

# **Center of Excellence for Chemical Hydrogen Storage**

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Project ID #  
STP60

This presentation does not contain any proprietary or confidential information

[Chemical Hydrogen Storage Center](#)

# 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

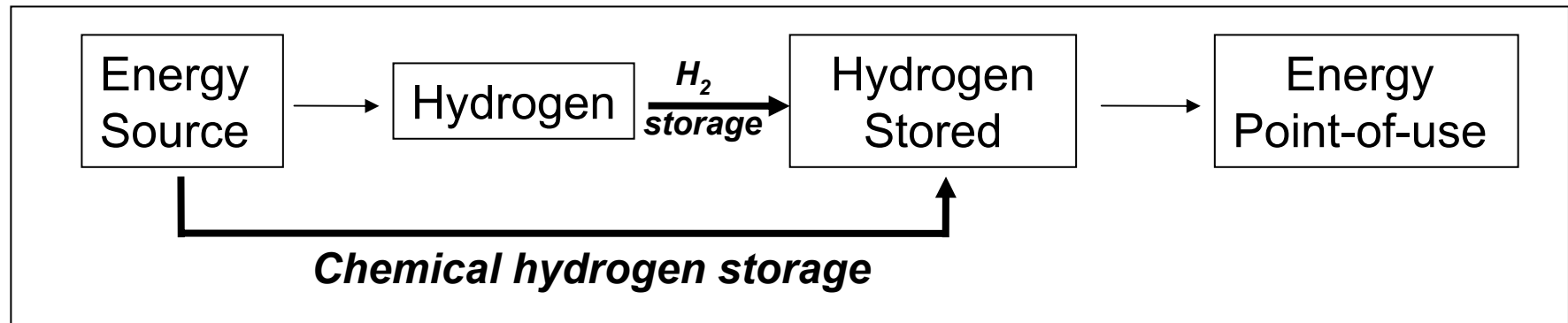
Pennsylvania State University  
University of California at Davis  
Northern Arizona University  
University of Pennsylvania  
University of California at Los Angeles  
University of Washington  
University of Alabama

## Companies

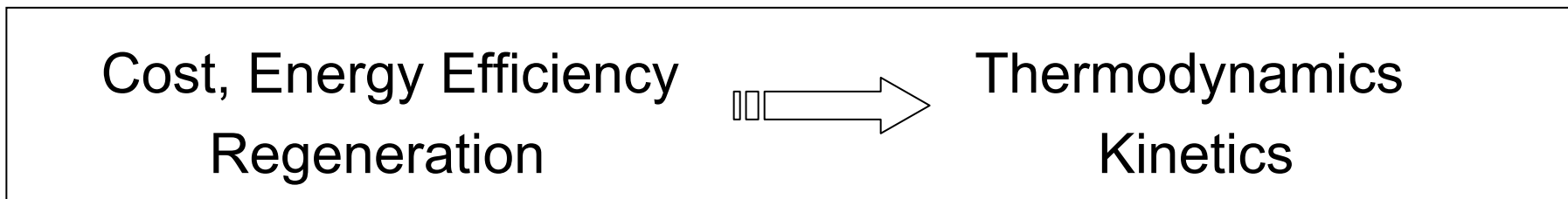
Rohm and Haas  
Millennium Cell  
Intematix  
U.S. Borax



# Overview: Chemical Hydrogen Storage



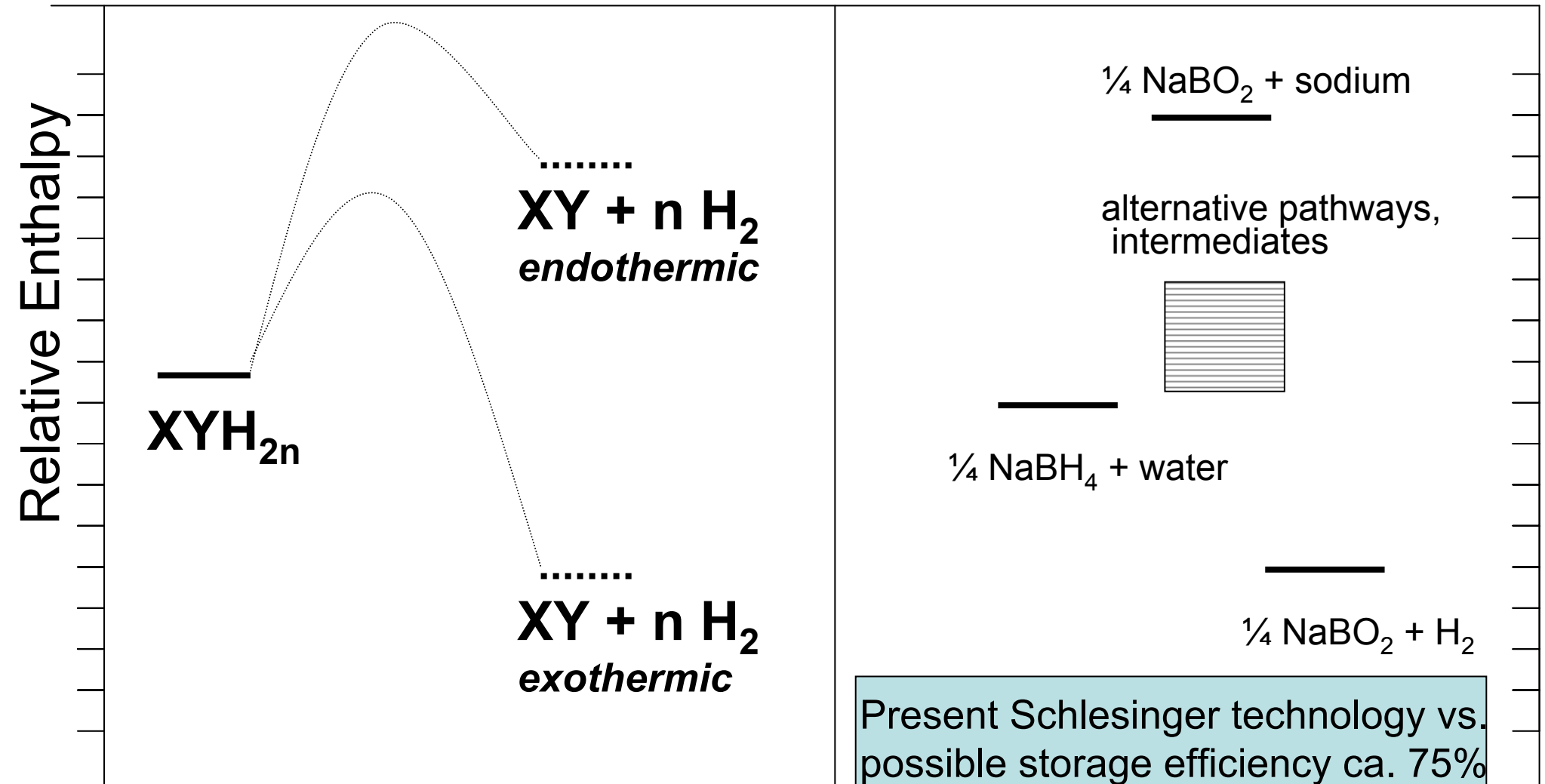
- Attractive Features:
  - Liquid or solid fuel infrastructure
  - Potential for no H<sub>2</sub> handling by consumer
  - Diversity of options
  - Off-board or on-board regeneration



