Chemical Hydrogen Storage R&D at Los Alamos National Laboratory

Project ID# ST_17_Burrell

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2009 DOE Annual Merit Review
Arlington, VA

This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Start: FY 05
- End: FY 09
- 80% Complete

Barriers

- Weight and Volume
- Flow Rate
- Energy Efficiency
- Cost
- Regeneration Process
- System Life-Cycle Assessments

Budget

- Estimated Project Funding
  - $9.61 M
- FY 08
  - $2,455 K
- FY 09
  - $2,750 K

Partners

- Chemical Hydrogen Storage Center of Excellence
- IPHE (Singapore, UK, New Zealand)
- Hiroshima University, Japan

Relevance - Objectives

- Provide preliminary cost analysis of LANL regen process
- Develop and demonstrate heterogeneous catalysts and continuous flow reactor operation
- Develop liquid ammonia-borane (AB) fuels and increase rate and extent of hydrogen release
- Identify and demonstrate new materials and strategies for near-thermoneutral hydrogen release (ΔG° = ideally no less negative than ca. –0.8 kcal/mol)
- Develop materials and processes to minimize gas-phase impurities, and demonstrate adequate purity of hydrogen stream

Relevance - Milestones

	Ranked list of heterogeneous catalysts vs. capacity and rate (3Q09)
	Ranked list of liquid fuel formulations with hydrogen content and liquid range (3Q09)
	Demonstrate catalyst-fuel combinations with potential to achieve DOE 2010 performance targets for capacity and rate, and determine volatile byproduct speciation and quantity (4Q09).
	Deliver optimal, demonstrated AB regeneration scheme using the thiacatechol approach with highest thermodynamic and chemical efficiency (3Q09)
	Go/ No Go Decision on formic acid process (1Q09)
	Demonstrate integrated regeneration cycle (2Q09)
	Initiate assessment of regenerating spent liquid fuels (1Q09)
	Demonstrate >2 integrated regeneration cycles (4Q09)
	Tabulations of compound formulae vs. hydrogen content and rates of release (4Q09)
	Summary of preliminary hydrogenation experimental results (4Q09)
	Complete assessment of hydrogen capacity, release rate, and energetics of release and potential rehydrogenation of metal amidoboranes having > 7 wt. % hydrogen (4Q09)
	Provide recommendation to DOE for future research in metal amidoboranes (4Q09)
	Decision on formic acid as a hydrogen transfer reagent (1Q09)
	Decision on direct rehydrogenation as an approach to M-H recycle (1Q09)
	Operational cyclic regeneration reactor system (2Q09)
	Integrated communication plan with Hydrogen Storage Engineering Center of Excellence (3Q09) assuming 1Q09 start for ECoE.

Approach: Los Alamos Technical Contributions

- Engineering Guided Research
  - Gas cell analysis of impurities in hydrogen release
  - Fabricate and operate continuous flow reactor for heterogeneous catalyst testing
  - Cost Analysis of LANL regen scheme with Rohm & Hass
  - Interfacing with Engineering CoE
- New hydrogen storage materials for portfolio
  - Design and synthesis of near-thermoneutral release materials
  - Design and synthesis of liquid fuel compositions
- Hydrogen Release
  - Identify reaction pathways to maximal storage and release rates
  - Design, synthesize, and demonstrate heterogeneous catalysts with high rates at T < 100 °C
  - New Base Metal catalysts
- Regeneration
  - Demonstrate all individual steps to ammonia borane from spent fuel and begin process integration
  - Refined stoichiometry, concentrations, separations, substitutions, reaction times, materials properties etc
  - Cost Analysis of LANL regen scheme with Rohm & Haas completed
  - Use theory to guide toward most energy efficient matching of regeneration reactions
  - New reagent development
- Patents
  - Published – 8
  - Pending – 8
  - Disclosures – 6

Technical Accomplishments since last review

- Cost Analysis on LANL regen process completed in collaboration with Rohm & Haas
- New materials have been prepared that have lower exothermicity, higher rates and higher extents of release compared to ammonia borane which exceed 2010 targets
- Liquid fuel compositions have been expanded with both alkylamine and ionic liquid options
- Heterogeneous base metal catalysts for hydrogen release have been prepared and demonstrated to have high rates of release to > 9 wt % H_2
- A complete cycle “first pass” regen cycle has been proven with overall yield of spent fuel digestion through reduction steps exceeding 70%
- Flow reactor for catalyst screening and liquid fuel assumed using gas phase analysis assembled and underway
- Hydrogen stream purity analysis system has been assembled and is operating to identify and quantify impurities in H_2 stream

Approach – New Materials Development

Materials must meet CHSCoE 2008 down select criteria

2008-09 Discovery → **2009 Analysis** → **2009-10 Go-NoGo**

2008-09 Discovery

- Literature search
- Prescreen materials
  - H_2 Wt% must be in excess of 7%
  - Example $W(NH_2BH_3)_6$ = 8.3 wt%
- Materials synthesis

2009 Analysis

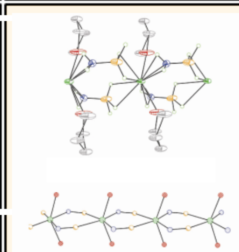
- Hydrogen release profile
- Characterization
- X-ray Structure
- Thermodynamics
- Impurities
- Feedback to discovery

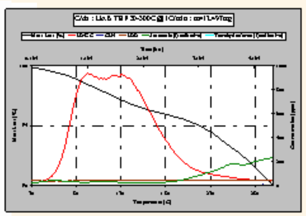
2009-10 Go-NoGo

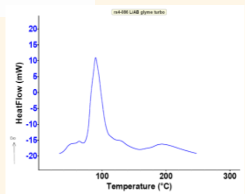
- Exothermic or endothermic?
- Improved release rates?
- Improved release volume?
- Fewer impurities?

$MgCl_2 + 2NaNH_2BH_3 \rightarrow Mg(NH_2BH_3)_2 + 2NaCl$
$MgCl_2 + NaNH_2BH_3 \rightarrow Mg(NH_2BH_3)Cl + NaCl$
$ZnCl_2 + 2NaNH_2BH_3 \rightarrow Zn(NH_2BH_3)_2 + 2NaCl$
$TiCl_4 + 4NaNH_2BH_3 \rightarrow Ti(NH_2BH_3)_4 + 4NaCl$
$LiNH_2 + NH_3BH_3 \rightarrow LiNH_2BH_3 + NH_3$

AB derivative	H_2 wt%
$LiNH_2BH_3$	13.70 (2008)
$Ti(NH_2BH_3)_4$	12.05
$Mg(NH_2BH_3)_2$	12.00
$Sc(NH_2BH_3)_3$	11.24
$Li_2[Zn(NH_2BH_3)]_4$	10.15
$Ca(NH_2BH_3)_2$	10.10 (2008)
$NaNH_2BH_3$	9.54 (2008)
$LiZn(NH_2BH_3)_3$	9.34
$Zn(NH_2BH_3)_2$	8.06
KNH_2BH_3	7.31 (2009)
$Al(NH_2BH_3)_3$	12.97 (2009)







Compound	Normalized 1st exother mJ/g (onset/°C)	Normalized 2nd exother mJ/g (onset/°C)	Normalized 3rd exother mJ/g (onset/°C)	On Board
LiAB	-621.9 (77) *			No
KAB	+70 (71)	-48.6 (75)		No
Mg (AB) 2	-6.7 (78)	-188 (108)		No
Ca (AB) 2	-102 (101)	-56 (120)		No
Al (AB) 3	-38.5 (66)	-5.1 (106)	-5.9 (154)	No

Onboard options using new materials:

The search for improved thermodynamics and kinetics

AB derivative	H_2 wt%
$LiNH_2BH_3$	13.70 (2008)
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Pacific Northwest NATIONAL LABORATORY ST18

