Center of Excellence for Chemical Hydrogen Storage

William Tumas

Los Alamos National Laboratory

May 24, 2005

Project ID # ST11

Overview

Timeline

Project Start Date: FY05
Project End Date: FY09
New Start

Budget

Total project funding (requested)

- $ 29.9 M DOE share
- $ 3.34 M Cost share

Funding for FY05: $ 3.9 M (DOE)
$ 425K (Cost share)

Barriers Addressed

Cost
Weight and volume
Energy efficiency
System life-cycle assessment
Spent material removal
Regeneration processes
Heat removal

Chemical Hydrogen Storage Center

National Laboratories

- Los Alamos, Pacific Northwest

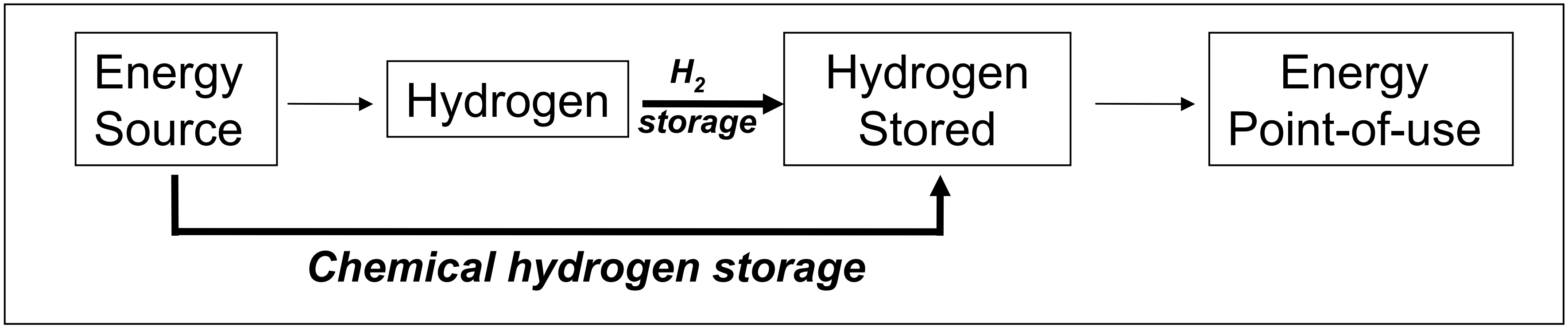
Universities

- Pennsylvania State University
- University of California at Davis
- Northern Arizona University
- University of Pennsylvania
- University of California at Los Angeles
- University of Washington
- University of Alabama

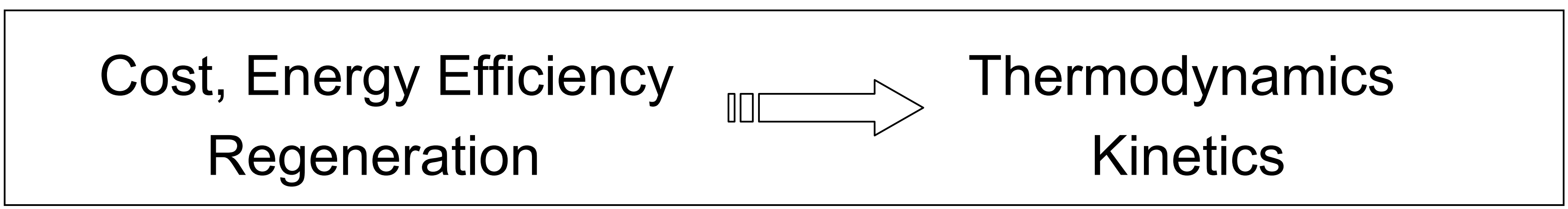
Companies

- Rohm and Haas
- Millennium Cell
- Intematix
- U.S. Borax

Overview: Chemical Hydrogen Storage

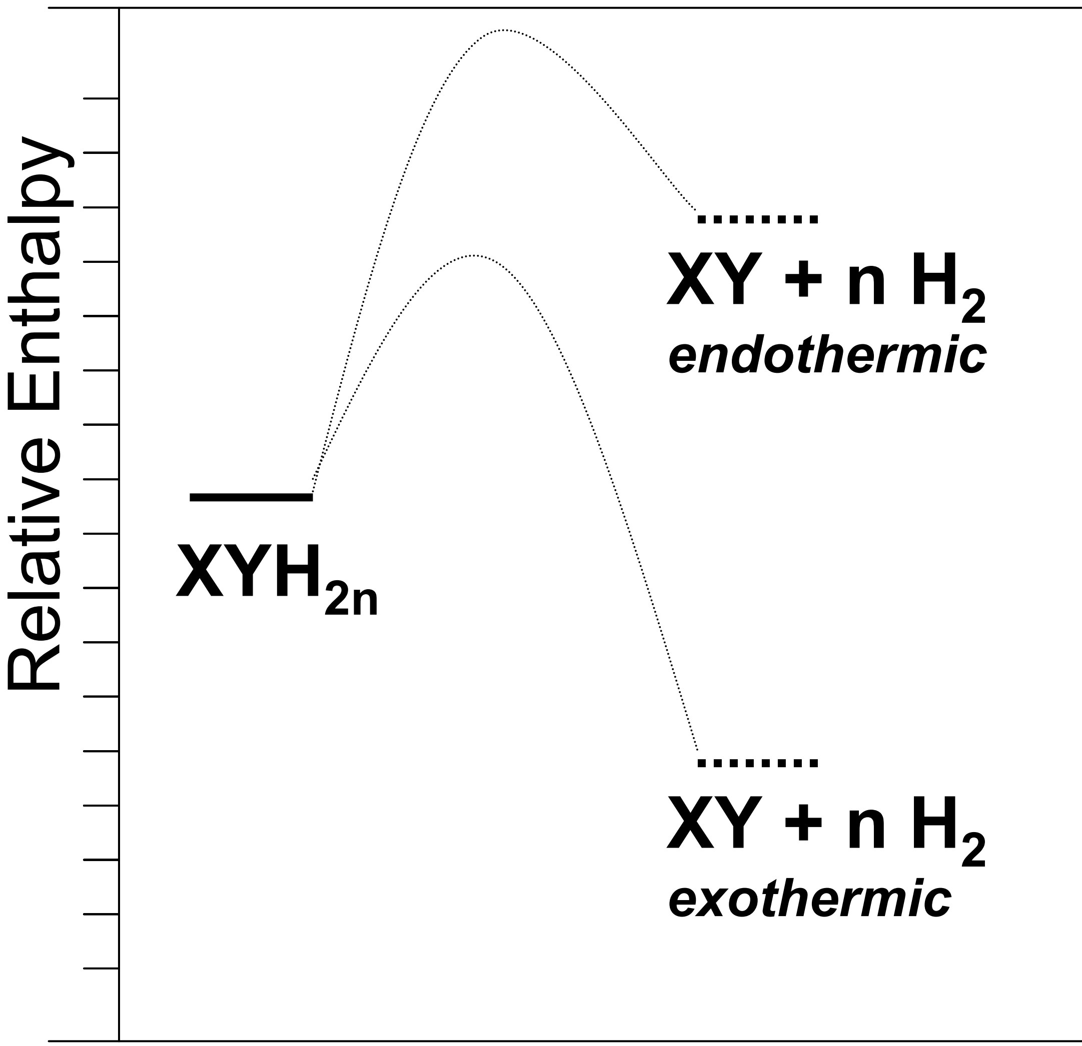


- Attractive Features:
  - Liquid or solid fuel infrastructure
  - Potential for no H_2 handling by consumer
  - Diversity of options
  - Off-board or on-board regeneration

