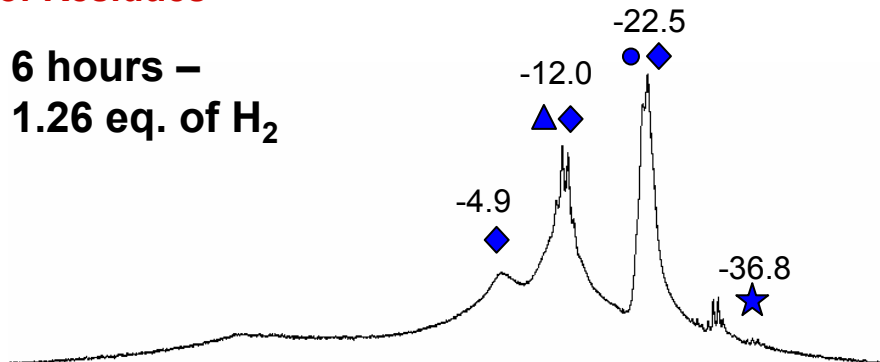
19 hours –
0.83 eq. of H₂



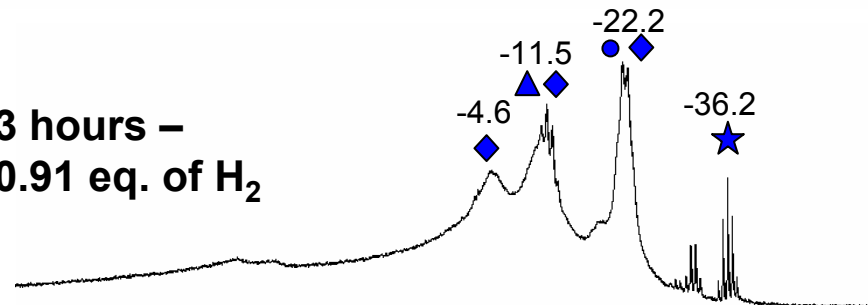
3 hours –
0.04 eq. of H₂



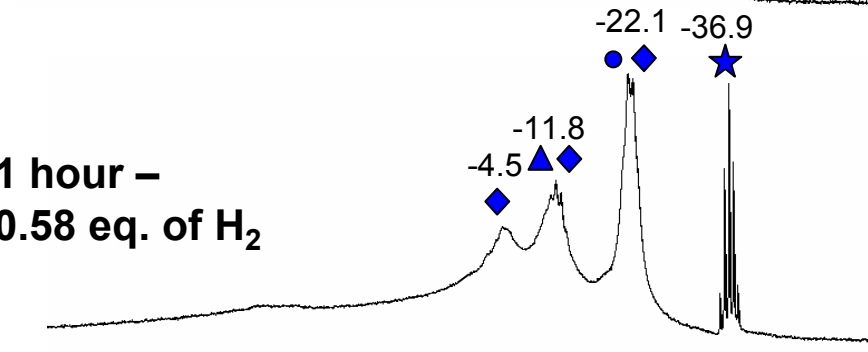
6 hours –
1.26 eq. of H₂



3 hours –
0.91 eq. of H₂



1 hour –
0.58 eq. of H₂



ppm (F1) 50

0

-50