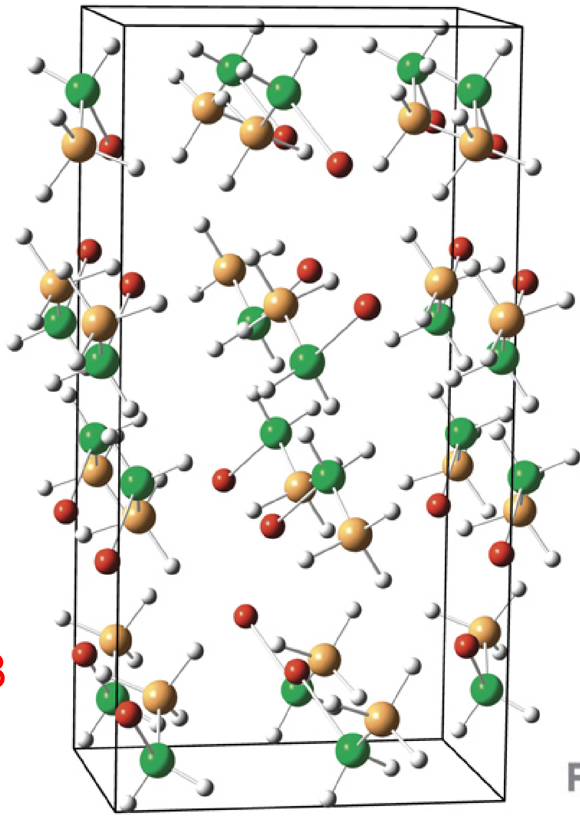
Mizzou University of Missouri STP20

ISIS

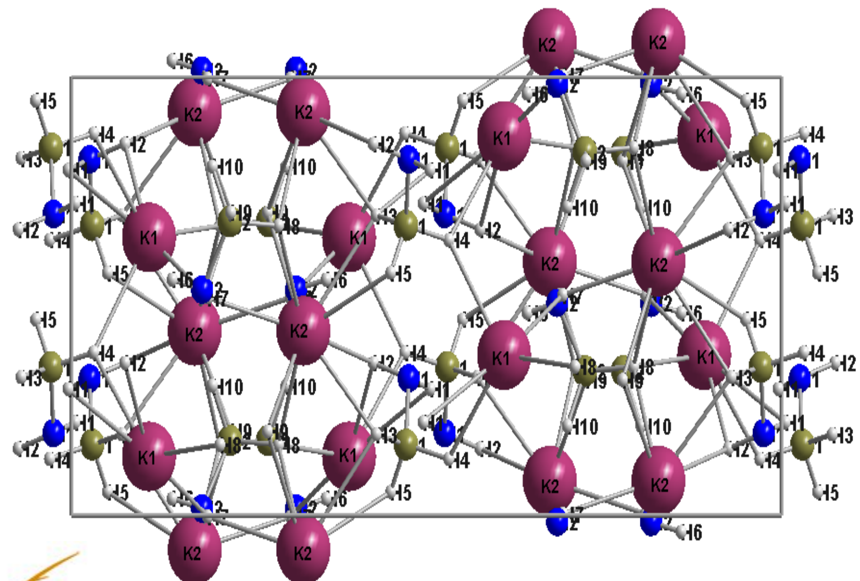
INDUSTRIAL RESEARCH LIMITED

HIROSHIMA UNIVERSITY

Structures of alkali metal salts changes at potassium



See ST18

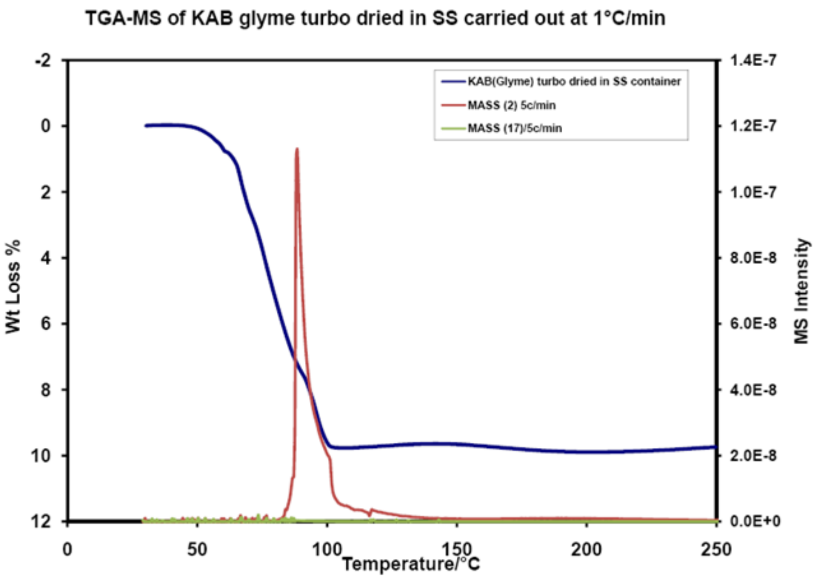


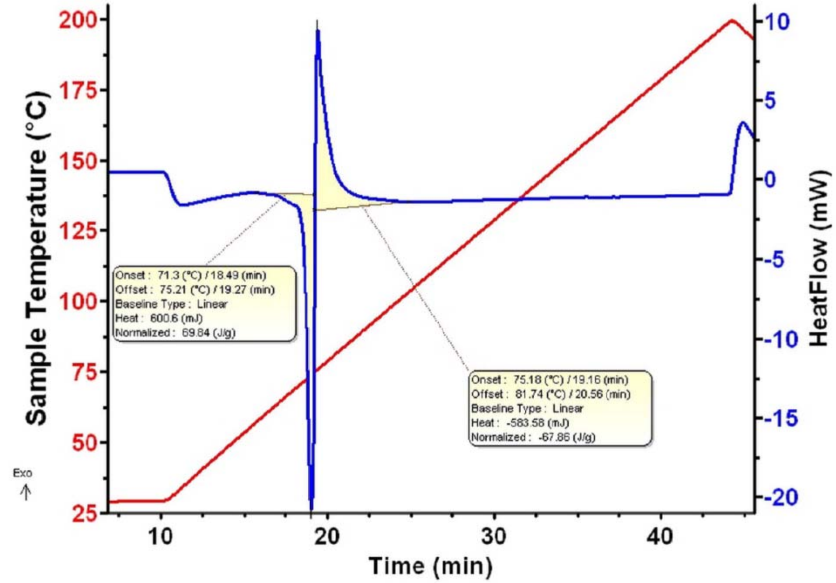
High-capacity hydrogen storage in lithium and sodium amidoboranes
Zhitao Xiong[1], Chaw Keong Yong[1], Guotao Wu[1], Ping Chen[1,2], Wendy Shaw[3], Abhi Karkamkar[3], Thomas Autrey[3], Martin Owen Jones[4], Simon R. Johnson[4], Peter P. Edwards[4] & William I. F. David[5]
Nature Materials **2008**

K has a much more complex structure

Li and Na isostructural

2009 Hydrogen release from solution prepared KAB

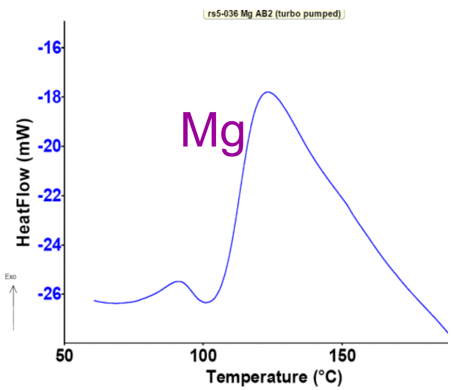


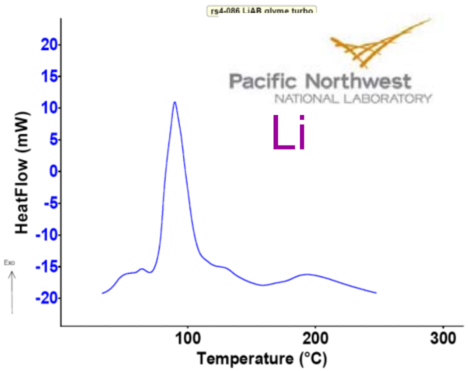


Less exothermic hydrogen release in one step with no impurities observed in the gas phase (yet)

2009 Thermal release profiles vary significantly

So far all have exothermic hydrogen release but there are differences!





