Chemical Hydrogen Storage R&D at Los Alamos National Laboratory (Project ID # ST29)

DOE Hydrogen Program

2007 DOE Hydrogen Program Review
May 17, 2007 Arlington, VA

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Overview

DOE Hydrogen Program

Timeline

- Start: FY 05
- End: FY 09
- 45% Complete

Budget

- Total project funding
  - $8.1M
- Funding received in FY06
  - $1600K
- Funding for FY07
  - $1700K

Barriers

- System Weight and Volume
- Hydrogen Release Rate
- Energy Efficiency
- Cost
- Regeneration Processes
- System Life-Cycle Assessment

Partners

- All Partners - DOE Chemical Hydrogen Storage Center of Excellence
- IPHE (Singapore, UK, New Zealand)

Los Alamos Technical Contributions

DOE Hydrogen Program

Tier 1: B-O to B-H

Materials and synthesis support for PSU electrochemistry

- provided ultrapure ionic liquids and modified electrodes

Tier 2: B-N Compounds

Amine-borane dehydrogenation, regeneration and engineering

- Mechanistic studies identified metal-catalyzed reaction pathways to allow for optimal hydrogen storage capacity
- Storage capacity increased using liquid amine-borane fuels
- Significant experimental progress on energy matching of spent fuel digestion and subsequent reduction
- Identified new potentially energy efficient sulfur-based regeneration scheme

Tier 3: Advanced Concepts

IPHE project - prepared and characterized new M-B-N-H storage materials

Engineering Support - GC-based system for hydrogen quantification

- bread-boarding for AB dehydrogenation/regeneration

Objectives

- Provide materials chemistry support for PSU work on electrochemical conversion of B-O to B-H
- Liquefy ammonia-borane (AB) fuel and increase rate and extent of hydrogen release
- Demonstrate chemistry and conduct engineering assessment for energy efficient AB regeneration process
- Continue to identify coupled chemical reactions that release hydrogen with near thermoneutrality
- Work with *International Partnership for the Hydrogen Economy* partners to investigate M-B-N-H chemistry to identify potentially reversible storage systems
- Increase engineering efforts towards continuous processing

Technical Approach

DOE Hydrogen Program

- Support Penn State electrochemistry B-O to B-H regen effort
  - Prepare and supply ultrapure ionic liquid electrolytes and modified electrodes
- Mechanistic studies of metal-catalyzed AB dehydrogenation
  - Reaction pathways dictate extent of hydrogen release
  - Use theory and rapid hydrogen quantification to support catalyst design for better rates
- Investigate spent fuel digestion and reduction chemistry
  - Perform digestion and reduction experiments on variety of BNH_x spent fuels
  - Optimize regeneration of MH reducing agent and B-H capture
  - Use theory and engineering analysis to assess energy efficiency
- Optimize reaction conditions and chemistry to develop hydrogen storage system based on coupled reactions
  - Identify new systems that couple endo- and exothermic reactions
- Prepare and characterize IPHE hybrid M-B-N-H compounds and assess their potential as high capacity (≥ 2H per main-group element), potentially reversible hydrogen storage materials

Technical Accomplishments: Hydrogen Release from Amine-Boranes

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$$H_3NBH_3 \rightarrow n\,H_2 + (H_2NBH_2)_n \rightarrow n\,H_2 + (HNBH)_n \rightarrow n\,H_2 + BN$$

6.5 wt% 13.1 wt% 19.6 wt%

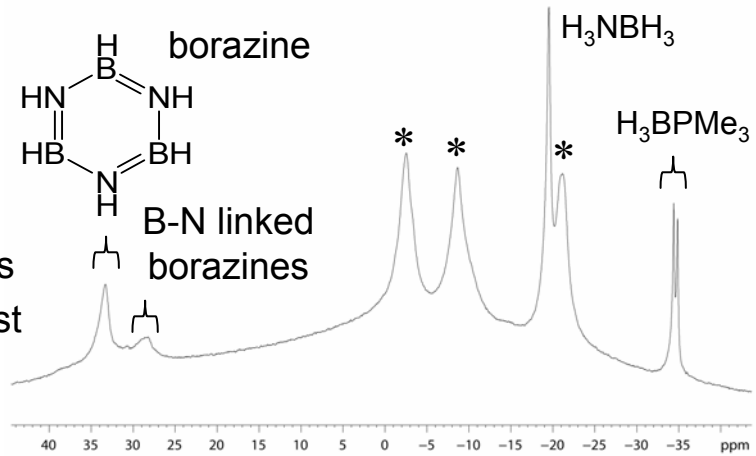
Acid Catalysis

- ✓ Combined theory (**Alabama**) and experiment to show that strong Lewis and Brønsted acids facilitate hydrogen release from ammonia-borane (AB) via reactive boronium cation $[BH_2(NH_3)(S)]^+$ (S = ether solvent)
- ✓ Work was discontinued due to insufficient rates

Transition Metal Catalysis

- ✓ Evaluated hundreds of precious and base metal catalysts using gas burette to measure hydrogen and ^{11}B NMR spectroscopy to characterize BNH_x products
- ✓ Discovered high capacity Ni and Ru catalysts

$^{11}B\{^1H\}$ NMR of soluble products from H_3NBH_3 + Fe-PMe_3 catalyst after 4 days @ 20°C



* is intermediate that converts directly to borazine!

