

DOE Chemical Hydrogen Storage Center of Excellence STP29

Identify, research, develop and validate advanced on-board chemical hydrogen storage systems to overcome technical barriers and meet 2010 DOE system goals with the potential to meet to 2015 goals:

- Develop materials, catalysts and new concepts to control thermochemistry and reaction pathways
- Assess concepts and systems using engineering analysis and studies
- Select most promising chemical systems for engineering development
- Develop life cycle inventory and demonstrate a 1 kg storage system



- More efficient borate-to-borohydride (B-OH to B-H) regeneration
- Alternative boron chemistry to avoid thermodynamic sinks using polyhedral boranes (B_xH_y) or amine-boranes
- Concepts using coupled endo/exothermic reactions, nanomaterials, heteroatom substitution for thermodynamic control



Overview

Timeline

- Start – Jan-Apr 2005
- Finish – Jan 2010
- ca. 28 % complete

Barriers

- Cost
- Weight and volume
- System Life-Cycle Assessment
- Energy Efficiency
- Regeneration Processes

	2010	2015
Gravimetric Capacity	6 wt %	9 wt %
Volumetric Capacity	.045 kg/L	0.081 kg/L
Minimum Flow Rate (g/s)/kW)	0.02	0.02
Regeneration Efficiency (Center goal)	50 %	50 %

Overview

- **On-board hydrogen storage is a formidable problem**
 - Scientific advances and engineering assessment needed
 - Multi-disciplinary collaborative approach is being pursued at the project level
- **Chemical hydrogen storage offers a number of opportunities**
 - A potential “game-changer” for transportation
- **We’re making advances in hydrogen release**
 - A number of promising new developments
 - Hydrogen release rates and pathways
- **Regeneration concepts and efficiency will be key**
 - Already under development
- **Engineering assessment tools being developed**

Science of Chemical Hydrogen Storage

- **CAPACITY**

- Develop, synthesize, test compounds with high hydrogen density, proper energetics, and potential pathways
- Theory and modeling for insight

- **HYDROGEN RELEASE**

- Pathways: avoid large thermodynamic sinks, byproducts
- Rates: study mechanisms
- Develop and optimize catalysts and catalytic processes

- **REGENERATION**

- Develop pathways closer to thermodynamic limits
 - » Avoid high energy intermediates
 - » Use regenerable intermediates

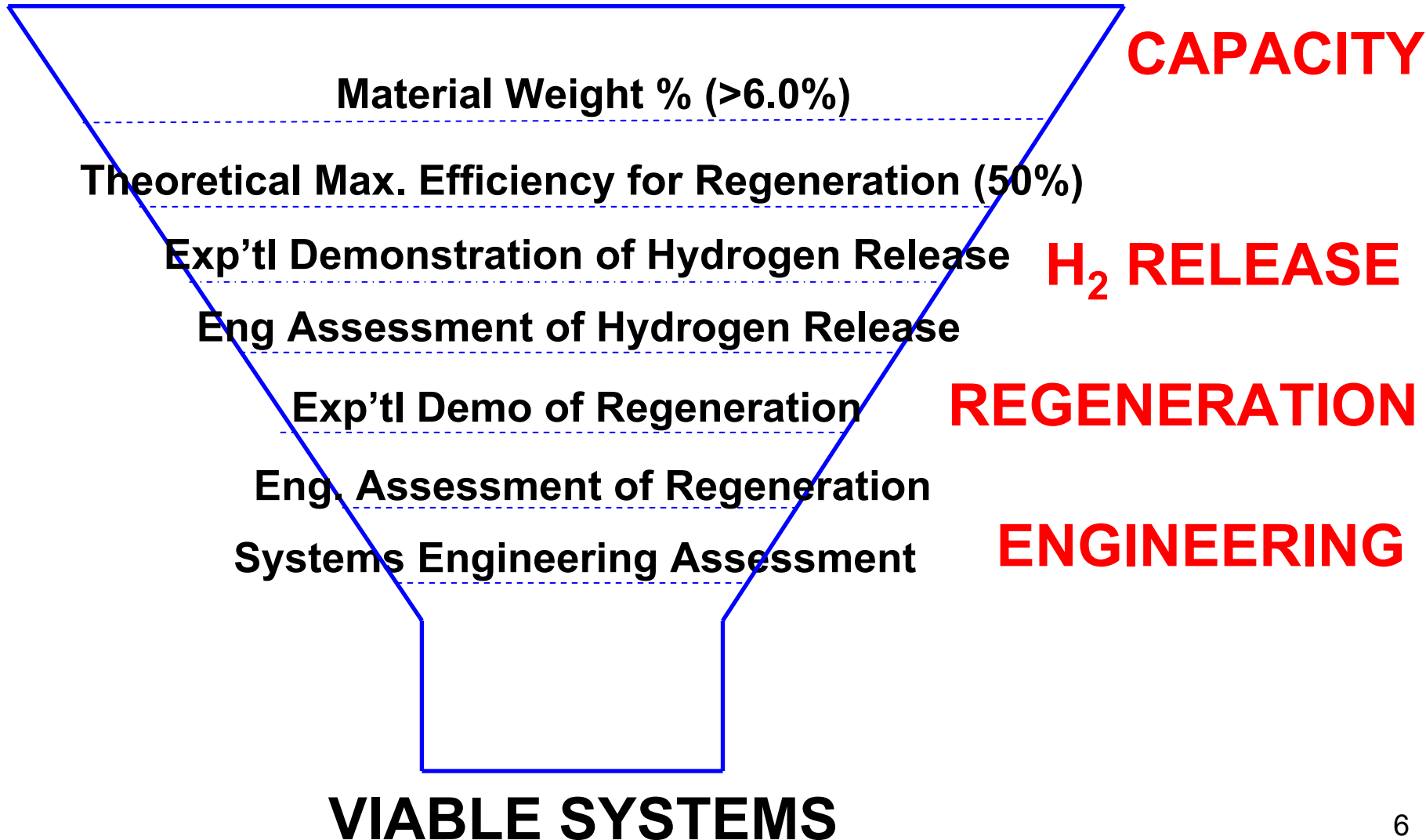
Theory ↔ *Experiment* ↔ *Assessment*

Center Projects

	Project	Partners
1.1	B-O to B-H Engineering Guided Research	ROH, MCEL, PSU, Ala, USB, PNNL, LANL
1.2	Engineering Assessment of Hydrogen Generation Systems	MCEL, ROH, LANL, PNNL
2.1	Polyhedral Borane Chemistry	UCLA, IMX, PSU, PNNL, LANL
2.2	Amine-Borane Chemistry	Penn, UW, NAU, Ala, IMX, PNNL, LANL
2.3	Amine-Borane Systems Engineering, Safety	PNNL, NAU, LANL
3.1	Organics and Coupled Reactions	Ala, PNNL, LANL
3.2	Nanoparticles and Main Group Hydrides	UC Davis, Ala, LANL

Performance-Based Approach

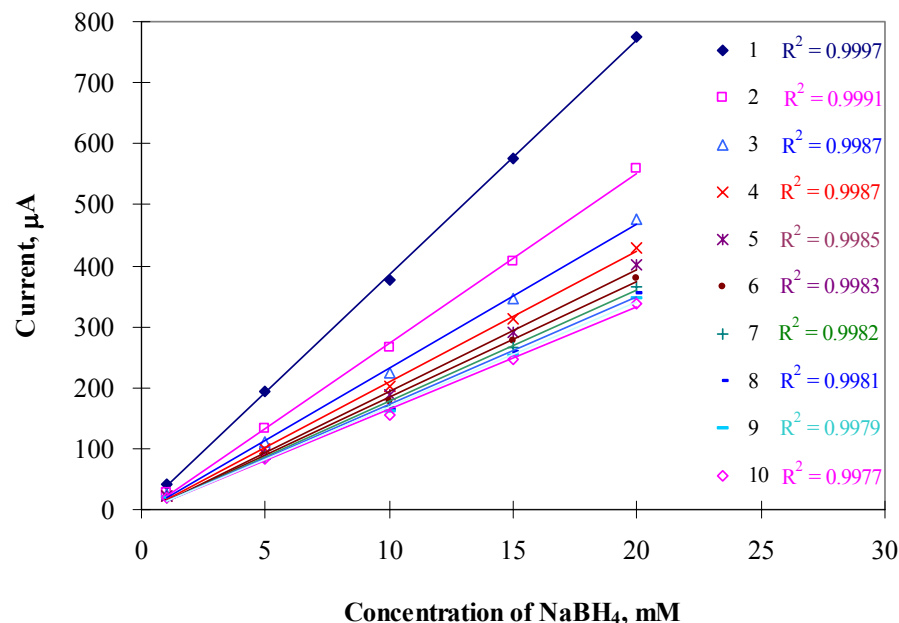
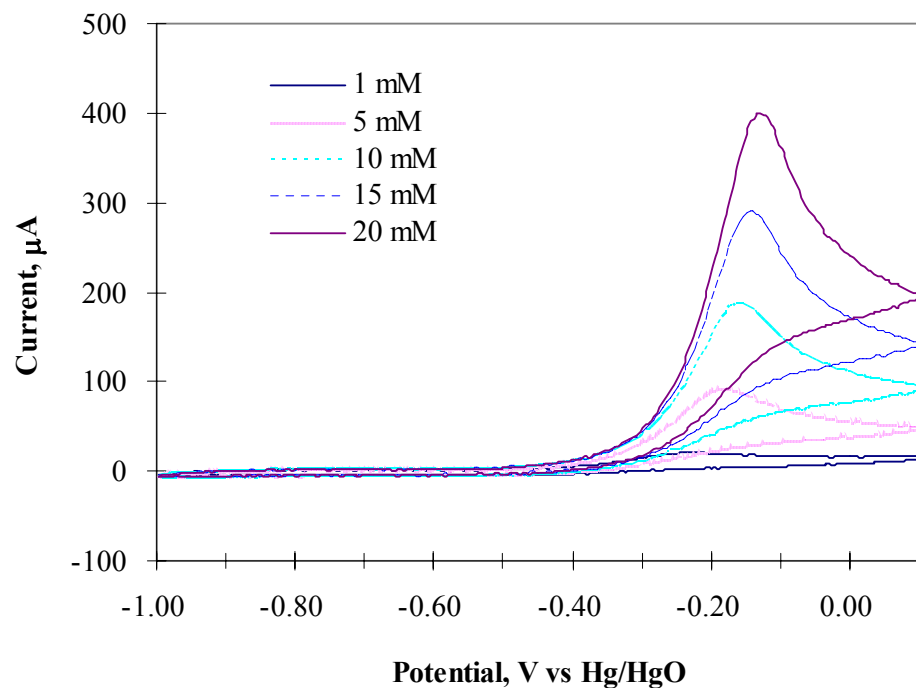
POTENTIAL CANDIDATES



Engineering Guided R&D for B-OH to B-H

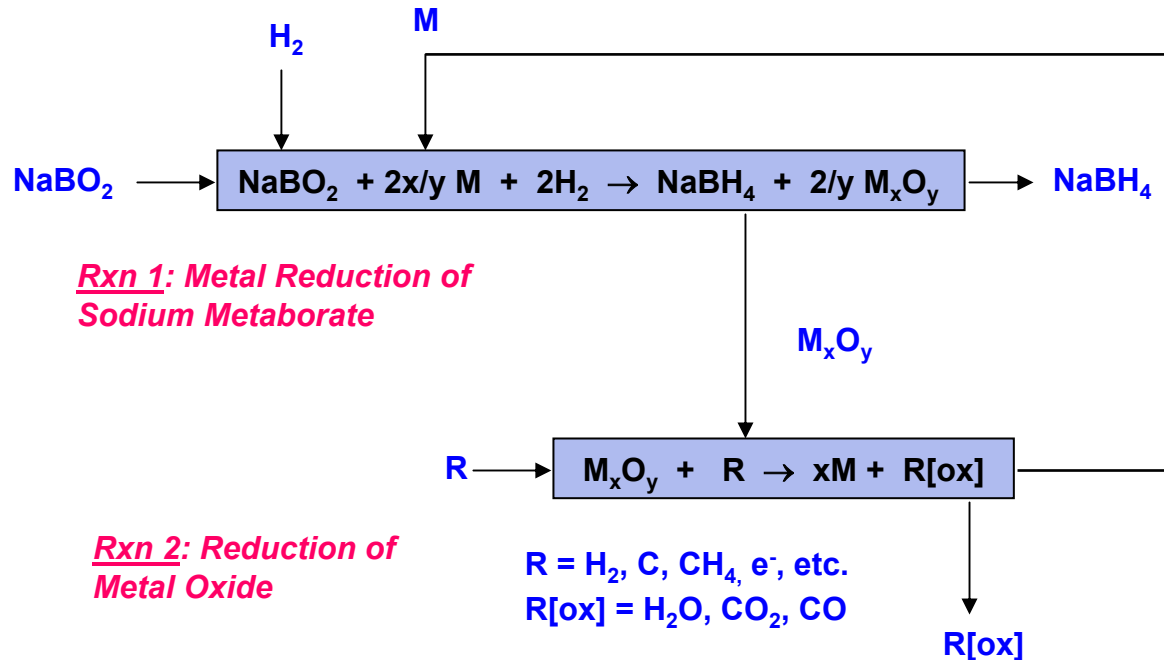
- Data mining of prior work, including proprietary information
 - Investigate electrochemical methods for borate reduction
 - Develop concepts for borate complexation and reduction
-
- Established performance-based metrics
 - Identified potential regeneration routes
 - Metal reduction of borate
 - Borane-based routes
 - Two electrolytic process routes identified
 - In-situ Analysis; laboratory evaluations
 - Boron substrate: borate, alkyl borates, alkoxyborohydrides
 - Solvent systems: aqueous, non-aqueous
 - Cathode materials: hydrophobic composites, high hydrogen overpotential systems, gas diffusion cathodes
 - 1-step direct conversion to NaBH_4
 - 2-step conversion through $\text{NaBH}(\text{OCH}_3)_3$
 - Established framework for Analysis
 - Life Cycle Inventory

Electroanalysis of BH_4^- Ion



- We have demonstrated cyclic voltammetry as a quantitative electroanalytical method for BH_4^-
- Excellent selectivity towards BH_4^- ion observed even in high concentrations of sodium borate ($\text{BO}_2^-/\text{BH}_4^- \geq 10$).
- Method is simple and inexpensive with the advantage of allowing for real-time, *in situ* monitoring of BH_4^- concentration.