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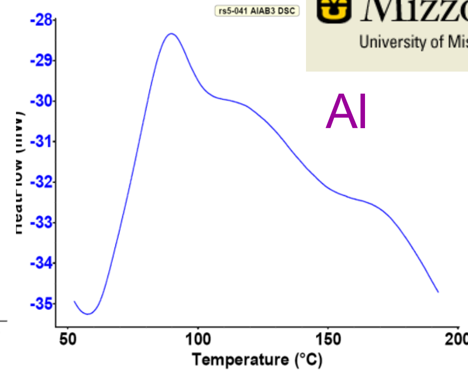
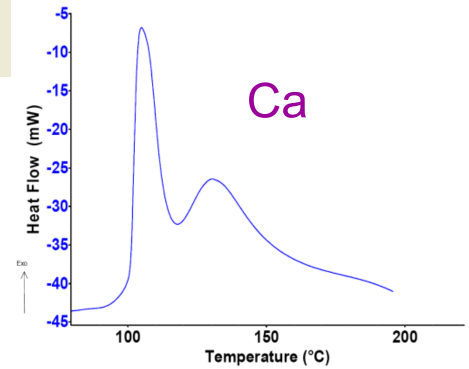
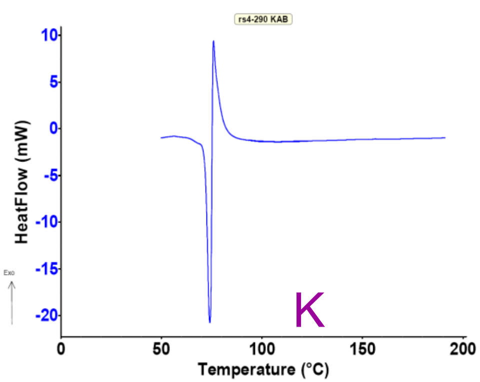


Mizzou University of Missouri





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These compounds cannot be on-board regenerated. Work with adducts and mixtures will continue

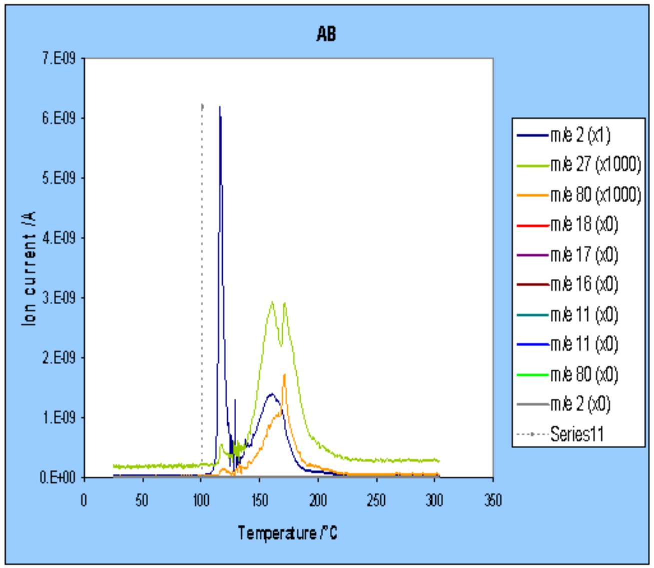
Approach – Hydrogen release

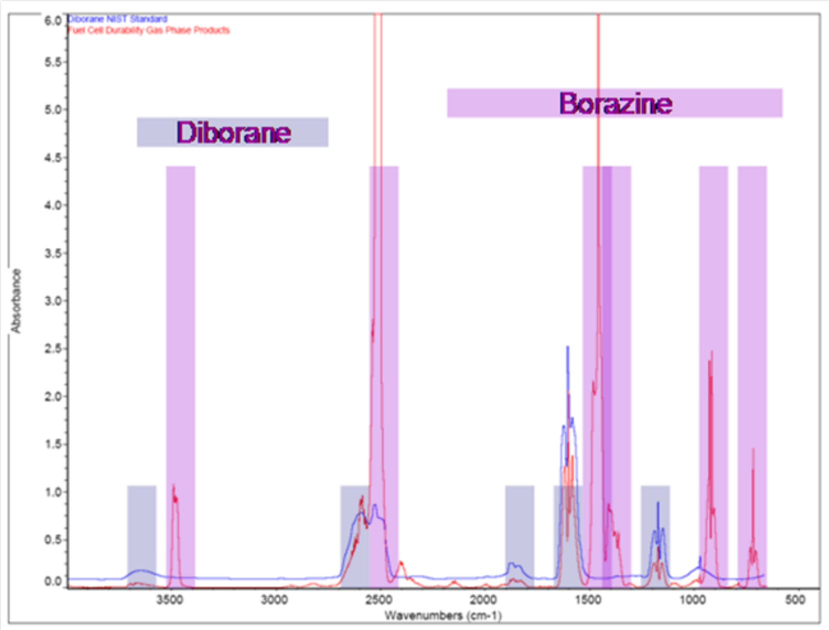
For continued release development materials must be able meet DOE targets CHSCoE criteria for materials are:

Criterion	Description	Metric
Gravimetric Capacity	Maximum calculated hydrogen weight fraction	> 7 wt. % H_2
Potential to Regenerate On-Board	Potential to rehydrogenate spent fuel directly	yes/no/?
Regenerable	Ability to chemically reprocess spent fuel off board	yes/no/?
Acceptable Phase Change	Problematic liquid to solid phase change, or volatile byproducts	yes/no/?
Acceptable Release Rate	Maximum rate of hydrogen release, T< 125 °C	> .02g H_2/s/kg material
Material Stability	Stable in fuel tank< 50 °C	yes/no/?
Endothermic Release	Hydrogen release occurs endothermically	yes/no/?
Low Temperature	For endothermic reactions, temperature of release <200 °C (with potential for lower T, i.e., 80 °C, release)	Temperature

