

Chemical Hydrogen Storage Using Polyhedral Borane Anion Salts

Part of the DOE Chemical Hydrogen Storage Center of Excellence

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Project ID: **ST5**

This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Project start date: Fiscal year 2005
- Project end date: Fiscal year 2009
- Percent complete: 25%

Budget

- Total project funding
 - DOE share: 1,123,132 (proposed)
 - Contractor share: 224,627
- Funding received in FY'05: 236,400
- Funding for FY'06: 180,000

Barriers

- Barriers addressed for Chemical Hydrogen Approach
 - Efficiency
 - Regeneration Processes
 - By-product/Spent Material Removal

Partners

- Penn State University (Digby McDonald)
 - Electrochemical studies of polyhedral boranes
- LANL (Tom Baker)
 - Amine borane species
- PNNL (Tom Autrey)
 - Kinetic studies of hydrolysis of polyhedral boranes using microcalorimetry.

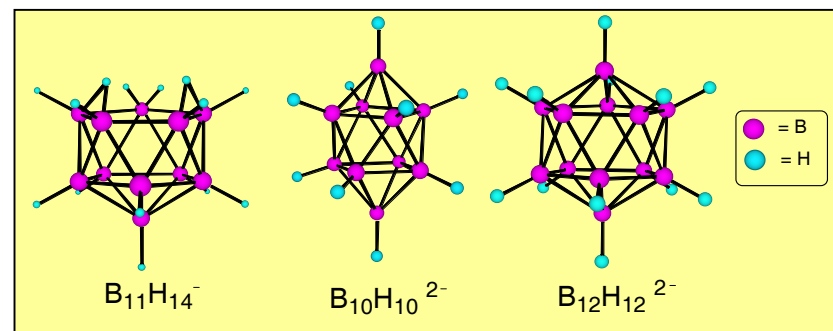
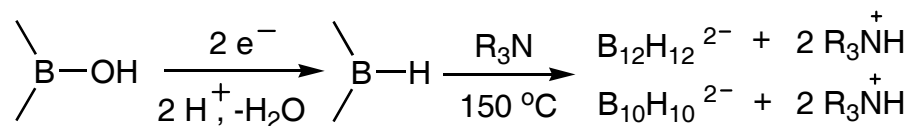
Objectives

- Develop heterogeneous catalysts for the controlled release of hydrogen from the hydrolysis of salts of $B_{12}H_{12}^{2-}$, $B_{10}H_{10}^{2-}$ and $B_{11}H_{14}^{-}$ ions.
- Determine the kinetics and mechanisms of these catalyzed polyhedral borane anion hydrolysis reactions to provide design data for large-scale hydrogen storage devices.
- Optimize existing processes for the conversion of diverse $>BH$ sources to $B_{12}H_{12}^{2-}$ and $B_{10}H_{10}^{2-}$ salts for direct use in hydrogen storage without extensive purification.

Approach

Polyhedral Hydridoborates - Electron Reservoirs

The UCLA team will provide the overall program focal point for the investigation of polyhedral borane anions $B_nH_n^{2-}$ ($n = 10$ and 12), $B_{11}H_{14}^-$ and their derivatives as reservoirs for stored electrons available for proton reduction and hydrogen release upon catalyzed hydrolysis.



Properties of $B_{12}H_{12}^{2-}$ and $B_{10}H_{10}^{2-}$

- Very H_2O soluble alkali metal salts
- Non-toxic ($LD_{50} = 1.2g Na_2B_{12}H_{12}/Kg$ body weight in mice)
- Thermally stable $>500^\circ C$
- No decomposition on storage in H_2O solution at elevated temperatures

Approach Cont.