Reaction Pathways Dictate Extent of Hydrogen Release

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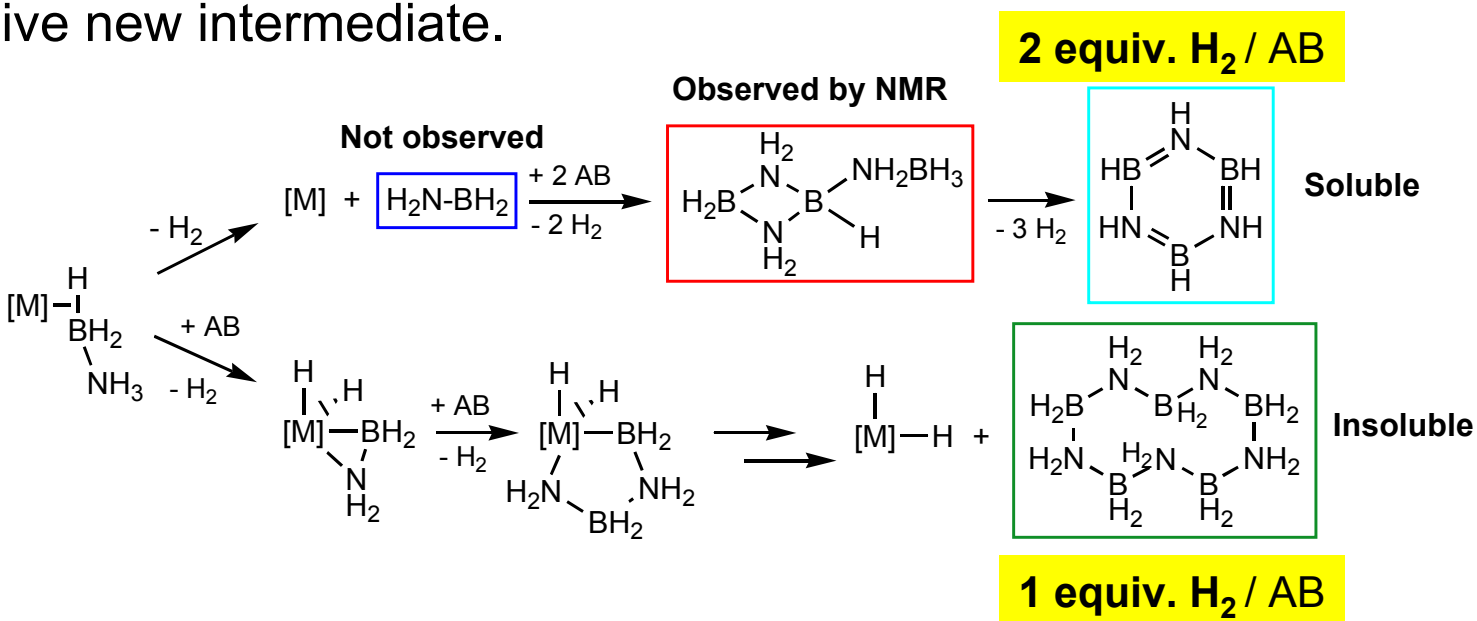
- Isotopic labeling and kinetic studies were consistent with first order formation of transient aminoborane (H_2NBH_2) which is trapped by AB to give new intermediate.

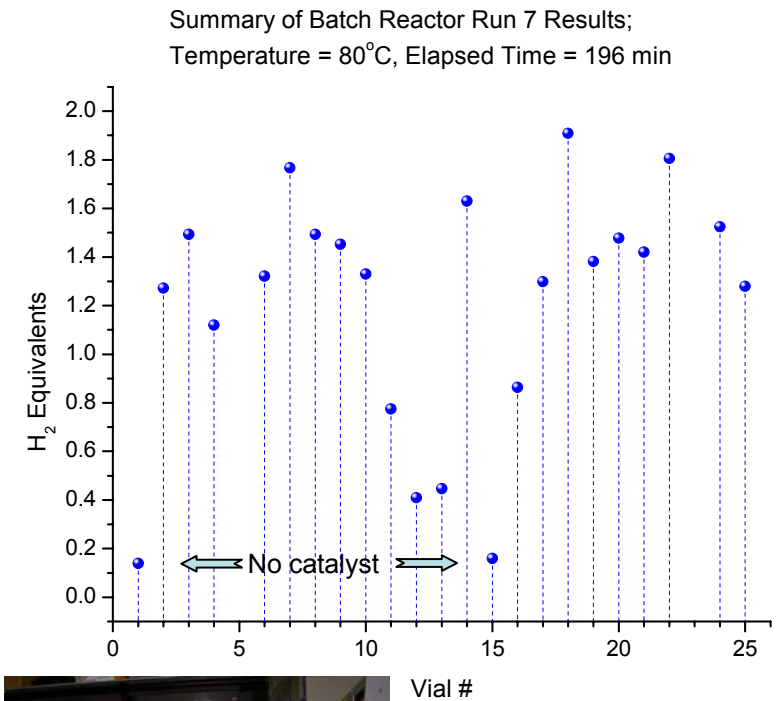


- Less productive pathway results presumably from metal coordination of aminoborane and dehydrogenative metallacycle-based ring formation.