2008 Purity issues with hydrogen released from NH_3BH_3

Simple thermal release results in impurities in the hydrogen released





Diborane and borazine detected by IR as impurities from thermal release

$$n\,NH_3BH_3 \rightarrow (NH_2BH_2)_n + n\,H_2 \rightarrow (NHBH)_n + n\,H_2$$

80-110 °C

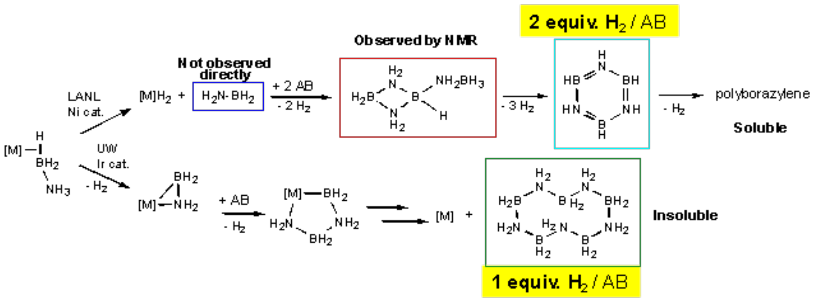
6.5 wt%

150 °C

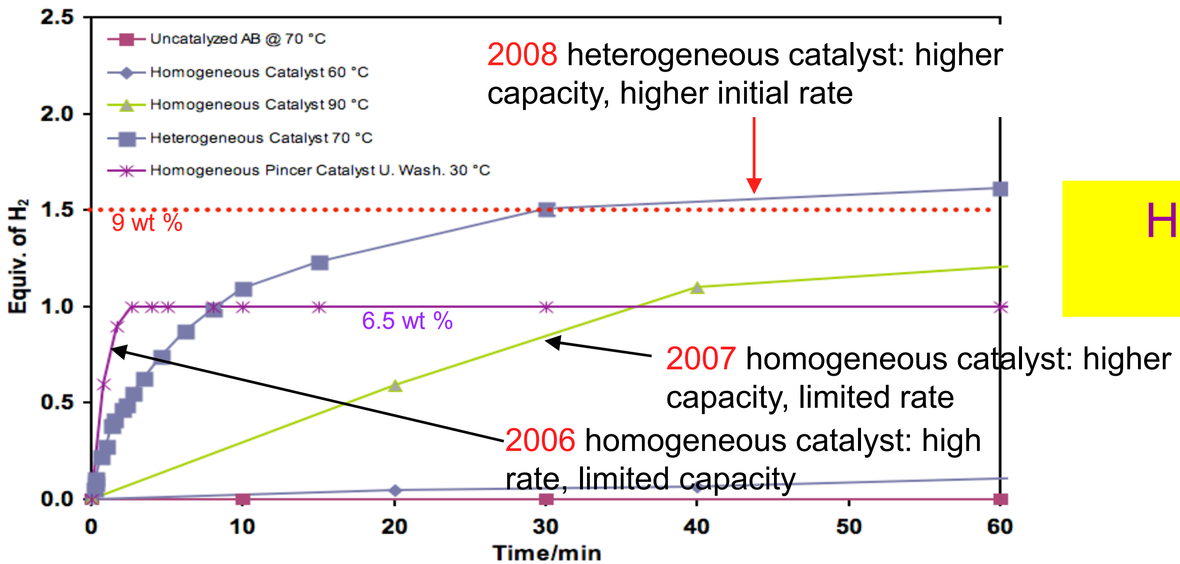
6.5 wt%

Total 13 wt% below 150 ˚C

Previous (2005-2008) work elucidated the mechanism of catalyzed H_2 release from Ammonia-Borane



Work from 2005-2008 shows catalysis can change the release mechanism and thereby change and eliminate the impurities

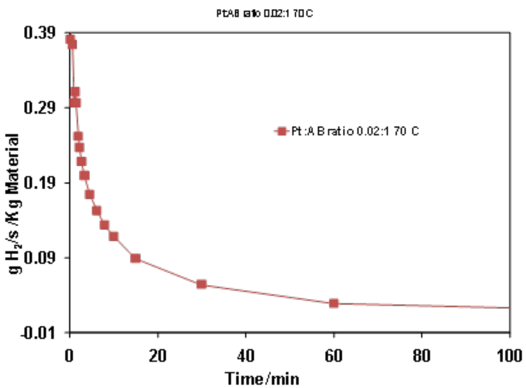


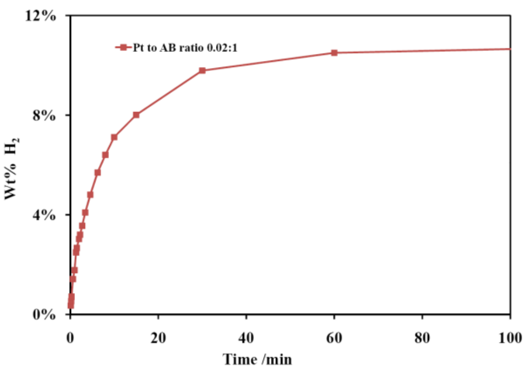
Hydrogen release rates have continued to be improved

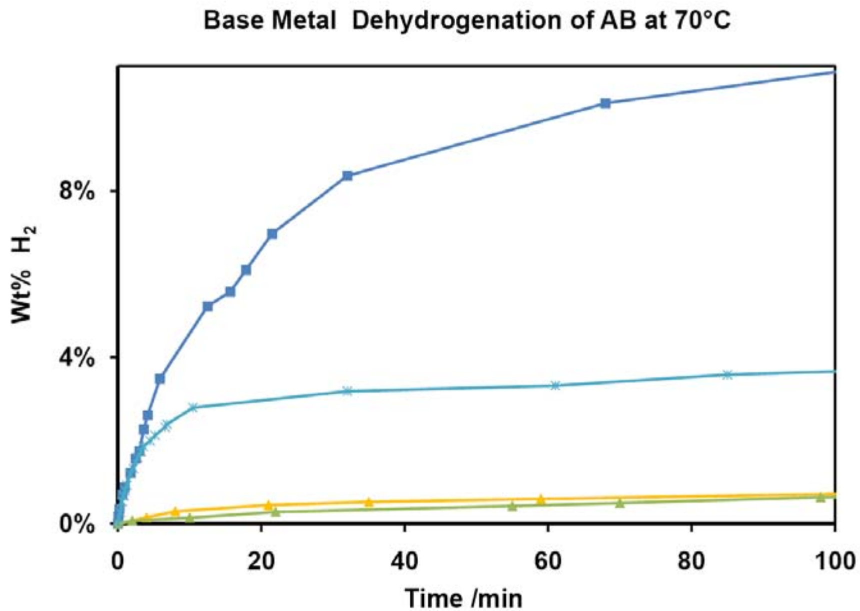
2009 Heterogeneous Catalysts

Release rates using catalysts have potential to exceed DOE targets

Platinum catalyst is fast 70 ˚C







titanium	vanadium	chromium	manganese	iron	cobalt	nickel	copper	zinc
22	23	24	25	26	27	28	29	30
Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
47.867	50.942	51.996	54.938	55.845	58.933	58.693	63.546	65.39

H_2 Release rates with base metals potential to exceed DOE materials target with base metal at lower temp. with the same capacities as the Pt catalyst

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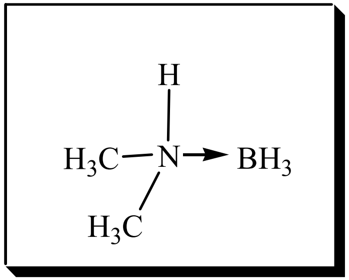
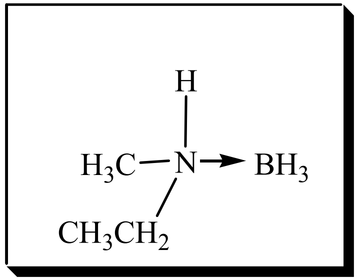
2009 Liquid Fuels (several options under investigation)