General Pathway for Metal Reduction of Borate



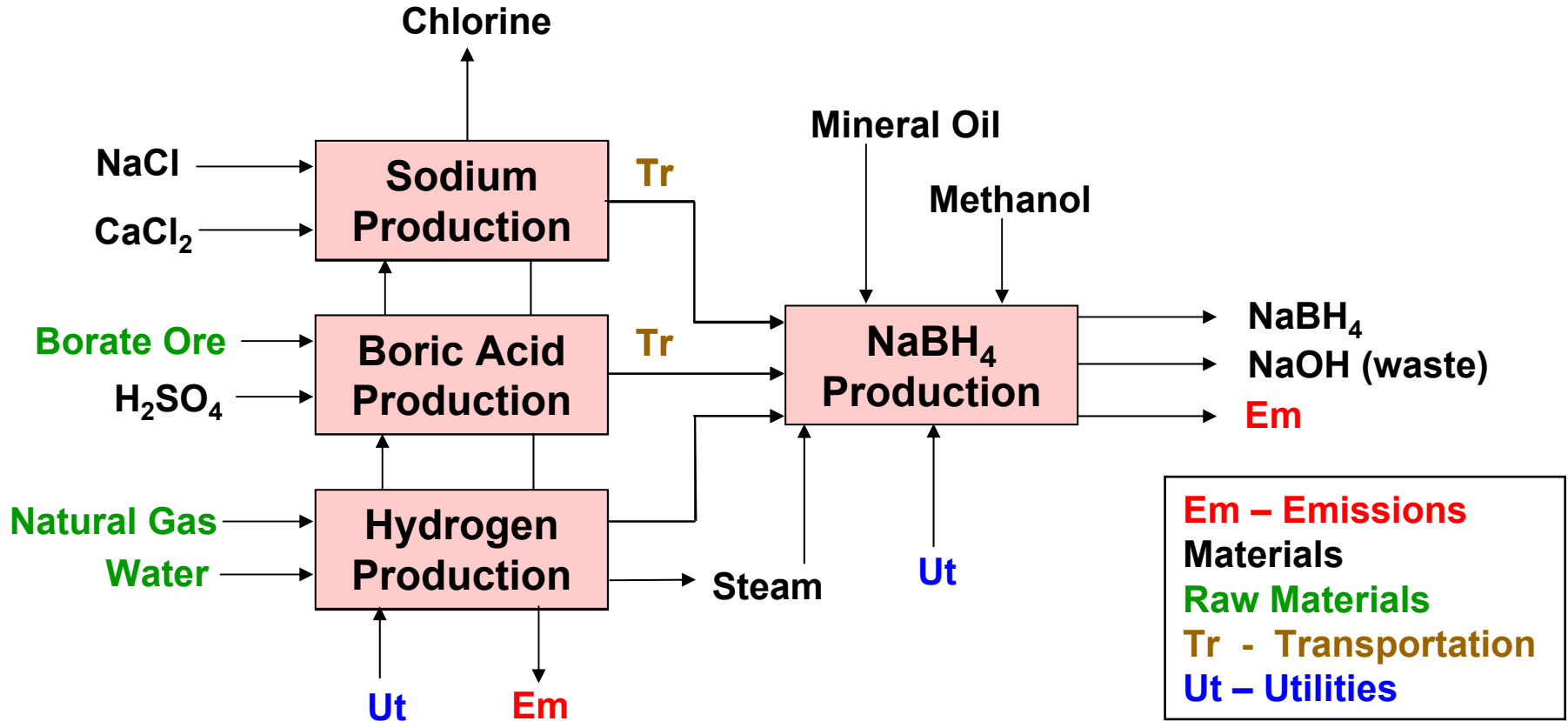
Fast-fail Metrics

- Energetics of both reaction steps
- Metal reductant regeneration requirements
- Energy costs
- Raw material cost and availability

$$\begin{aligned} \% \text{ Regen Eff} &= \text{Usable Energy Released} / \text{Total Energy Used}^* \\ &= 100 * \Delta G_{\text{cmb}} \text{ H}_2 \text{ prod} / (\Delta G_{\text{cmb}} \text{ reductant} + \Delta G_{\text{rxn}} \text{ NaBO}_2 \rightarrow \text{NaBH}_4) \\ &= 75\% \text{ ideal} \end{aligned}$$

* Described at DOE H₂ Storage Engineering Analysis meetings, Argonne National Lab (10/12/05) and Palm Springs (11/18/05)

Life Cycle Inventory (LCI) Established for NaBH_4 via Current Brown-Schlesinger Process



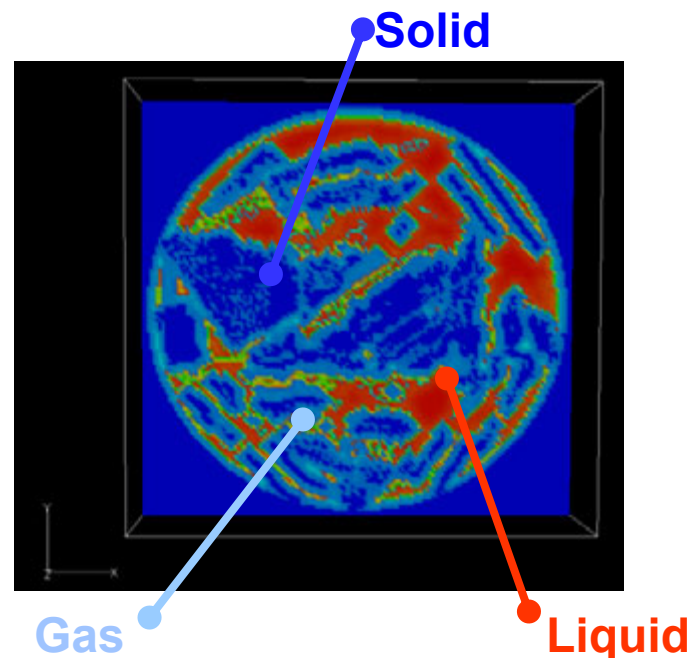
Life cycle analysis addresses technical barrier: Lack of understanding of environmental impacts (energy usage and emissions) of the generation process

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Catalytic Reactor Modeling

- Center Reactor Modeling Activity
 - Developed reactor packing sub-module
 - Completed Lattice Boltzmann microscopic modeling of reactant flow in the reactor
 - Established macroscopic reactor model that matches the experimentally observed parameters
- Generated experimental data to validate modeling results.
- Started to use the model to predict performance parameters
- Begin to build the experience and modeling tool that can be applied to other chemical hydrogen storage systems

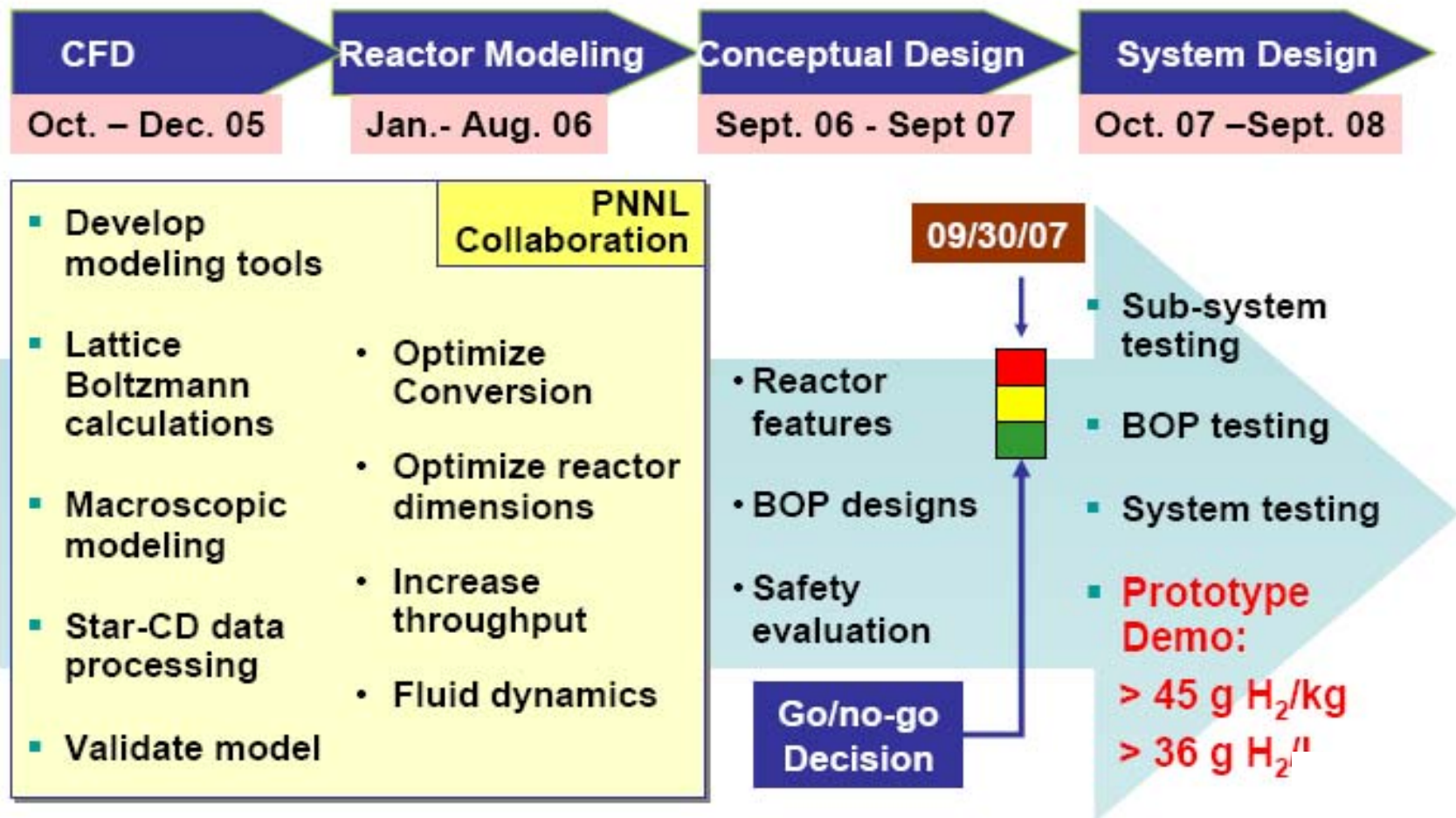
CATALYTIC REACTOR MODEL



- Initial model based on SBH. Straightforward to adapt to other chemical systems
- Process
 - SEM cross-sections used to build 'virtual' reactor
 - Lattice-Boltzmann coupled to CFD
 - Kinetics taken from available databases

System Development Approach

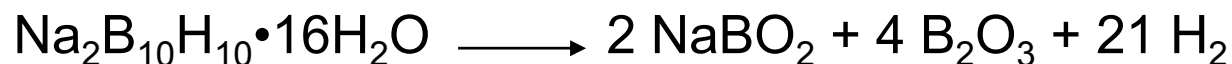
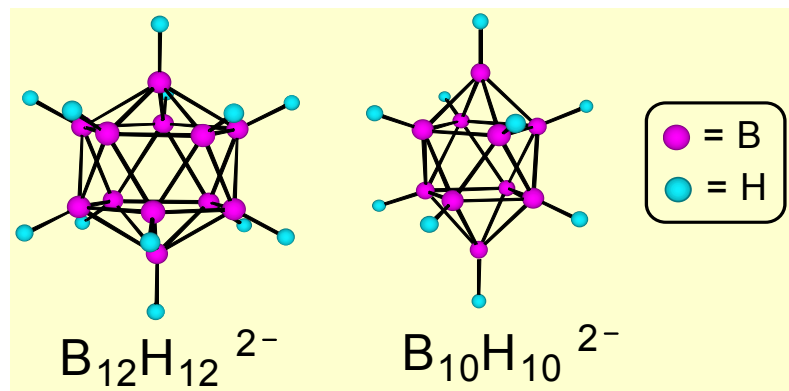
Using NaBH_4 as Example