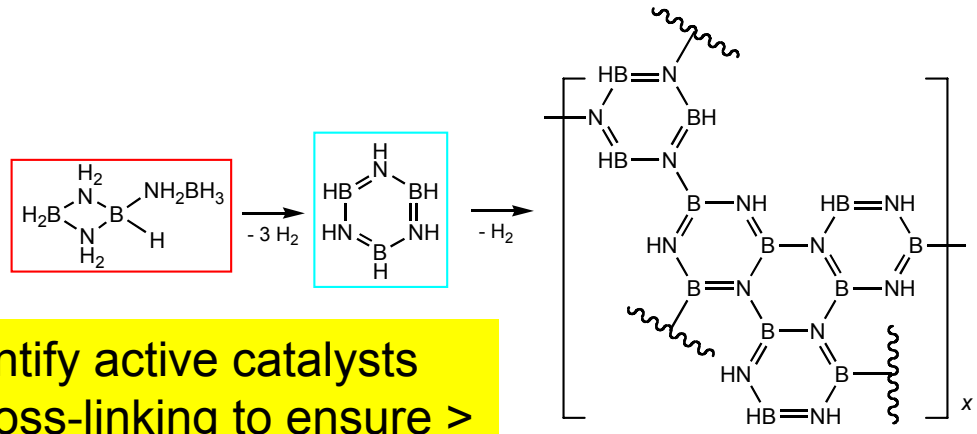
Mechanistic knowledge will focus search for best catalyst

^{11}B NMR shifts of intermediate agree well with Penn DFT calculations

Hydrogen Quantification using Rapid Throughput GC-based System



- New instrumentation allows 25 experiments per run
  - ✓ evaluate catalysts, kinetics and reaction conditions
- In run at left most catalysts afforded 1.3 - 1.5 equiv. H_2 / AB
  - ✓ simultaneous operation of both reaction pathways



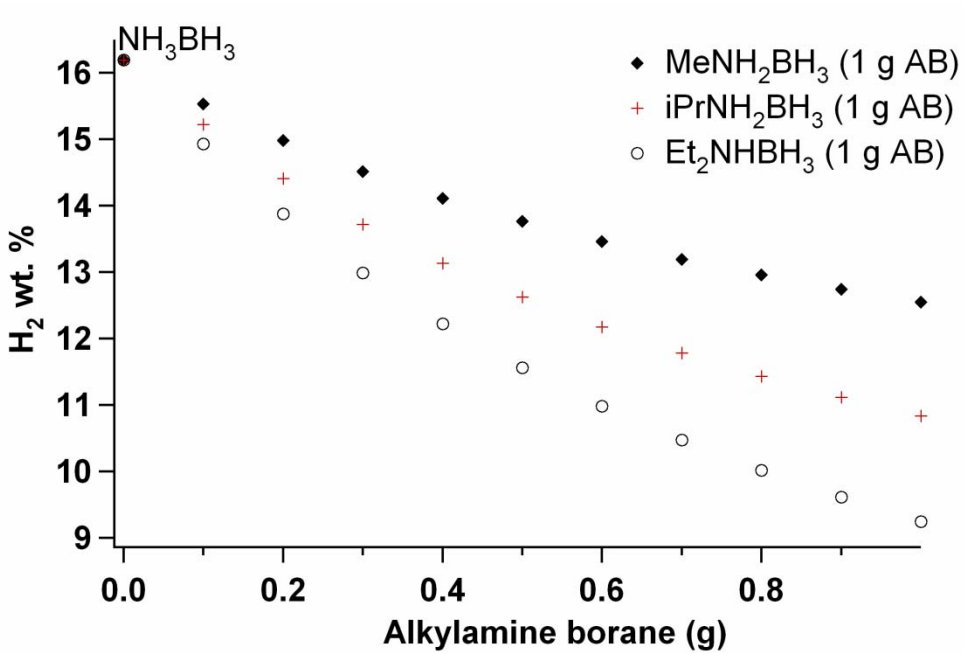
Soluble B-N linked borazines

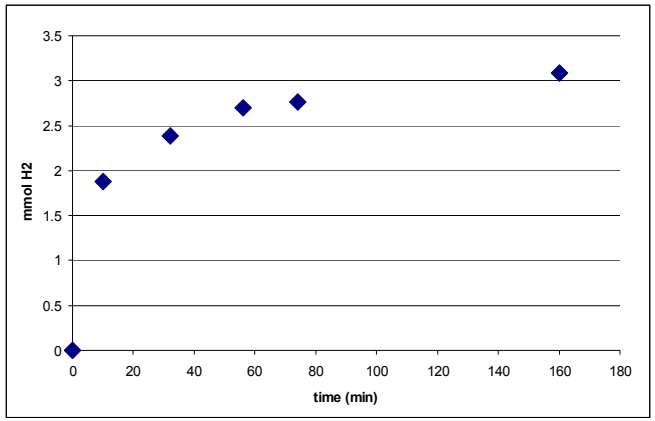
Working to identify active catalysts for borazine cross-linking to ensure > 2.5 equiv. H_2 from AB

Liquid Amine-Borane Fuels

- Liquid mixed amine-borane fuels mitigate capacity loss due to non-hydrogen releasing solvents

$$RNH_2BH_3 \Longrightarrow 1/3\ [RNBH]_3 + 2\ H_2$$





✓ Preliminary experiments with 5 mol% Ni carbene cat. in 1:1 AB:MeAB at 80°C gave 5.7 wt% hydrogen vs. 10.5 wt% theoretical

Northern Arizona, UW, PNNL posters

Need to optimize catalysts in amine-borane solvents

Materials Comparisons and Progress

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Metrics	Catalysis						
	UW Ir, MeAB/AB w/solvent, 23 °C	LANL Ni, MeAB/AB (neat) 80 °C	1: 1 MeAB/AB Theoretical, 2 equivalents H_2	LANL Ni cat 2% AB, in solvent 80 °C	Extrapolated Ni AB, saturated sol'n	LANL Ru cat, 2% AB in solvent 80 °C	LANL Bronsted Acid; 20 wt % AB, 60 °C 18 hr
Grav. density (Mat. wt%)	0.4 4.9 - no solvent (ns)	5.7	11	.015 10.8 - ns	1.8	0.019 13.5 - ns	1.7
Vol. density (Kg-H_2/L Mat.)	0.005	0.06	0.12	0.00015 .08 - ns	.03	.00019 .1 - ns	0.016
H_2 Flow Rate (g/s) per kg Material	0.068 0.82 - ns	0.02	-	0.00002 .016 - ns	.004	0.0001 .01 - ns	18 hrs -- too slow
Kg of Mat. for 0.8 mol/sec	23 2 - ns	100	-	70,000 98 - ns	400	16,000 160 - ns	terminated