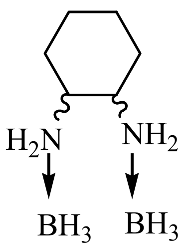


solid at RT, m.p. = 37°C



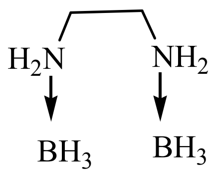
liquid at RT

liquid at RT



cis/trans cyclohexane-bisAB
pasty solid at RT

STP16



solid at RT

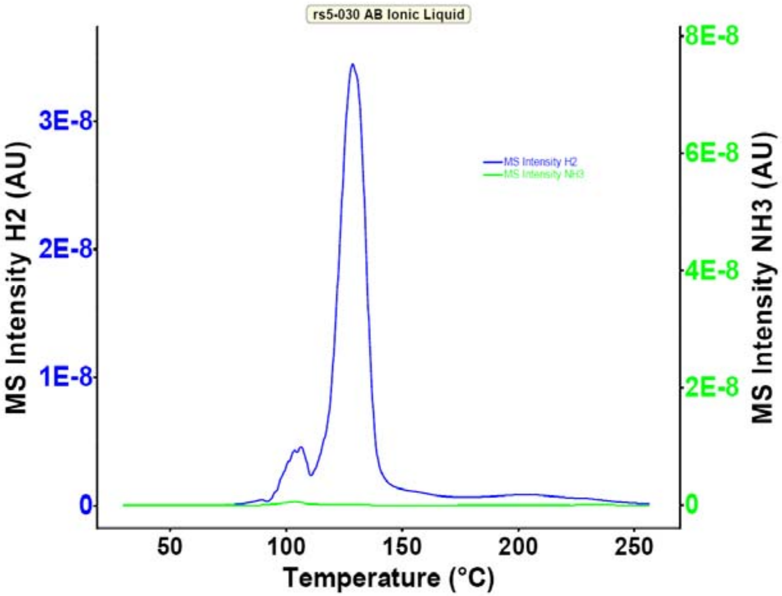
Alkylamine Boranes began in 2008

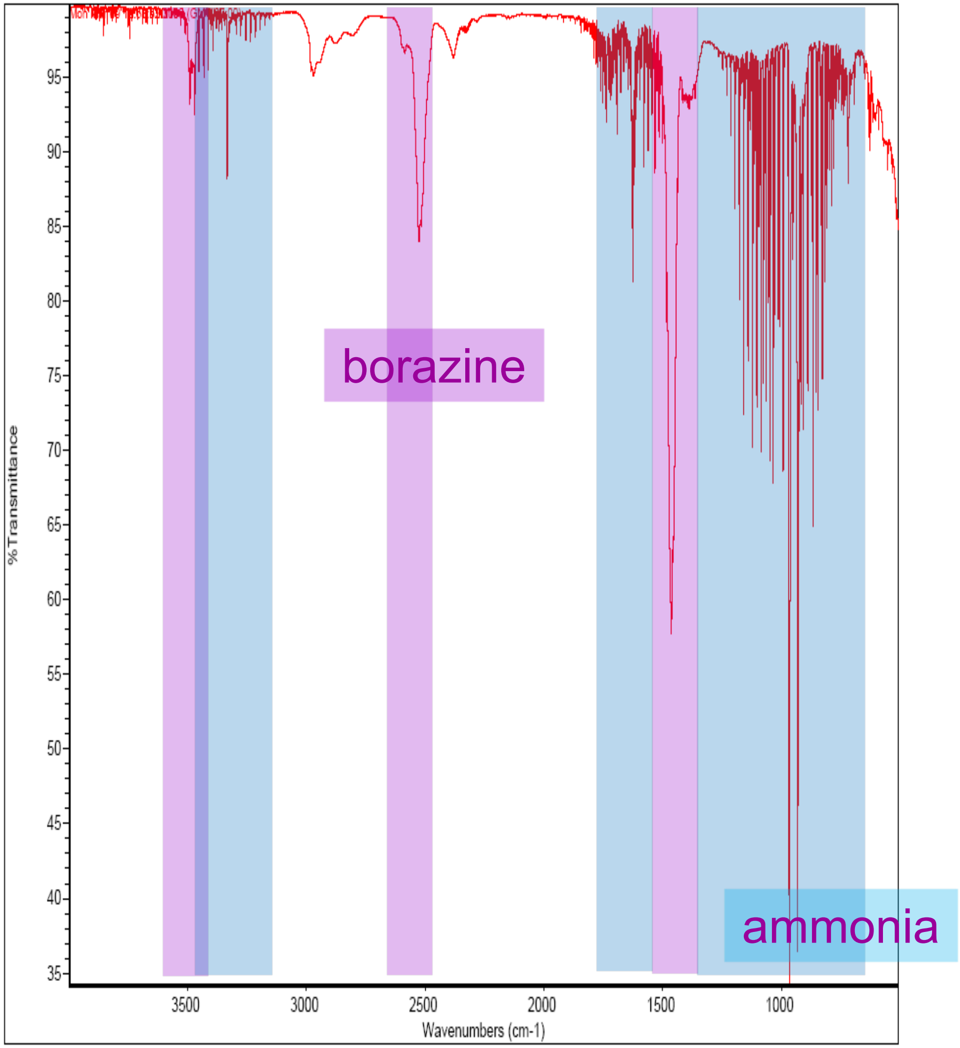
- New ionic liquid compositions based upon the work of Penn ST16
- Demonstrate excellent release rates
- Analysis of gas impurities underway at LANL

Ionic liquid systems new for 2009

Composite approach

2009 Impurities in Ionic Liquid based liquid fuels





Thermal release from liquids still gives impurities but not diborane

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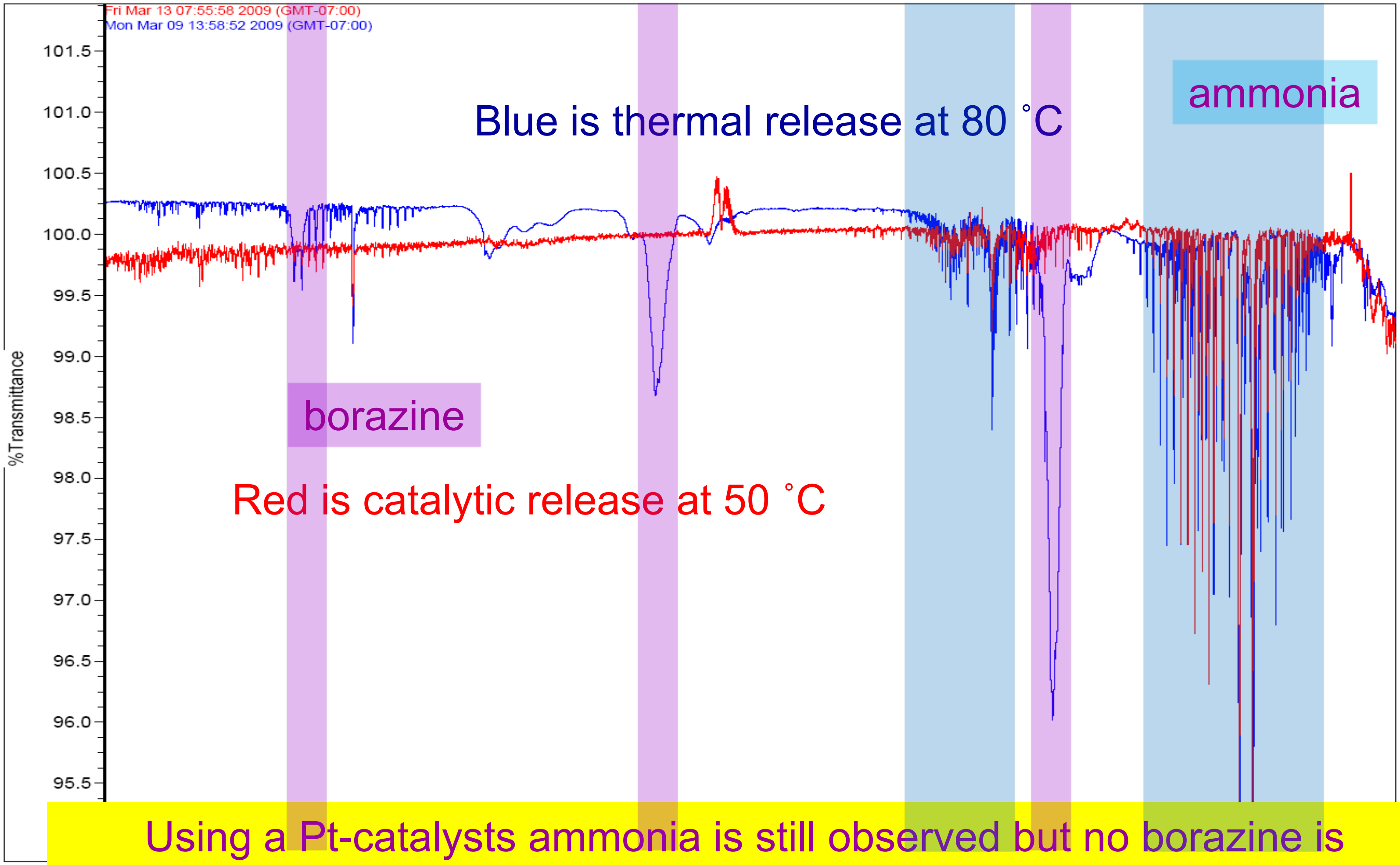
2009 Catalysis in the IL AB mix release at 50 ˚C