Polyhedral Boranes

Polyhedral boranes are more stable than borohydride and multiple electron sources

Objective: Develop catalysts for hydrolysis

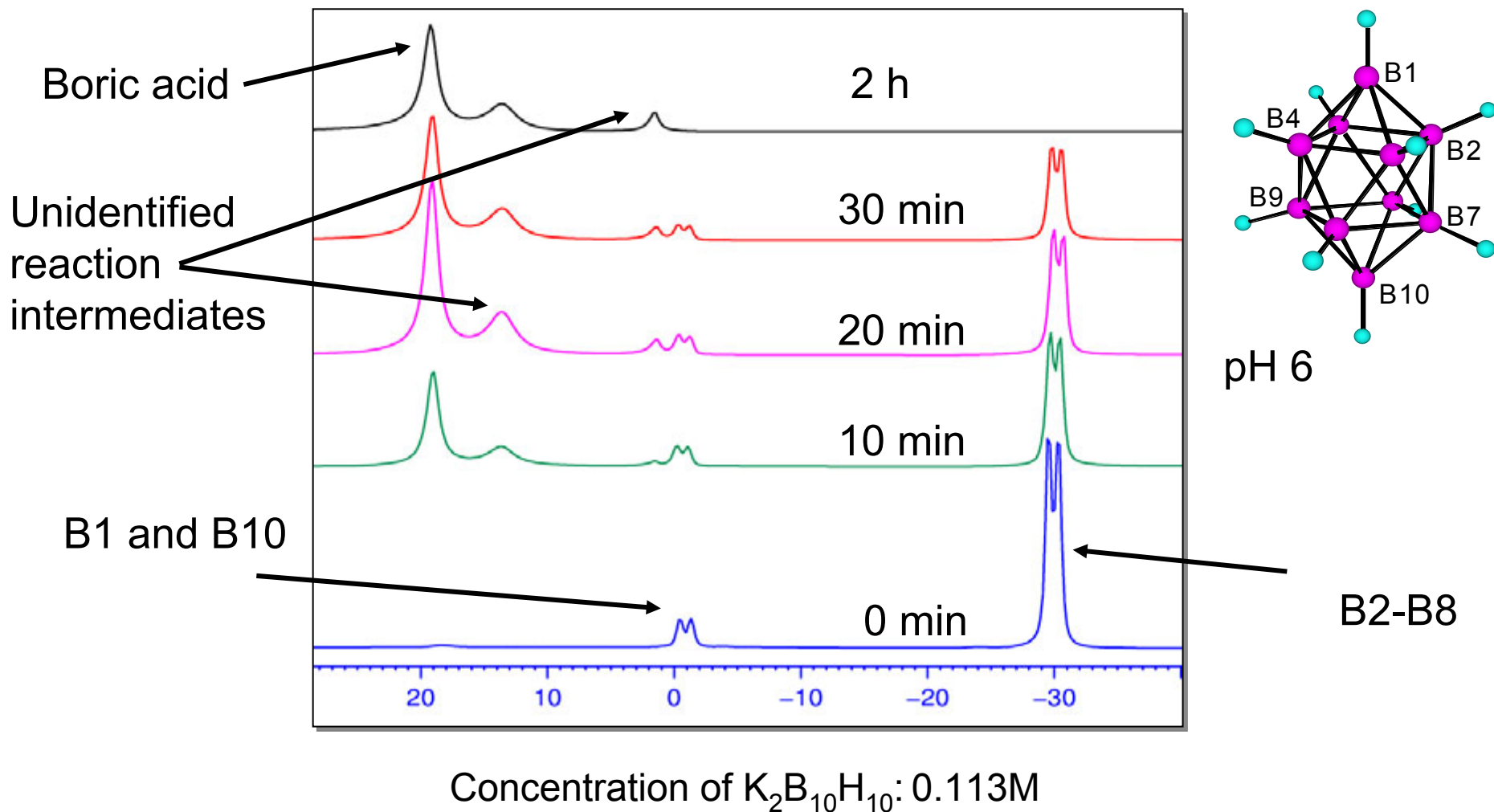


Material storage capacity 9.4 wt% hydrogen (including water)

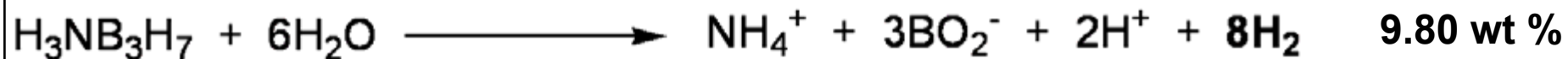
Borane salts investigated	Initial concentration	Reaction Time (mins)		
		10% reaction	25% reaction	50% reaction
$(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$	0.113M (0.45 mmol)	2.5	6.5	18
$\text{K}_2\text{B}_{12}\text{H}_{12}$	0.113M (0.45 mmol)	6.5	--	--
$\text{K}_2\text{B}_{10}\text{H}_{10}$	0.113M (0.45 mmol)	1.5	4.5	12

Reaction conditions: pH=6, 80 °C and 5 mol% catalyst in water.

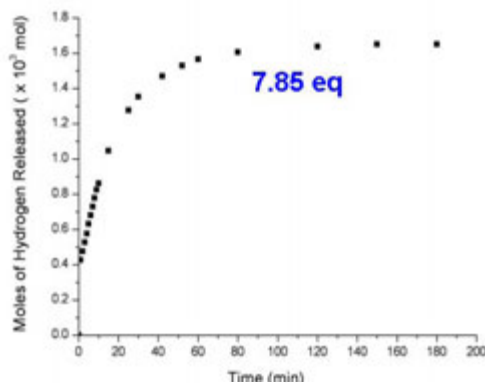
Rhodium-Catalyzed Polyhedral Borane Hydrolysis



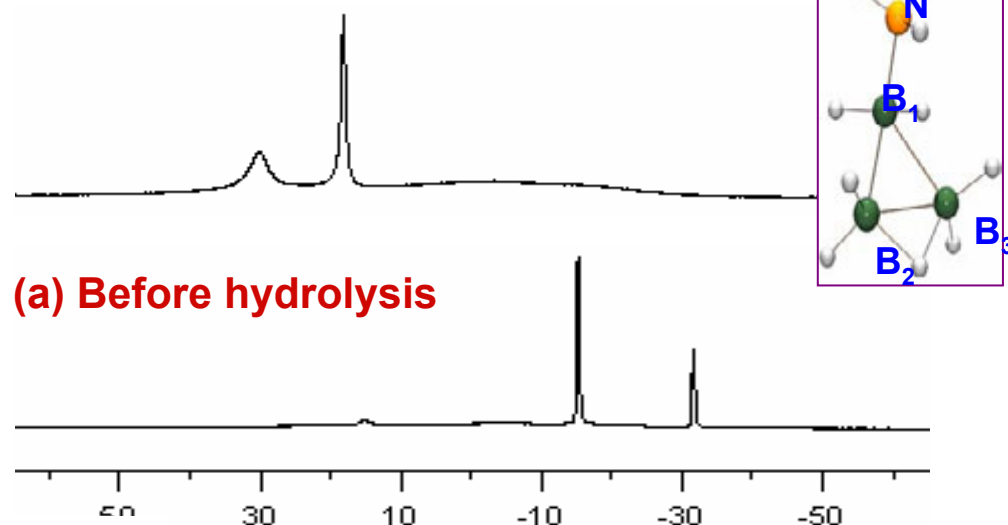
H₃NB₃H₇ (AT) Hydrolysis



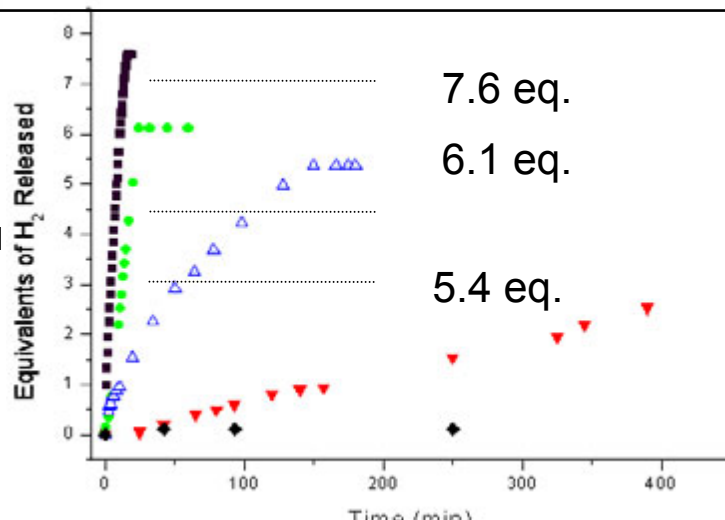
- Improved Synthesis of AT
- AT is Soluble and Stable in H₂O
 - > 33 wt% solubility
 - Reacts with acids (HCl)



(b) After hydrolysis ¹¹B NMR



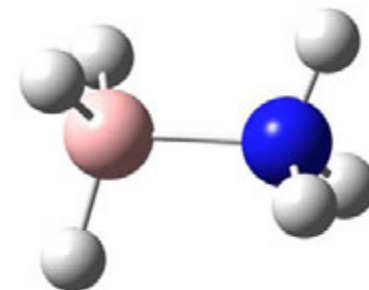
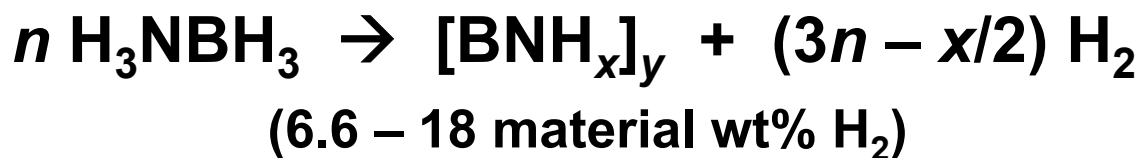
21 °C
[B₃H₇NH₃] ~0.088 M



Metal-Catalyzed Hydrolysis

- Rh/Al₂O₃, 5 wt % (7.0 mol%)
- [Rh(COD)(μ-Cl)]₂ (7.2 mol%)
- △ Rh/Al₂O₃, 5 wt % (1.4 mol%)
- ◆ Ru metal (29 mol%)
- ◆ Pd submicron size (10 mol%), Ir (5.0 mol%), Fe, or No catalyst

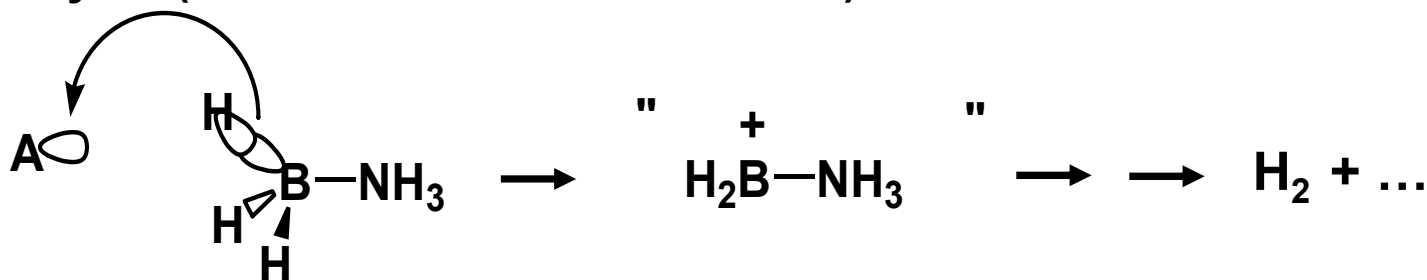
Ammonia-Borane for Hydrogen Storage



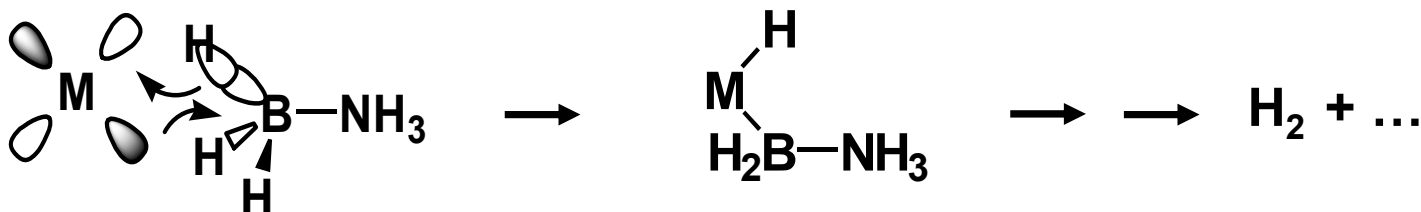
Objectives

- Understand and alter solid-state chemistry
- Identify catalysts for rapid, controlled release of hydrogen from ammonia-borane (AB) (determine capacity, kinetics and mechanisms)
- Fully characterize dehydrogenated BNH_x products obtained from different families of catalysts