DOE Total System Targets for Hydrogen Storage Systems

Gravimetric Density (wt%)
4.5 ***(2007)***, 6.0 ***(2010)***, 9.0 ***(2015)***

Volumetric Density (Kg-H_2/L)
0.036 ***(2007)***, 0.045 ***(2010)***, 0.081 ***(2015)***

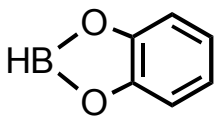
Accomplishments: Regeneration of Amine-Boranes

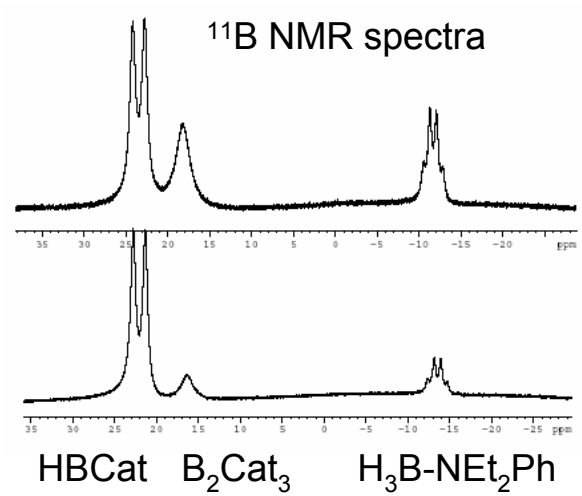
LANL – 2006

- ✓ **Initiated reduction** $BX_3 + MH \rightarrow BH_3{\cdot}L$

X = Cl, OAr
MH = $HSiEt_3$, $HSnBu_3$, regenerable tin formate

- ✓ **Demonstrated redistribution and ammoniation**

HBcat = 



- Diethylaniline drives redistribution of HBCat
- Ammonia reacts quantitatively with $H_3B\text{-}NEt_2Ph$ ($t_{½}$ < 30 min)

Now, tackle the more difficult aspects of digestion and optimization

LANL Regen FY07 Accomplishments

- Evaluated HX compounds for digestion of BNH_x spent fuel to BX_3
- Evaluated MH compounds for reduction of BX_3 to BH_3
- Combined above experimental findings with theory to demonstrate three steps of new sulfur-based regeneration scheme
- Conducted preliminary energy efficiency analysis of new regeneration scheme
- Identified routes to capture B-H from spent fuel prior to digestion

