

IV.B.5d University of Missouri-Columbia's Progress Towards Chemical Hydrogen Storage Using Polyhedral Borane Anion Salts

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Contract Number: DE-FC36-05GO15058

Collaborators:

- Pennsylvania State University
- Los Alamos National Laboratory

Project Start Date: September, 2005
Project End Date: September, 2009

- (R) Regeneration Processes
- (S) By-Product/Spent Material Removal

Technical Targets

Data reported are for hydrolysis of $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$ with 25% mol of Rh metal catalyst at 80°C. The values are material based where as the DOE targets are system based.

| DOE TARGET | MU 2006 Status | 2010 Center Goal |
|--|--|---|
| System Gravimetric Capacity (6 wt%) | 6.5% "in laboratory vessel" [[$(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$ + water consumed + catalyst] | >6.0 wt% Phase I: Material Phase II: System-2010 Phase II: 9% Material-2015 |
| System Volumetric Capacity 0.045 kg/L | 0.0833 kg H_2 /L laboratory vessel contents "in laboratory vessel" [[$(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$ + water consumed + catalyst] | >0.045 kg/L Phase I: Material Phase II: System-2010 Phase II: 0.060 Material-2015 |
| H_2 Flow Rate (0.02 (g/s)/kW) (80 kW stack) | 5268 ml laboratory reactor required for 0.80 mole H_2 /sec | Reactor volume Amount of catalyst |

Project Objective

- Develop heterogeneous catalysts for the controlled generation of hydrogen from the hydrolysis of salts of $\text{B}_{12}\text{H}_{12}^{2-}$, $\text{B}_{10}\text{H}_{10}^{2-}$ and $\text{B}_{11}\text{H}_{14}^-$ ions.
- Determine the kinetics and mechanism of these catalyzed borane anion hydrolysis reactions to provide design data for large-scale hydrogen generation devices.
- Optimize existing processes for the conversion of diverse >BH sources to $\text{Na}_2\text{B}_{12}\text{H}_{12}$ and $\text{Na}_2\text{B}_{10}\text{H}_{10}$ for direct use in hydrogen generation without extensive purification.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System cost
- (C) Efficiency

Accomplishments

- Identified an active Rh metal catalyst for the hydrolysis of borane anion salts.
- Determined that the rate of hydrolysis is first-order with respect to the concentration of borane anion salts and surface area of Rh metal catalyst.
- Determined that hydrogen ion concentration and the identity of the cation accompanying the polyhedral ions have insignificant effect on the rate of hydrogen generation.



Approach

Borohydride compounds offer the potential for significant hydrogen storage capacity, but most work to date has focused on one particular anion, BH_4^- , which requires high pH for stability and large energy costs for regeneration. Other borohydride compounds, in particular polyborane anions, may offer comparable hydrogen storage capacity without requiring high pH media and with significantly reduced energy costs for

| | | Material System weights % (wt. H ₂ / wt. Boranes + wt. H ₂ O) x 100 | | | | |
|---------------------|---|--|-----------------------|----------|---------|--------|
| | | Li salts | NH ₄ salts | Na salts | K salts | |
| $B_{11}H_{14}^-$ | + 32 H ₂ O $\xrightarrow{\text{Cat.}}$ | BO ₂ ⁻ + 10 B(OH) ₃ + 24 H ₂ | 6.61 % | 6.55 % | 6.51 % | 6.37 % |
| $B_{12}H_{12}^{2-}$ | + 38 H ₂ O $\xrightarrow{\text{Cat.}}$ | 2 BO ₂ ⁻ + 10 B(OH) ₃ + 25 H ₂ | 6.46 % | 6.28 | 6.20 % | 5.96 % |
| $B_{10}H_{10}^{2-}$ | + 32 H ₂ O $\xrightarrow{\text{Cat.}}$ | 2 BO ₂ ⁻ + 8 B(OH) ₃ + 21 H ₂ | 6.54 % | 6.34 % | 6.24 % | 5.95 % |

FIGURE 1. Material System Wt% Calculated for Material Consumed in the Reaction Vessel

regeneration. Figure 1 shows the system capacity of these polyhedral borane anions with respect to DOE targets.

The MU project provides the overall Metal Hydride Center of Excellence focal point for the investigation of polyhedral borane anions B_nH_n²⁻ (n = 10 and 12), B₁₁H₁₄⁻ and their derivatives as reservoirs for stored electrons available for hydrogen release upon catalyzed hydrolysis.