• Acid Catalysis (Lewis Acid or Bronsted Acid)

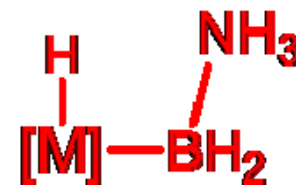
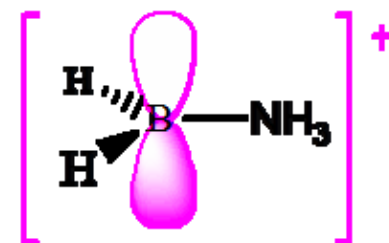
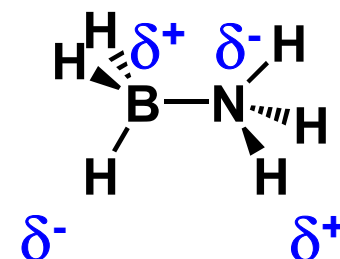


• Metal Catalysis

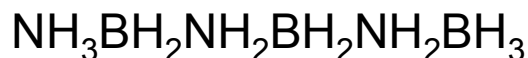
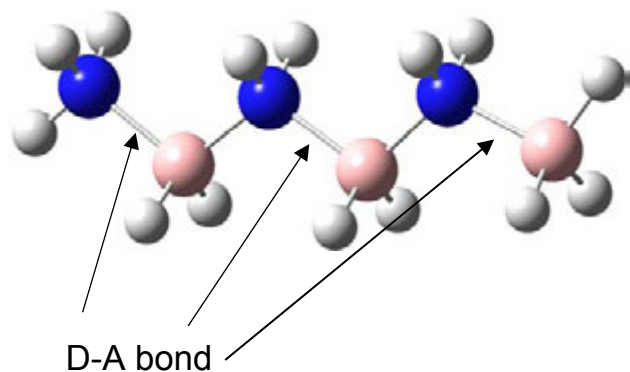


Key Developments for Ammonia-Borane

- Theory for thermodynamics and energetics of reaction intermediates
- Mechanism and thermodynamics of solid state reactions
- Inclusion in mesoporous materials alters rate and selectivity
- Rapid single dehydrogenation with Ir catalysts
- Acid catalysts can lead to multiple dehydrogenation from AB
- Multiple dehydrogenation of AB is facile with homogeneous electron-rich precious metal complexes
- The first examples of non-precious metal catalysts have been discovered
- Heterogeneous catalysts have been discovered (including rapid screening)
- Alternative reaction media can open up new reaction pathways
- Evaluation of safety and properties
- Kinetics and mechanistic studies underway
- Regeneration concepts developed and key steps demonstrated

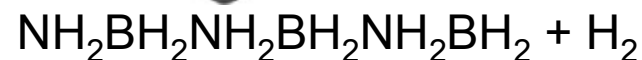
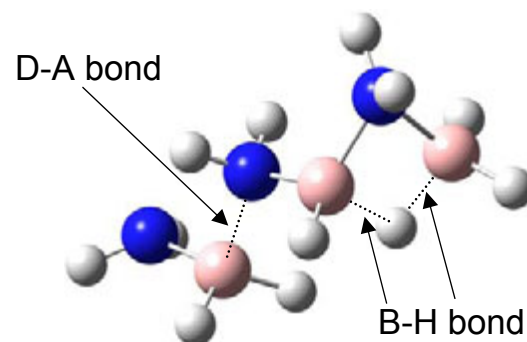
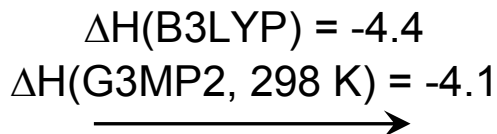


Theory: Energetics (kcal/mol) for H₂ Release in Polymeric Chains



Donor-Acceptor N-B bond $\approx 1.66 \text{ \AA}$

Normal N-B bond $\approx 1.56 \text{ \AA}$

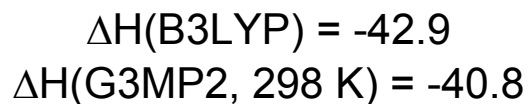
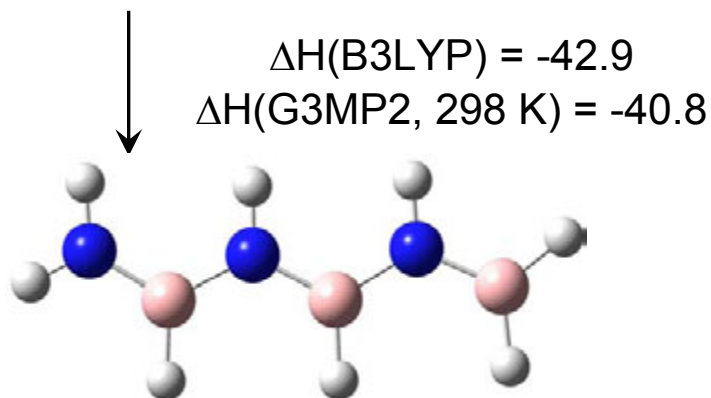
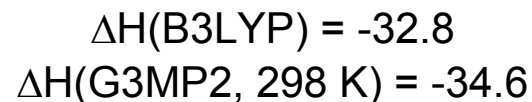


Bridge structure

Donor-Acceptor N-B bond = 1.73 \AA

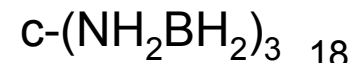
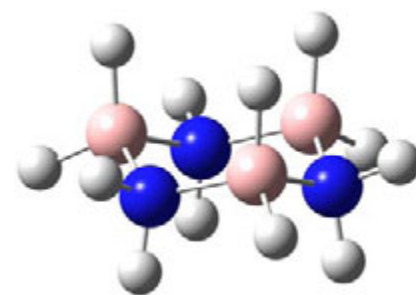
Normal N-B bond $\approx 1.54 \text{ \AA}$

B-H bond $\approx 1.34 \text{ \AA}$



N-B bond = 1.42 \AA and 1.45 \AA

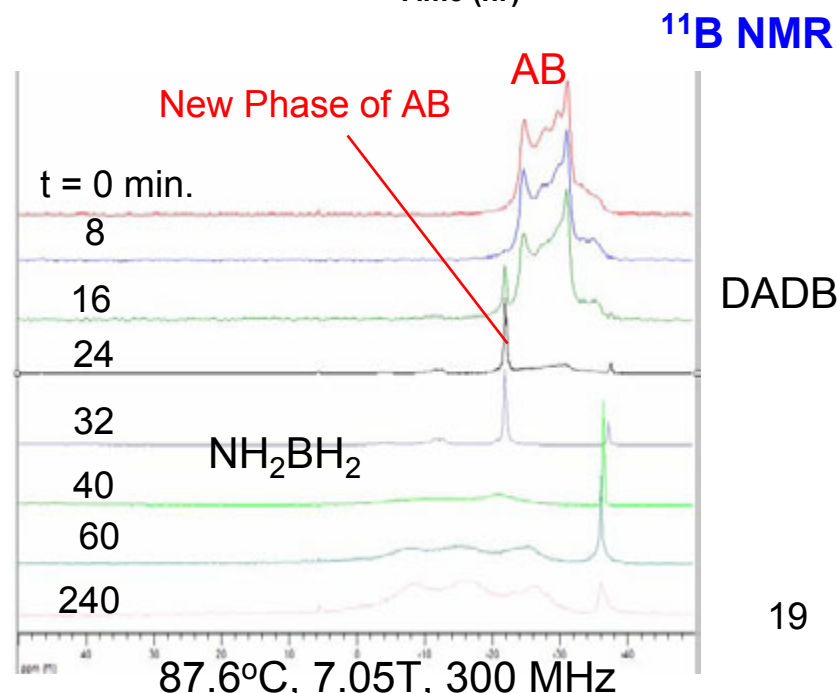
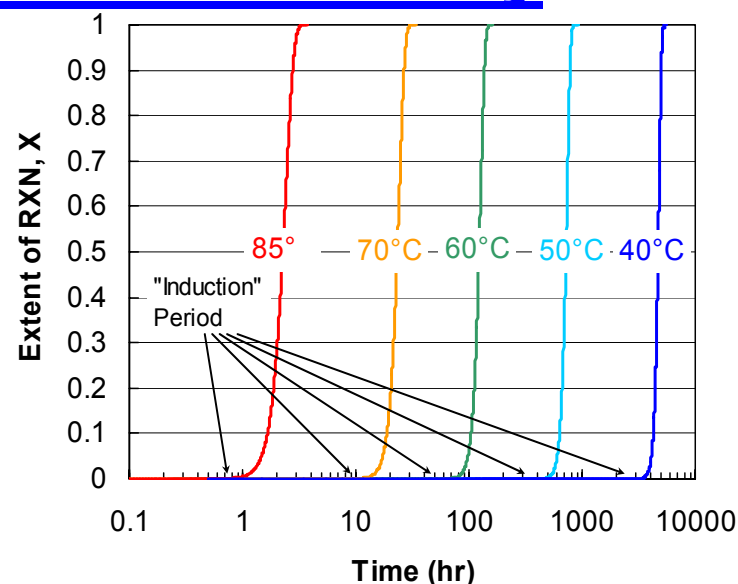
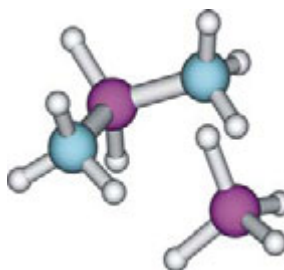
- Evidence that polymer to polymer is not as exothermic as forming the ring – need condensed phase interactions.



N-B bond = 1.59 \AA

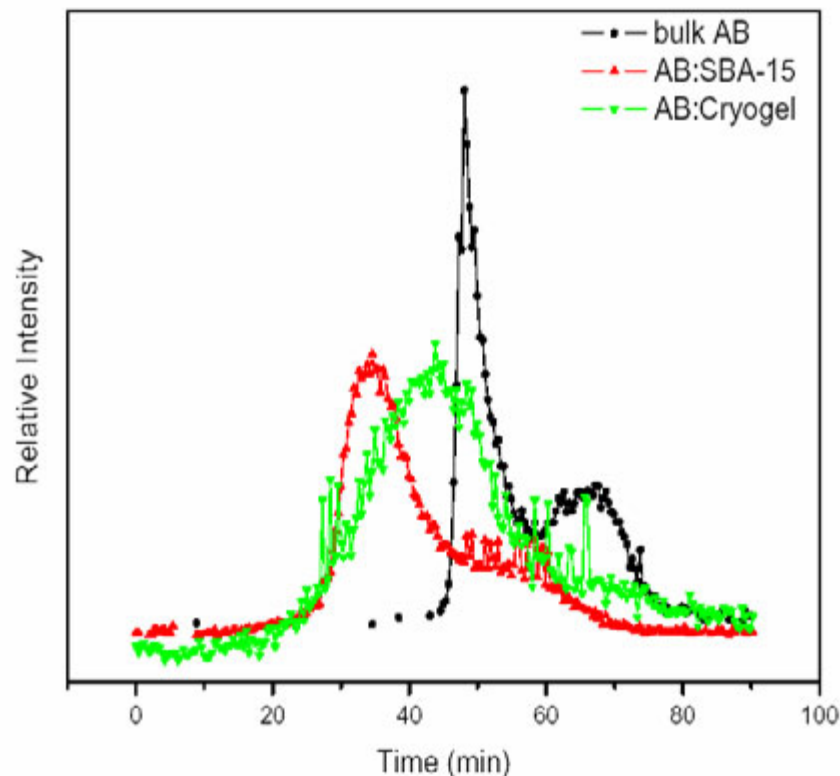
Solid-State Ammonia-Borane Reactivity

- Mechanism and Kinetics
 - Avrami Kinetics
 - $X = 1 - \exp[-(kt)^n]$
 - Seeding or partial conversion of the AB fuel reduces the “induction” period
 - Reaction shows initial peak at -20 ppm (mobile AB phase), then growth of diammoniate of diborane (-36 ppm).
 - One of these two species is likely the seed compound.
- Better understanding of options for fuel formulation.
 - Heat management
 - Fuel stability



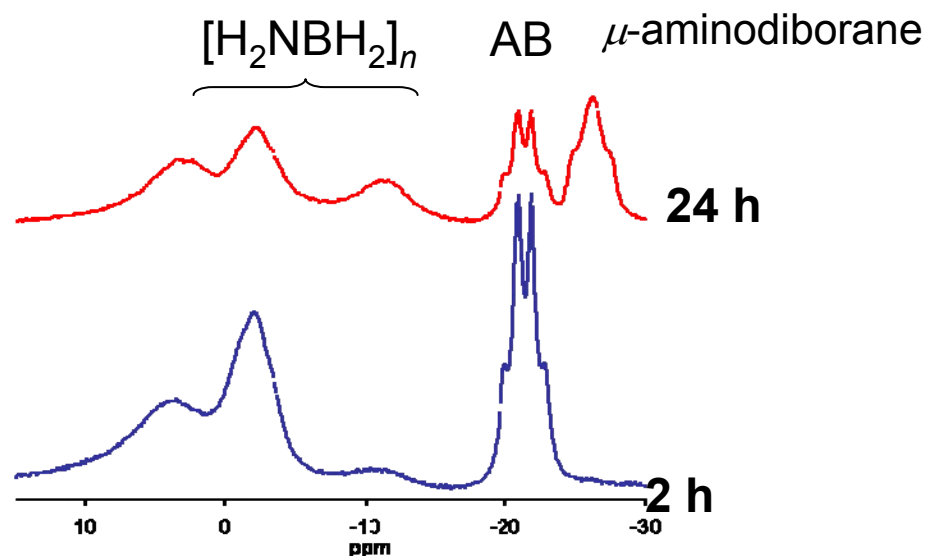
Ammonia-Borane in Scaffolds

- Preliminary data has been collected on carbon scaffolds.
- Driver for this work is to reduce the scaffold weight and drive closer to intrinsic H_2 density of AB.
- Enhancement of kinetics observed, but somewhat less of an effect than silica scaffold.
- Indicates that surface chemistry of the scaffold should be examined further.