LANL Regeneration Schemes

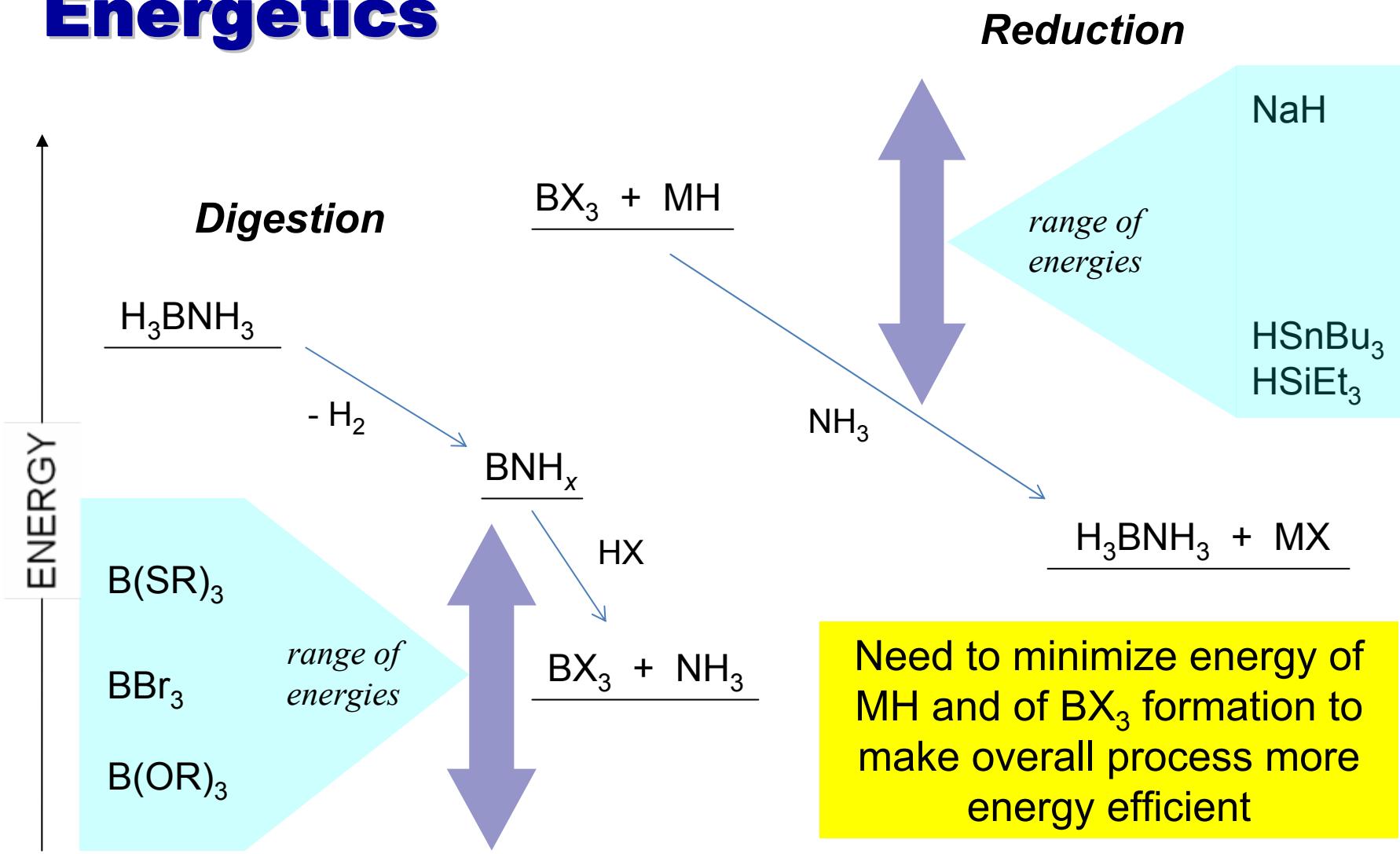
- Energy efficiency depends on X and MH

1) Digestion: $BNH_x + 3\,HX \longrightarrow BX_3 + NH_3 + H_2$
2) Reduction: $BX_3 + 3\,MH + NH_3 \longrightarrow H_3BNH_3 + 3\,MX$
3) MH Recycle: $MX + H_2 \longrightarrow MH + HX$

- May need to capture residual B-H from spent fuel

1) B-H Capture: $BNH_x + L \longrightarrow BNL_y + H_3BL$
2) Digestion: $BNL_y + 3\,HX \longrightarrow BX_3 + NH_3 + L$
3) Reduction: $BX_3 + MH + NH_3 \longrightarrow H_3BNH_3 + MX$
4) MH Recycle: $MX + H_2 \longrightarrow MH + HX$

Matching Digestion/Reduction Energetics



Need to minimize energy of MH and of BX_3 formation to make overall process more energy efficient

Experiment guided by theory (Alabama)

Digestion/Reduction Results

Spent Fuel + Digesting Agent

↓

$BX_n + HBX_m + NH_3$

↓ + MH

H_3NBH_3

Digesting Agent	Reaction Product
Ar(OH)	**$HB(OAr)_2$, $B(OAr)_3$**
Ar(OH-OH)	**$\{B[(O\text{-}O)Ar]_2\}^-$**
$Ar(NH_2\text{-}NH_2)$	**HB[(NH-NH)Ar]**
Ar(SH)	**$[B(SAr)_4]^-$**
Ar(SH-SH)	**HB[(S-S)Ar], $B_2[(S\text{-}S)Ar]_3$**

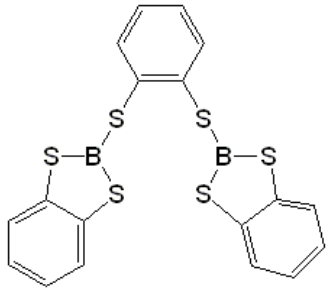
Survey of likely digestion agents revealed that sulfur compounds digest and B-S bonds are reduced with energy efficiency

Compound	NaH/LAH	$HSiEt_3$	$HSnBu_3$
BBr_3	**Y**	**Y**	**Y**
BCl_3	**Y**	**Y**	**Y**
$BHCl_2{\cdot}SMe_2$	**Y**	**Y**	**Y**
$BH_2Cl{\cdot}SMe_2$	**Y**	**Y**	**Y**
ClBCat	**Y**	**--**	**Fast**
Bu_2BOTf	**Y**	**Y**	**Y**
$B_3N_3Cl_3H_9$	**Y**	**N**	**Y?**
$BF_3{\cdot}OEt_2$	**Y**	**Slow**	**Slow**
$B(SPh)_3$	**Y**	**Slow**	**Y**
$B_2[(S\text{-}S\}Ar]_3$	**--**	**--**	**Y?**
HB[(NH-NH)Ar]	**Y?**	**N**	**N**
$B(OC_5F_5)_3$	**Y**	**N**	**N**
$(C_6F_4)OBCat$	**--**	**N**	**N**
HBCat	**--**	**Slow**	**slow**
B_2Cat_3	**--**	**Slow**	**Slow**
$B(OMe)_3$	**Y**	**N**	**N**

Formation of B-S Bonds for Digestion/Reduction

Digestion with thiols

kcal/mol

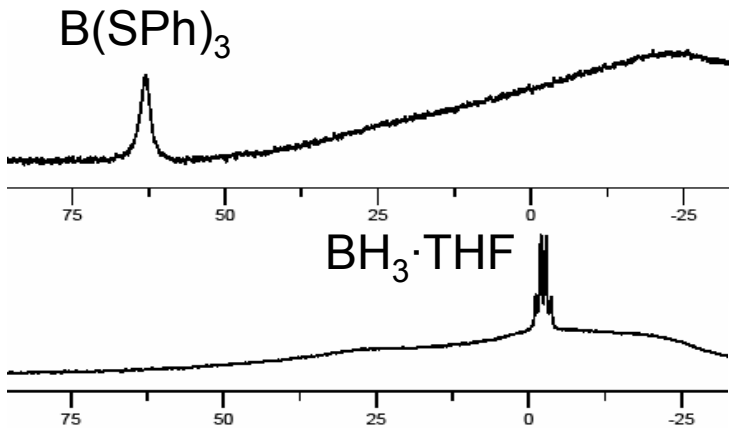
	ΔH(298K)	ΔG(298K)
$2\ B_3N_3H_6 + 9\ [1,2\text{-}C_6H_4(SH)_2] \rightarrow 3$  $+ 6\ NH_3 + 6\ H_2$	-5.9	-18.0