- Polyhedral boranes production:
 - The $B_{12}H_{12}^{2-}$ ion is readily formed in excellent yield by heating $>B-H$ containing species with a base (R_3N).
 - Crude materials containing $>B-H$ may be converted to a $B_{12}H_{12}^{2-}$ salt which is extracted with water and used directly for catalytic generation of hydrogen.
 - Useful $>B-H$ sources obtainable from many different routes can be exploited.
 - Tetrahydridoborate salts of any purity are easily converted to $Na_2B_{12}H_{12}$.
 - Both $Na_2B_{10}H_{10}$ and $NaB_{11}H_{14}$ may be easily obtained from $NaBH_4$.
- Polyhedral borane applications:
 - Hydrogen generation from $Na_2B_{12}H_{12}$ and $Na_2B_{10}H_{10}$ will be catalyzed and slower than in the case of $NaBH_4$.
 - Blends of $NaBH_4$ and/or $NaB_{11}H_{14}$ with $Na_2B_{12}H_{12}$, etc. will yield hydrogen just as blends of hydrocarbons provide gasoline.
 - Polyhedral hydridoborate salts would be ideal for fixed installations requiring great safety and reliable hydrogen production after prolonged storage times (years).

Collaboration and Partners:

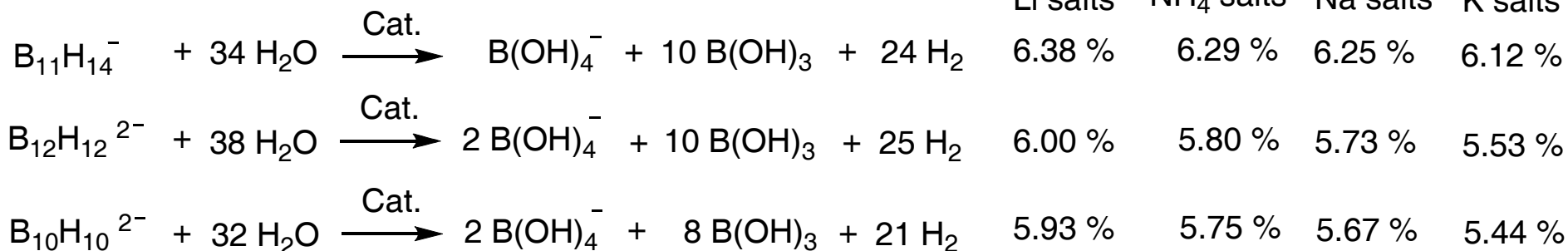
- Electrochemical studies of reversible electron (hydrogen) storage mediated by electrochemical reactions of polyhedral borane anion and their derivatives (Penn State University) will be supported by UCLA as follows:
 - Through UCLA and Penn State consultation, promising candidate polyhedral borane derivatives will be identified for electrochemical studies at Penn State.
 - Feasible polyhedral borane derivatives will be supplied to Penn State for study following their synthesis at UCLA.
- Polyhedral amine borane derivatives sought by the DOE Chemical Hydrogen Storage Center of Excellence for reversible hydrogen uptake and release will be supplied by UCLA.
- Polyhedral borane derivatives are desired by the Pacific Northwest National Laboratory for catalyzed hydrolysis studies using microcalorimetry measurements to determine reaction kinetics and thermodynamics. These species will be supplied by UCLA following compound selection through consultation and mutual agreement of the two partners.

Metal Catalyzed Hydrolysis of Polyhedral Boranes

- Metal catalyst is needed to hydrolyze $B_{11}H_{14}^-$, $B_{12}H_{12}^{2-}$ and $B_{10}H_{10}^{2-}$ anion salts.
- In each case the rate of hydrogen release depends upon the following variables:

- ★ *Choice of metal catalyst*
- ★ *Temperature*
- ★ *Concentration of the catalyst*
- ★ *pH of the reaction mixture*
- ★ *Choice of cation for polyhedral borane salt*

System weights %
(wt. H_2 / wt. Boranes + wt. H_2O) x 100



DOE targets for system wt. **2005**: 4.5%; **2010**: 6.0%; **2015**: 9.0%

- Rate of reaction and efficiency can be measured by ¹¹B NMR of the reaction mixtures or by hydrogen evolution as a function of time.