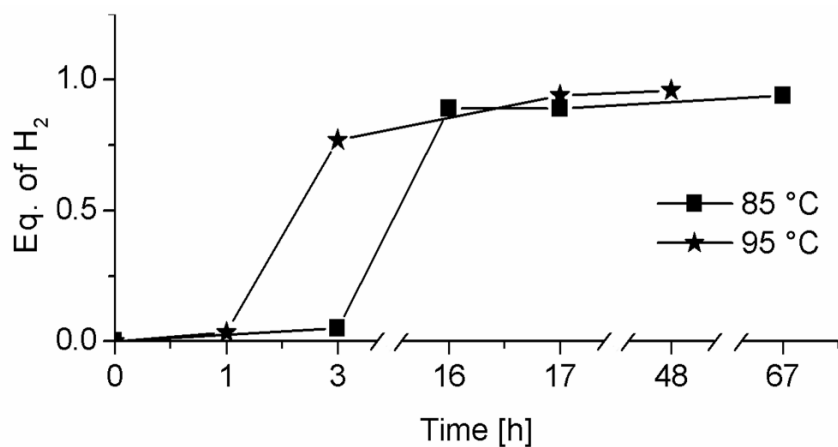
ppm (F1) 50

0

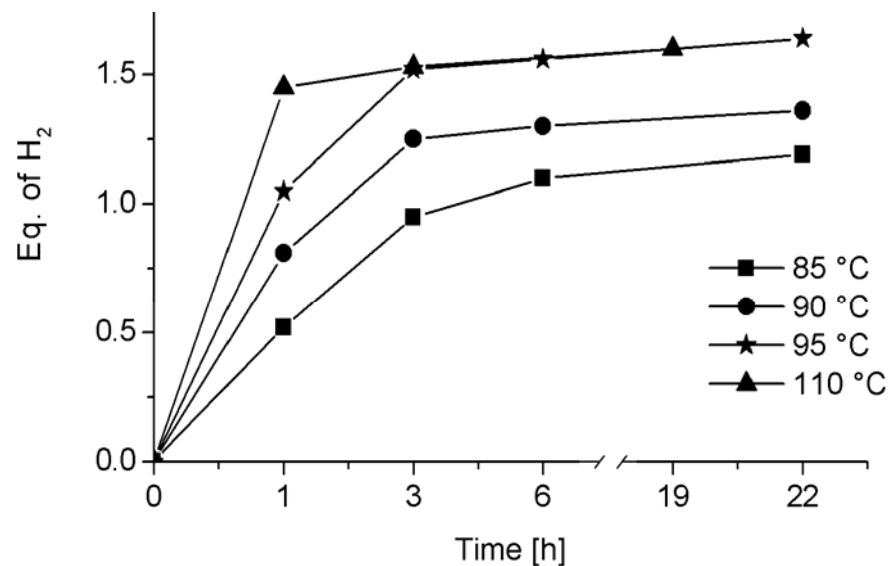
-50

● ammonia borane, ★ BH₄⁻, ▲ BH₂⁺, ◆ polyaminoborane, # 1-Butyl-3-methylimidazolium chloride

Neat NH_3BH_3



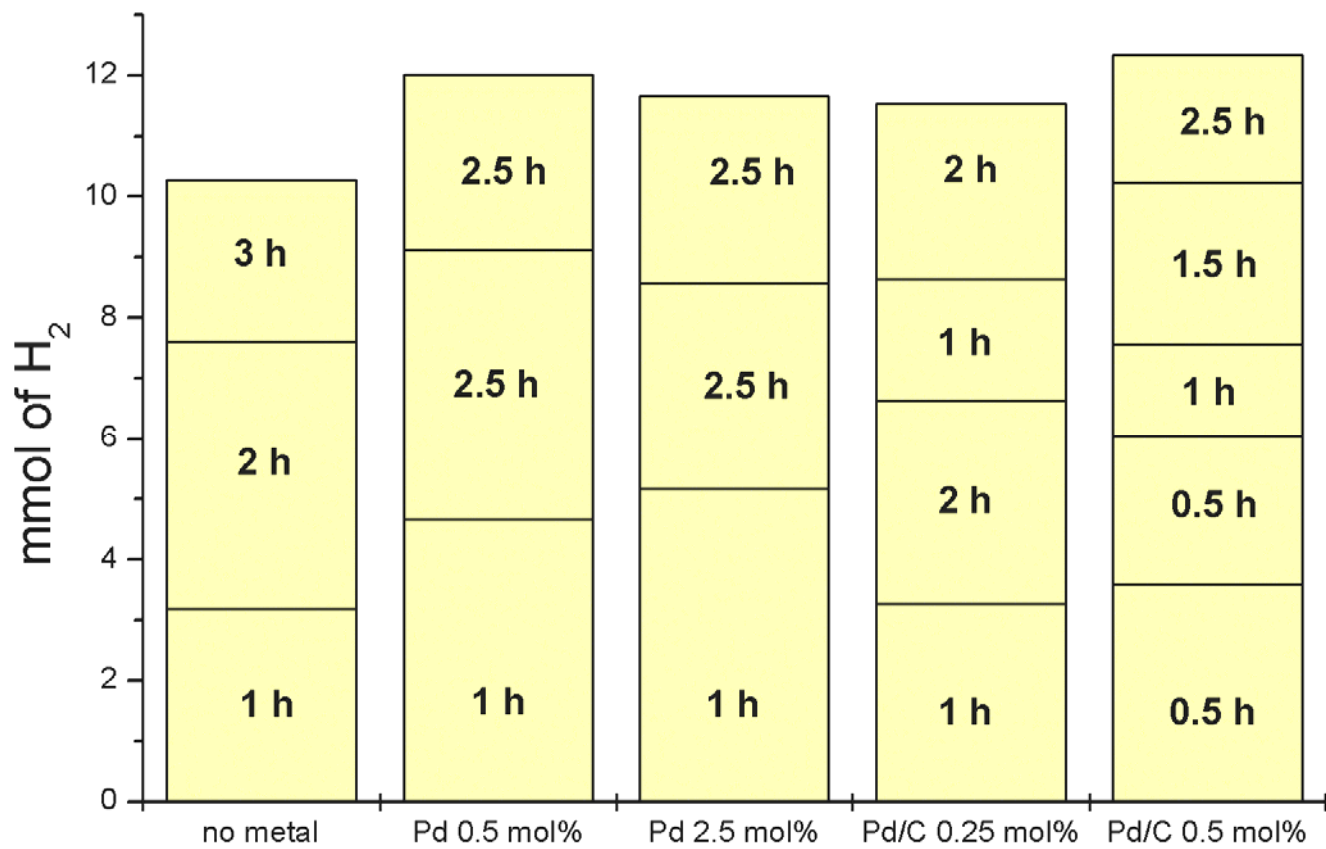
NH_3BH_3 + Ionic Liquid[‡]