B3LYP/DGDZVP2

- Successful digestion using *o*-benzene-dithiol predicted using theory (**Alabama**), and demonstrated experimentally
  - ✓ Reaction of borazine results in a mixture of HB(SCat), $B_2(SCat)_3$, and polyborazylene;
- Rapid reduction of B-S bonds in $B(SPh)_3$ has been achieved using tin hydrides

Reaction optimization will include ammonia recovery

^{11}B NMR spectra



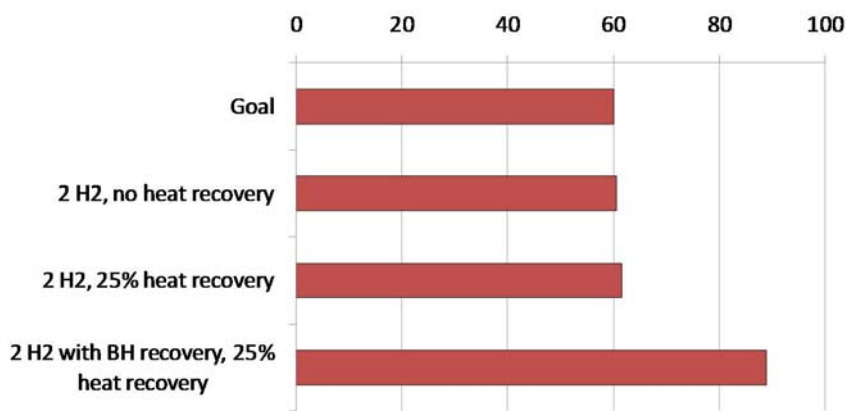
Energy Efficiency of Sulfur-Based Regeneration

Alabama

	REACTION ENTHALPY (condensed phase)
DIGESTION: 1/3 $B_3N_3H_6$ + 3/2 Ar(SH-SH) → 1/2 $B_2[(S\text{-}S)Ar]_3$ + NH_3 + H_2	10 kcal/mol
REDUCTION: 1/2 $B_2[(S\text{-}S)Ar]_3$ + 3 "HSn" + NH_3 → AB + 3/2 [Ar(S-S)]("Sn")$_2$	-14
MH RECYCLE: 3/2 [Ar(S-S)]("Sn")$_2$ + 3 H_2 → 3/2 Ar(SH-SH) + 3 "HSn"	8
DIRECT: 1/3 $B_3N_3H_6$ + 2 H_2 → H_3BNH_3	4

- When the energy of this reaction scheme is compared to the energy of the net direct reaction, we get the **system efficiency**:

$$\frac{(\text{Equiv. H}_2\text{ stored})(57.8)}{(\text{Equiv. H}_2\text{ used})(57.8)+\sum(\Delta H_{endo})-(\%\text{ heat recovery})\sum(-\Delta H_{exo})}=efficiency$$



Increasing Regen Efficiency: Reducing Agent Recycle and B-H Capture from Spent Fuel

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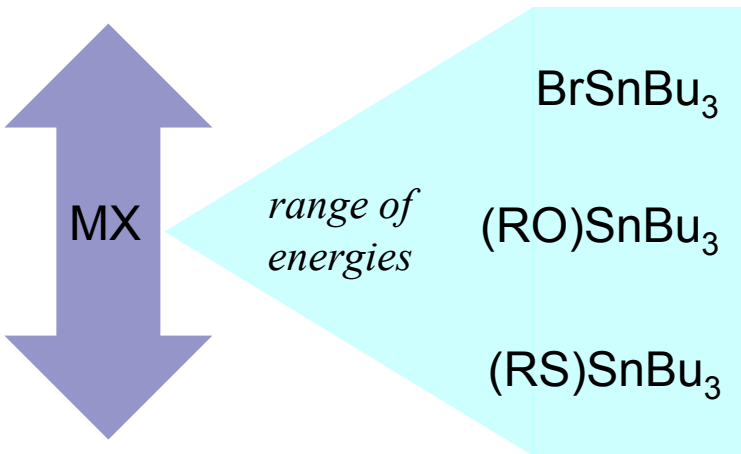
Recycle of MH from MX

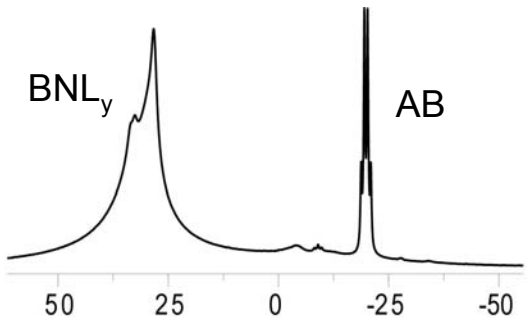
$$BX_3 + MH \longrightarrow BH_3 + MX$$

- **M-X bond strength key to energy efficient recycle**



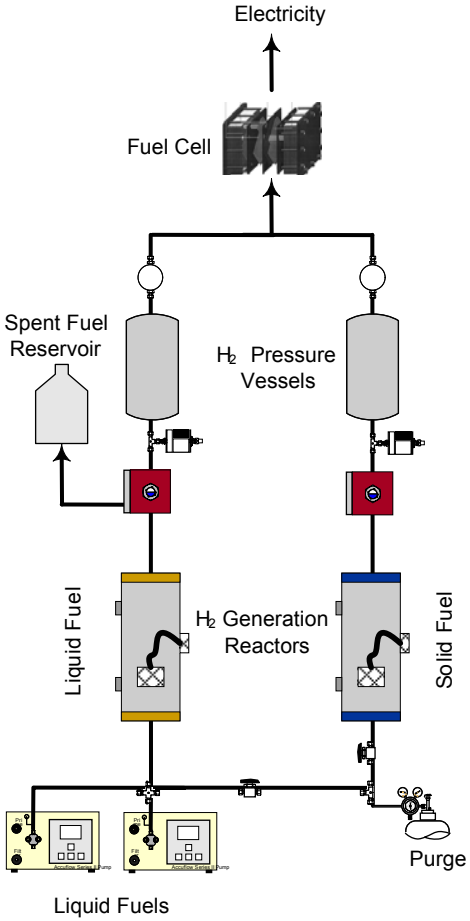
Extraction of BH from spent fuel

- **Liquid ammonia reacts with polyborazylene within hours at 20°C**
- **Currently optimizing yield, reaction conditions**