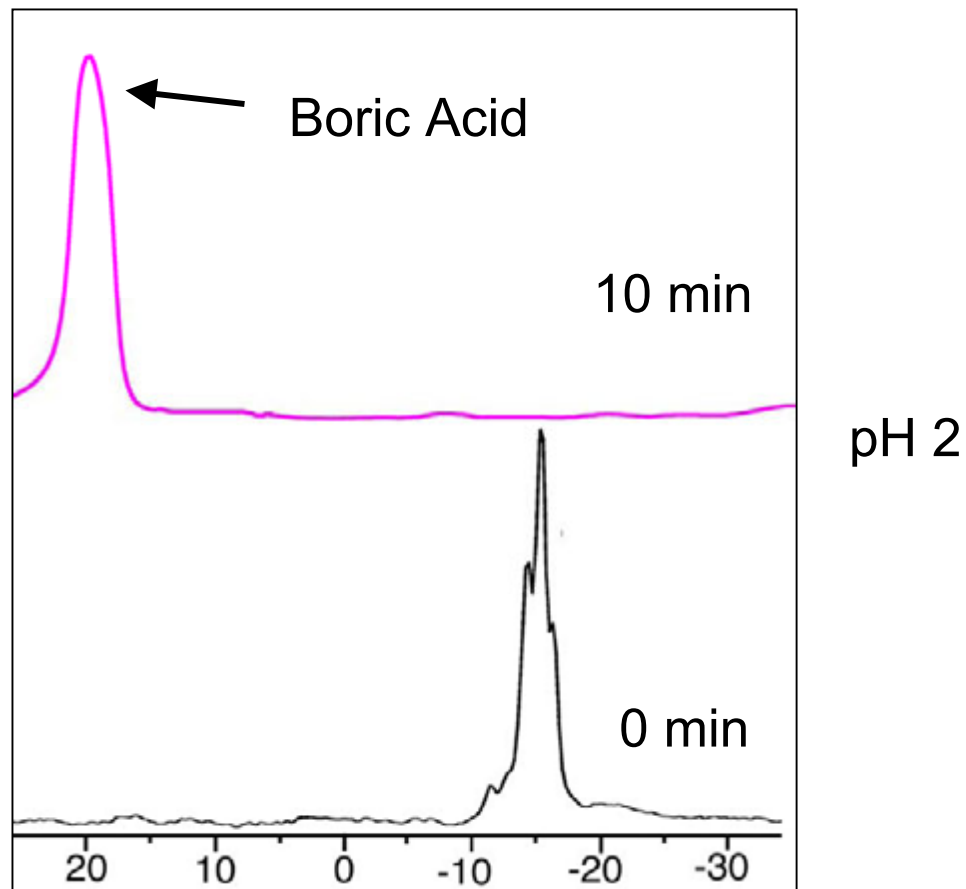
Search for the Optimum Metal Catalyst

- Transition metal ions, such as cobalt, nickel, palladium and rhodium are known to form metal borides in the presence of reactive borane species.
- Transition metal borides are good first choice catalysts since transition metal ion borane hydrolysis catalysts would most likely be converted to the respective borides during the hydrolysis reactions.
- This complicating possibility is removed by purposely employing transition metal borides as exploratory catalysts that are inert to modification by reaction with borane species present.
- For purposes of initial exploration, rhodium boride, nickel boride and cobalt boride were examined for their catalytic activity in the hydrolysis of $\text{NaB}_{11}\text{H}_{14}$, $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$, $\text{K}_2\text{B}_{12}\text{H}_{12}$ and $\text{K}_2\text{B}_{10}\text{H}_{10}$.