Using a Pt-catalysts ammonia is still observed but no borazine is detected and release temperatures lowered yet again

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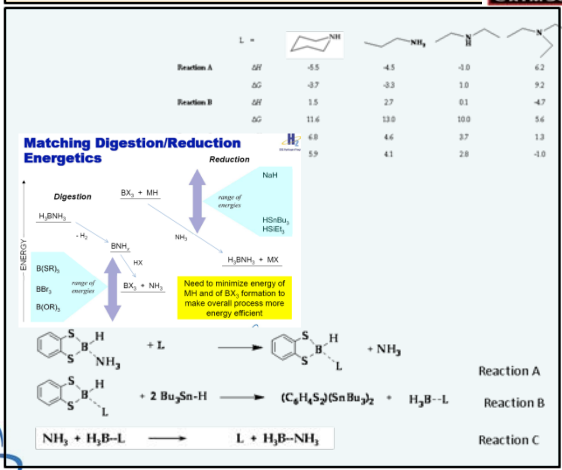
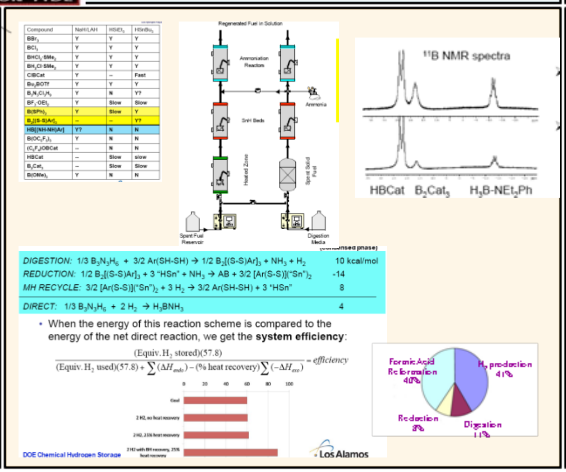
Approach - Off-Board Regeneration

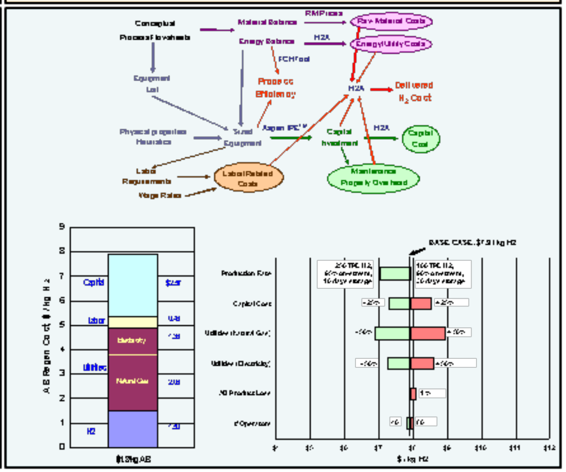
2007-08 Discovery	2008 Demonstration	2009 Cost Analysis
•Literature search •Theory •Scoping reactions	•Test reactions •Characterization •Scaling •Modeling •Thermodynamic assessment •Feedback to discovery	•Process conceptualization •Flow sheet development •Iterate w/experiments ➢separations ➢kinetics ➢yield •Aspen •H2A Tool

ST19

ST20







Off-Board Regeneration Required (timeline 2008-2009)

3 Ammonia Borane (H_3N-BH_3) $\rightarrow$ **Spent fuel** ($B_3N_3H_4$) + **7H_2↑**

2007 – Thiol based digestion of spent fuel first demonstrated

Mid 2007 – Tin hydrides observed to form ammonia borane (AB)

2008 – Digestion/reduction combined into one cycle

Mid 2008 – Feedback from TT, AMR increases emphasis on process analysis, cost; optimization of reactions, reducing unit operations

August 2008 – Center 'Engineering Summit' in Philadelphia with R/H

Fall/Winter 2008/2009 – Iterative process modifications with R/H input;
current scheme to R/H for baseline cost analysis

$\Delta H \approx$ -7 kcal/mol

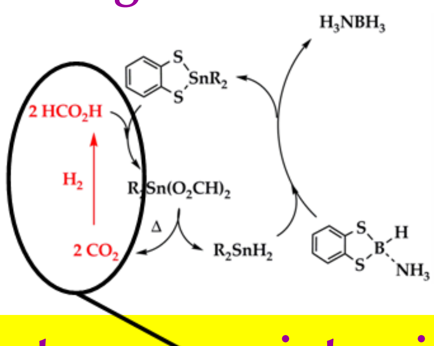
(Miranda and Ceder 2007)

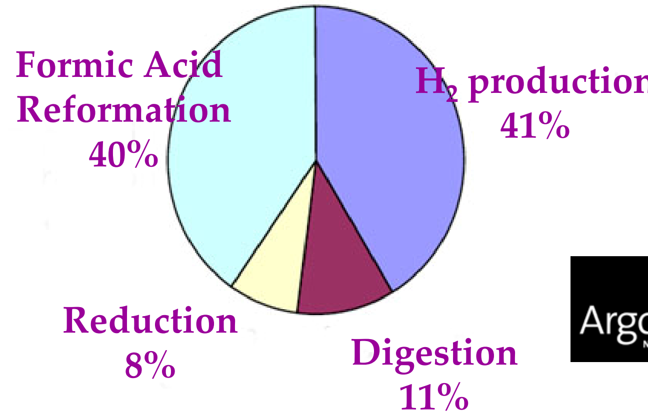
- Jan 2008 Regeneration Scheme
- ANL Assessment
- June 2008 Scheme
- Work to R/H Baseline Analysis
- R/H Improvement Areas
- Ultimate Goal

Center of Excellence Targets: 60% process efficiency for regeneration
$2-4 gallon of gas equivalent for H_2 stored