[‡] 1-Butyl-3-methylimidazolium chloride

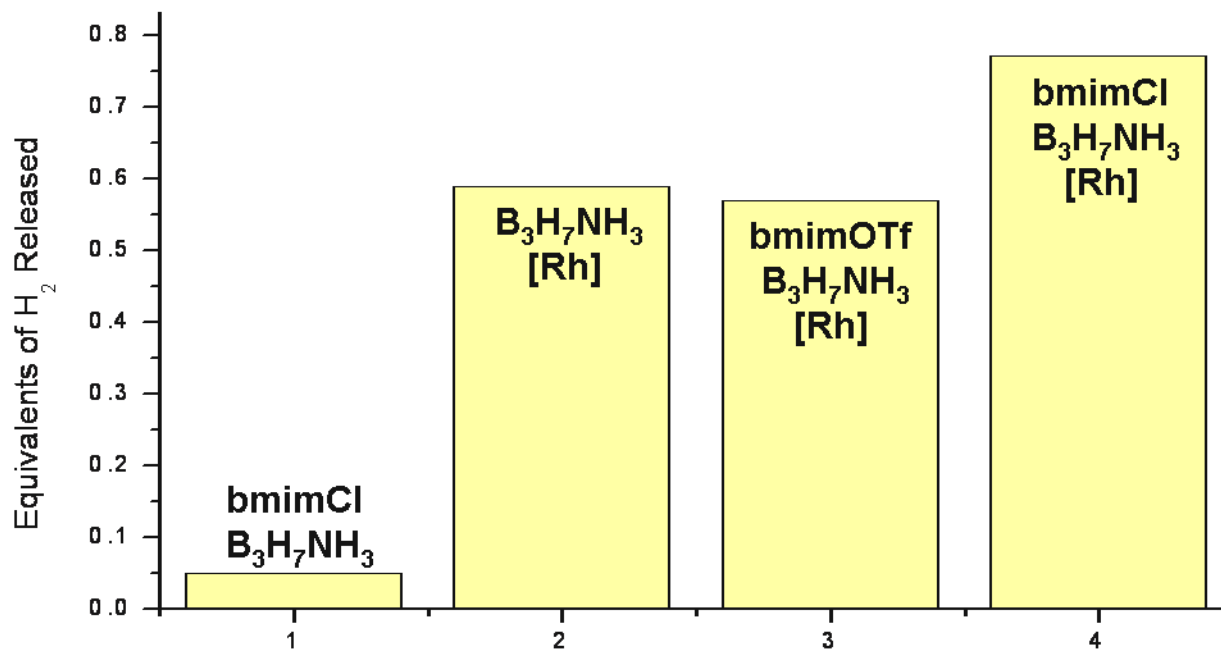
Ionic liquids accelerate the hydrogen release from NH_3BH_3 !