Preliminary Results

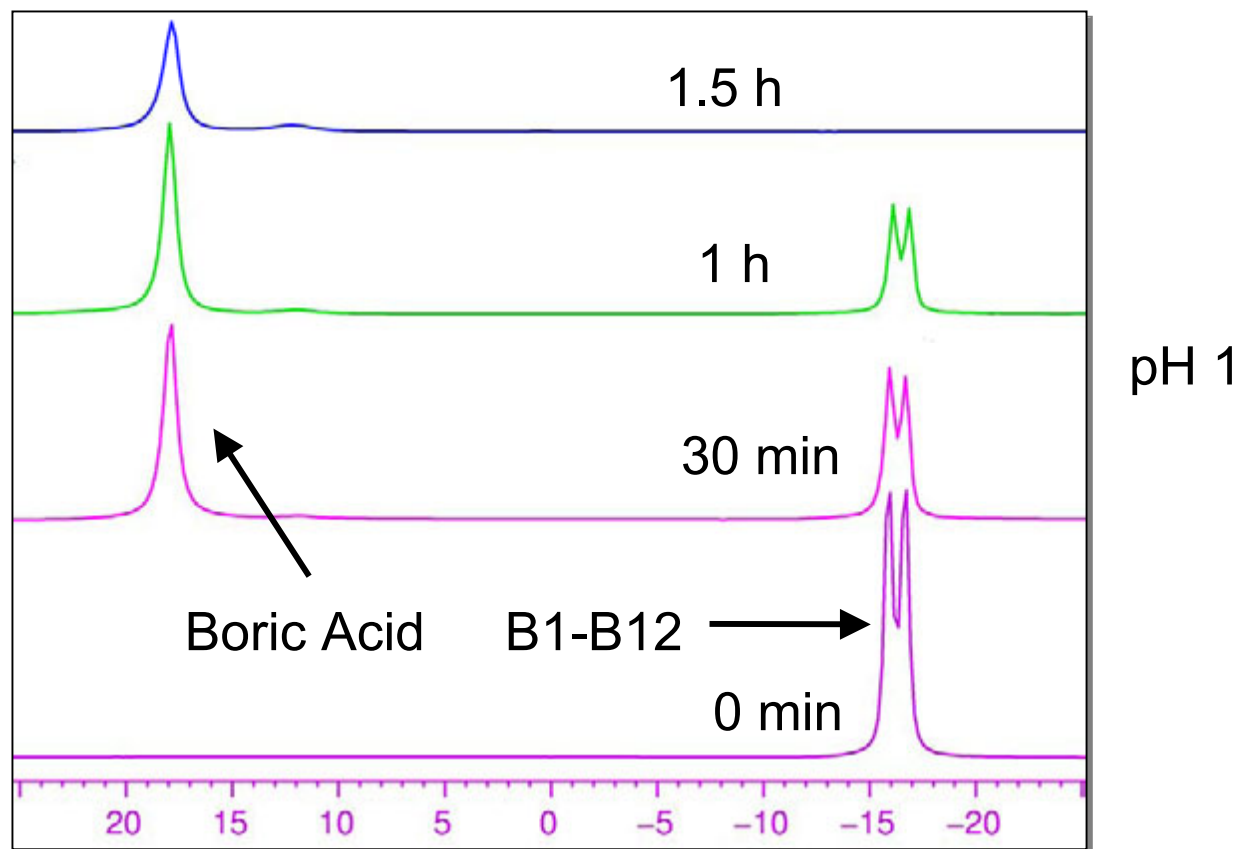
- Of the three boride catalysts investigated, only rhodium boride was able to catalyze the hydrolysis of the generally inert $B_{12}H_{12}^{2-}$ and $B_{10}H_{10}^{2-}$ ions. These ions were inert to nickel boride and cobalt boride catalysts.
- Hydrolysis of $NaB_{11}H_{14}$ was faster than any $B_{12}H_{12}^{2-}$ and $B_{10}H_{10}^{2-}$ salts investigated and proceeded in the presence of all the three boride catalysts. The hydrolysis rate was faster with rhodium boride compared to nickel and cobalt borides.
- Choice of cation can affect the rate of hydrolysis; $(NH_4)_2B_{12}H_{12}$ hydrolysis is faster than $K_2B_{12}H_{12}$ using rhodium boride catalyst.
- Both temperature and pH affect the rate of hydrolysis of all polyhedral borane ions under investigation. Additional studies are required to determine the mechanistic meaning and usefulness of the pH effects and their applications in large scale hydrogen generation.
- All hydrolysis reactions proceed to completion giving quantitative hydrogen and boric acid production.