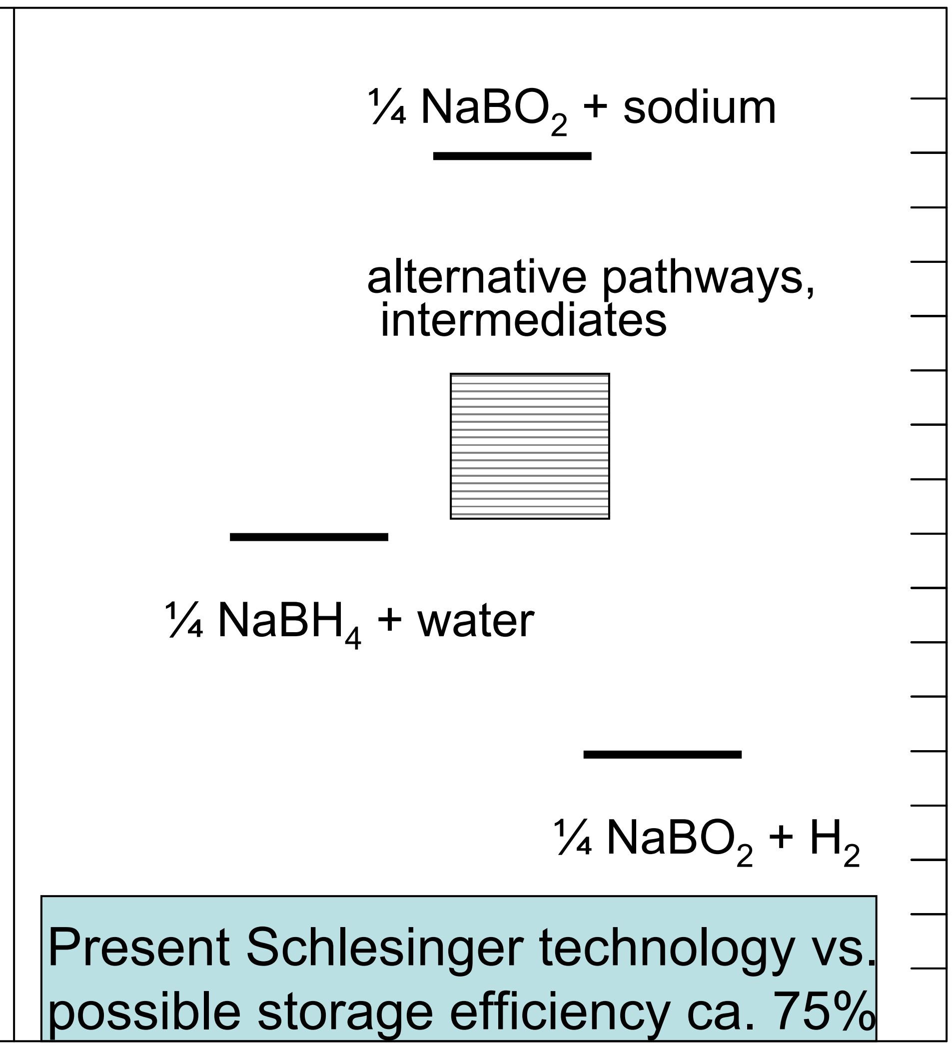


Chemical Hydrogen Storage and Regeneration

Thermodynamics & Kinetics



Example: $NaBH_4$



Chemical Hydrogen Storage

It's the right combination of a material and a reaction

Hydrolysis:	Dehydrogenation:
$XH_n + n\ H_2O = n\ H_2 + X(OH)_n$ (e.g. $NaBH_4$, LiH)	$H_nX\text{---}YH_n =\ n\ H_2 + XY$ (e.g. decalin -> naphthalene)
Dehydrocoupling: $XH_n + YH_n = n\ H_2 + XY$ (e.g. $NH_3 + BH_3$)	… and families of reactions yet to be developed

Each reaction family has numerous opportunities

Center Objectives

- Identify, research, develop and validate the best chemical hydrogen storage systems to overcome technical barriers and meet 2010 DOE goals
- Develop materials, catalysts, catalytic processes, and new concepts for hydrogen release and regeneration
- Design, synthesis, and testing of structures/compositions to control thermochemistry of H_2 release and spent fuel regeneration
- Engineering assessment for H_2 release and regeneration
- Engineering scale studies to assess performance in hydrogen delivery systems
- Life cycle inventory to assess regeneration energy requirements
- Demonstration of a 1 kg storage system

Center Approach

- Capitalize on a broad spectrum of expertise
  - Engineering, manufacturing
  - Computation and modeling
  - Chemical and materials synthesis and characterization
  - Mechanisms, electrochemistry, analysis
  - Catalyst discovery, high throughput screening
  - Safety analysis
  - Systems engineering
- Support synergistic, integrated effort
  - "Fail fast:" identify early what will not work
  - "Engineering guided research:" identify what is worth making work
  - Core capabilities in computation, experimental facilities and engineering analysis
  - IP agreement: Promote vetting ideas and cooperative R&D, reward success

Three Tier Structure of Center

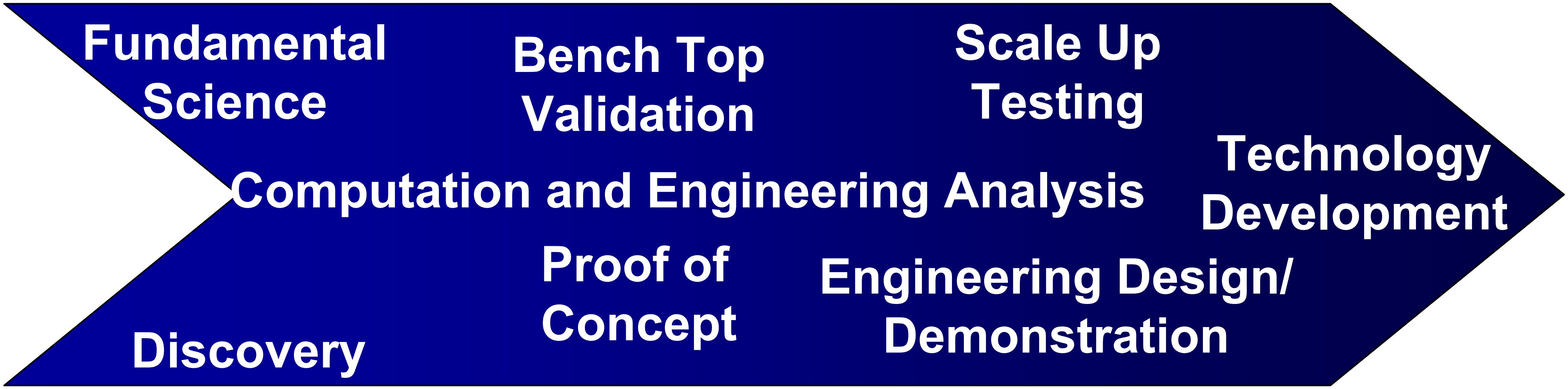
- Tier I:
  - Develop borate-to-borohydride (BO to BH) regeneration alternatives and assess economics and life cycle analysis of borohydride/water to hydrogen
    - Millennium Cell, Rohm and Haas, Penn State, Alabama, PNNL, LANL
- Tier II:
  - Avoid water and thermodynamic sinks. Alternative boron chemistry approaches include polyhedral boranes (B_xH_y), amine-boranes and BCNP chemistry
    - Penn, Penn State, UCLA, Washington, Northern Arizona, Alabama, Intematix, PNNL, LANL
- Tier III:
  - Beyond boron:
    - Develop concepts for coupled endo/exothermic reactions, Investigate nanomaterials
    - Use heteroatom substitution for thermodynamic control
    - UC Davis, Alabama, Intematix, PNNL, LANL

Center Core Capabilities

- Computation (PNNL, Alabama)
  - Access to Molecular Scale Computational Facility for theoretical studies through Grand Challenge grant award
  - Access to high performance codes
  - Access to collaborative staff to help center partners with theoretical needs
- Engineering assessment (Rohm and Haas, PNNL)
  - Industrial engineering assessment on new concepts and results
  - Pre-research engineering guidance
  - Foster relationship between Center partners and the standards testing lab being established at Southwest Research Inst.
- Complex instrumentation (PNNL, LANL)
  - Access to user facilities at LANL & PNNL
  - Developing measurement protocols for thermodynamics and kinetics
  - Specialized characterization of materials (thermochemistry, NMR, spectroscopy, etc.)
- IP management (IP Management Committee)
- Safety (PNNL, LANL, Northern Arizona)
- Center coordination, meetings, technical planning (LANL)

Tier	Project	Partners
1	**Tier 1: Borohydride**	
1.1	BO-> BH Engineering Guided R&D	ROH, MCEL, USB, PSU, Ala, PNNL, LANL
1.2	Engin. assessment for H2 generation systems	PNNL, MCEL, ROH
2	**Tier 2: Novel Boron Chemistry**	
2.1	Polyhedral Borane: Hydrolysis/Aminolysis	UCLA, IMX, PNNL, LANL
2.2	Polyhedral Borane Electrochemistry	PSU, UCLA, Ala, PNNL, LANL
2.3	Amine-Borane Dehydrogenation/Hydrogenation	Penn, NAU, PNNL, LANL
2.4	Amine-Borane: Mechanistic work	UW, PNNL, LANL
2.5	Amine-Borane: Scaffolds	PNNL
2.6	AB H2-gen systems engin. assessment, safety	PNNL, NAU
3	**Tier 3: Innovation Beyond Boron**	
3.1	Coupled reactions	LANL
3.2	Organics	Ala, PNNL, LANL
3.3	Nanoparticles	UC Davis, LANL
3.4	Main group hydrides	UC Davis, PNNL, LANL

Center Integration



Computational assessment of approaches (energetics)
Experimental and catalytic studies on high capacity storage systems
Catalyst development
State-of-the-art experimental techniques
Life cycle assessment, systems engineering
Demonstration

Technical Accomplishments and Future Work

- New Start FY05
- A number of preliminary results
  - See posters of all Center partners
  - Some preliminary results presented in talk
- Work plan developed for all Center projects
  - Collaborative projects launched
  - Several collaborative project meetings already held
    - Tier 1, Tier 2
  - Objectives and milestones developed

Tier 1: Borohydride

Project	Partners
B-O to B-H (Engineering Guided Research)	ROH, PSU, MCEL, PNNL, USB, Ala, LANL
Engineering Analysis for Hydrogen Generation Systems	ROH, MCEL, PNNL

Objectives

- Data mining of prior work, including proprietary information
  - From Rohm & Haas, US Borax, Millennium Cell, Redstone Arsenal
  - Share information on past studies and analytical characterization
- Investigate electrochemical methods for borate reduction
  - Mechanisms, electrodes and electrocatalysts, complexants
- Develop concepts for borate complexation and reduction
- Engineering assessment of findings and concepts
  - Define equipment requirements
  - Energy and economic analysis
- Engineering analysis for H_2 generation systems (liquids and solids)