mmol of H ₂ :	10.18	12.01	11.66	11.53	12.34
System wt%	4.1	4.8	4.5	4.5	4.6



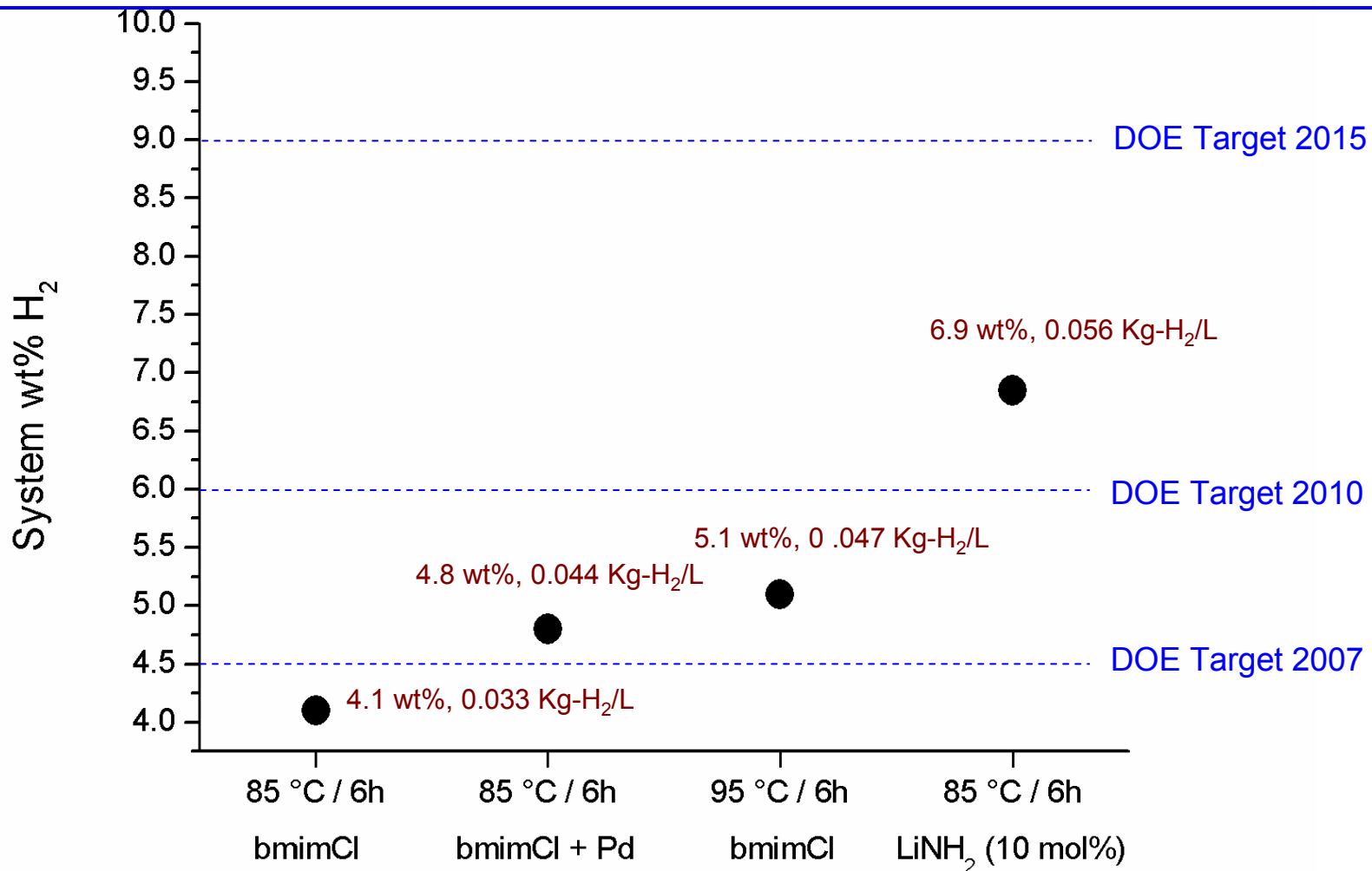
“System” = wt of H₃NBH₃ + Catalyst + bmimCl

Metals Catalyze Ammonia Triborohydride Dehydrogenation as Low as 50 °C



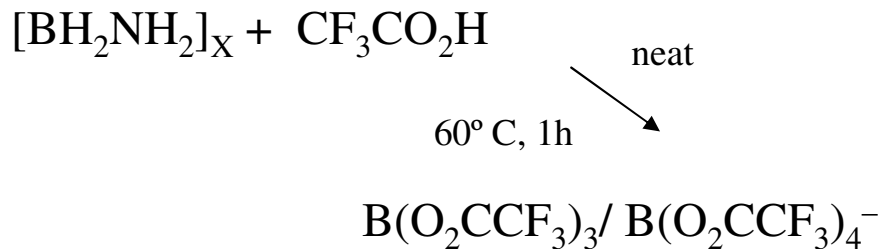
[Rh] = [Rh(COD)Cl]₂ (COD=1,5-cyclooctadiene)
 bmimCl = 1-butyl-3-methylimidazolium chloride
 bmimOTf = 1-butyl-3-methylimidazolium trifluoromethanesulfonate