Hydrolysis of $\text{NaB}_{11}\text{H}_{14}$ with 5 mol% Rh Catalyst at 80 °C



Concentration of $\text{NaB}_{11}\text{H}_{14}$: 0.113M

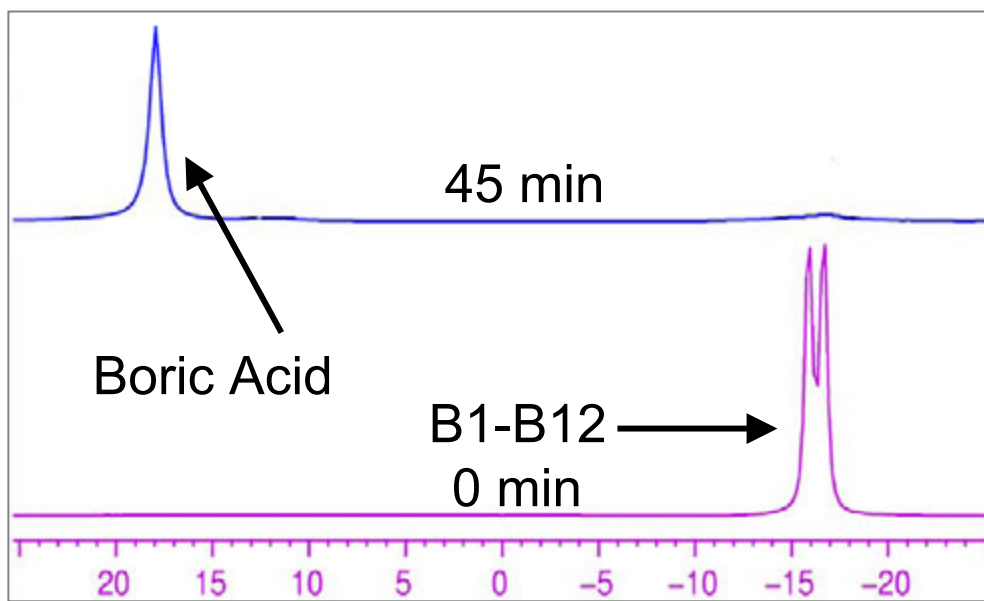
Hydrolysis of $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ with 5 mol% Rhodium boride Catalyst at 80 °C



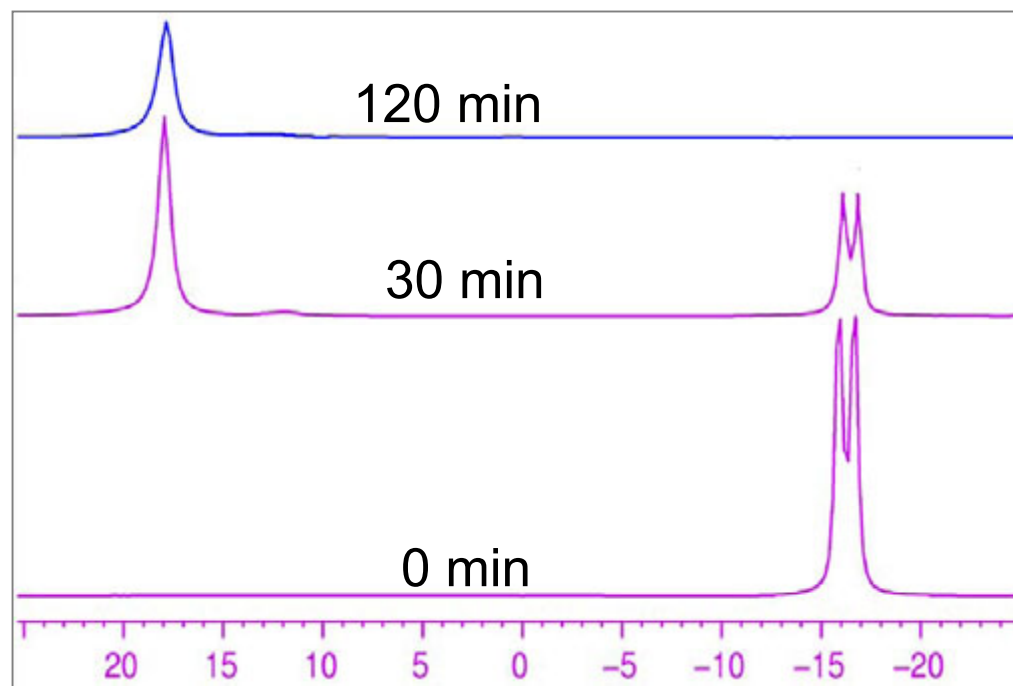
Concentration of $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$: 0.113M