Electrochemical Reduction of Borates
($BO_2^- + 6H_2O + 8e^- \rightarrow BH_4^- + 8OH^-$)

Los Alamos National Laboratory (1943 - 2003) — *Ideas That Change the World*

- Advanced electrode preparation
- Alternative reaction media

Rohm and Haas

- Engineering analysis
- Positive results from past studies (aqueous systems)
- Advise/direct experimental program

B-O to B-H

Penn State (1855)

- Fundamental insight
- Mechanistic studies
- Advanced analytical development

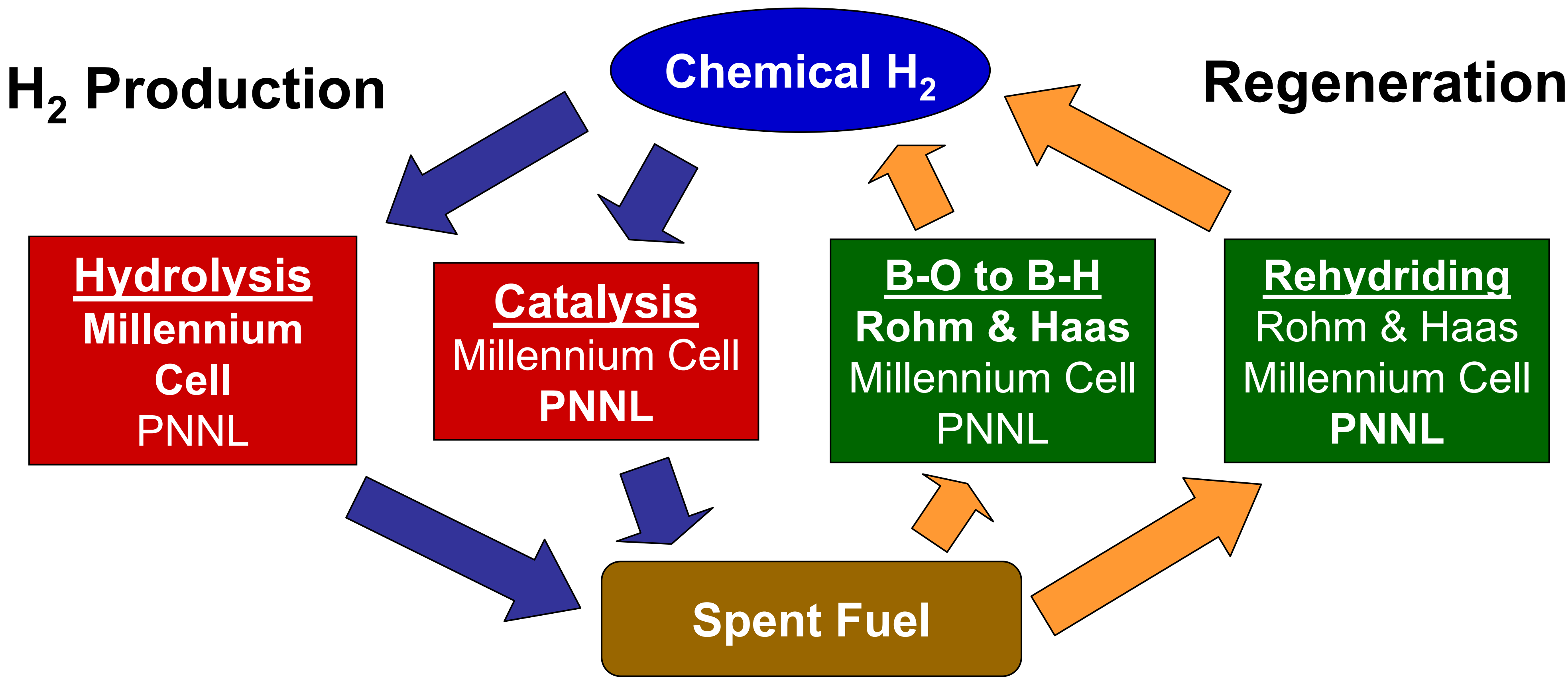
Millennium Cell

- Past experience with aqueous and non-aqueous systems

ROH, PSU, MCEL, LANL Posters

Engineering & Analysis Activities

- Regeneration of the fuel likely off-board
- Engineering aspects of the work are divided into two pieces: production & regeneration



PNNL, MCEL, ROH Posters

Tier 1: First Year Milestones

- Establishment of economic and engineering criteria (ROH, PNNL, LANL)
- Data mining on B-O to B-H with assessment of preliminary candidates; Report in Year 2 (ROH, MCEL, USB, PNNL, LANL)
- Initiation of technical evaluation of process engineering for borate reduction (ROH, MCEL)
- Experimental survey of complex borates started (LANL, PNNL, USB, ROH)
- Computational results for B-O to B-H energetics including complexed borates (Ala)
- Development of analytical and electrochemical methods for B-O to B-H (PSU, LANL)
- Reactor system analysis for liquids and solids (PNNL, MCEL)

Tier 2: New Boron Chemistry

Project	Partners
Polyhedral borane (PHB): hydrolysis/aminolysis	UCLA, Intematix, PNNL, LANL
PHB Electrochemistry	UCLA, PSU, Ala, LANL
Amine-Borane (AB) Dehydrogenation/Hydrogenation	Penn, NAU, PNNL, LANL
AB Mechanistic Work	UW, PNNL, LANL
AB Scaffolds	PNNL
AB H2 Gen Eng Analysis; Safety	PNNL, NAU

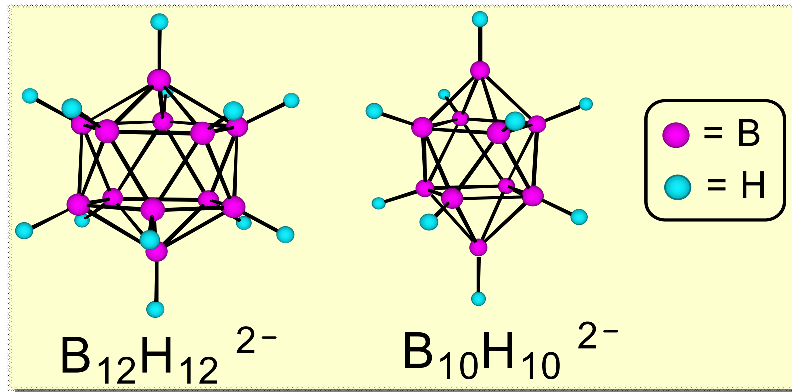
Objectives

- Investigate high capacity hydrogen storage systems for:
  - controlled hydrogen release
  - energy efficient regeneration
  - compatibility with fuel cells
- Initial targets are polyhedral boranes and amine-boranes

Polyhedral Boranes

Polyhedral boranes are more stable than borohydride and multiple electron sources

Objective: Optimize catalysts for hydrolysis of polyhedral borane anions using rapid throughput heterogeneous catalyst synthesis and testing



$$Na_2B_{10}H_{10} \bullet 16H_2O \rightarrow 2\ NaBO_2 + 4\ B_2O_3 + 21\ H_2$$

Material storage capacity 9.4 wt% hydrogen (including water)

Future Work:

Thermodynamics, theory and calorimetry

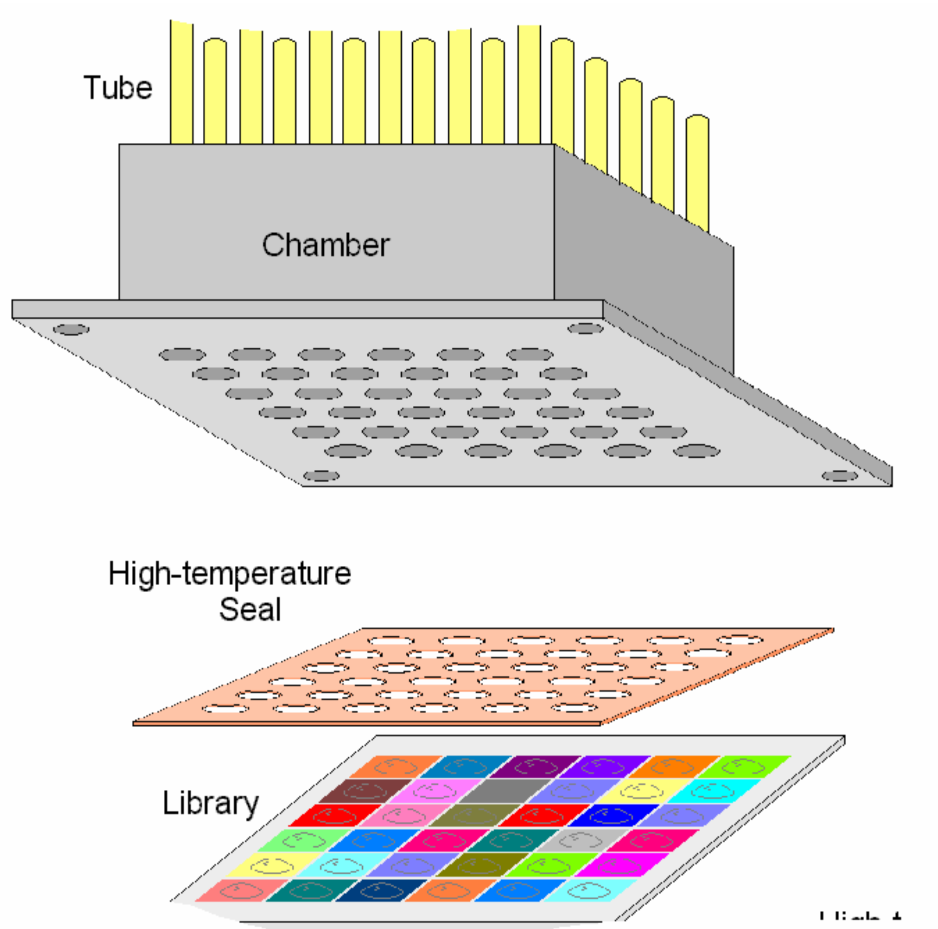
Other H_2 generation routes

- Aminolysis
- Electrochemistry

New regeneration routes from borate

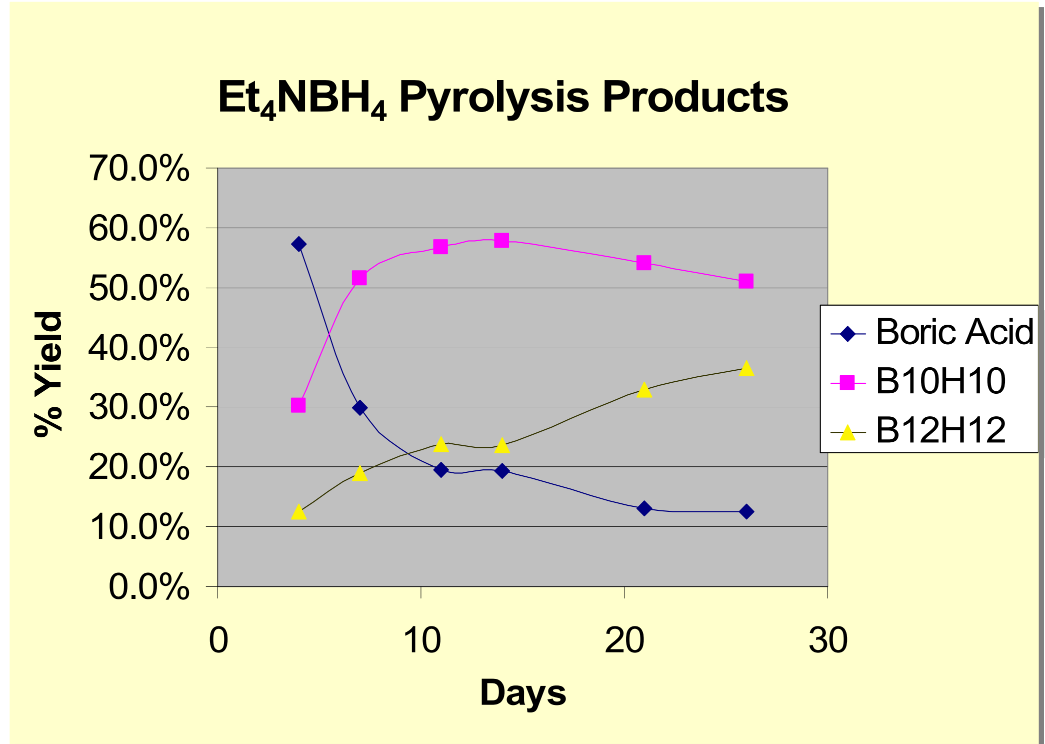
UCLA, Intematix, PNNL, LANL Posters

Rapid Throughput Catalyst Synthesis and Testing



Intematix poster

Production/Regeneration of Polyhedral Boranes



- Selective synthesis of $B_nH_n^{2-}$

UCLA Poster

Amine-Borane Dehydrogenation/Regeneration

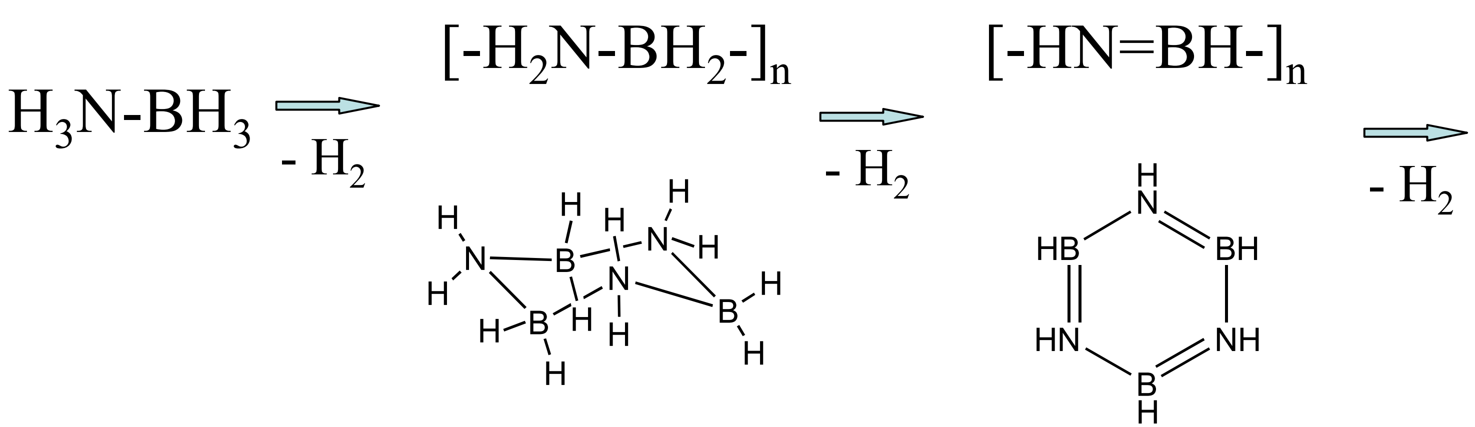
$NH_4BH_4 \longrightarrow BN + 4\ H_2$ (24.5% H_2)

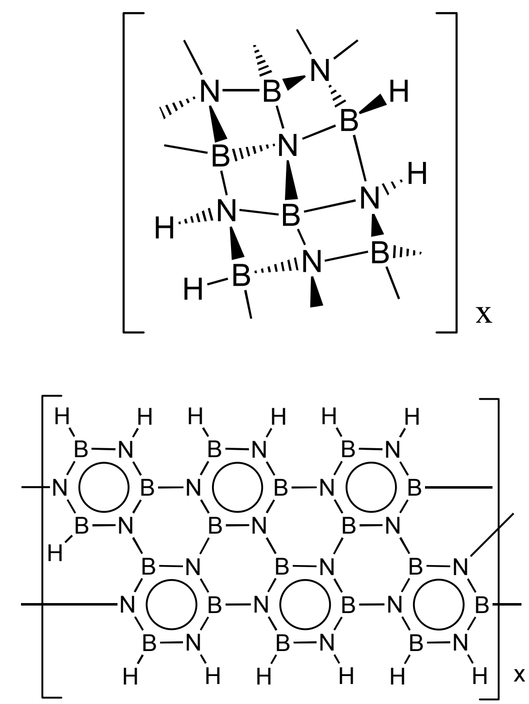
$NH_3BH_3 \longrightarrow BN + 3\ H_2$ (19.6% H_2)

$B_3N_3H_{12} \longrightarrow 3\ BN + 6\ H_2$ (14% H_2)

$B_3N_3H_6 \longrightarrow 3\ BN + 3\ H_2$ (7.5% H_2)

$NH_3B_3H_7 \longrightarrow B_3N + 5\ H_2$ (17.8% H_2)





Penn, NAU, Ala, UW, PNNL, LANL Posters

AB Dehydrogenation/Regeneration

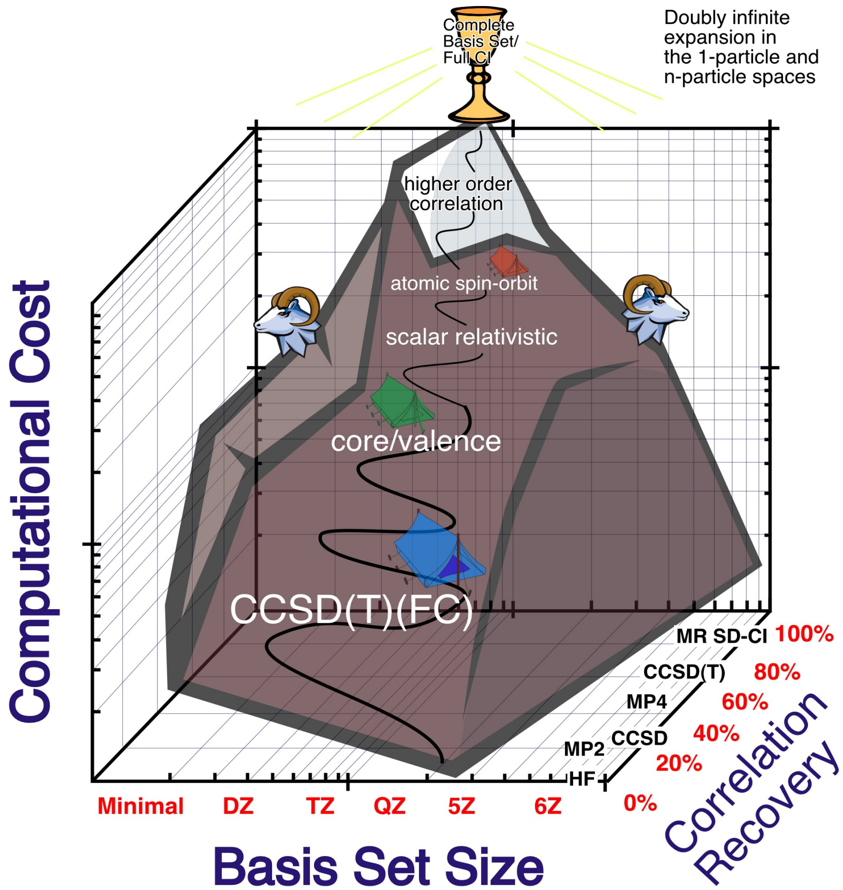
Objective:

- Achieve controlled release of hydrogen from amine-boranes to products that can be efficiently regenerated

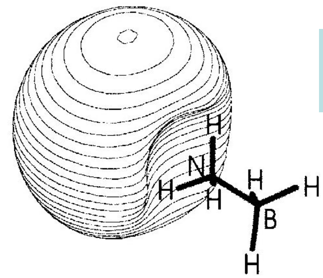
Approaches:

- Kinetics and mechanistic studies to understand amine-borane dehydropolymerization
- Computational guidance on thermochemistry, medium effects
- Catalyst development to control kinetics and selectivity
  - homogeneous, heterogeneous catalysts
- Medium and substituent effects
  - scaffold effects, alternative reaction media
- Properties and safety data
- Engineering systems analysis

Theory and Computation



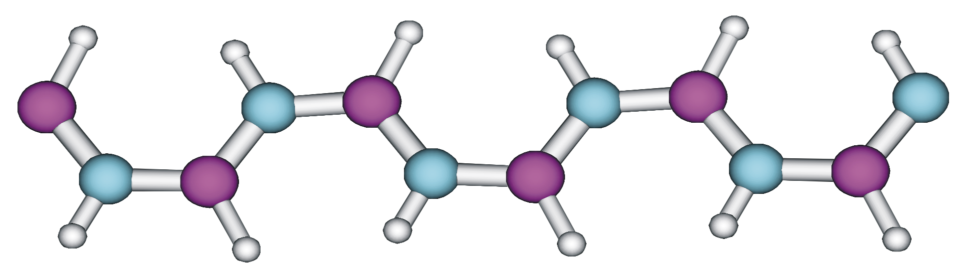
Calculate accurate molecular heats of formation (±1 kcal/mol) by ab initio molecular orbital theory



Alabama, PNNL Posters

Results (Solids)

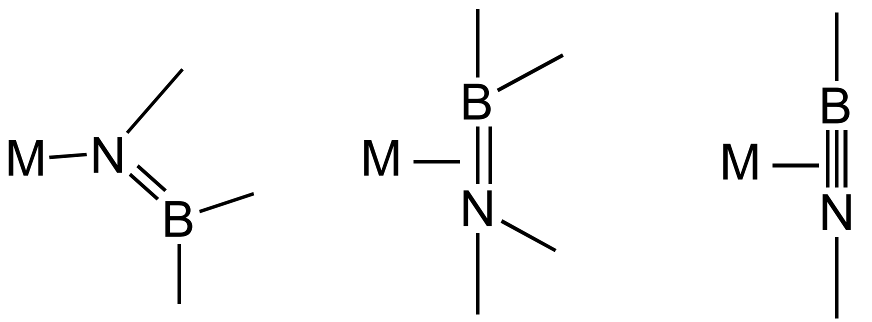
- $H_3B \leftarrow :NH_3$ Electron donor-acceptor bond
  - Large dipole moment of 5.3 D
  - The $H_3B\text{-}NH_3$ bond energy is 25 kcal/mol
- $NH_2BH_2 \rightarrow NHBH + H_2$; $\Delta H = -3$ kcal/mol
- $NHBH \rightarrow BN + H_2$; $\Delta H = -9$ kcal/mol
- Undoped NH_2BH_2 and NHBH are insulators

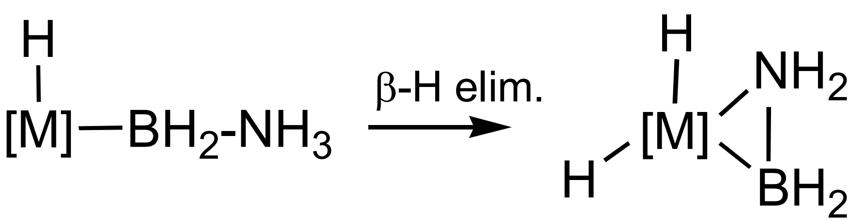


Computational Design of Materials for Hydrogen Storage
- 900,000 node-hours per year for 3 years

Amine-Borane R&D

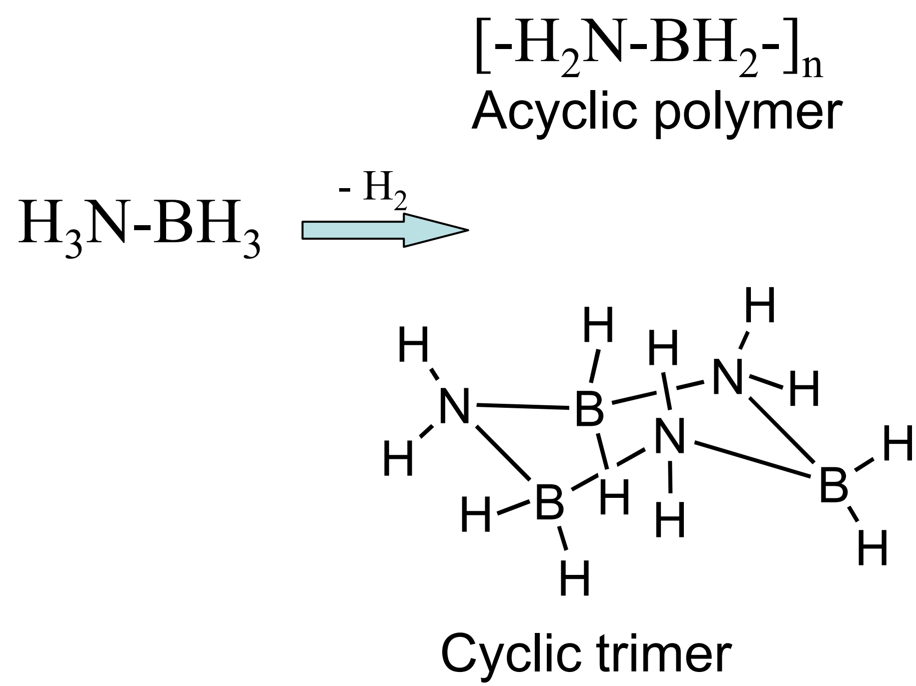
Mechanisms for AB Dehydrogenation





UW, PNNL, LANL Posters

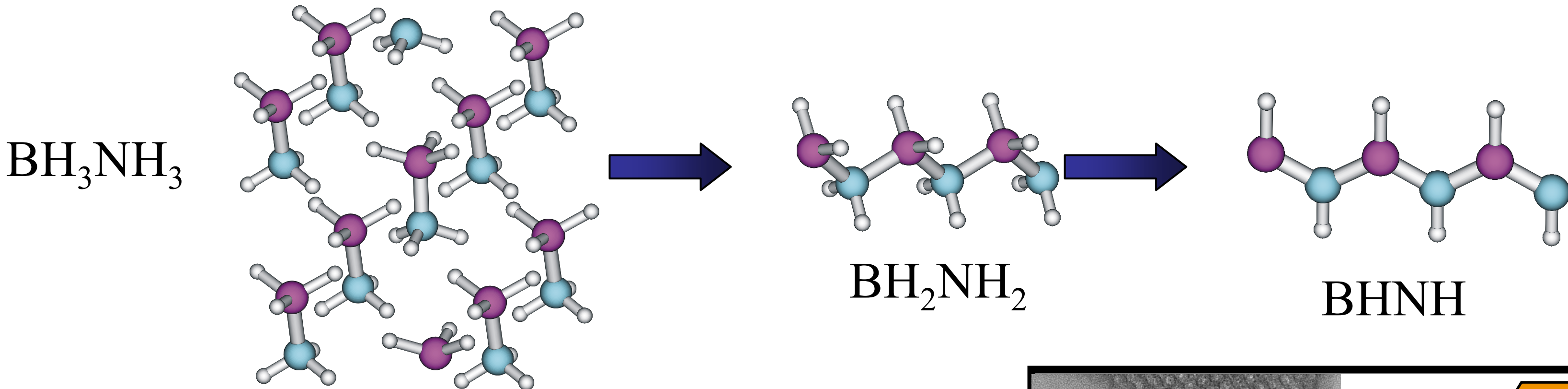
Catalyst Development Kinetics/ Selectivity