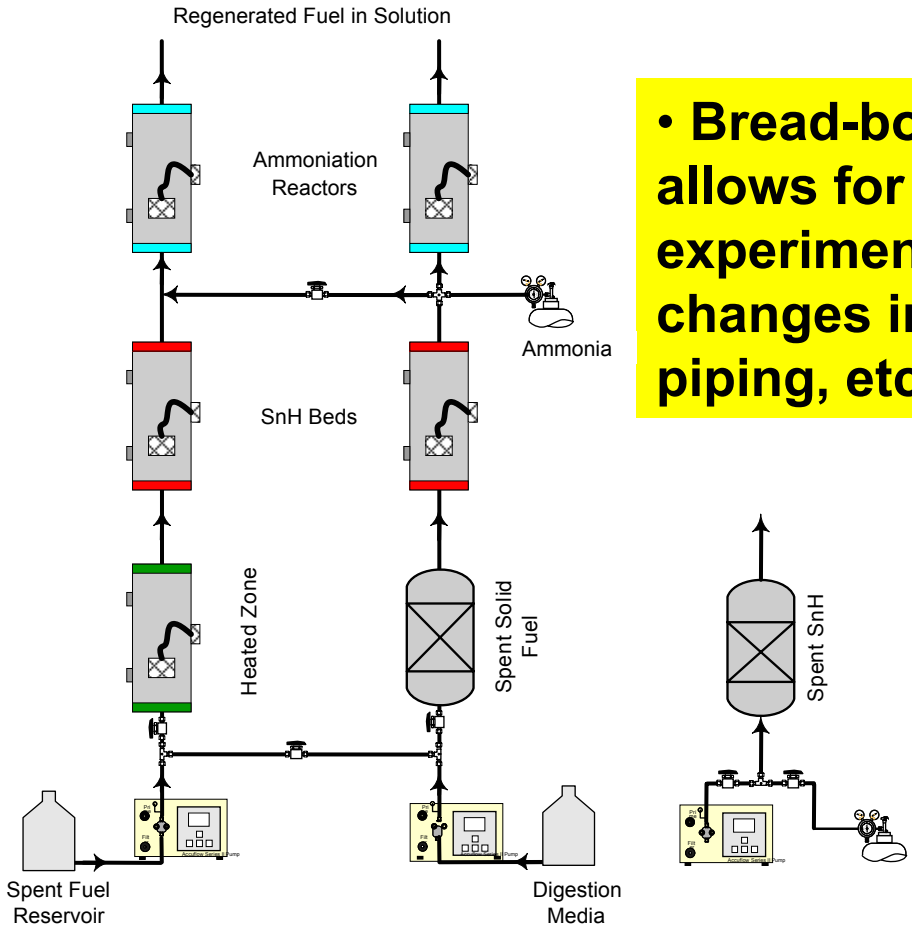


^{11}B NMR spectrum

Engineering Support for AB Dehydrogenation / Regeneration



Hydrogen Release



Spent Fuel Regeneration

- **Bread-boarding allows for rapid experimental design changes in reactors, piping, etc.**

Tier 3 Research on Advanced Concepts

- Work on imidazole-based organics and nanoparticles was terminated due to insufficient storage capacity
- Work on coupled reactions was postponed to implement rapid throughput hydrogen quantification and focus more resources on IPHE project
- For newly started IPHE project LANL is preparing and characterizing a new family of metal amine-borane compounds as potentially reversible hydrogen storage media

