Chemical Hydrogen Storage Using Polyhedral Borane Anion Salts

Part of the DOE Chemical Hydrogen Storage Center of Excellence

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STP7

Overview

Timeline

- Project start date: Fiscal year 2005
- Project end date: Fiscal year 2009
- Percent complete: New Start

Barriers

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

Budget

- Total project funding
  - DOE share: 1,123,132 (proposed)
  - Contractor share: 224,627
- Funding received in FY04: 0.0
- Funding for FY05: 236,400

Partners

- DOE Center of Excellence for Chemical Hydrogen Storage

Objectives

- Develop heterogeneous catalysts for the controlled generation 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 mechanism of these catalyzed borane anion hydrolysis reactions to provide design data for large-scale hydrogen generation device.

- Investigate blends of two or more anionic polyhedral borane salts of variable purity as commercially viable sources of hydrogen (analogous to hydrocarbon blends for optimized gasoline blends) with cost and performance as working parameters.

- Optimize existing processes for the conversion fo diverse >BH sources to $Na_2B_{12}H_{12}$ and $Na_2B_{10}H_{10}$ for direct use in hydrogen generation without extensive purification.

Objectives, cont.

Collaboration and Partners

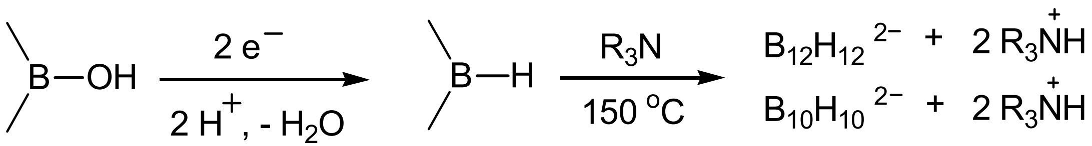
Interactions with the DOE Chemical Hydrogen Storage Center of Excellence:

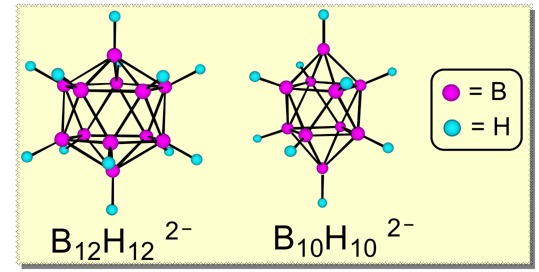
- UCLA project will provide the overall program focal point for the investigation of polyhedral borane anions $B_nH_n^{2-}$ (n = 10 and 12), $B_{11}H_{14}^-$ and their derivatives as reservoirs for stored electrons available for hydrogen release upon catalyzed hydrolysis; as substrate for electrochemical studies leading to reversible electron storage, and as reactants in reversible hydrogen storage.

- Specific Partners:
  - Penn State University (Digby McDonald) for electrochemical studies of polyhedral borane species identified through consultation with UCLA and supplied by UCLA.
  - Los Alamos National Laboratory (Tom Baker) for collaborative studies of selected amine borane derivatives supplied by UCLA and used in reversible hydrogen uptake reactions.
  - Pacific Northwestern National Laboratory (Tom Autrey) for collaborative kinetic studies of catalyzed polyhedral borane hydrolysis using microcalorimetry to obtain reaction kinetics and thermodynamic data.

Approach

Polyhedral Hydridoborates - Electron Reservoirs





H_2 Production

$B_{12}H_{12}^{2-} + 38\,H_2O \xrightarrow{\text{Cat.}} 2\,B(OH)_4^- + 10\,B(OH)_3 + 25\,H_2$	26.7 %	g H_2/g Na salt x 100
$B_{10}H_{10}^{2-} + 32\,H_2O \xrightarrow{\text{Cat.}} 2\,B(OH)_4^- + 8\,B(OH)_3 + 21\,H_2$	25.6 %	" "
$BH_4^- + 4\,H_2O \xrightarrow{\text{Cat.}} B(OH)_4^- + 4\,H_2$	21.1 %	" "

Properties of $Na_2B_{12}H_{12}$ and $Na_2B_{10}H_{10}$

- Very H_2O soluble
- Non-toxic (LD50 = 1.2g $Na_2B_{12}H_{12}$/Kg body weight in mice)
- Thermally stable >500°C
- Chemically inert in absence of a catalyst
- No decomposition on storage in H_2O solution at high temperatures

Approach, cont.

Production of Polyhedral Hydridoborates

- 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 $B_{12}H_{12}^{2-}$ 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 $Na_2B_{12}H_{12}$.

Approach, cont.

Applications of Polyhedral Hydridoborates

- Hydrogen generation from $Na_2B_{12}H_{12}$ and $Na_2B_{10}H_{10}$ will be catalyzed and probably slower than in the case of $NaBH_4$.
- Blends of $NaBH_4$ and $Na_2B_{12}H_{12}$, etc. will yield hydrogen just as blends of hydrocarbons provide gasoline.
- Polyhedral hydridoborate salts would be ideal for fixed installations requiring great safety and steady hydrogen production over very long storage times (years).

Approach, cont.

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 desired by the Pacific Northwest National Laboratory for catalyzed hydrolysis studies using microcalorametry measurements to determine reaction kinetics and thermodynamics will be supplied by UCLA following compound selection through consultation and mutual agreement of the two partners.