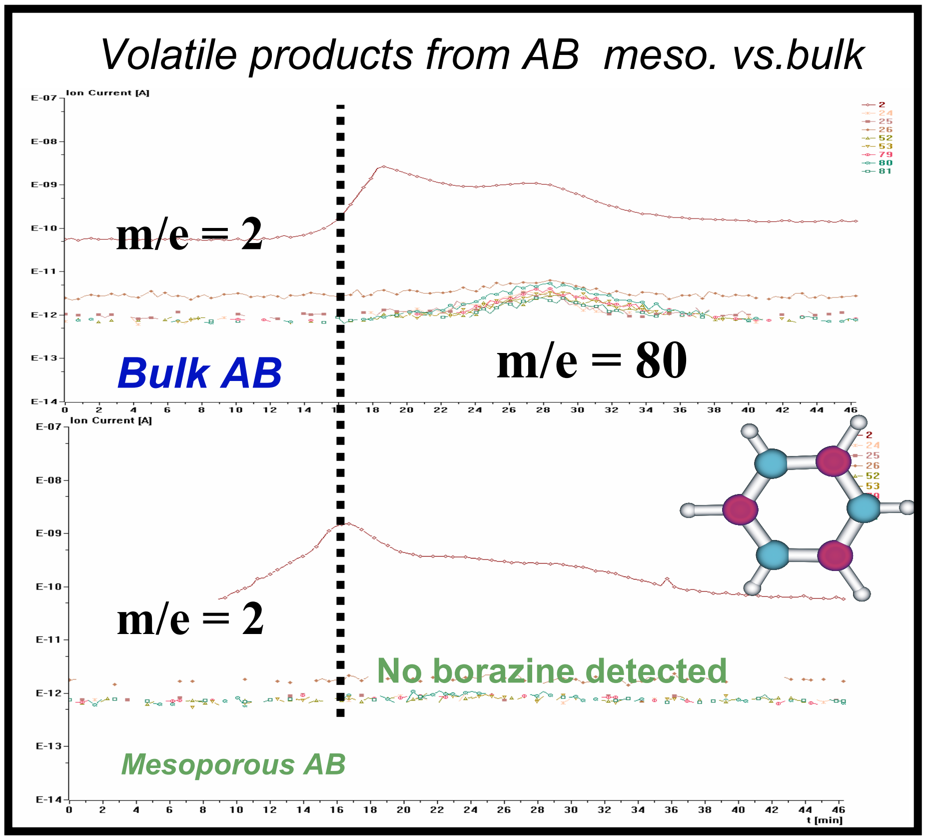


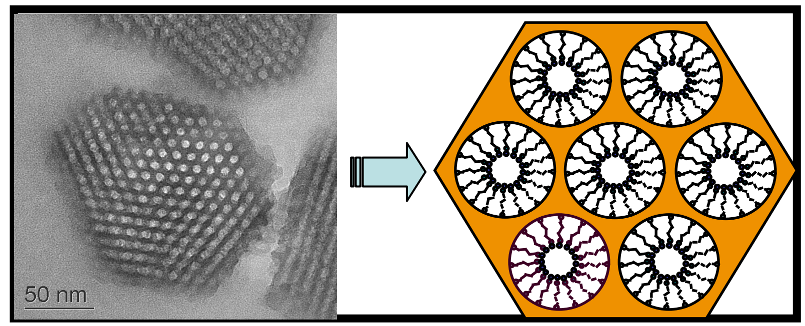
- New proprietary catalysts developed

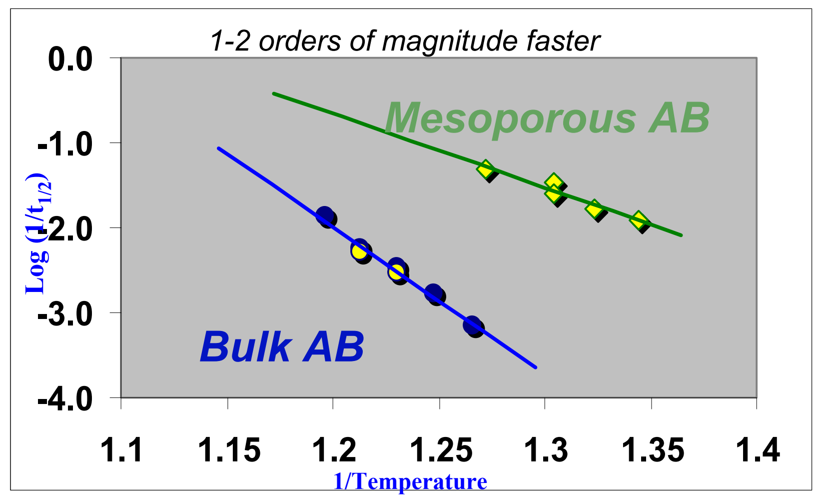
Penn, NAU, PNNL, LANL Posters

NH_xBH_x in Mesoporous Oxide Scaffolds





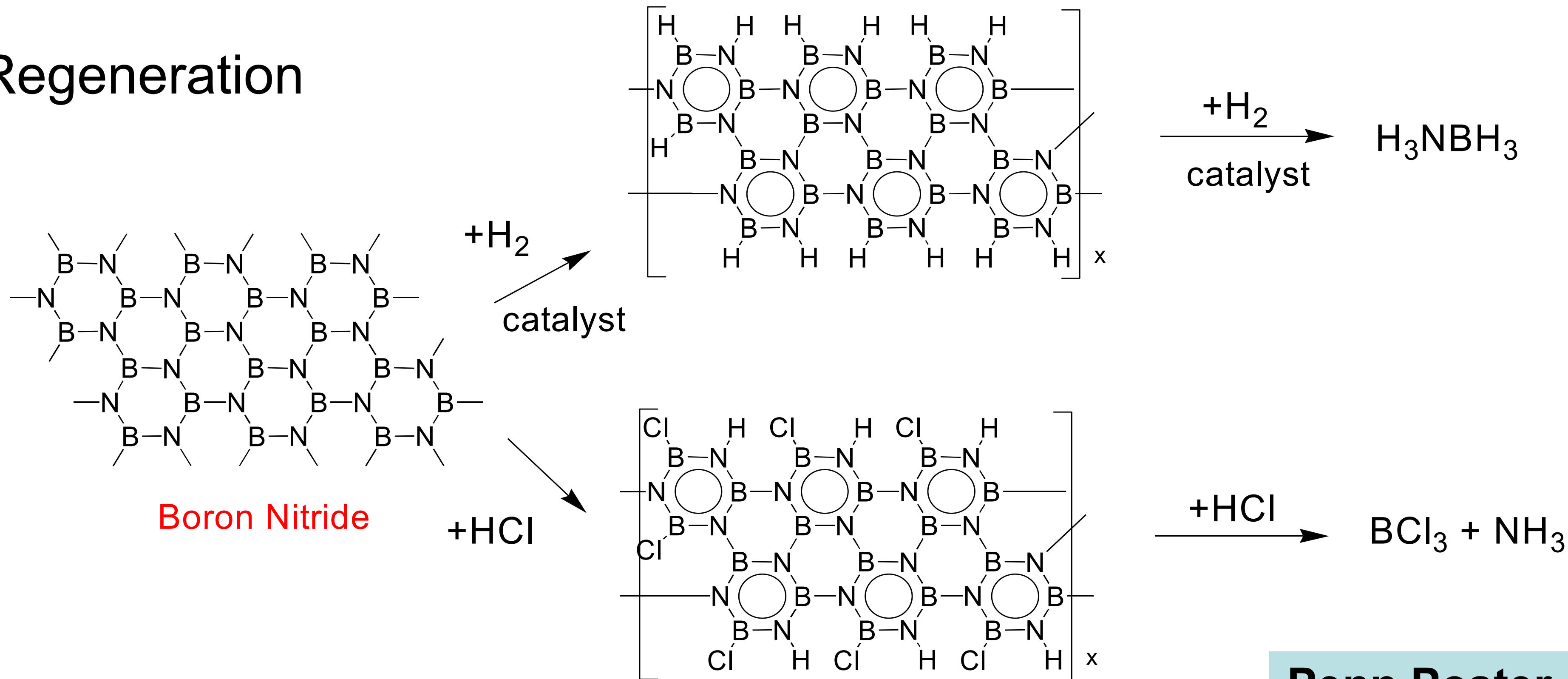




PNNL Poster

Amine-Borane R&D

Regeneration



Penn Poster

Safety

- Safe handling of amine-borane compounds
- Safety guidance for chemical hydrogen storage center
- Preparation, solubility, stability and hydrogen evolution from substituted amineborane compounds