Results

Various metal catalysts were investigated for the hydrolysis of B₁₁H₁₄⁻, B₁₂H₁₂²⁻ and B₁₀H₁₀²⁻ anion salts. Transition metal ions, such as cobalt, nickel, palladium and rhodium are known to form metal borides in the presence of reactive borane species. For purposes of initial exploration, rhodium, nickel, cobalt, ruthenium, palladium, platinum and iridium catalysts were examined for their catalytic activity in the hydrolysis of NaB₁₁H₁₄, (NH₄)₂B₁₂H₁₂, K₂B₁₂H₁₂ and K₂B₁₀H₁₀. In each case the rate of hydrogen release depends upon the following variables:

- Choice of polyhedral borane anion
- Choice of metal catalyst
- Concentration of polyhedral borane anion
- Temperature
- Concentration of the catalyst
- pH of the reaction mixture

Of these catalysts, only rhodium (Rh), ruthenium (Ru) and Rh-Co mixtures (1/1 and 1/3) were active in catalyzing the hydrolysis of borane salts. Table 1 shows various transition metal catalysts investigated for borane hydrolysis. Rhodium catalyst was found to be the most active catalyst. Activity of Rh-Co mixtures depended upon the Rh content in the catalyst, showing greater activity at higher percentage of Rh content in the catalyst.

Kinetic Studies

Kinetic studies of (NH₄)₂B₁₀H₁₀, K₂B₁₀H₁₀ and Cs₂B₁₂H₁₂ hydrolysis were carried out at different salt

TABLE 1. Various Transition Metal Catalysts Investigated for the Hydrolysis of Borane Anion Salts

| Catalyst | Borane Anions | Borane Anions | Borane Anions |
|------------------|--|---|---|
| | B ₁₁ H ₁₄ ⁻ | B ₁₀ H ₁₀ ²⁻ | B ₁₂ H ₁₂ ²⁻ |
| Rh Metal | Very Active | Very Active | Very Active |
| Rh/Co 3:1 | Activity Corresponds to Rh Content | Activity Corresponds to Rh Content | Activity Corresponds to Rh Content |
| Rh/Co 1:1 | | | |
| Rh/Co 1:3 | | | |
| CoB ₂ | Active | Inactive | Inactive |
| NiB ₂ | Active | Inactive | Inactive |
| Ru Metal | Inactive | Inactive | Inactive |
| Ir sponge | Inactive | Inactive | Inactive |
| Pd Metal | Inactive | Inactive | Inactive |
| Pt Metal | Inactive | Inactive | Inactive |

concentrations, catalyst concentrations, and hydrogen ion concentrations. In general it was found that the rate of hydrolysis is first-order with respect to the concentration of borane anion salt and surface area of Rh catalyst. We also found that the rate of hydrolysis does not depend upon the pH of the reaction or choice of cation used. These results are illustrated in Figures 2 and 3. Table 2 shows the initial rate of hydrogen release with respect to initial concentration of borane anion salts.

Catalyst Characterization

The most active catalyst, "Rh metal powder," was characterized by different physical methods:

- Elemental analysis of material showed that the catalyst is pure rhodium metal;
- The catalyst has Brunauer-Emmett-Teller surface area of 55 m²·g⁻¹;
- Particle size determination data show that the catalyst is almost monodisperse, with particle size of

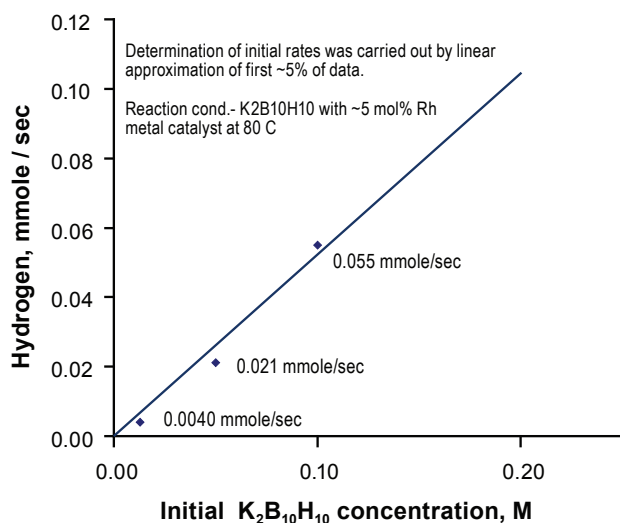


FIGURE 2. Dependence of Rate of Hydrogen Release on Initial Borane Anion Salt Concentration (reaction conditions: 80°C, pH ~6, 5% mol of Rh metal catalyst)