2008 ANL Assessment Identifies CO_2 Recompression as a Major Energy Concern

Must replace CO_2 as a hydrogen transfer reagent



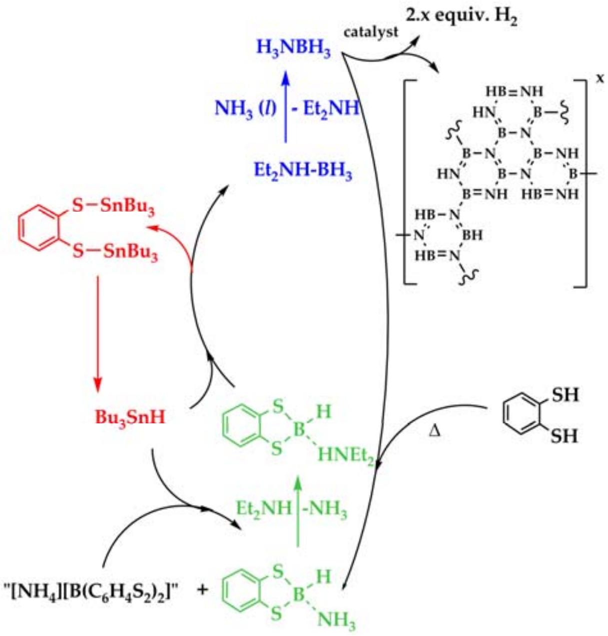


Recompression too energy intensive

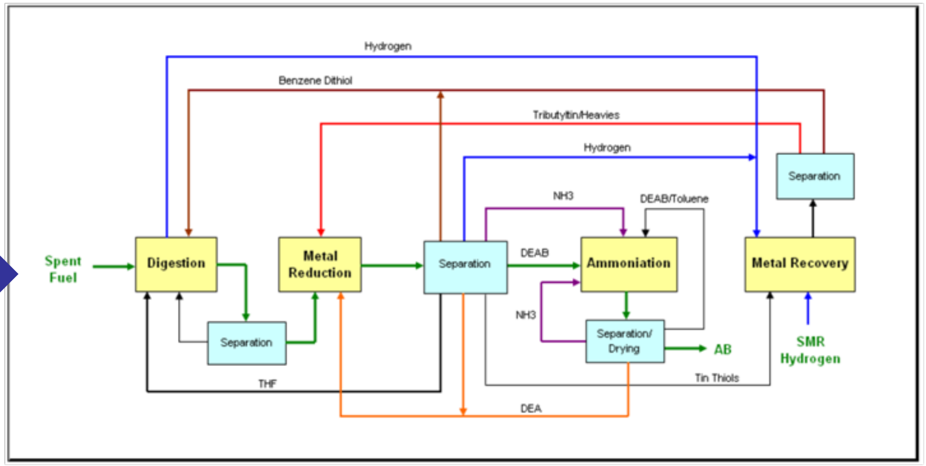
2009 Launched multiple efforts to address reductant recycle as a major energy concern

- Methane to formic acid to replace H_2 MSR (LANL, R&H)
- More efficient tin format recycle (UC-Davis STP18)
- Electrochemical recycle of metal hydrides (PSU STP19)
- Replacements for CO_2 (LANL)
- Transition metal hydrides (PNNL)
- Direct hydrogenation of tin-sulfur (LANL)

2009 Lessons Learned from Rohm & Haas Cost Analysis



translates to



2009-2010 Focus Area
Reduce Mass Flow

- Combine Steps
- Optimized digestion stoichiometries
- Optimize amine exchange/ammoniation
- Consider lower MW reducing agents

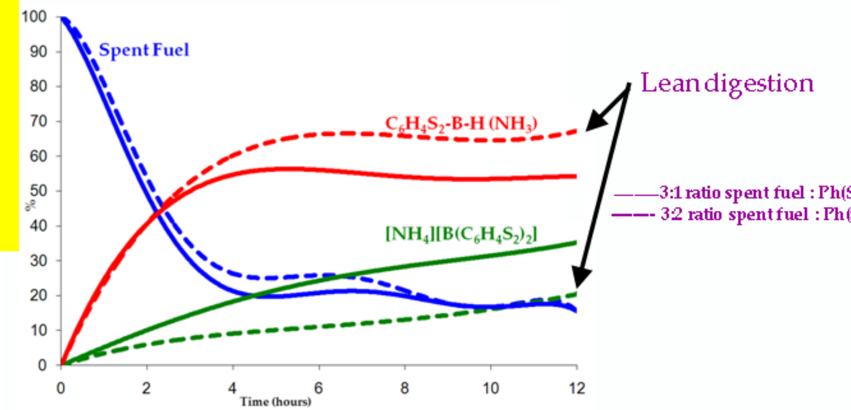
ST20

2009 Actions Taken based upon Rohm & Haas Cost Analysis

2009 Analyzed

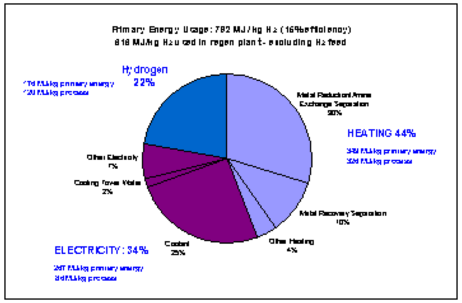
- Combining reactors
- Stoichiometry
- Concentrations
- Separations
- Reagent Substitutions
- Solvent effects
- Reaction Times
- Optimal Product
- Product Distributions

Example. Lean digestion with recycle increased overall efficiency



2009 Analysis by R&H indicates mass and separations are major energy costs

Nearly 90% of Utility Use Related to Separations



Rohm & Haas Report Detail

ST20

	Digestion	Metal Reduction / Amine Exchange	Ammoniation	Metal Recovery
H_2		431		1,145
NH_3		15,645	3,303	
$(Et)_2NH$		14,930	67,187	
THF	86,989	86,989		
Toluene			88,773	
BNH	5,272			
$C_6H_4(SH)_2$	22,505	2,250		222,795
Bu_3SnH		162,797		906,777
$(Et)_2NHBH_3$		79,896	8,877	
$HB(C_6H_4S_2)NH_3$	69,895	17,258		17,258
$(NH_4)B(C_6H_4S_2)_2$	156,278	17,364		17,364
$HB(C_6H_4S_2)NH(Et)_2$		22,985		22,985
$(C_6H_4)(SH)(SSnBu_3)$		276,252		27,625
$C_6H_4(SSnBu_3)_2$		792,217		79,222
NH_3BH_3			28,354	
Total, kg/hr	340,938	1,489,015	196,494	1,295,171

2009 New Kinetics and Separation Methodology Under Development

Scheme Detail

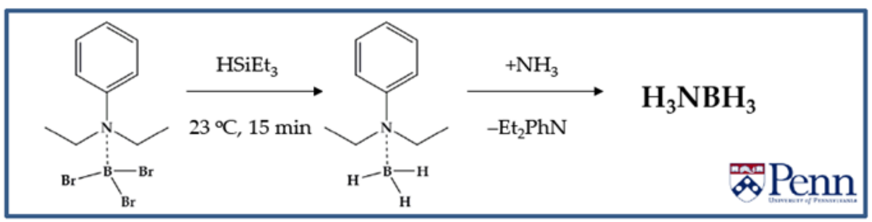
$Et_2NH\text{-}BH_3 \xrightarrow[NH_3]{-\ Et_2NH} H_3NBH_3$

Changes to

Et_3NBH_3 (neat) $\xrightarrow{NH_3\ 100\ psi}$ $\xrightarrow[Decant]{Vent}$ H_3NBH_3 Crystallizes

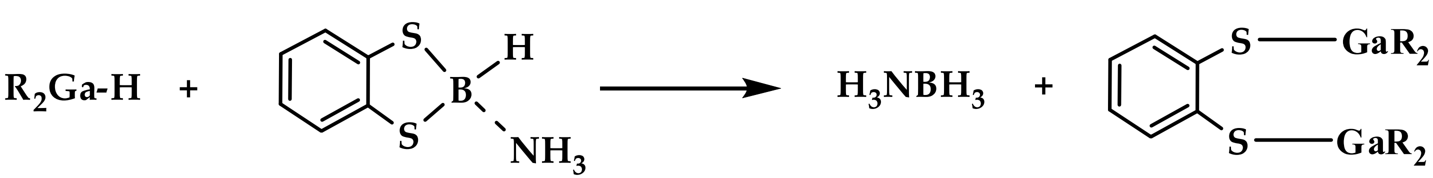
Changes in conditions = energy savings
- No solvent
- No distillation