NAU Poster

Tier 2: First Year Milestones

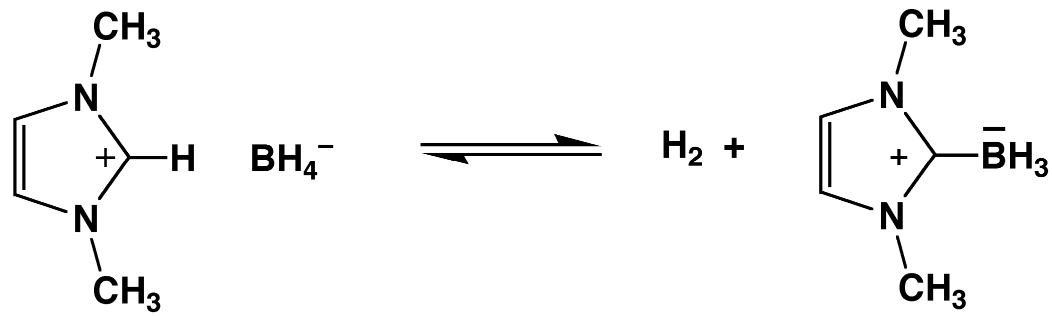
- Synthesis of quantities of complex boranes (UCLA)
- Catalyst development for complex borane hydrolysis (UCLA, LANL, IMX)
- Preliminary demonstration of electrochemical transformations in the B-H systems and oxidation state changes (PSU, LANL, UCLA)
- Screening of homogeneous and nanocatalysts for amine borane dehydrogenation (PNNL, LANL, Penn)
- Screening of haloacid reactivity with BN oligomer/polymer (Penn)
- Model studies of BN compounds with transition metals (UW)
- Safety data and properties of amine boranes (NAU)
- Computation of thermochemistry for BN compounds and intermediates (Ala)
- Amine borane and intermediate characterization within scaffolds (PNNL)

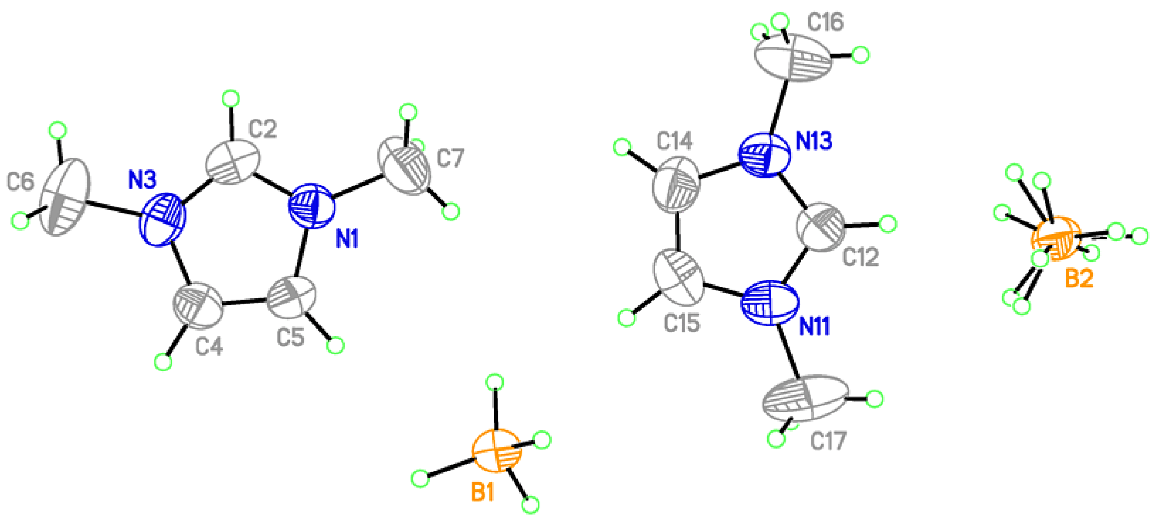
Tier 3: Beyond Boron

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

Imidazolium Borohydride



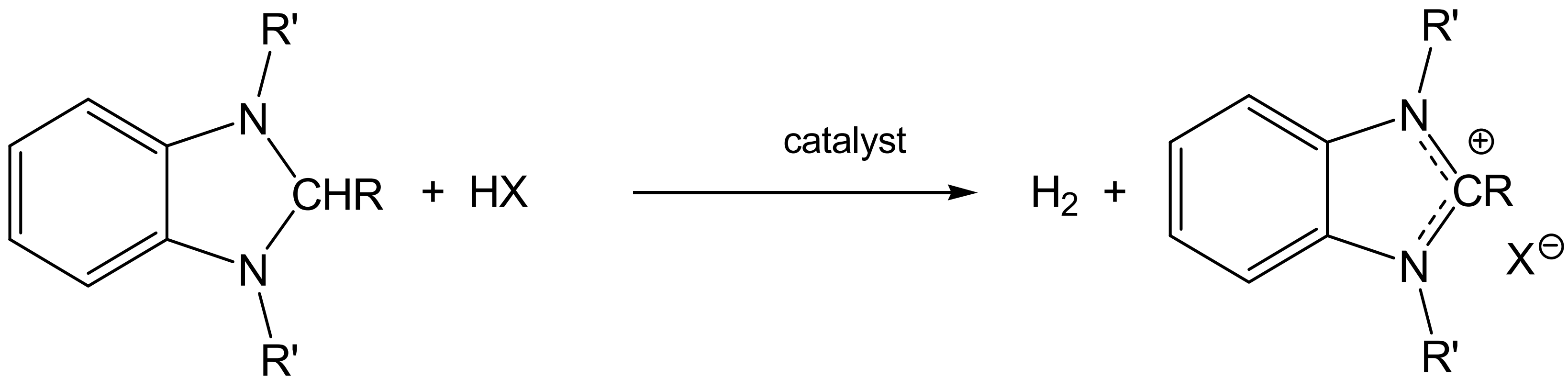


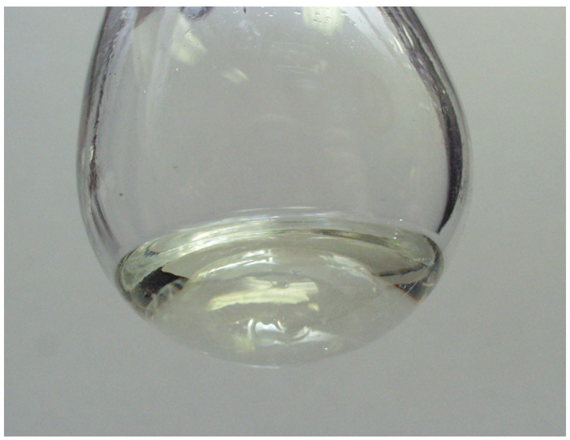
The first X-ray structure of an imidazolium borohydride was determined.

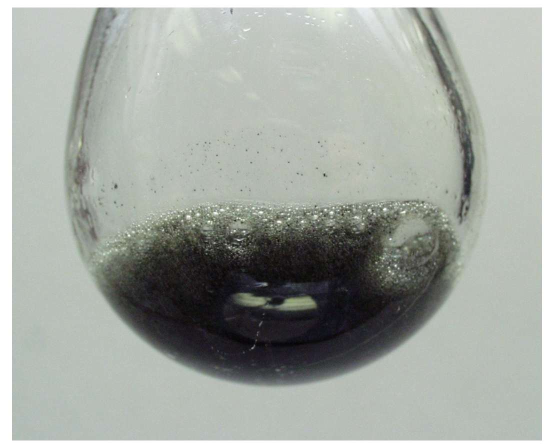
Structure shows interactions between hydrogen at C-2, C-4 and the borohydride and evidence for an H-H "hydrogen bond"

Alabama Poster

Exergonic H_2 Evolution at Ambient Temperature: A Chemical Hydride







- Demonstration of judicious heteroatom substitution
- Future work to focus on
  - Improving wt% H_2 in related and other systems
  - Increasing rate of H_2 evolution
  - Regeneration

Tier 3

- Coupled Reactions
  - Couple reactions in such a way that endothermic H_2 evolution can be driven by exothermic co-reaction
    - {Organic substrate} + H_2O + {inorganic component} $\longrightarrow$ H_2 + {recyclable coproduct}
    - LANL-proprietary concepts, with hypothetical H_2 capacity > 6 wt% (> 0.09 kg H_2/liter)
    - Proof of concept, patent filing

- Main-group compounds
  - Hydrogen-active E=E bonds
  - Heterosubstituted organic compounds

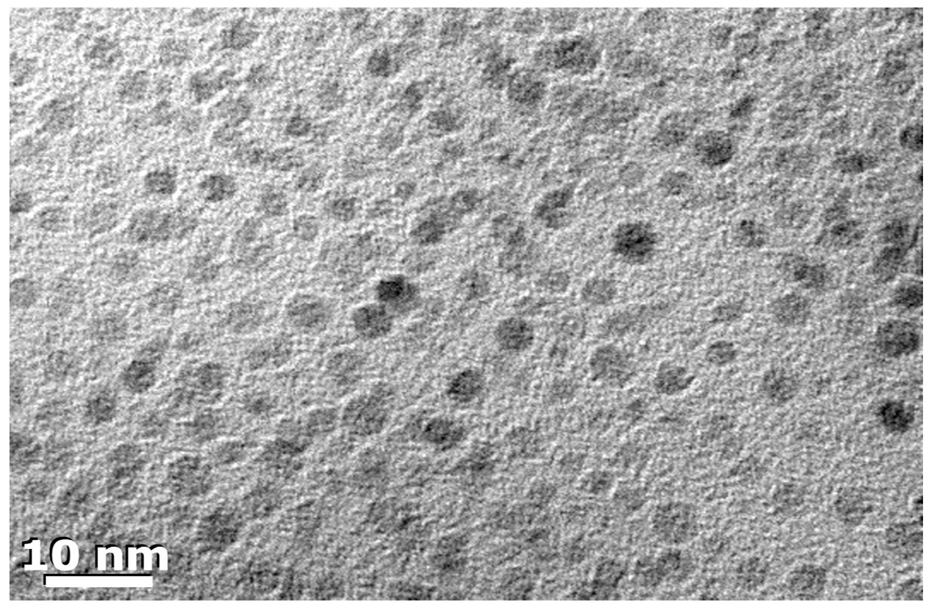
LANL, PNNL, UC Davis, Ala Posters

Nanoscale Materials

- Realize the potential to store and release hydrogen
  - Doped-B, Si nanoparticles by solution core-shell synthesis
  - Metal-based nanoparticles by gas-solid synthesis
  - Targets: 1-2 nm particles, compositions
    - $M_{1.0}H_{1.0}$, $M_{1.0}(NH_2)_{1.0}$, $M_{1-x}M'_xH_{1.0}$, $M_{1-x}M'_x(NH_2)_{1.0}$