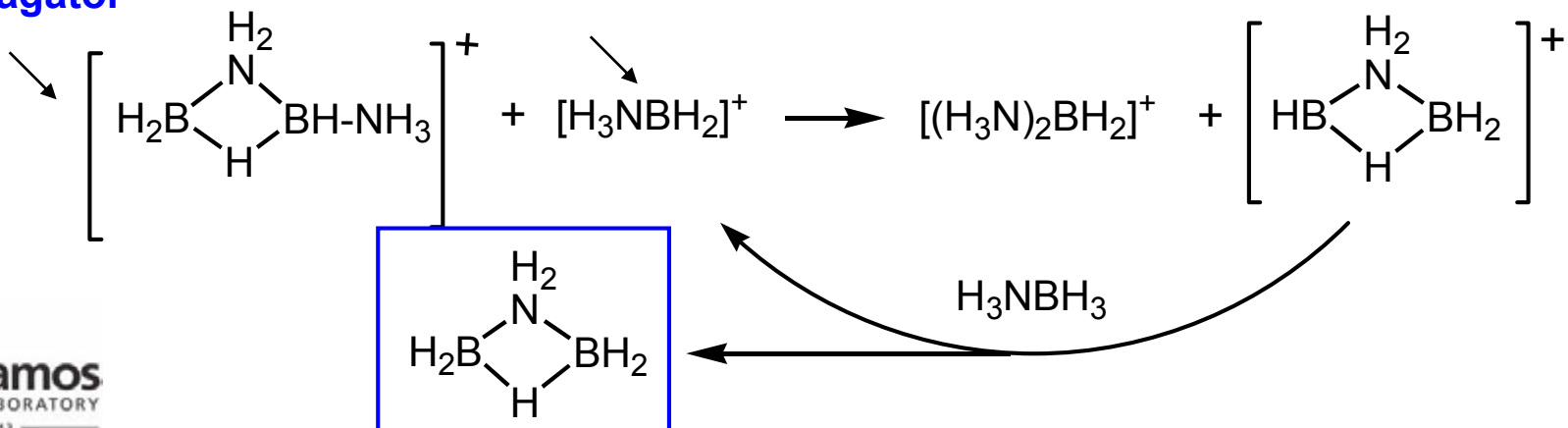
Results: Acid Catalysis

- Strong Bronsted and Lewis acids enable H_2 release at room temp
- Experimental and theory studies (w/ Alabama):
 - cationic initiator
 - acyclic BNH_x products
 - < 1 eq. hydrogen, due to μ -aminodiborane by-product
 - By-product formation leads to free NH_3 which quenches cation and chain propagation
- Reducing acid/AB ratio eliminates
- μ -aminodiborane and affords $> 2 H_2$

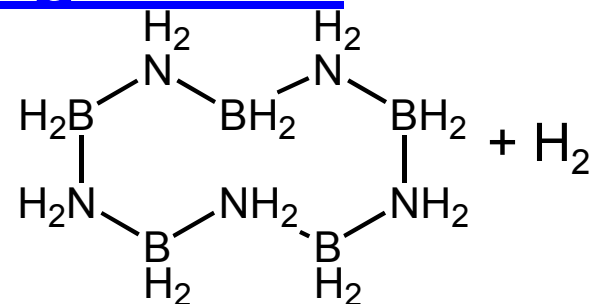
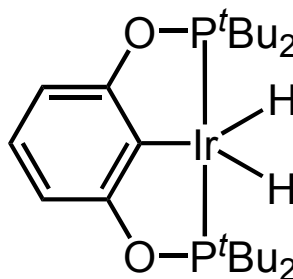
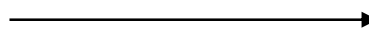


H-coupled ^{11}B NMR of AB and 0.1 equiv. triflic acid in diglyme at 24°C

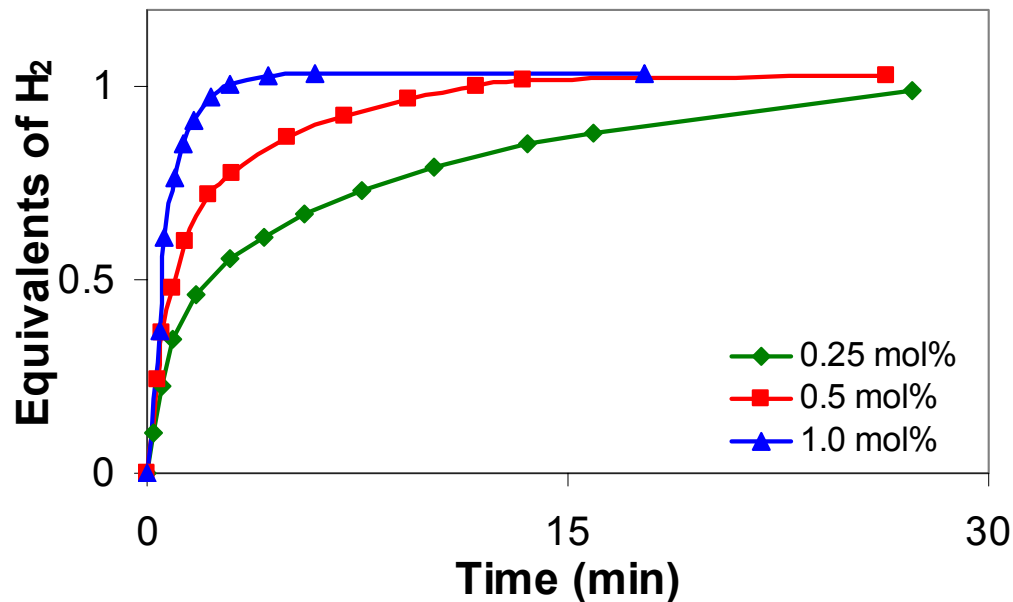
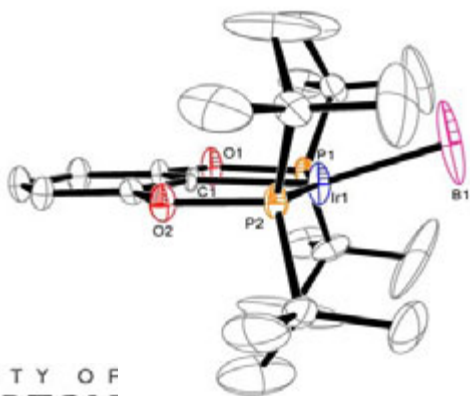
propagator



Ir Catalysts for Rapid Dehydrogenation



- Single well characterized non-volatile product
- Reaction complete in < 15 min at 25 °C
- All other reported reactions of this type lead to mixtures including borazine
- Eventually, catalyst forms a dormant state



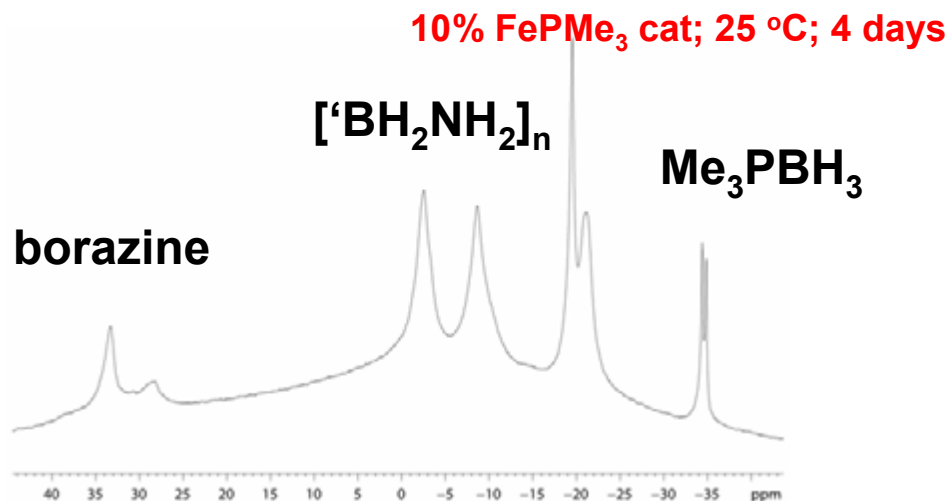
Homogeneous Catalysts: Base Metals

APPROACH

- Examine electron-rich metal complexes
- “Base” metal complexes with electron-rich phosphine and carbene ligands

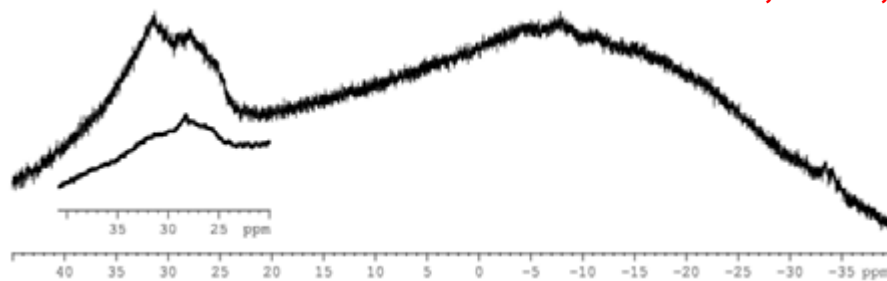
RESULTS

- Iron and nickel phosphine complexes are slow and short-lived due to inactive metal boride formation
- Metal carbene complexes afford long-lived catalysts that afford linked borazines without build-up of $[\text{BH}_2\text{NH}_2]_n$ intermediates



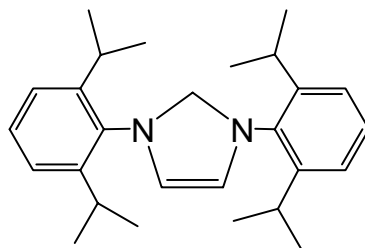
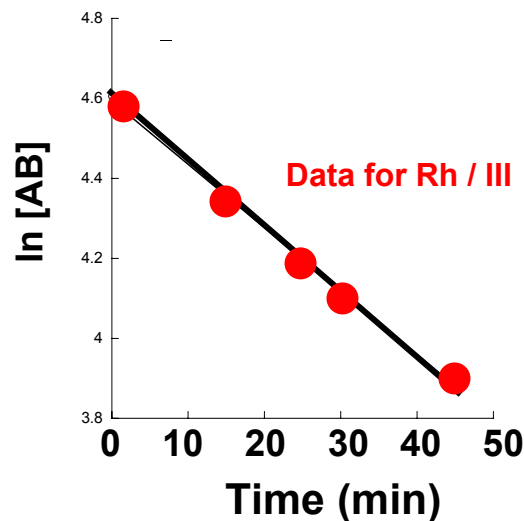
linked borazines

10% Ni carbene; 60 °C; 6 hrs



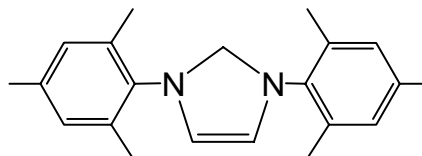
Rates Depend on Metal and Ligands

- Kinetics of Ni, Ru, and Rh carbene complexes
- Best catalyst to date is Ni complex with Enders' triazacarbene III



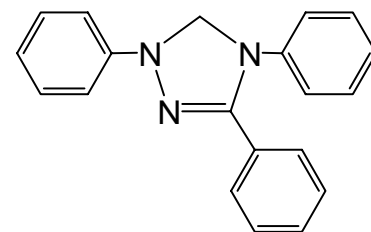
I-dipp

I



I-Mes

II

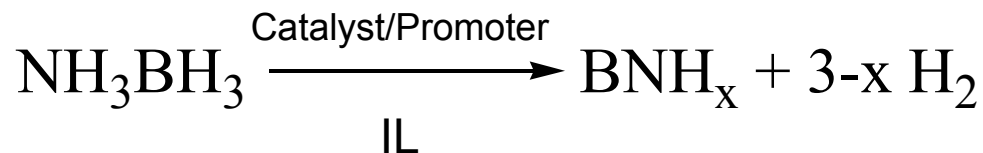


Enders'