# Chemical Hydrogen Storage and Regeneration

Thermodynamics & Kinetics

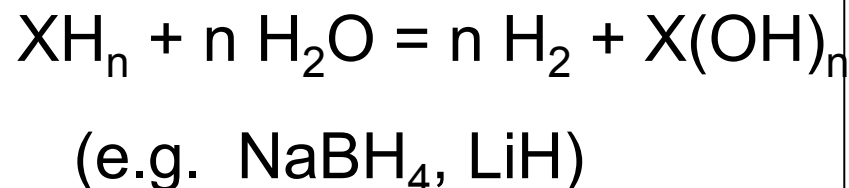
Example:  $\text{NaBH}_4$



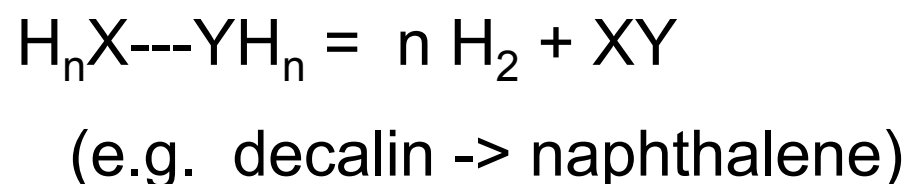
# Chemical Hydrogen Storage

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

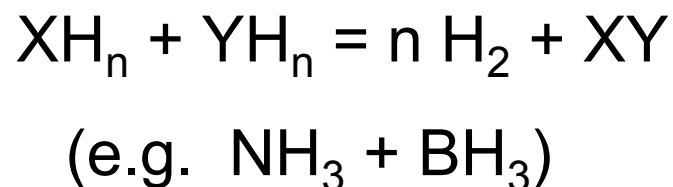
Hydrolysis:



Dehydrogenation:



Dehydrocoupling:



... 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<sub>2</sub> release and spent fuel regeneration
- Engineering assessment for H<sub>2</sub> 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

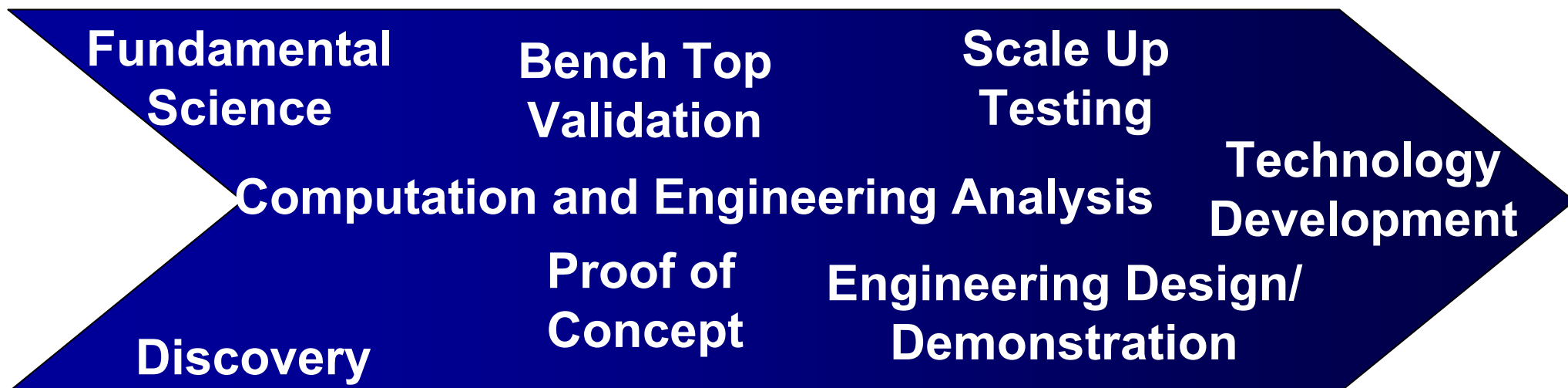
- Tier I:
  - Develop borate-to-borohydride (BO to BH) regeneration alternatives and assess economics and life cycle analysis of borohydride/water to hydrogen
    - Millennium Cell, Rohm and Haas, Penn State, Alabama, PNNL, LANL
- Tier II:
  - Avoid water and thermodynamic sinks. Alternative boron chemistry 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)

| <b>Tier</b> | <b>Project</b>                              | <b>Partners</b>                      |
|-------------|---|--------------------------------------|
| <b>1</b>    | <b>Tier 1: Borohydride</b>                  |                                      |
| 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                      |
|             |   |                                      |
| <b>2</b>    | <b>Tier 2: Novel Boron Chemistry</b>        |                                      |
| 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                            |
|             |   |                                      |
| <b>3</b>    | <b>Tier 3: Innovation Beyond Boron</b>      |                                      |
| 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

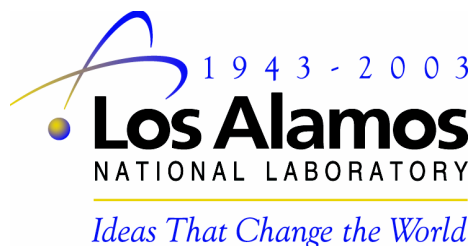
# Tier 1: Borohydride

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

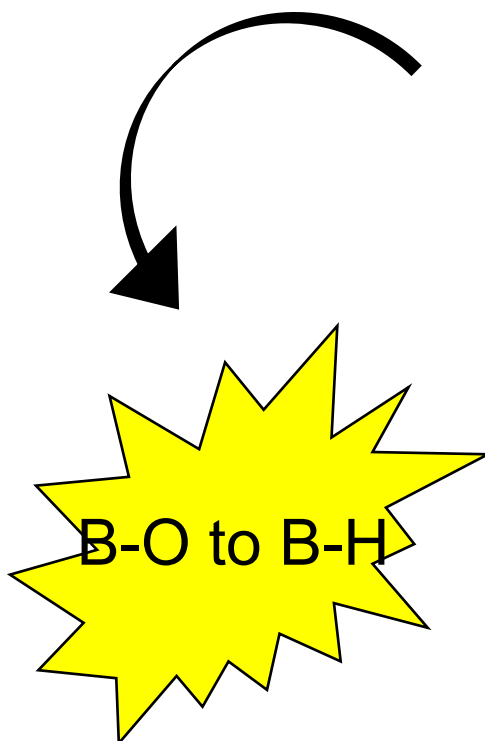
## Objectives

- 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<sub>2</sub> generation systems (liquids and solids)

# Electrochemical Reduction of Borates



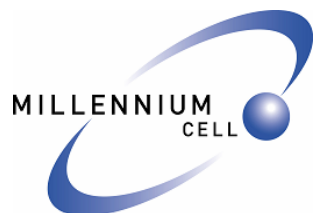
- Engineering analysis
- Positive results from past studies (aqueous systems)
- Advise/direct experimental program