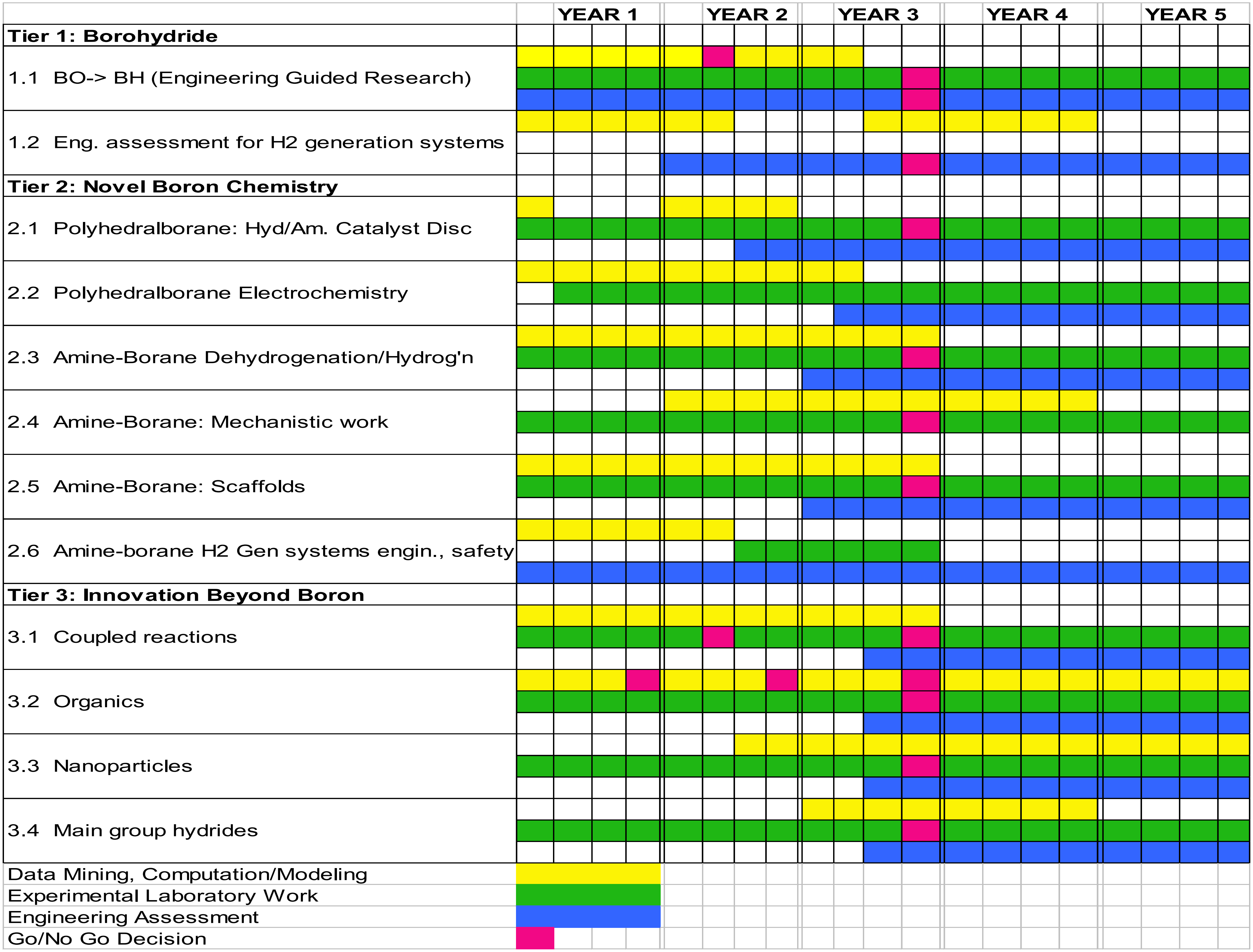
      (M, M' = B, Al, Si, C)
  - Establish ability to hydrogenate, dehydrogenate

Capped Si nanoparticles obtained by oxidation of Mg_2Si



Tier 3: First Year Milestones

- Proof of concept of coupled reaction and patent filing (LANL)
- B_xH_yN and NH_z-capped Si nanoparticle synthesis and characterization (UC Davis, LANL)
- Computation of thermochemistry for heteroatom-containing organic structures (Ala)
- Computation of thermochemistry for imidazolium complexes (Ala)
- At least one storage candidate containing heteroatoms (LANL)
- C-N oligomer synthesis and characterization (Ala)
- Main-group compound synthesis (UC Davis)


YEAR 1
YEAR 2
YEAR 3
YEAR 4
YEAR 5
Tier 1: Borohydride
1.1 BO-> BH (Engineering Guided Research)
1.2 Eng. assessment for H2 generation systems
Tier 2: Novel Boron Chemistry
2.1 Polyhedralborane: Hyd/Am. Catalyst Disc
2.2 Polyhedralborane Electrochemistry
2.3 Amine-Borane Dehydrogenation/Hydrog'n
2.4 Amine-Borane: Mechanistic work
2.5 Amine-Borane: Scaffolds
2.6 Amine-borane H2 Gen systems engin., safety
Tier 3: Innovation Beyond Boron
3.1 Coupled reactions
3.2 Organics
3.3 Nanoparticles
3.4 Main group hydrides
Data Mining, Computation/Modeling
Experimental Laboratory Work
Engineering Assessment
Go/No Go Decision

Center Project 1.1: B-O to B-H
(ROH, MCEL, Alabama, PSU, PNNL, LANL)

TASK	Year 1	Year 2	Year 3	Year 4	Year 5
Data mining	Goals, criteria established; options documented				
Engineering Guided Reduction R&D	Identification of leading options	✦			
		Leading options development			
			Design data		
Computation of Energetics	Energetics of intermediates; reaction pathways				
Electrochemical Mechanistic Work	Borate and complexed borates		✦		
				Pathways detailed	
Electrode/Catalyst Development	Laboratory-scale experimental work				
				Optimization	
Complexation and Reduction of Borate	Solution chemistry, stoich. rxns		✦	thermochemistry, mechanisms	
Engineering Assessment		Assessment of exptl results			
				Eng. design	

✦ **Go/No Decision Point**

Center Coordination

- Objectives
  - Real collaboration and information sharing within Tiers
  - Collaborative project structure
  - Share background information
  - Foster joint discovery/inventions
  - Reward and manage success
- Status
  - Joint development projects (Center projects) defined
  - Framework for IP management developed
    - **Defines management of joint inventions**
    - **Enables technology transfer**
  - Website developed
  - Center project meetings, conference calls
  - Frequent center-wide electronic communication

Chemical Hydrogen Storage CoE

- Penn: Prof. Larry Sneddon
  - Martin Bluhm (PD), Prof. Mark Bradley, William Ewing (GS)
- UCLA: Prof. Fred Hawthorne
  - Satish Jalisatgi (PD), Bhaskar Ramachandran (PD), Robert Kojima (GS), Thomas Quickel (GS), Colin Carver (GS)
- Penn State: Prof. Digby Macdonald
  - Justin Tokash (GS), Jason McLafferty (GS), Yancheng Zhang (PD)
- 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)
- UC Davis: Profs. Susan Kauzlarich, Phil Power
  - Japhe Raucher (GS), Li Yan Wang (PD)
- NAU: Prof. Clint Lane

Chemical Hydrogen Storage CoE

- Rohm and Haas: Sue Linehan
  - Frank Lipiecki, Arthur Chin, John Yamamoto, Leo Klawiter,, James Vouros,, Sam November, Aaron Sarafinas, Alan Keiter, Wendy Bingaman Jay Soh, and Robert Wilczynski; Larry Guilbault and Duane Mazur (consultants)
- Millennium Cell: Ying Wu
  - Jeffrey Orgeta, Robert Molter, Rick Mohring, Todd Randal, Roxanne Spencer
- Intematix: Xiao-Dong Xiang
  - Wei Shan, Jonathan Belman
- US Borax: Dave Schubert
  - Jonathan Owen
- PNNL: Chris Aardahl
  - Chris Aardahl, Tom Autrey, Maciej Gutowski, Anna Gutowska, John Linehan, Scot Rassat, Wendy Shaw, Ashley Stowe, Mike Thompson
- LANL: Bill Tumas
  - R. Thomas Baker, Anthony Burrell, Fernando Garzon, P. Jeffrey Hay, Neil Henson, Kevin John, Karl Jonietz, Richard Keaton (PD) , Dan Kelly, Kevin Ott, Bobbi Roop, Dan Schwarz (PD), Frances Stephens (PD), David Thorn