Effect of Catalyst Concentration on the Hydrolysis of $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$

Reaction conditions: 0.45mmol of borane (0.113M) + Rh Catalyst at 90 °C and pH=1

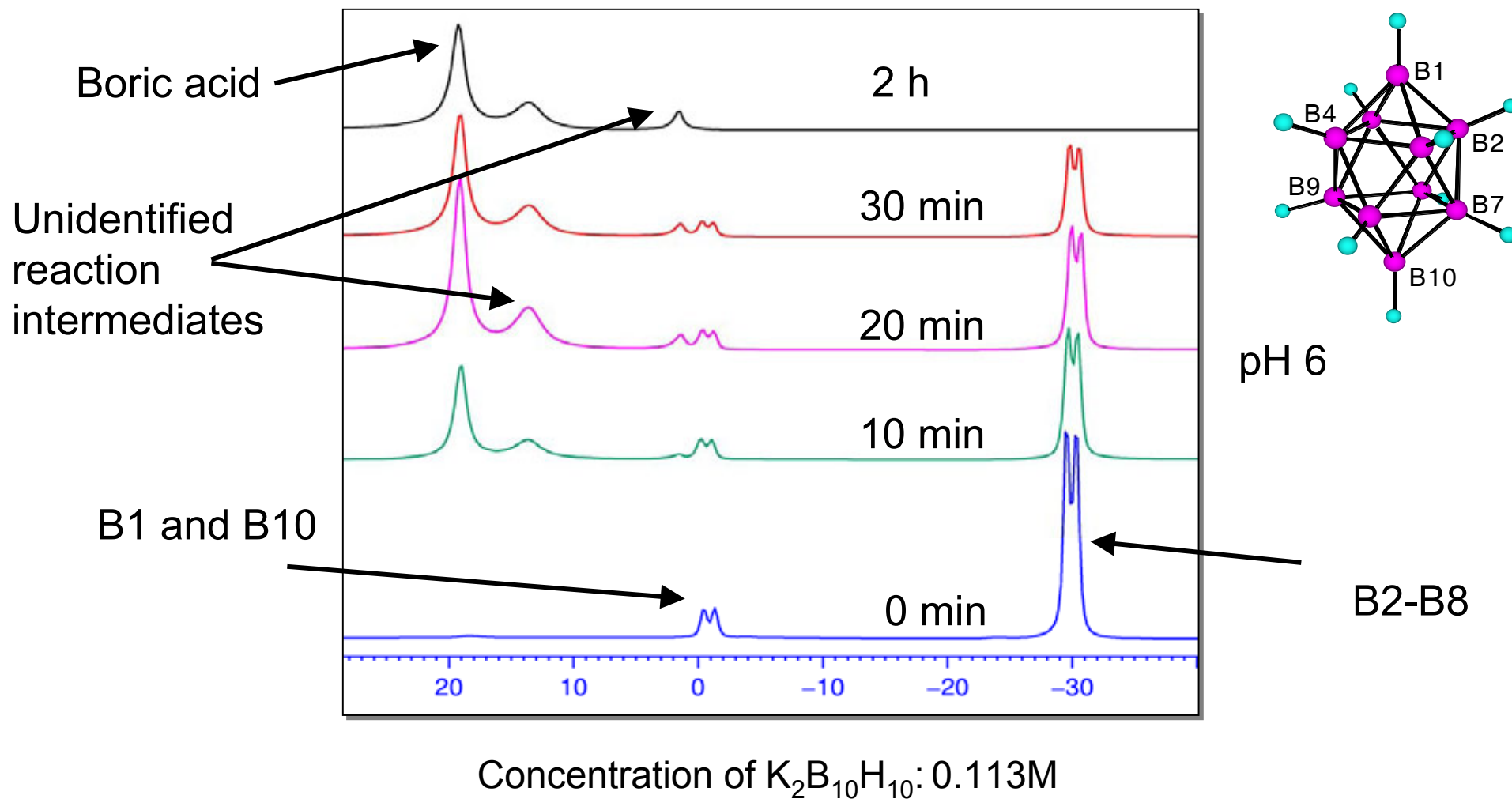


5 mol% Rh catalyst



2.5 mol% Rh catalyst

Hydrolysis of $K_2B_{10}H_{10}$ with 5 mol% Rh boride Catalyst at 80 °C



Comparative Reaction Rates of Rhodium Catalyzed Hydrolysis of $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$, $\text{K}_2\text{B}_{12}\text{H}_{12}$ and $\text{K}_2\text{B}_{10}\text{H}_{10}$

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.
- Hydrolysis rate: $\text{K}_2\text{B}_{10}\text{H}_{10} > (\text{NH}_4)_2\text{B}_{12}\text{H}_{12} > \text{K}_2\text{B}_{12}\text{H}_{12}$

Summary of Hydrolysis of Polyhedral Borane Salts

Polyhedral boranes	Weight of salt	Water consumed (mg)	RhB catalyst (mg)	System wt. (mg)	T (°C)	pH	Relative rate ($\times 10^{-3} \text{ min}^{-1}$)	H ₂ released	
								mmol	wt%*
NaB ₁₁ H ₁₄	70.2mg (0.450 mmol)	279.0	4.7 (5.0 mol%)	354.7	80	2	0.1	10.9	6.15
K ₂ B ₁₀ H ₁₀	88.4mg (0.450 mmol)	261.0	4.7 (5.0 mol%)	354.7	80	6	8.3	9.6	5.41
(NH ₄) ₂ B ₁₂ H ₁₂	80.1mg (0.450 mmol)	311.0	4.7 (5.0 mol%)	396.7	80	1	11	11.4	5.74