- Advanced electrode preparation
- Alternative reaction media

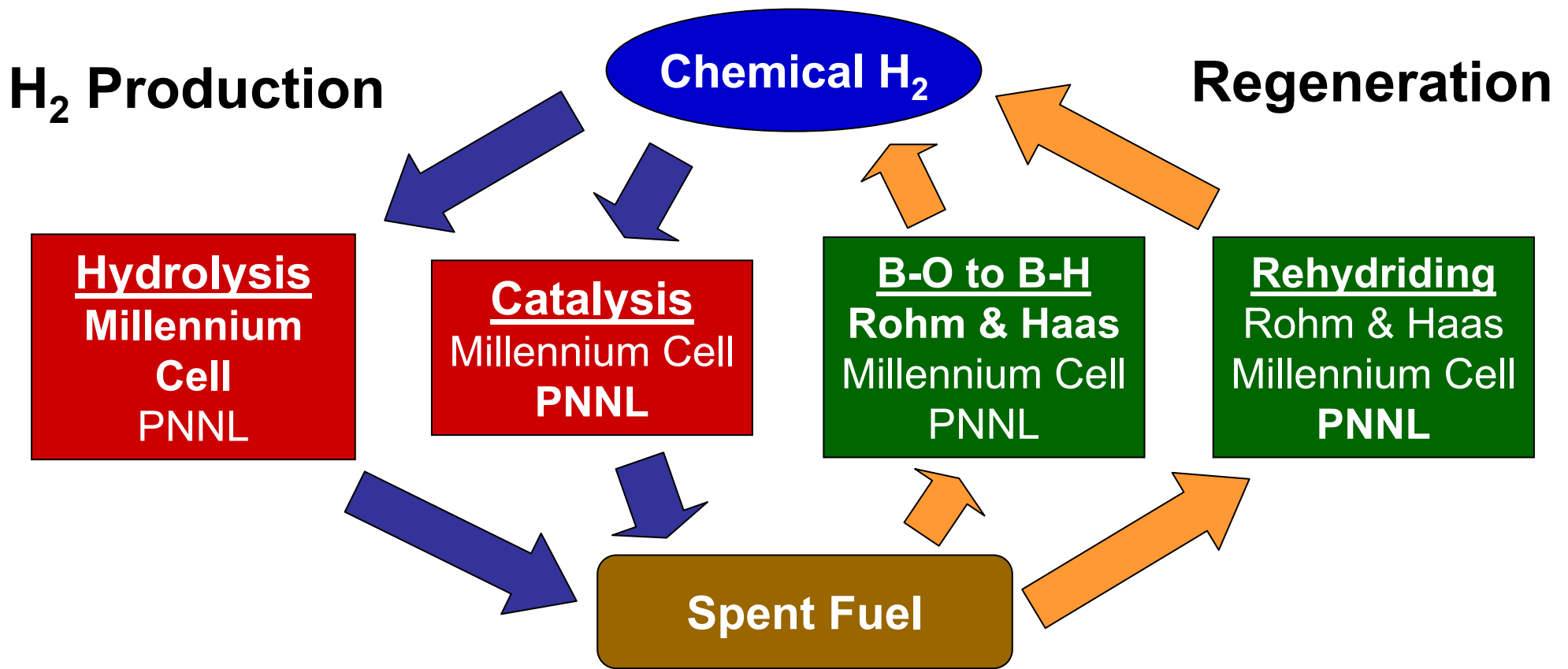
- Fundamental insight
- Mechanistic studies
- Advanced analytical development

- Past experience with aqueous and non-aqueous systems



# Engineering & Analysis Activities

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





# 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

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

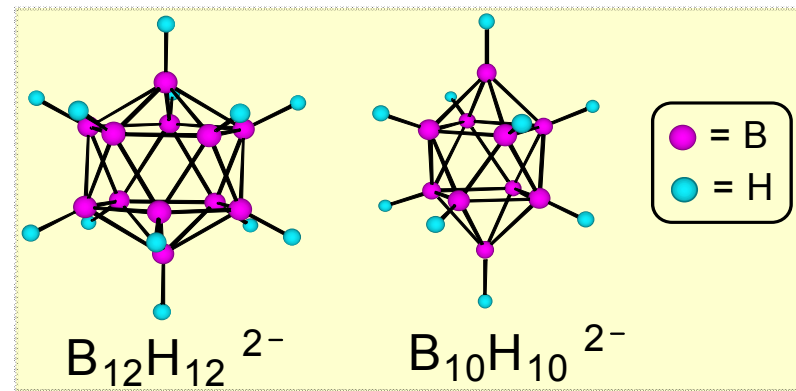
## Objectives

- 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



Material storage capacity 9.4 wt% hydrogen (including water)