2009 Lighter hydrogen transfer agents under evaluation



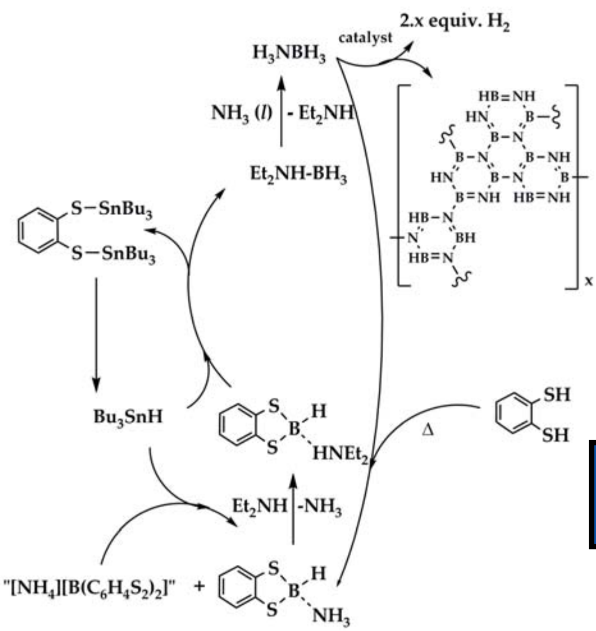
demonstrated

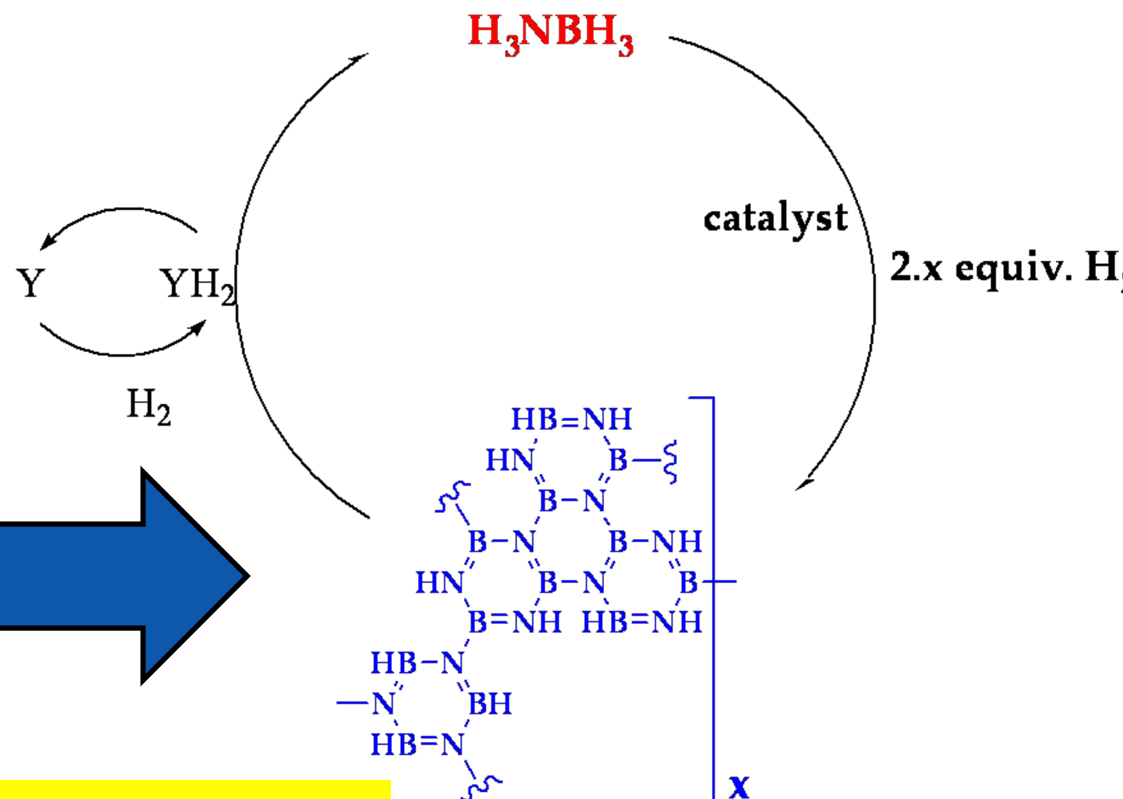
Calculations suggest less massive main group hydrides will work



ΔG (298K) -13.0 kcal/mol

2009 Ultimate Goal for LANL Regen





Spent fuel

Reduction in the number of chemical transformations and reducing overall mass flow is key

Proposed Future Work

- Storage
  - Prepare fuels that meet DOE targets for operability
  - Identify, test metal AB derivatives (mixed metal systems) with potential for on-board regen
  - Long term stability of fuel form
  - Temperature stability and range of liquid fuel

- Release
  - Identify, demonstrate additional non-precious metal heterogeneous catalyst with yet higher rates and with high durability,
  - Cold start up issues
  - Potential catalyst deactivation to be examined using flow reactors – in unison with the Engineering Center of Excellence.
  - Liquid fuels compatibility with catalyst and longevity issues to be examined using flow reactor in unison with the Engineering Center of Excellence
  - Purity of hydrogen – identification, quantification, and mitigation

- Regen
  - Improve process efficiency and reduce cost
  - Confirm capability of liquid fuel with regen

- Engineering Guided Research
  - Hydrogen purity testing of release materials
  - Flow reactor catalysis testing of catalyst kinetics, durability, extent of hydrogen release

Summary

- Engineering integration is now the major driver for the chemical storage systems under development
- Heterogeneous catalysis have been identified and proven to be effective with hydrogen release from AB
- Liquid storage options for AB fuels are major priority and have multiple paths forward
- Large numbers of new materials are now under investigation for direct rehydrogenation potential
- Regen scheme is being optimized with input from Cost analysis, with replacement of major energy intensive steps the priority
- Hydrogen gas stream purity is a priority
- As we move forward communication with the new Engineering Center of Excellence will be is developing; LANL is a partner as is PNNL

LANL Materials Comparisons and Progress; Selected Results

Metrics	2005	2006	2007	2008	2009
Grav. density (Mat. wt%)			2007 AB Mixtures	2010 Metal AB's	2010 Liquid AB 2010 Metal AB's
Vol. density (kg-H_2/L)					2010 Liquid AB 2015 Metal AB's
Minimum full flow rate				Platinum catalysts	NON-Platinum catalysts
Operating Temperature				70 ˚C	70 ˚C
Fuel Purity				inline filter required	inline filter required
Fuel cost					\$7-8 1st process

Table 3.3.2 Technical Targets: On-Board Hydrogen Storage Systems				
Storage Parameter	**Units**	**2007**	**2010**	**2015**
System Gravimetric Capacity				
Usable, specific-energy from H_2	kWh/kg	1.5	2	3
(net useful energy / max system mass) [a]	(kg H_2/kg system)	(0.045)	(0.06)	(0.09)
System Volumetric Capacity				
Usable energy density from H_2	kWh/L	1.2	1.5	2.7
(net useful energy / max system volume)	(kg H_2/L system)	(0.036)	(0.045)	(0.081)
Storage System Cost [b]	\$/kWh net (\$/kg H_2)	6 (200)	4 (133)	2 (67)
Fuel cost [c]	\$/gge at pump	---	2-3	2-3
Durability / Operability				
Operating ambient temperature [d]	°C	-20/50 (sun)	-30/50 (sun)	-40/60 (sun)
Min/max delivery temperature	°C	-30/85	-40/85	-40/85
Cycle life (1/4 tank to full) [e]	Cycles	500	1000	1500
Cycle life variation [f]	% of mean (min) at % confidence	N/A	90/90	99/90
Min delivery pressure from tank; FC = fuel cell, ICE = internal combustion engine	Atm (abs)	8FC / 10 ICE	4FC / 35 ICE	3FC / 35 ICE
Max delivery pressure from tank [g]	Atm (abs)	100	100	100
Charging / Discharging Rates				
System fill time (for 5 kg)	min	10	3	2.5
Minimum full flow rate	(g/s)/kW	0.02	0.02	0.02
Start time to full flow (20 °C) [h]	s	15	5	5
Start time to full flow (- 20 °C) [h]	s	30	15	15
Transient response 10%-90% and 90% - 0% [i]	s	1.75	0.75	0.75
Fuel Purity (H_2 from storage) [j]	% H_2	99.99 (dry basis) See Appendix C		
Environmental Health & Safety				
Permeation and leakage [k]	Scc/h	Meets or exceeds applicable standards		
Toxicity	-			
Safety	-			
Loss of useable H_2 [L]	(g/h)/kg H_2 stored	1	0.1	0.05