(NH ₄) ₂ B ₁₂ H ₁₂	80.1mg (0.450 mmol)	311.0	4.7 (5.0 mol%)	396.7	90	1	22	11.4	5.74
(NH ₄) ₂ B ₁₂ H ₁₂	80.1mg (0.450 mmol)	311.0	2.3 (2.5 mol%)	394.3	90	1	8.3	11.4	5.78

* The calculations are based upon water consumed.

System wt: wt of boranes + water consumed + catalyst

Hydrogen wt% : wt of H₂ / wt (boranes + water + catalyst) X 100

DOE targets for hydrogen storage wt% for **2005**: 4.5%; **2010**: 6.0%; **2015**: 9.0%

Future Work

- Investigate alternative transition metal boride catalysts.
- Identify and characterize rhodium boride catalyst useful for $B_{11}H_{14}^-$, $B_{12}H_{12}^{2-}$, and $B_{10}H_{10}^{2-}$ anion hydrolyses.
- Study the kinetics of the reaction; effect of pH, cation identity and ionic strength; determination of activation parameters; determine the reaction mechanisms.
- Examine $B_{12}X_{12}^{2-}$ ($X = Cl, CH_3, OR$) in catalyzed hydrolysis reactions and the mechanistic implications of these results.
- Identify appropriate polyhedral borane-amine complexes and ammonium salts for catalytic dehydrogenation studies (with Center).

Demonstration of Rhodium Catalyzed Hydrolysis



Hydrolysis of NaB₁₁H₁₄



Hydrolysis of (NH₄)₂B₁₂H₁₂