*Future Work:*

Thermodynamics, theory and calorimetry

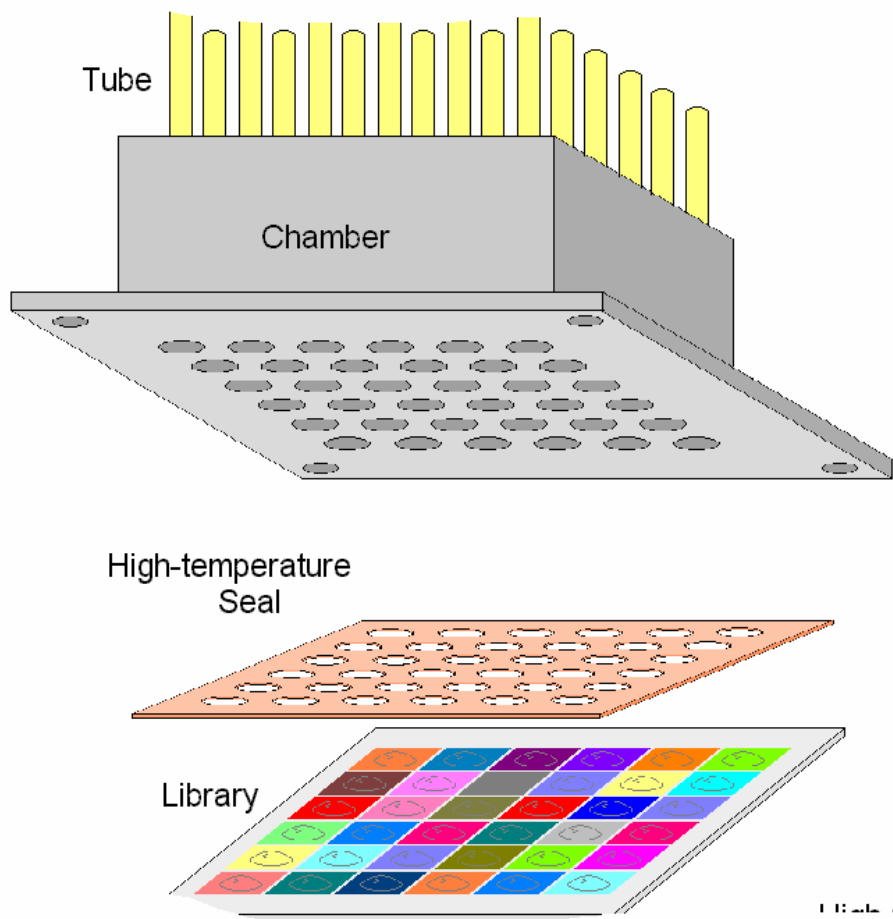
Other  $H_2$  generation routes

- Aminolysis
- Electrochemistry

New regeneration routes from borate

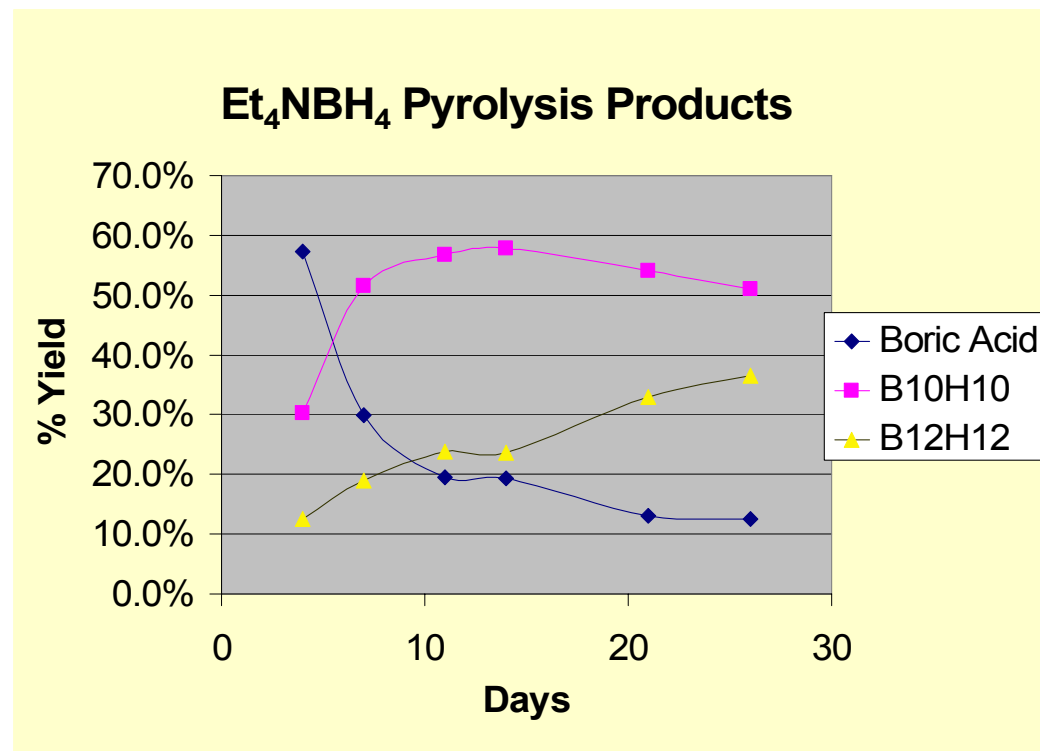
**UCLA, Intematix,  
PNNL, LANL Posters**

# Rapid Throughput Catalyst Synthesis and Testing



Intematix poster

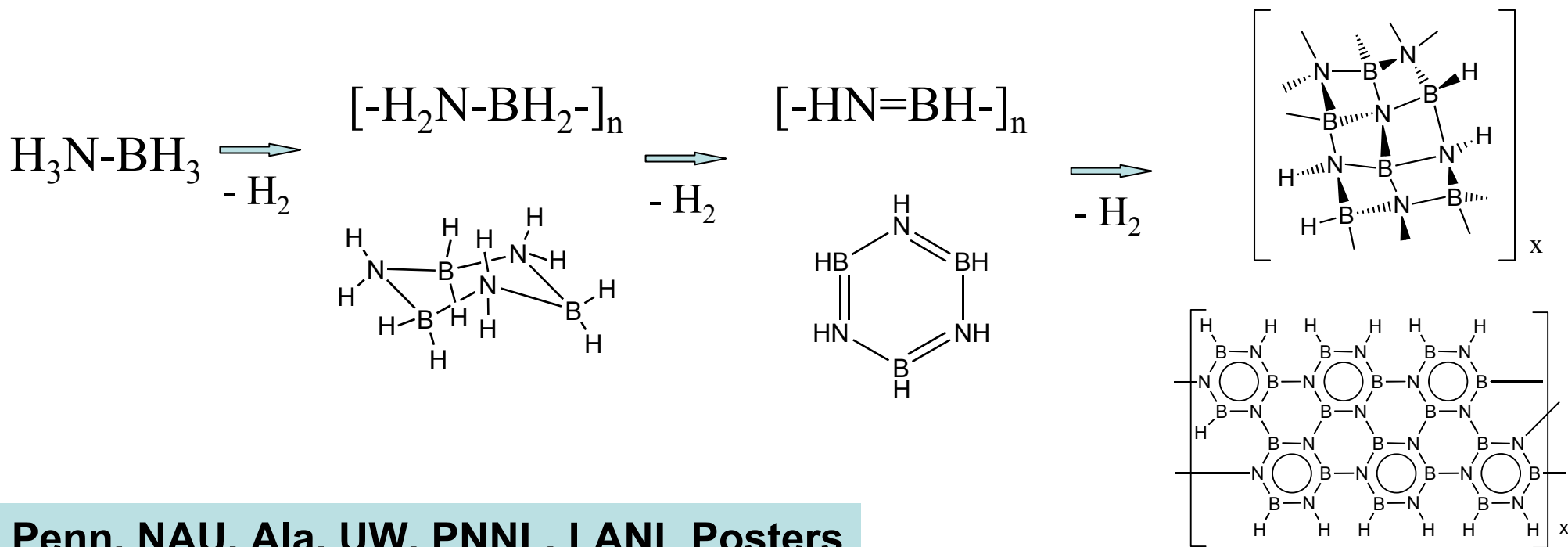
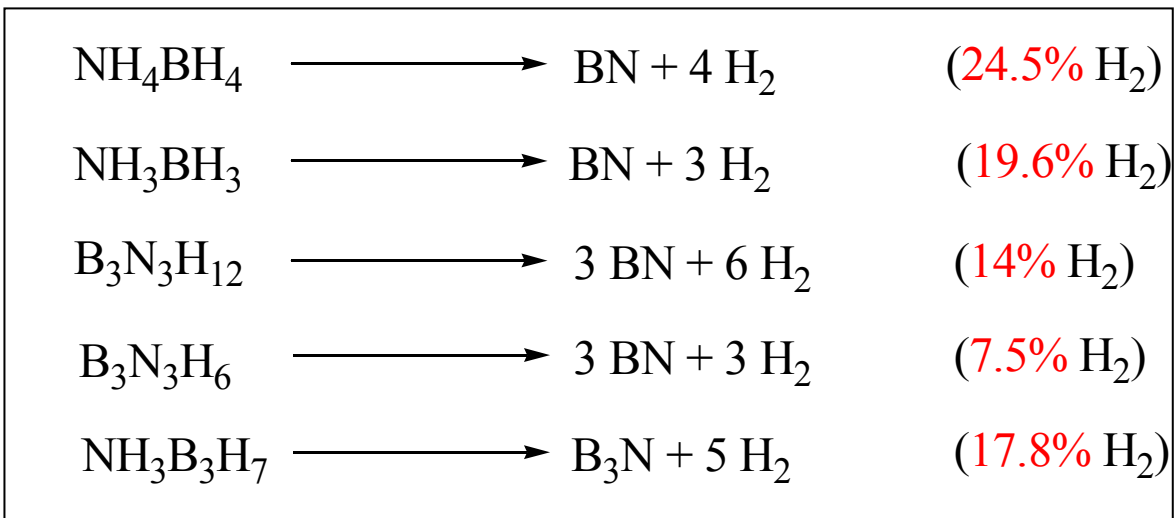
# Production/Regeneration of Polyhedral Boranes