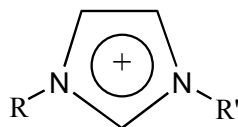
III

Catalyst	Ni / I	Ni / II	Ni / III	Ru / III	Rh / III
Rates at 60°C (10 ⁻³ min ⁻¹)	5.6	7.3	64.6	34.7	15.8

Ionic Liquids (IL) and Catalysts for AB

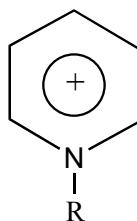


Cations:



N,N'-imidazolium

bmim

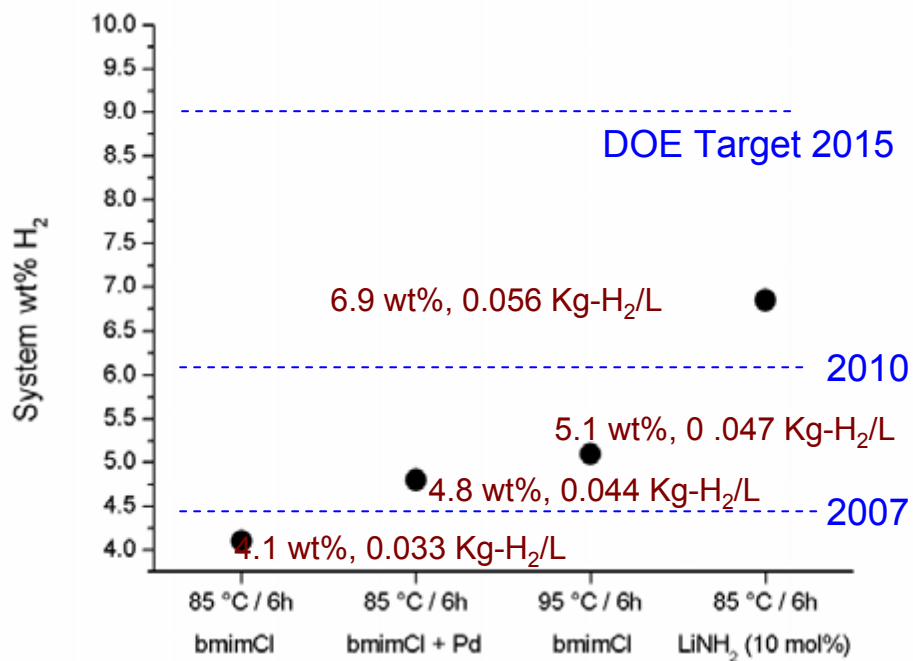


N-pyridinium

Anions:

Reactive: AlCl_4^- , Al_2Cl_7^-

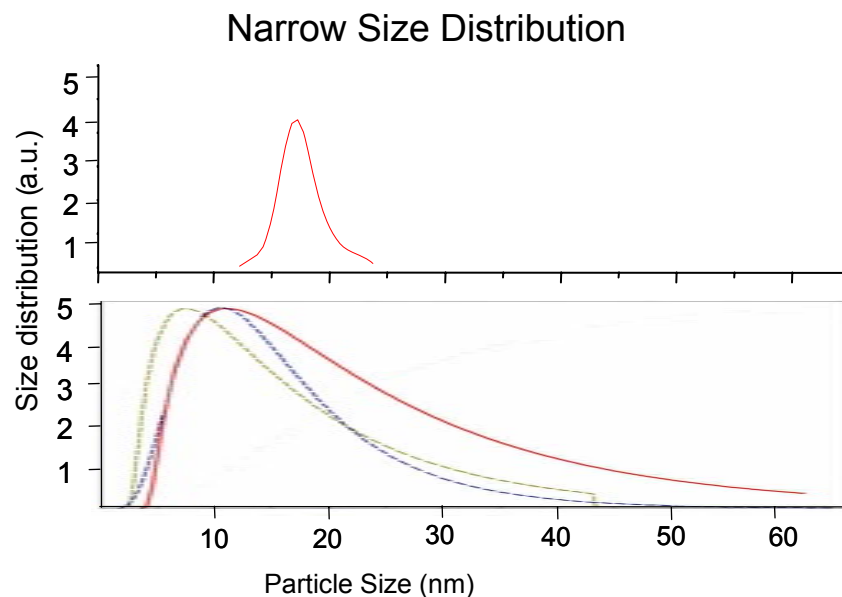
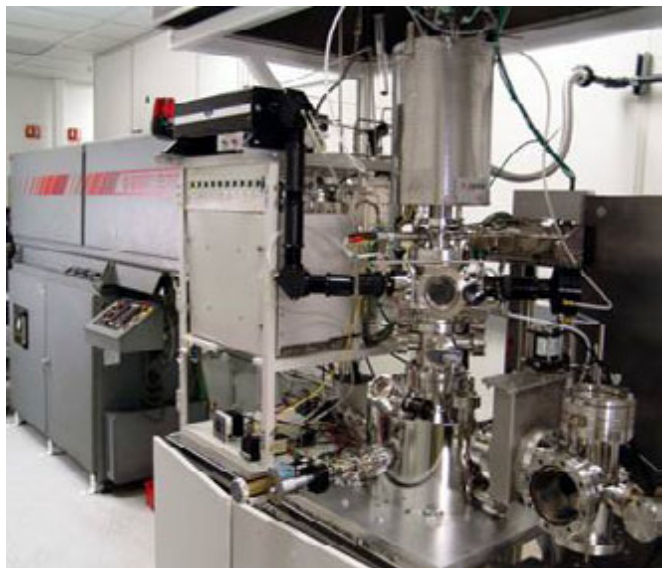
Inert: PF_6^- , BF_4^- , Cl^-



“System” = wt of H_3NBH_3 + Catalyst/Additive/Solvent

Rapid Screening of Catalysts

- **Approach**
 - Create combinatorial libraries consisting of both higher cost known catalytic metals and lower cost metals
 - Qualitatively screen libraries for catalytic activity
 - Quantitatively measure activity in microreactor
 - Test scaled-up system to confirm bulk activity

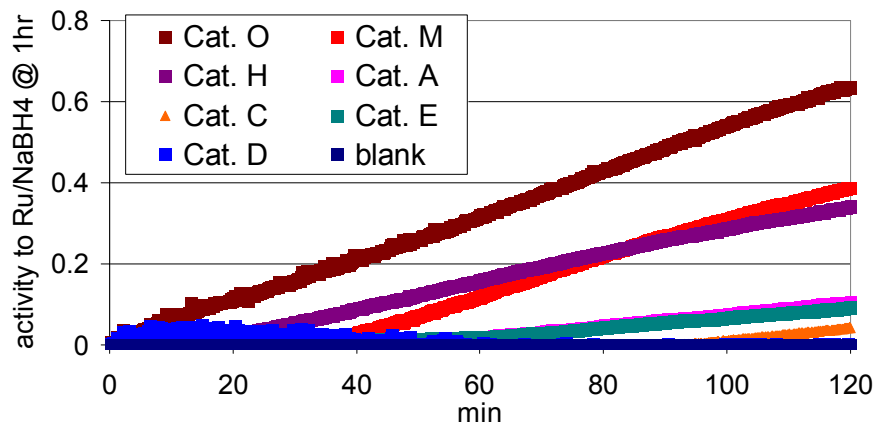


- Precise particle size control enables direct correlation between size and property
- Broad size distributions obscure size dependent properties
- Same size particles, different composition
- Same composition, different sizes

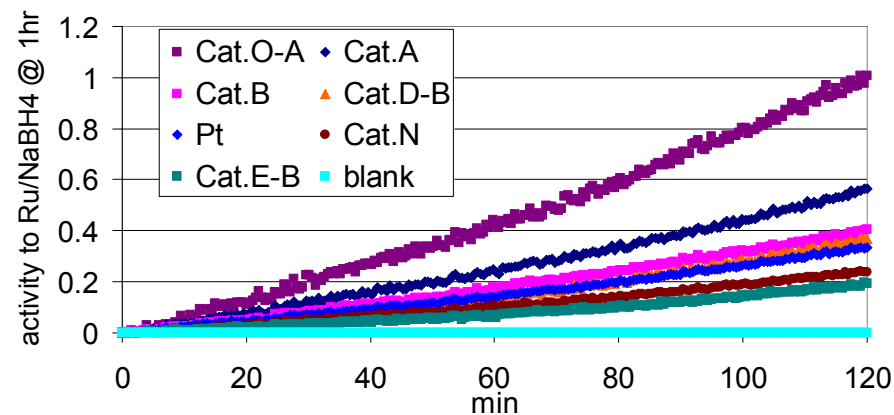
Rapid Screening for Boron-Based Storage

Accomplishments

- Screened hundreds of combinatorial compositions for catalytic H_2 generation via NH_3BH_3 dehydrogenation
 - » Found a several compositions with catalytic activity
- Screened a hundred combinatorial compositions for catalytic H_2 generation via NH_3BH_3 hydrolysis
 - » Found a few low-cost compositions with catalytic activity on par with than Ruthenium/ $NaBH_4$ systems
- Screened a hundred combinatorial compositions for catalytic H_2 generation via polyhedral borane hydrolysis
 - » Found little activity under neutral aqueous conditions



AB Dehydrogenation



AB Hydrolysis

Safety Analysis and Applied Research on the Use of Borane-Amines for Hydrogen Storage

- **Objectives**

- Safety analysis of amine-borane compounds and dissemination of this information throughout the Chemical Hydrogen Storage Center.
- Evaluation of hydrogen on-board generation and off-board regeneration capability and capacity of N-substituted amine-borane compounds to determine if a system can be developed that safely meets the DOE 2010 target of 6-wt% hydrogen.

- **Approach**

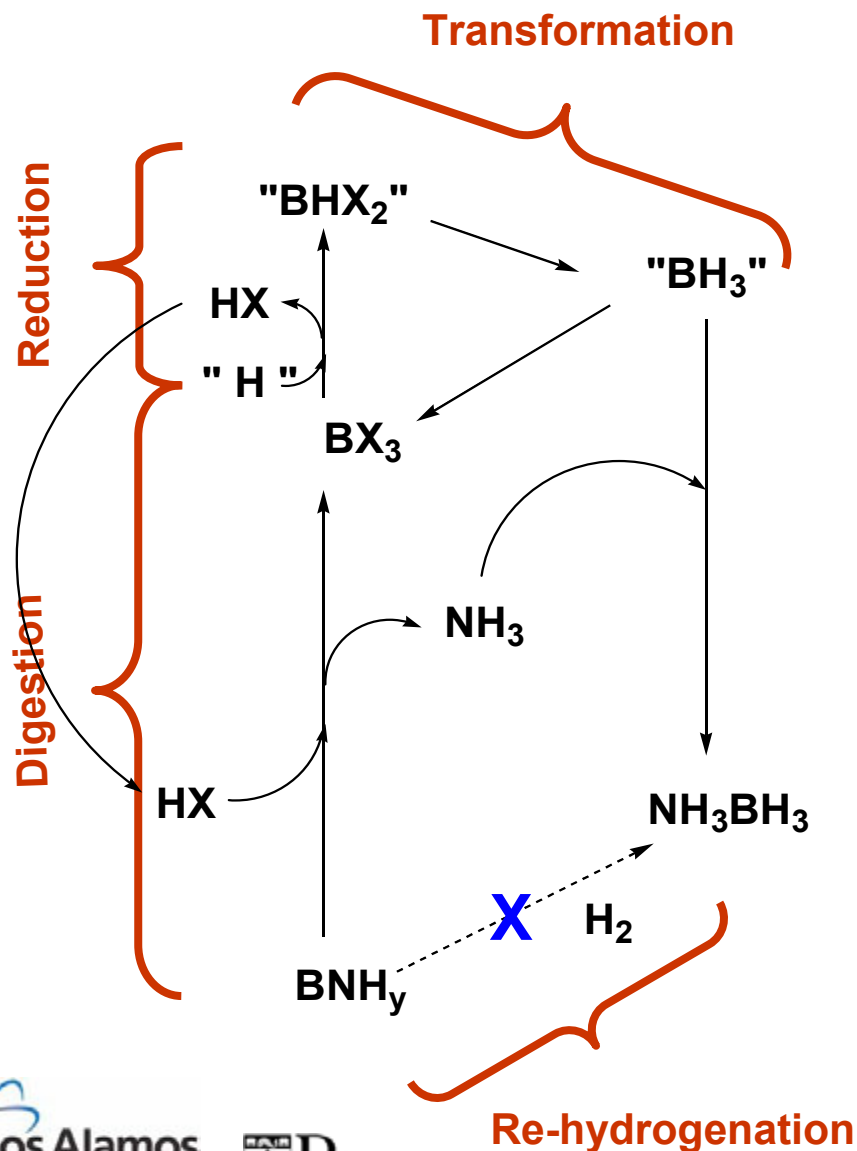
- Literature searching for preparation, physical properties, chemical properties and safety aspects of amine-borane adducts and related N-B-H compounds.
- Collection of Material Safety Data Sheets and technical information from manufacturers of amine-borane compounds and borazine.
- Anecdotal observations from organizations and research groups currently or formerly active in amine-borane chemistry.