Accomplishments: New M-B-N-H Compounds

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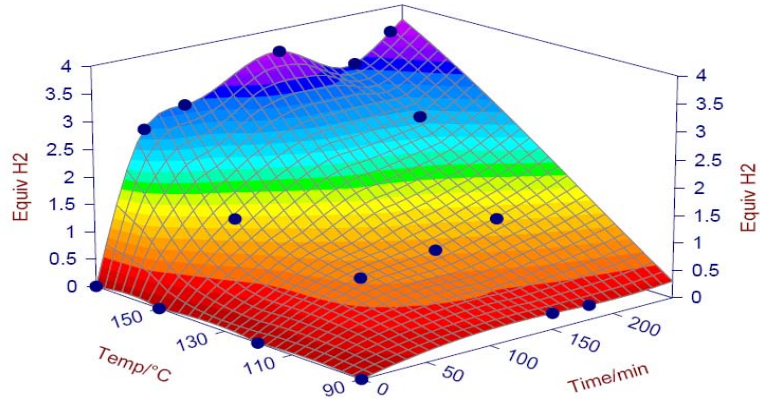
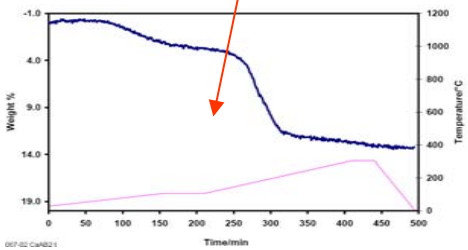
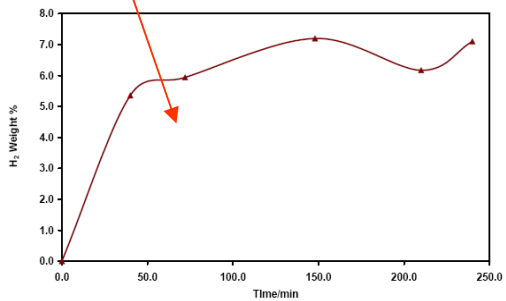
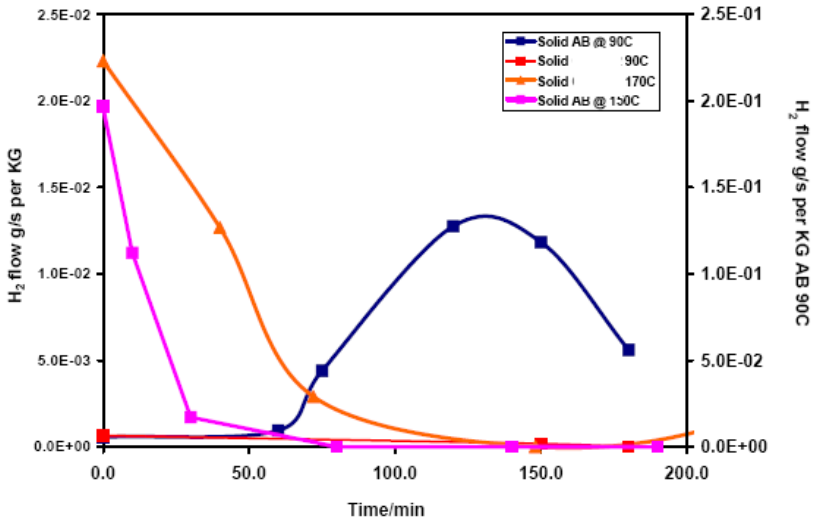
Wt. % H_2 for new compounds

	tot H	opt H	obs H
A	10.0	8.0	7.4
B	12.8	10.3	
C	13.6	10.9	
D	10.9	8.7	
E	11.9	9.5	
F	11.9	8.7	









Compound A

- ✓ 7.4 wt. % H_2 quantified by GC
- ✓ Excellent thermal stability
- ✓ Potential for reversibility

Future Work

DOE Hydrogen Program

- Hydrogen Release from Amine-Boranes
  - Use mechanistic results and theory to guide catalyst design for optimal rates and extent of hydrogen release from liquid amine-borane fuels
  - Use GC-based rapid throughput hydrogen quantification system to identify best catalysts and reaction conditions
- Amine-Borane Regeneration
  - Identify best match of HX for spent fuel digestion with MH for reduction of BX_3
  - Optimize recycle of MX to MH and B-H capture
  - Expand engineering analysis of most promising regeneration schemes
- Evaluate additional coupled reaction systems with ≥ 2 H/element
- Prepare and characterize variety of IPHE M-B-N-H compounds for high capacity, potentially reversible hydrogen storage

Project Summary

DOE Hydrogen Program

Relevance - High storage capacity chemical hydrogen storage materials have potential to meet DOE targets

Approach - Combine theory, experiment and engineering assessment to:

- Support Tier 1 effort on electrochemical B-O to B-H
- Refine catalyst design to increase rate extent dehydrogenation of liquid amine-borane fuels
- Optimize energy efficiency of AB regeneration process
- Identify new M-B-N-H compounds with potential for reversible storage

Accomplishments - Made major progress on effective hydrogen release from amine-boranes and regeneration of BNH_x spent fuels including:

- ✓ Increased understanding and resources to identify fast, inexpensive AB dehydrogenation catalyst with > 2 H_2/AB
- ✓ Identified new potentially energy efficient sulfur-based AB regeneration scheme
- ✓ Prepared and characterized new stable M-B-N-H compounds that release hydrogen with potential for reversibility

Collaboration - Integrated catalysis efforts and refined IPHE roles

Future Work - Optimize catalyst performance for hydrogen release from liquid amine-borane fuels and energy efficiency of AB regeneration process

- Identify new coupled reactions with potential release of ≥ 2H per element
- Increase engineering assessment for on-board hydrogen release and off-board regeneration
- Work with IPHE partners to identify and characterize new M-B-N-H hydrogen storage compounds

Project Summary Table

Metrics	LANL 2007				
	LANL Bronsted Acid; 20 wt % AB solution, 60 °C 18 hr	LANL Ni cat 2% AB, in solvent 80 °C	LANL Ru cat, 2% AB in solvent 80 °C	LANL Ni, MeAB/AB (neat) 80 °C	IPHE Theory
Grav. density (Mat. wt%)	1.7	.015 10.8 - no solvent (ns)	0.019 13.5 - ns	5.7	Measured 7.2 Max 10 - 11.9 Opt. 8-10.9
Vol. density (Kg-H_2/L Mat.)	0.016	0.00015 .08 - ns	.00019 .1 - ns	0.06	Measured 0.072
H_2 Flow Rate (g/s) per kg Material	18 hrs -- too slow	0.00002 .016 - ns	0.0001 .01 - ns	0.02	Measured 0.02
Kg of Mat. for 0.8 mol/sec	completed	70,000 98 - ns	16,000 160 - ns	100	Measured 80

DOE Total System Targets for Hydrogen Storage Systems

Gravimetric Density (wt%)
4.5 ***(2007)***, 6.0 ***(2010)***, 9.0 ***(2015)***

Volumetric Density (Kg-H_2/L)
0.036 ***(2007)***, 0.045 ***(2010)***, 0.081 ***(2015)***