- Selective synthesis of  $\text{B}_n\text{H}_n^{2-}$

UCLA Poster

# Amine-Borane Dehydrogenation/Regeneration



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

# AB Dehydrogenation/Regeneration

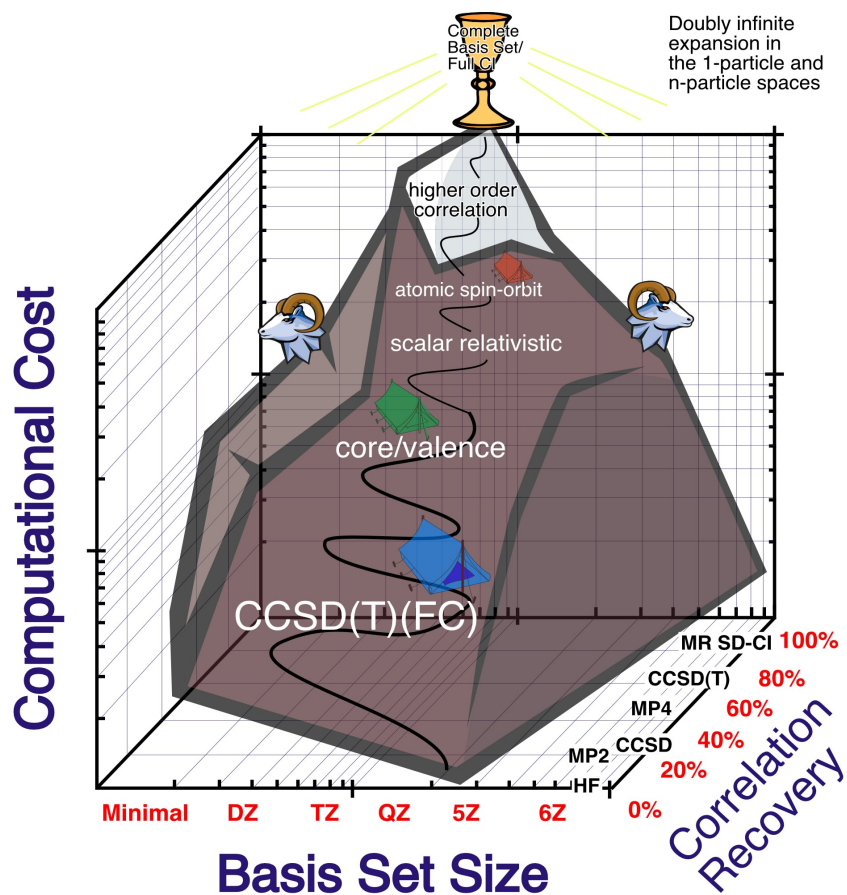
## *Objective:*

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

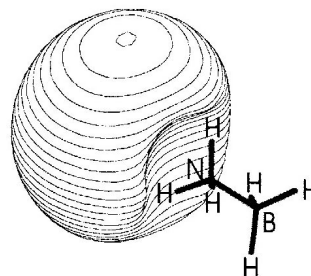
## *Approaches:*

- 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



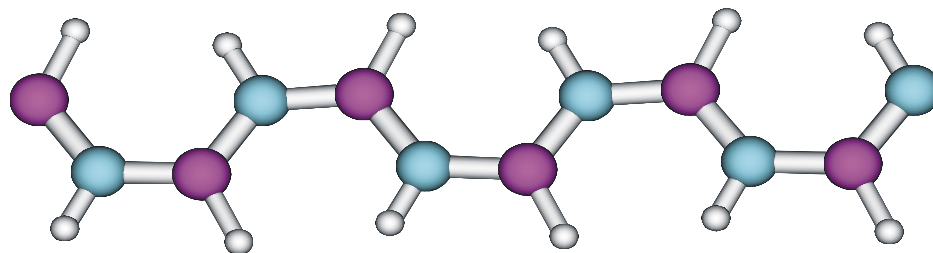
Calculate accurate molecular heats of formation ( $\pm 1$  kcal/mol) by ab initio molecular orbital theory



Alabama, PNNL Posters

## Results (Solids)

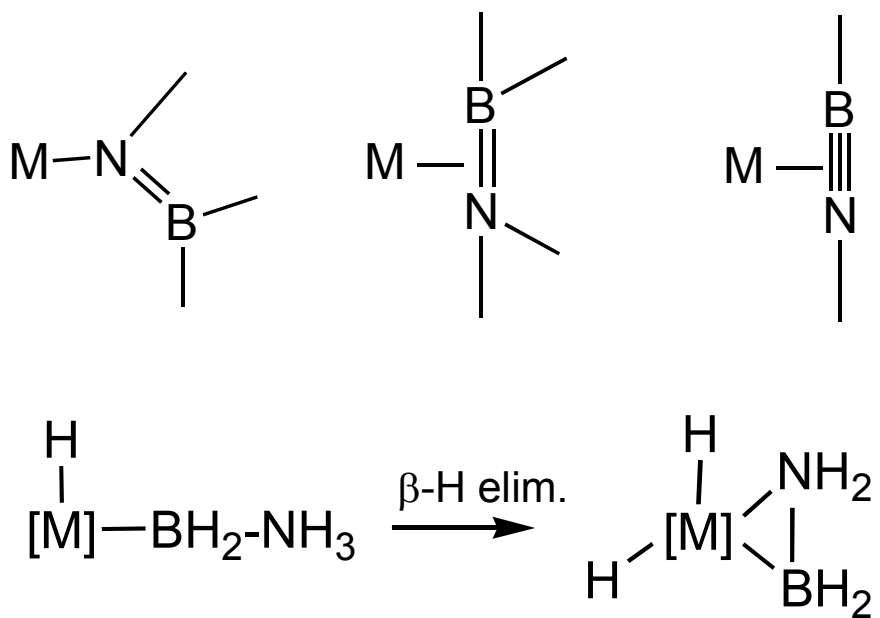
- $\text{H}_3\text{B}\leftarrow:\text{NH}_3$  Electron donor-acceptor bond
  - Large dipole moment of 5.3 D
  - The  $\text{H}_3\text{B}-\text{NH}_3$  bond energy is 25 kcal/mol
- $\text{NH}_2\text{BH}_2 \rightarrow \text{NHBH} + \text{H}_2$ ;  $\Delta H = -3$  kcal/mol
- $\text{NHBH} \rightarrow \text{BN} + \text{H}_2$ ;  $\Delta H = -9$  kcal/mol
- Undoped  $\text{NH}_2\text{BH}_2$  and  $\text{NHBH}$  are insulators