- **Accomplishments**

- All the information collected about amine-borane compounds has now been compiled in a document entitled:

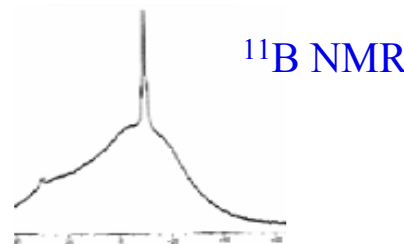
Ammonia-Borane and Related N-B-H
Compounds and Materials: Safety Aspects,
Properties and Applications

Toward Regeneration of Ammonia Borane



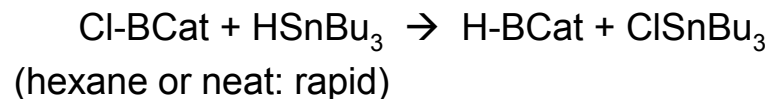
Penn

- Digestion with CF₃CO₂H
- Reduction of BX₃/BX₄⁻ with AlH₃NH(CH₃)₂ to regenerate amine-borane

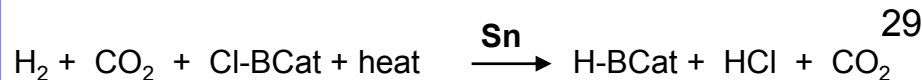
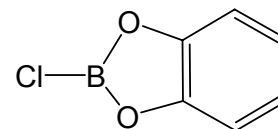
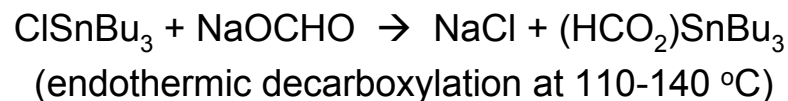


LANL

- Demonstrated reduction of Cl-BCat



- Metal-hydride regeneration



Non-Boron Hydrogen Storage Concepts under Study

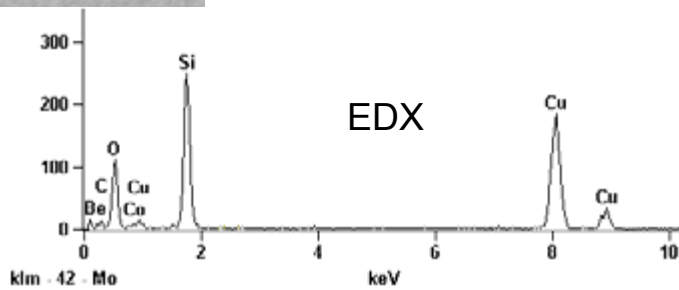
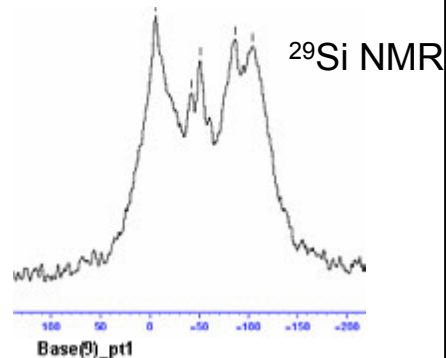
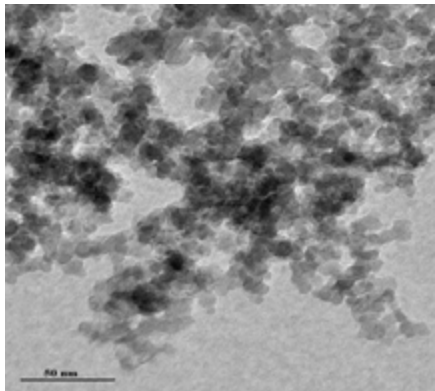
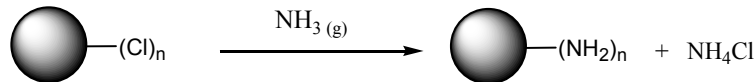
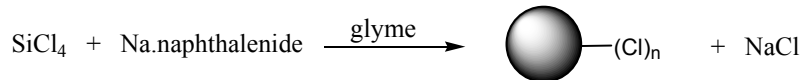
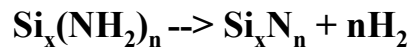
Project	Partners
Heteroatom-substituted organics	Alabama, PNNL, LANL
Coupled reactions	LANL
Nanoscale materials	UC Davis, Intematix, LANL
Main-group hydrides	UC Davis, Alabama, PNNL

Objectives

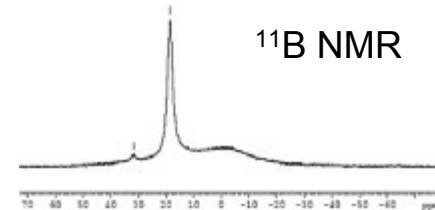
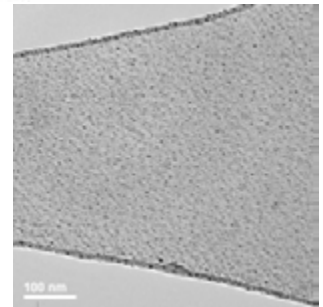
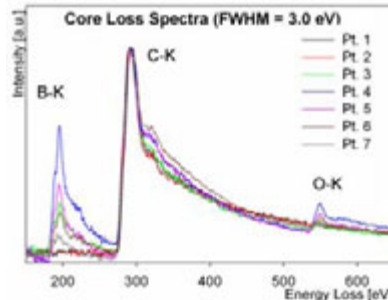
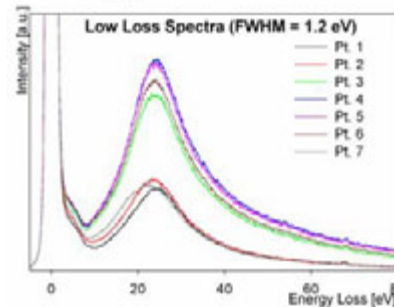
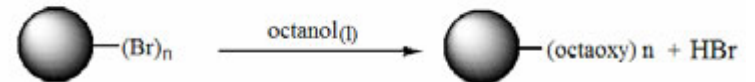
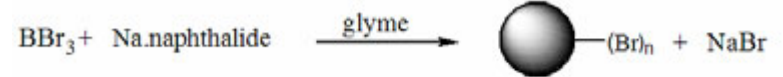
- Develop new concepts for hydrogen generation
- Control and tune thermodynamics and kinetics
- Synthesize and characterize new materials
- Calculate thermochemistry for promising concepts
- Use high-throughput catalyst discovery, materials development
- Redirect work based on developments, discovery
- Engineering assessment of promising results

Nanoscale Materials

- **Objective**
 - Assess potential for hydrogen storage of main group element clusters of Si, B, Al, and alloys
 - Design synthetic routes using mild conditions to provide commercially viable materials
 - Characterize materials and measure hydrogen uptake
- **Accomplishments**
 - Room temperature synthesis of amide-capped silicon nanoparticles
 - Solution and solid-state synthesis of nanocrystalline silicon with hydrogen
 - First synthesis of organo-capped boron nanoparticles
 - Synthesis of molecular compounds by addition of hydrogen across a multiply-bonded system



Boron Nanoparticles



Organic-Based Materials for Hydrogen Storage

BACKGROUND

- Organic compounds contain considerable hydrogen
- Offer potential advantages as storage materials
- Hydrogen release from most C-H bonds occurs endothermically at elevated temperature

OBJECTIVE

- Identify compounds and chemical reactions that release H₂ from organic materials with near thermoneutrality at ambient temperature

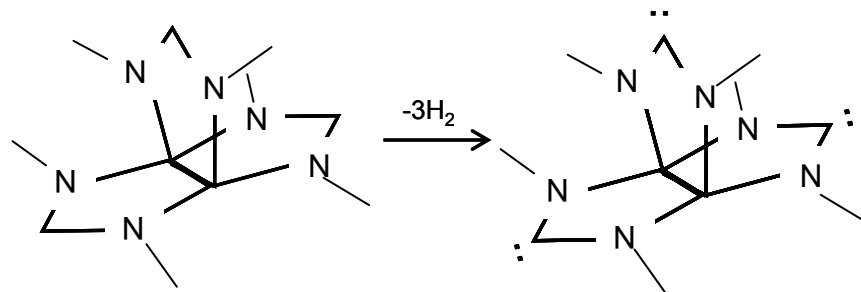
APPROACH

- Use heteroatom substitution to lower the enthalpy of H₂ release
 - 1,1-Elimination to form heteroatom stabilized carbenes
 - Dihydrobenzimidazoles act as “organic hydrides,” with acids
 - Exothermic release of H₂
- Use simultaneous or tandem “coupled reactions” to balance an endothermic H₂ release with an exothermic reaction step

1,1-Elimination for Hydrogen Storage: Increasing Capacity

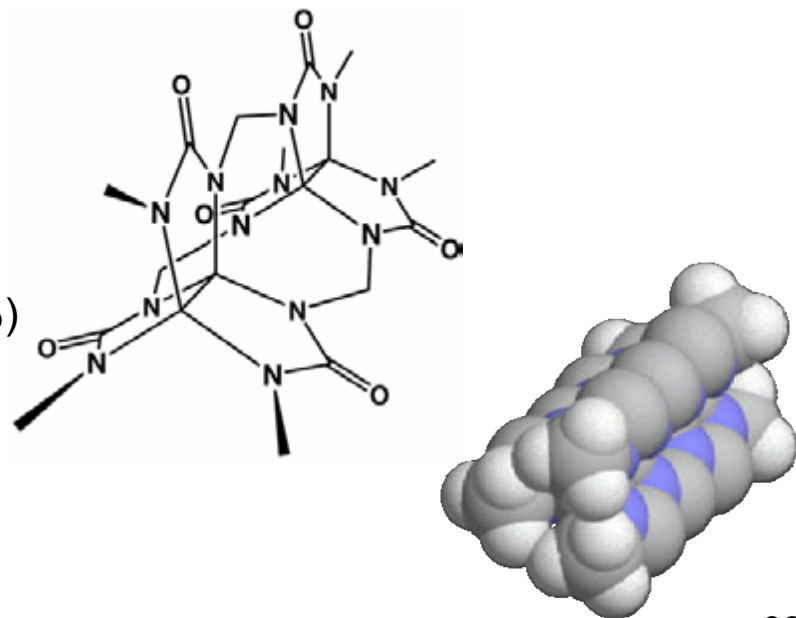
Developed new chemistry concept to increase capacity

- Fusing 3 dihydroimidazole rings into “propellane” structure:
- Lightest possible material is $C_5H_{12}N_6$, forming $C_5H_6N_6 + 3 H_2$ (3.9 wt %)
- Reaction currently under study for N-substituted analogs



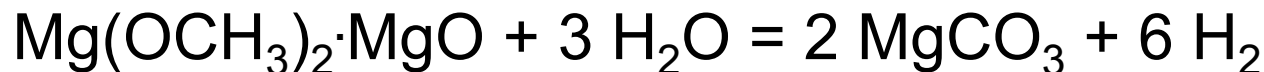
Ultimate goal:

- Lateral condensation with $-CH_2-$ links gives material $C_8H_{12}N_6$, forming $C_8N_6 + 6 H_2$ (6.3 wt %)
- Routes to such materials under study: one possible precursor is the urea compound
- Designed poly-carbene product