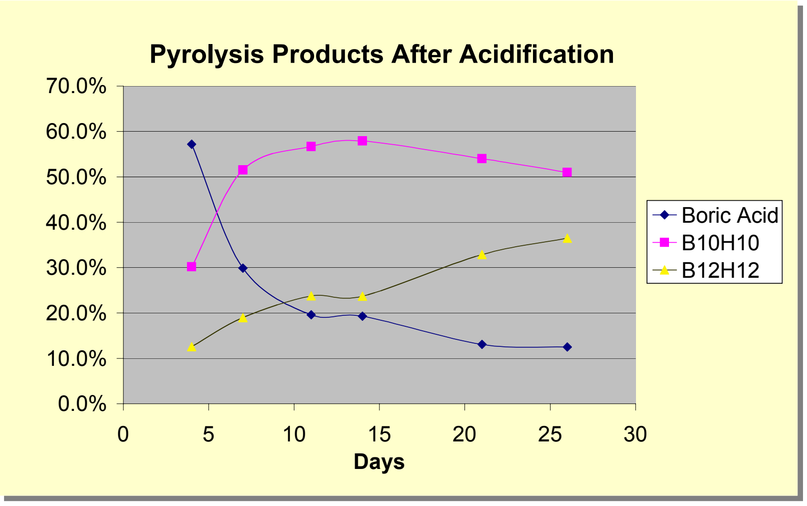
Technical Accomplishments/ Progress/Results

Conversion of Et_4NBH_4 to *Closo*-$B_{10}H_{10}^{2-}$ and *Closo*-$B_{12}H_{12}^{2-}$ Ions by Thermolysis

$$Et_4NBr + NaBH_4 \xrightarrow[100\%]{CH_3CN} Et_4NBH_4$$

$$Et_4NBH_4 \xrightarrow[185\ ^{o}C,\ 11d]{1\ atm} B_{10}H_{10}^{2-} + B_{12}H_{12}^{2-} + \text{Boranes} \xrightarrow{2M\ HCl} \underset{51\%}{B_{10}H_{10}^{2-}} + \underset{37\%}{B_{12}H_{12}^{2-}} + \underset{12\%}{B(OH)_3}$$

- Et_4NBH_4 purified by filtration only.
- Borane Yields determined by ^{11}B NMR, ^{1}H NMR and $B_{10}H_{10}^{2-}$ confirmed by azo coupling.



Future Work

- **Remainder of FY 2005:**
  - Prepare appropriate quantities of $Na_2B_{10}H_{10}$, $Na_2B_{12}H_{12}$ and $NaB_{11}H_{14}$ to support catalyst studies.
  - Identify active catalyst for $B_{11}H_{14}^-$ hydrolysis.
  - Identify appropriate polyhedral borane anions for electrochemical regeneration (with Penn State).
  - Identify appropriate polyhedral borane-amine complexes and ammonium salts for catalytic dehydrogenation studies (with Center).

- **FY 2006:**
  - Identify catalyst for polyhedral borane anion hydrolysis reactions.
  - Determine mechanism of polyhedral borane anion hydrolysis. reactions and secure an efficient catalyst for same.
  - Identify appropriate polyhedral borane anions for electrochemical regeneration (with Penn State).
  - Identify appropriate polyhedral borane-amine complexes and ammonium salts for catalytic dehydrogenation studies (with Center).

Go/No-go Decision Points:

- Choose high-activity hydrolysis catalysts and optimize hydrogen generation at the end of Q12.
- Choose best complex boranes for electrochemical regeneration (with Penn State) by end of Q12.
- Choose best borane-amine complexes or ammonium salts and catalysts for catalytic dehydrogenation (with Center) by end of Q16.
- Choose best borane-amine complexes or ammonium salts and catalysts for catalytic regeneration/hydrogenation (with Center and PNNL) by end of Q20.

Timeline of Project Tasks

TASKS	Year 1	Year 2	Year 3	Year 4	Year 5
Task 1 **Catalytic Hydrolysis of Polyhedral Borane Anions**	■	■	■	■	
Prepare appropriate quantities of $Na_2B_{12}H_{12}$ and $NaB_{11}H_{14}$	■				
Evaluate a variety of catalysts and reaction conditions for the rapid hydrolysis of $Na_2B_{12}H_{12}$ and $NaB_{11}H_{14}$	■	■	■		
Examine mechanism of the hydrolysis process		■	■	■	
Go/No-go Decision Active catalysts for $B_{11}H_{14}^{-}$ and $B_{12}H_{12}^{2-}$ hydrolysis			■		
Task 2 **Electrochemical Regeneration of Borates to Polyhedral Borane Anions (In collaboration with Penn State)**	■	■	■		
Prepare variety of complex boranes for electrochemical studies	■	■	■		
Synthesize new salts with a variety of counter cations to optimize electrochemical properties for reversible hydrogen storage		■	■		
Go/No-go Decision Choose best complex boranes for electrochemical regeneration			■		
Task 3 **Catalytic Dehydrogenation of Polyhedral Borane-Amine Complexes and Ammonium Salts (In collaboration with Center)**	■	■	■	■	■
Synthesize a variety of polyhedral borane amine complexes and ammonium salts for catalytic dehydrogenation studies with the center	■	■	■	■	
Work with the center to identify best catalysts and characterize dehydrogenated B-N residues			■	■	■
Go/No-go Decision Choose best amine-borane complexes for catalytic dehydrogenation				■	
Task 4 **Develop Efficient, Economical Routes to Polyborane Anions**					■
Task 5 **Project Management**	■	■	■	■	■