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

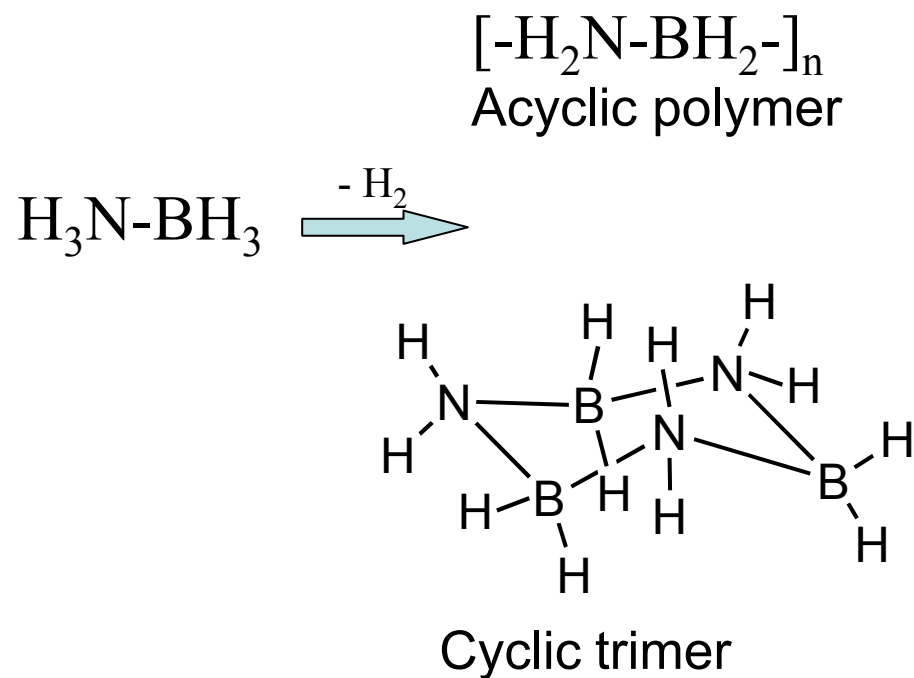
# Amine-Borane R&D

## Mechanisms for AB Dehydrogenation



UW, PNNL, LANL Posters

## Catalyst Development Kinetics/ Selectivity

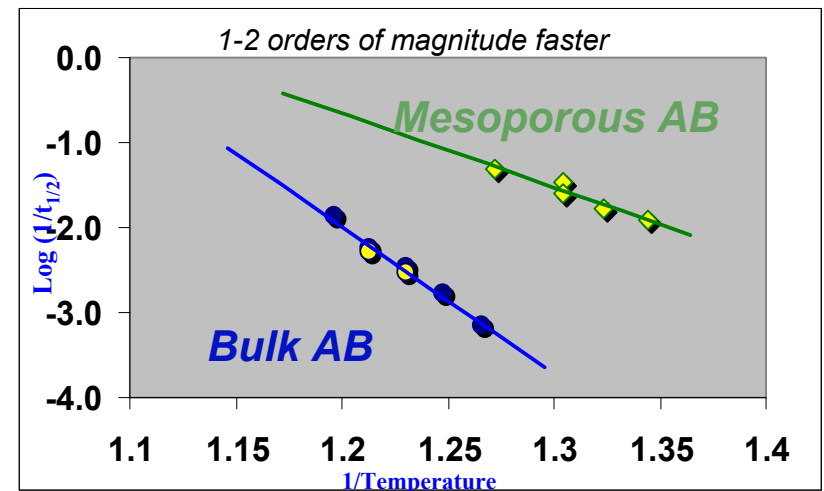
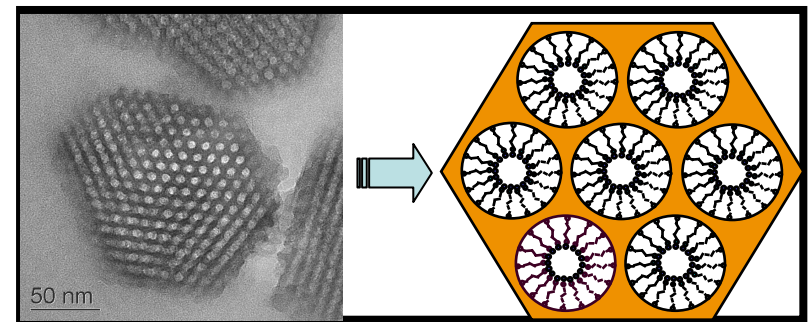
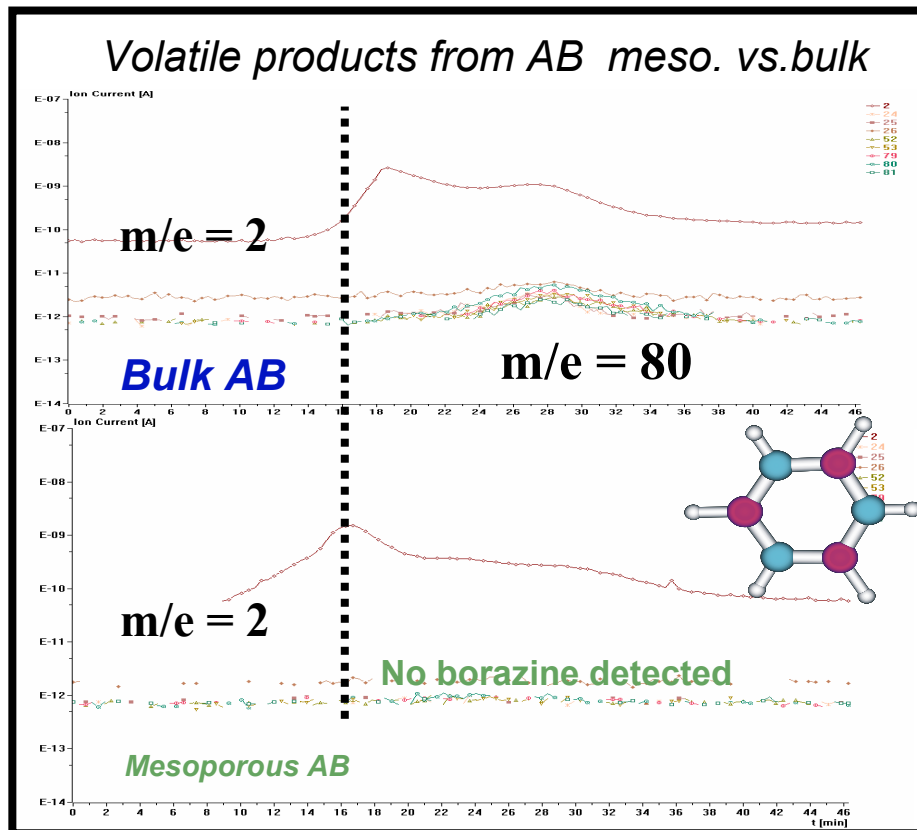
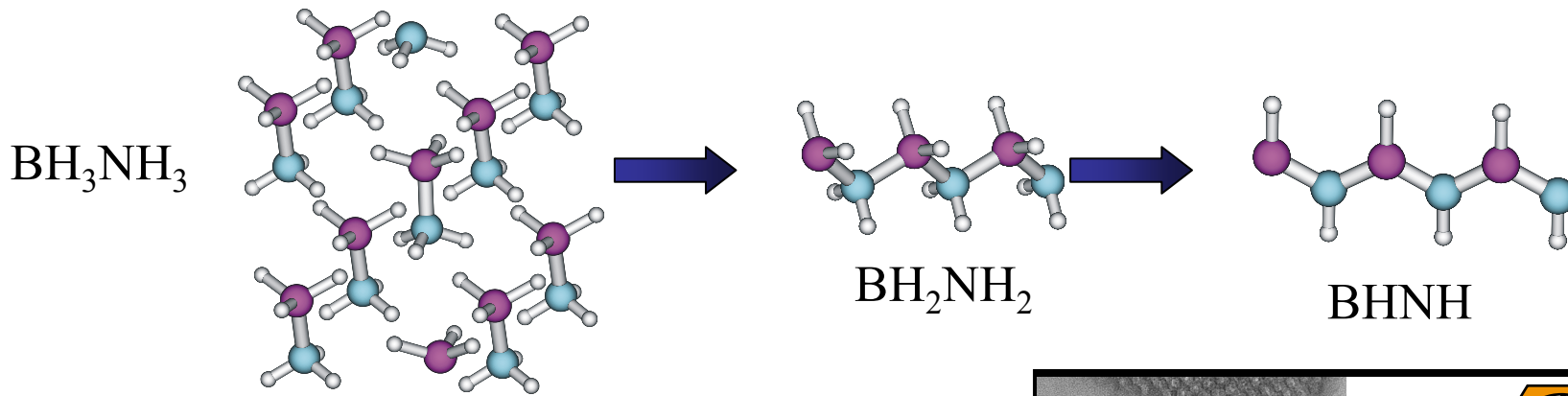