Summary of Weight H₂ Release from NH₃BH₃ Systems

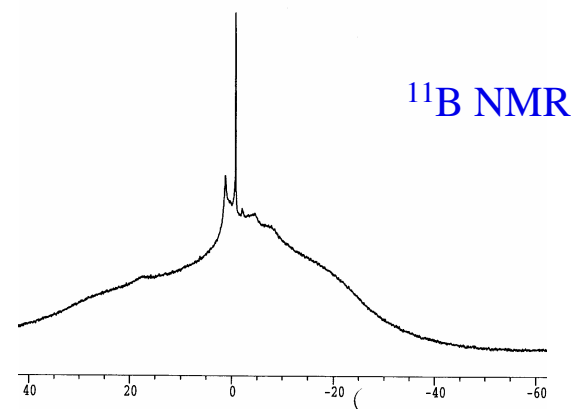


“System” = wt of H₃NBH₃ + Catalyst/Additive/Solvent

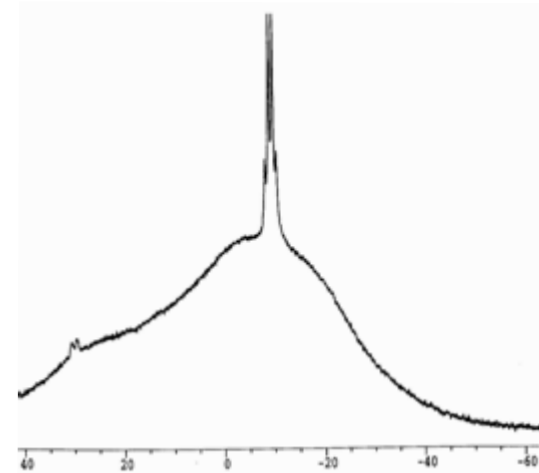
Polymer Digestion



- The polymer completely reacts with and dissolves in trifluoroacetic acid

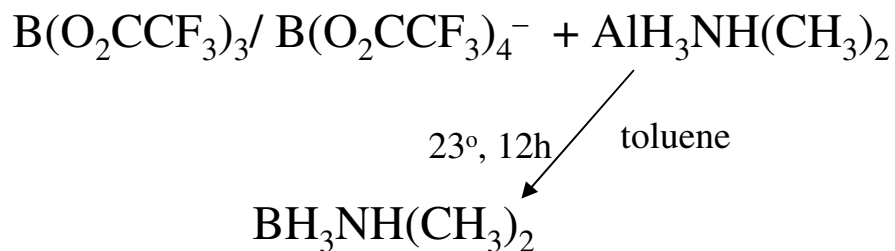


$\text{B}(\text{O}_2\text{CCF}_3)_3 / \text{B}(\text{O}_2\text{CCF}_3)_4^-$



$\text{BH}_3\text{NH}(\text{CH}_3)_2$

Reduction to Borane



- Reduction regenerates a borane amine adduct



Achievements

- Chemical additives, metal catalysts and ionic liquids have been shown to increase both the extent and rate of hydrogen release from amineboranes and several systems have been identified that have potential to meet DOE targets.
- Ammonia triborohydride has been shown to be a promising candidate for hydrogen storage.
- A new strategy for amineborane regeneration has been demonstrated.

Ongoing and Future Studies

- Develop new metal-catalyst and/or chemical-additive systems with improved hydrogen release rates for both the hydrolytic and thermolytic processes.
- Optimize the catalyzed ammonia triborohydride thermolysis process.
- Determine which of the AB or AT dehydrogenation products have the highest regeneration activities.
- Optimize regeneration processes.

Publications

M. E. Bluhm, M. G. Bradley, R. E. Butterick III, U. Kusari, and L. G. Sneddon “Amineborane Based Chemical Hydrogen Storage: Enhanced Ammonia Borane Dehydrogenation in Ionic Liquids” submitted.

M. E. Bluhm, M. G. Bradley, R. and L. G. Sneddon “Promoted Hydrogen Release from Amineborane” *Prepr. Sym., Div. Fuel Chem.* **2006**, submitted.

Presentations

M. E. Bluhm, M. G. Bradley and L. G. Sneddon “Promoted Hydrogen Release from Ammonia Borane” to be presented at the National American Chemical Society Meeting, San Francisco, September 2006.

M. E. Bluhm, M. G. Bradley, R. E. Butterick, U. Kusari and L. G. Sneddon “Enhanced Ammonia Borane Dehydrogenation in Ionic Liquids” poster to be presented at the National American Chemical Society Meeting, San Francisco, September 2006.

C. Y. Yoon and L. G. Sneddon “Ammonia Triborohydride: A Promising Candidate for Amineborane-Based Chemical Hydrogen Storage” poster to be presented at the National American Chemical Society Meeting, San Francisco, September 2006.