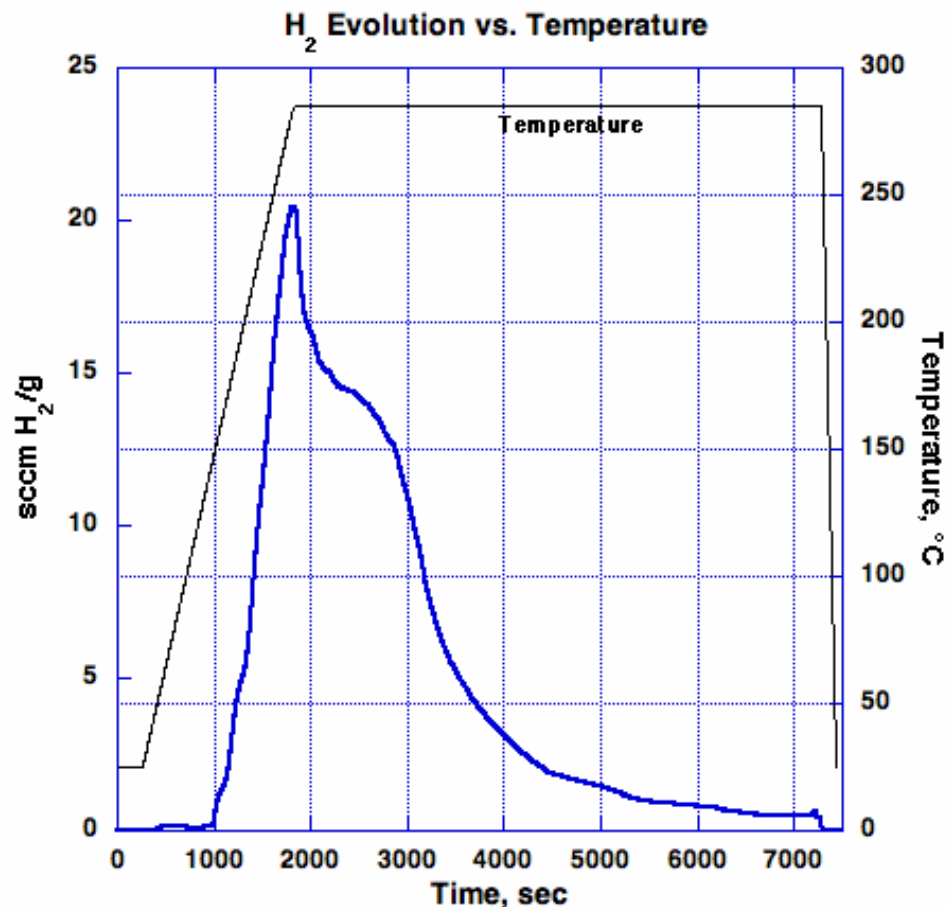


Results: Coupled Reactions

- Developed $\text{Mg}(\text{OCH}_3)_2 \cdot \text{MgO}$ -catalyst composites

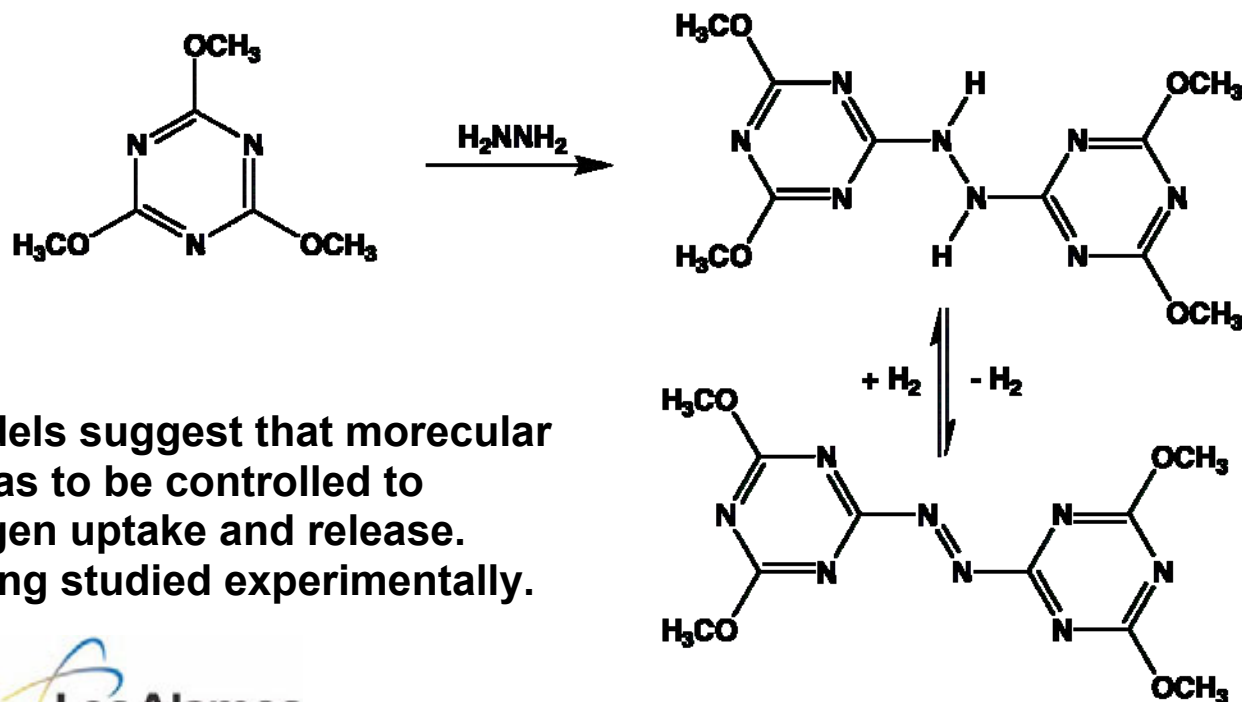
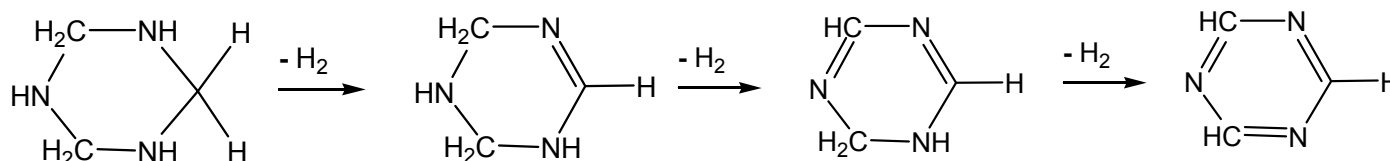


- Theoretical composite material capacity = 6.7 wt%
- > 0.09 kg/ H_2 /L w/o water
- Demonstrated yield to date:
 - 4.4 wt% H_2
 - 46% of theoretical
- Demonstrated H_2 release rate: 20 sccm/g at 260 °C
- At this release rate, 600 g would provide 0.02 g H_2 /sec



Future Work on Organic Systems

- A goal: dehydrogenation of hexahydrotriazine (6.9 wt% H₂)



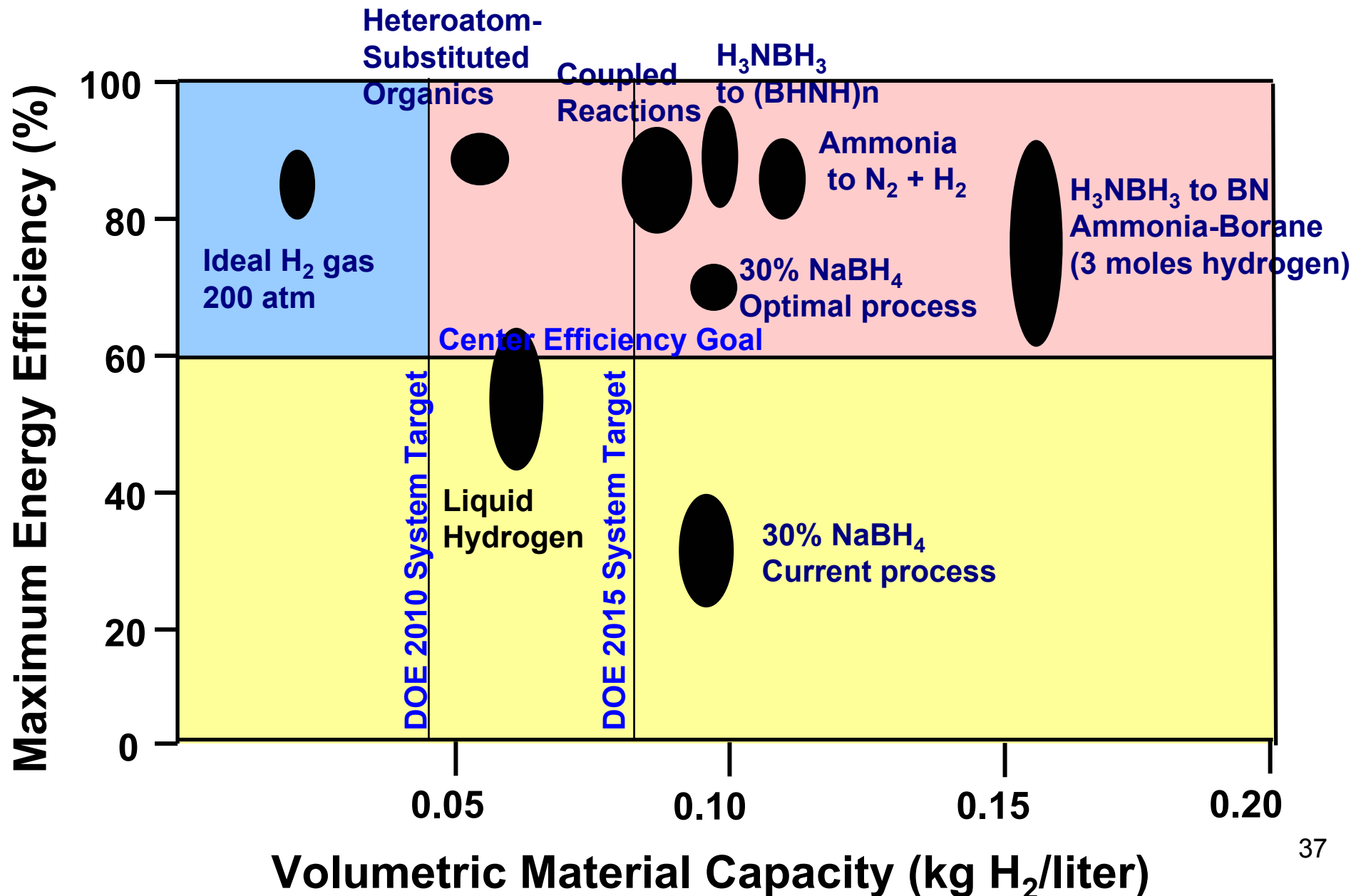
Theoretical models suggest that molecular re-orientation has to be controlled to manage hydrogen uptake and release. The issue is being studied experimentally.

Summary

- Collaborative project-based approach is leading to advances on a number of fronts
 - A number of options are being pursued
 - Energetics and reaction pathways being understood
 - On the path to understand what is possible for B-OH to B-H
 - Catalysts discovered for polyhedral borane hydrolysis
 - A number of dehydrogenation concepts being developed for amine-boranes
 - Regeneration concepts for ammonia-borane being developed
 - Heteroatom organic compounds appear to be promising
 - Benefits from nanophase materials under study
- Engineering assessment tools being developed and engineering analysis in progress
 - On-board reactor concepts using lessons learned from NaBH_4
 - Flowsheeting
 - LCI

Theory ↔ *Experiment* ↔ *Assessment*

Chemical Hydrogen Storage



Center Path Forward

- **Go/no-go on sodium borohydride (FY07)**
 - Determine feasibility and provide a go/no-go recommendation for Sodium Borohydride (SBH) hydrolysis on-board storage system based on modeling and laboratory-scale experimental demonstration of energy efficient regeneration off-board.
 - Criteria development
 - Center milestones by quarter
- **Ammonia-borane**
 - Increase rates for AB dehydrogenation
 - Enhance spent AB regeneration scheme
- **Optimization and evaluation of other boron-containing systems**
- **Coordinated effort on non-boron organic system**
- **Exploratory research on other options**
- **Prepare for down-selection of storage material**
 - Criteria development

FY07 Milestones

- **FY07 Milestones:**

- Complete assessment of the most energy-efficient routes for indirect regeneration of sodium borate to sodium borohydride (complexed borates)
- Down-select catalysts and chemical processes (2-3 candidates max) for hydrogen generation from ammonia-borane
- Down-select to organic materials and polyhedral boranes (3-5 candidates max) along with associated processes for hydrogen generation
- Down-select from chemical hydrogen regeneration processes for sodium borohydride.
- Complete assessment of ammonia borane regeneration routes to assist in down selection process
- Complete assessment of nanoparticles for hydrogen storage capacity
- Complete assessment for regeneration of organics and polyhedral boranes to assist in down-selection process

- **Go/No Go Decision on Sodium Borohydride (4QFY07)**

Center Partners

- **Penn: Prof. Larry Sneddon**
 - Martin Bluhm (PD), Prof. Mark Bradley, William Ewing (GS)
- **UCLA: Prof. Fred Hawthorne**
 - Satish Jalisetgi (PD), Bhaskar Ramachandran (PD), Robert Kojima (GS), Thomas Quickel (GS), Colin Carver (GS)
- **Penn State: Prof. Digby Macdonald**
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- **Alabama: Profs. Dave Dixon, A. Arduengo**
 - Owen Webster, Monica Vasiliu, Luigi Iconaru, Michael Phillips, Daniel Grant (GS), Jacob Batson (UGS), Myrna Hernandez Matus (PD), Prof. Minh Nguyen
- **UW: Profs. Karen Goldberg, Mike Heinekey**
 - Melanie Denney (PD), Vincent Pons (PD)
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 - Japhe Raucher (GS), Li Yan Wang (PD)
- **NAU: Prof. Clint Lane**
- **Rohm and Haas: Sue Linehan**
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- **Intematix: Xiao-Dong Xiang**
 - Wei Shan, Jonathan Melman
- **US Borax: Dave Schubert**
 - Jonathan Owen
- **PNNL: Chris Aardahl**
 - Tom Autrey, Maciej Gutowski, Anna Gutowska, John Linehan, Scot Rassat, Wendy Shaw, Ashley Stowe, Mike Thompson
- **LANL:**
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