- New proprietary catalysts developed

Penn, NAU, PNNL, LANL Posters

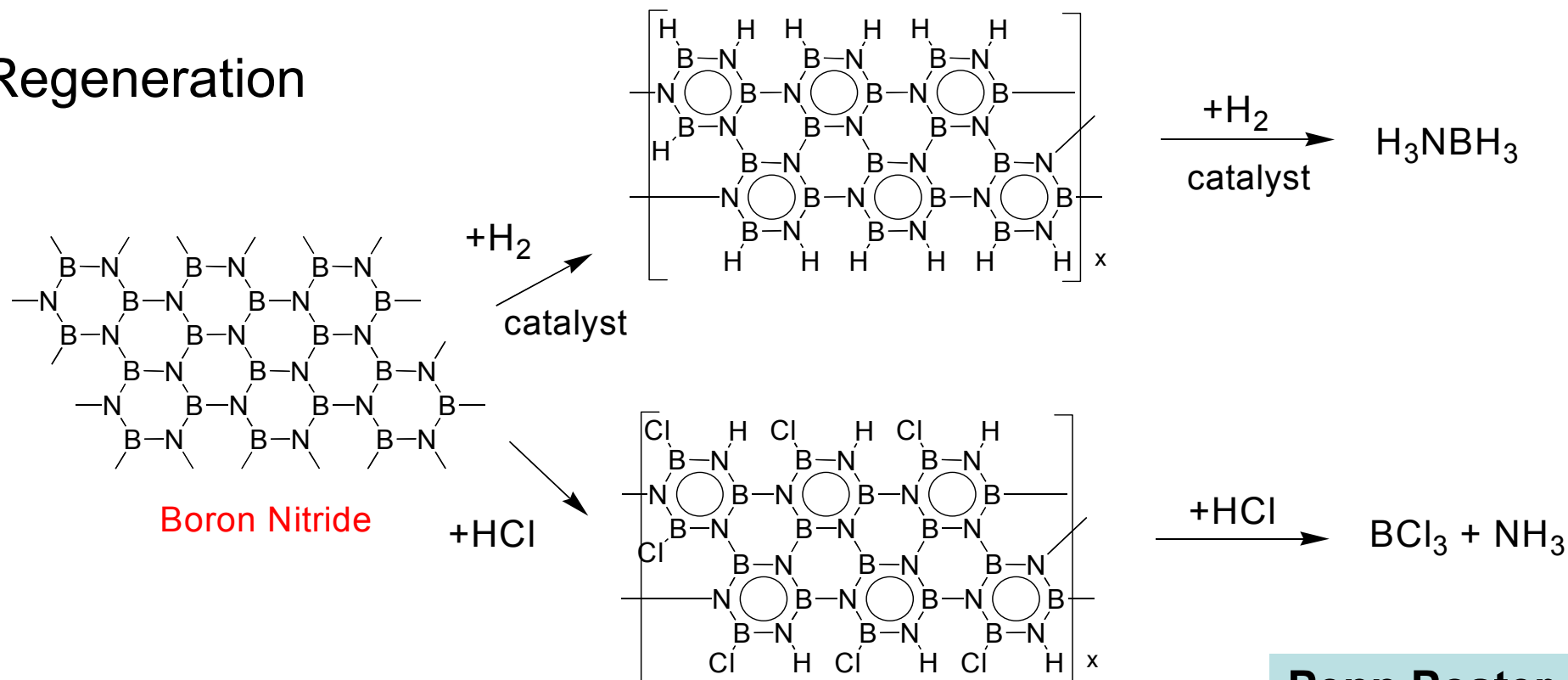


# NH<sub>x</sub>BH<sub>x</sub> in Mesoporous Oxide Scaffolds



# 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)

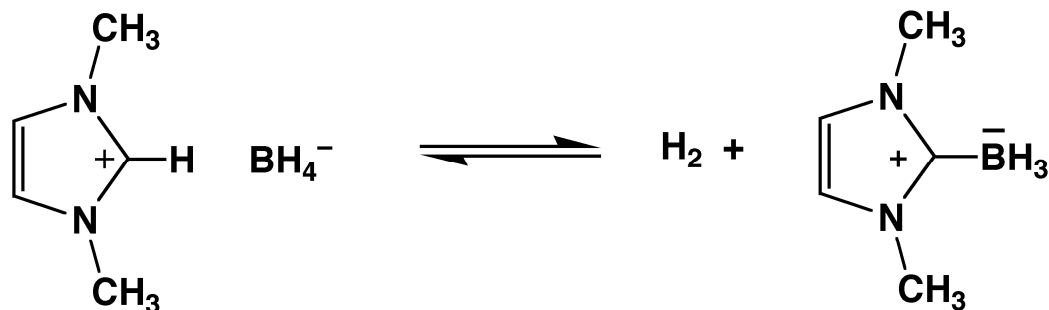
# Tier 3: Beyond Boron

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

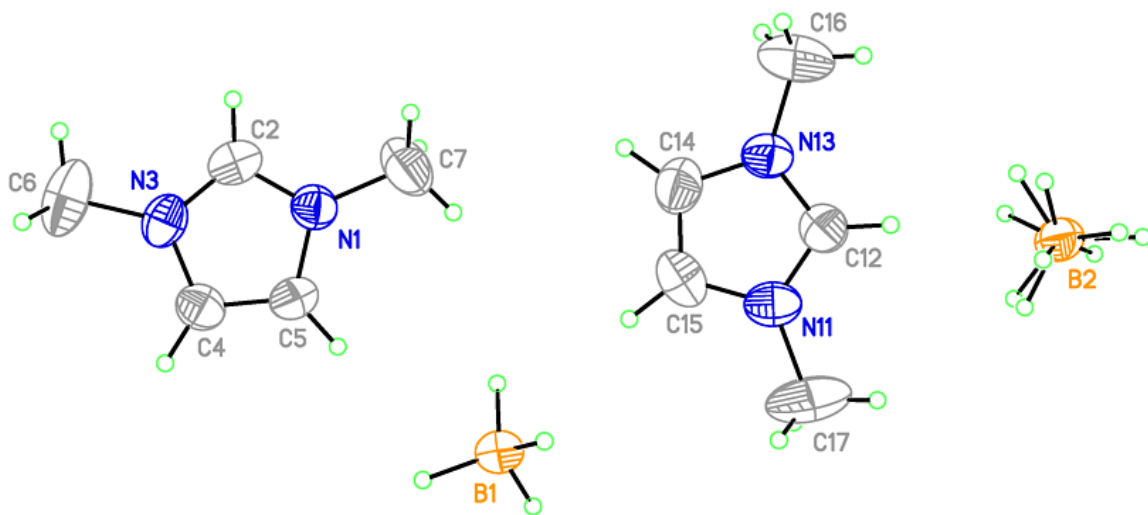
## Objectives

- 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

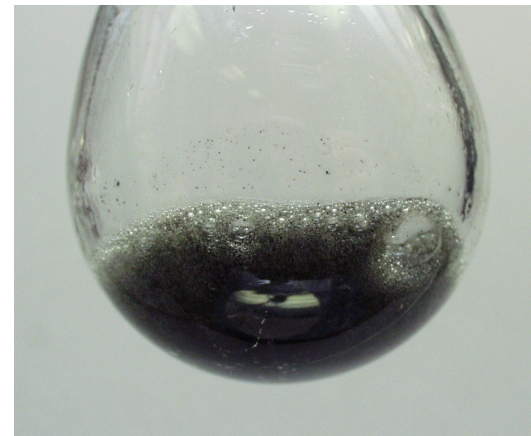
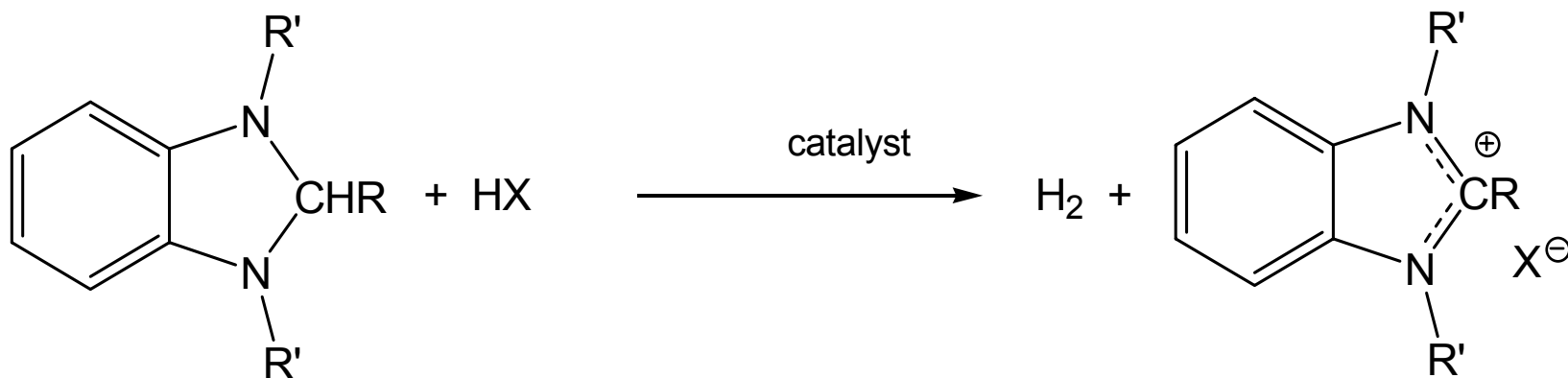


The first X-ray structure of an imidazolium borohydride was determined.



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

# Exergonic H<sub>2</sub> Evolution at Ambient Temperature: A Chemical Hydride



- Demonstration of judicious heteroatom substitution
- Future work to focus on
  - Improving wt% H<sub>2</sub> in related and other systems
  - Increasing rate of H<sub>2</sub> evolution
  - Regeneration

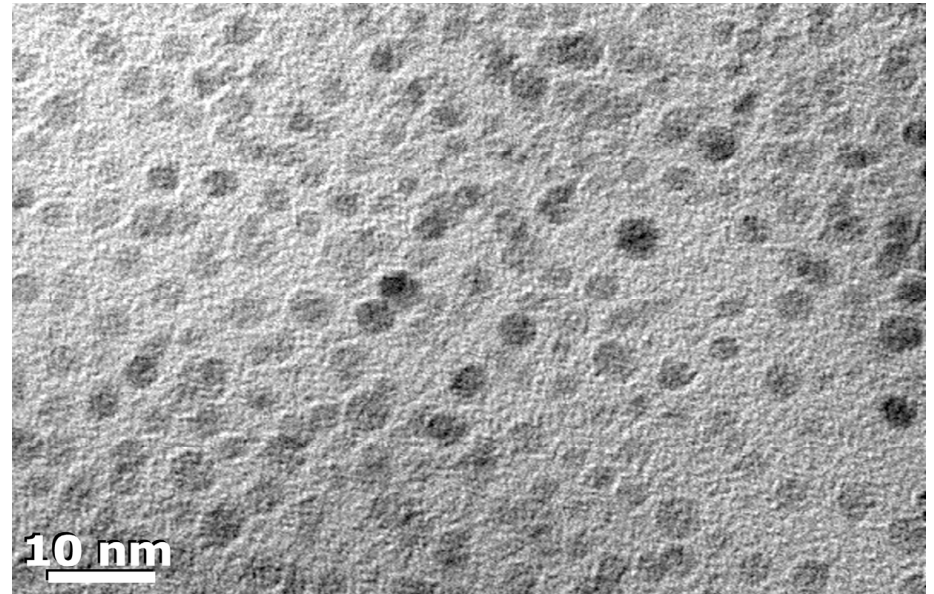
# Tier 3

- Coupled Reactions
  - Couple reactions in such a way that endothermic H<sub>2</sub> evolution can be driven by exothermic co-reaction
    - {Organic substrate} + H<sub>2</sub>O + {inorganic component} → H<sub>2</sub> + {recyclable coproduct}
    - LANL-proprietary concepts, with hypothetical H<sub>2</sub> capacity > 6 wt% (> 0.09 kg H<sub>2</sub>/liter)
    - Proof of concept, patent filing
- Main-group compounds
  - Hydrogen-active E=E bonds
  - Heterosubstituted organic compounds

# 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  $NH_2$ -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 |  |  |
|--|--------|--|--|--------|--|--|--------|--|--|--------|--|--|--------|--|--|
| <b>Tier 1: Borohydride</b>                     |        |  |  |        |  |  |        |  |  |        |  |  |        |  |  |
| 1.1 BO-> BH (Engineering Guided Research)      |        |  |  |        |  |  |        |  |  |        |  |  |        |  |  |
| 1.2 Eng. assessment for H2 generation systems  |        |  |  |        |  |  |        |  |  |        |  |  |        |  |  |
| <b>Tier 2: Novel Boron Chemistry</b>           |        |  |  |        |  |  |        |  |  |        |  |  |        |  |  |
| 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 |        |  |  |        |  |  |        |  |  |        |  |  |        |  |  |
| <b>Tier 3: Innovation Beyond Boron</b>         |        |  |  |        |  |  |        |  |  |        |  |  |        |  |  |
| 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                     |        |                    |                             |                   |
| Computation of Energetics            | Energetics of intermediates; reaction pathways  |        |                    |                             |                   |
|                                      | Borate and complexed borates                    |        |                    | Design data                 |                   |
| 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 |                   |
|                                      | Assessment of exptl results                     |        |                    |                             |                   |
| 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

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  - 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)
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  - Melanie Denney (PD), Vincent Pons (PD)
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  - Japhe Raucher (GS), Li Yan Wang (PD)
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# Chemical Hydrogen Storage CoE

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  - Wei Shan, Jonathan Belman
- US Borax: Dave Schubert
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- PNNL: Chris Aardahl
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  - 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