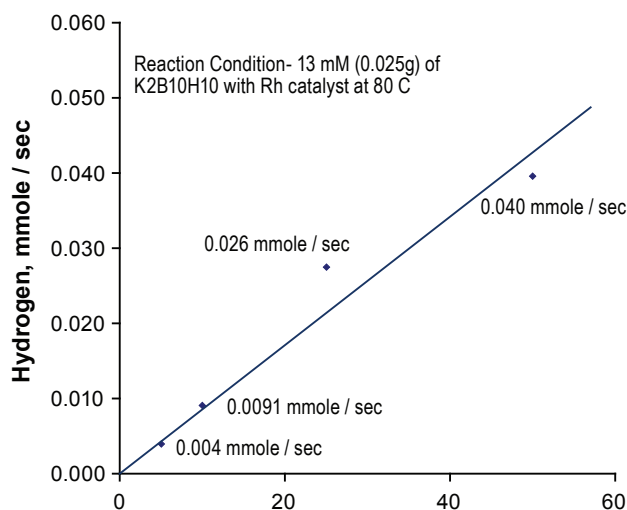


FIGURE 3. Initial Rates of Hydrogen Generation of $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$, $\text{K}_2\text{B}_{10}\text{H}_{10}$ and $\text{Cs}_2\text{B}_{10}\text{H}_{10}$ with Respect to Concentration of Rh Metal Catalyst (80°C, pH ~6, initial borane anion concentration 0.013 M)

237 nm; However, presence of a few agglomerates that are out of the instrument scale makes the z-average particle diameter equal to 938 nm. Figure 4 shows the particle size analysis of the Rh catalyst.

Conclusions and Future Directions

During year 2006, significant progress has been made in the investigation of hydrolysis of polyhedral borane anion salts. In general, we have a good working Rh metal catalyst for the hydrolysis and we have a good understanding of the kinetics of the hydrolysis reaction. The following summarizes our conclusions:

TABLE 2. Initial Hydrogen Generation Rates of $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$, $\text{K}_2\text{B}_{10}\text{H}_{10}$ and $\text{Cs}_2\text{B}_{10}\text{H}_{10}$ with Respect to Initial Borane Anion Concentrations (80°C, pH ~6, 5% mol of Rh catalyst [% of initial borane content])

| Polyhedral anion salts | $5.01 \cdot 10^{-7} \text{ M}$ (pH 6.6) (for $[\text{B}_{10}\text{H}_{10}]^{2-}$) / $2.51 \cdot 10^{-6} \text{ M}$ (pH 5.7) (for $[\text{B}_{12}\text{H}_{12}]^{2-}$) | 0.0001 M salt concentration | 0.01 M salt concentration |
|---|--|-----------------------------|---------------------------|
| $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$ | 0.0028 mmole/sec | 0.0037 mmole/sec | 0.011 mmole/sec |
| $\text{K}_2\text{B}_{10}\text{H}_{10}$ | 0.004 mmole/sec | 0.0081 mmole/sec | 0.017 mmole/sec |
| $\text{Cs}_2\text{B}_{12}\text{H}_{12}$ | 0.00059 mmole sec | 0.00059 mmole/sec | 0.0028 mmole/sec |

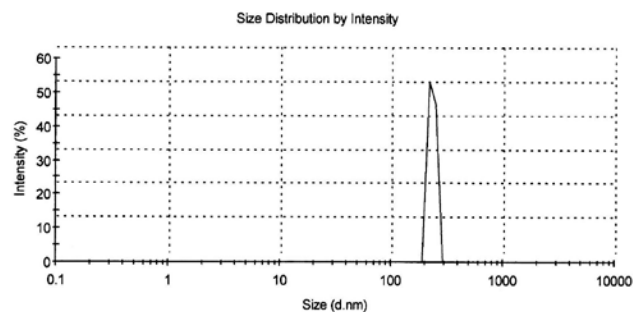


FIGURE 4. Particle Size Distribution of Rh Metal Catalyst Sample (in Water)

- The polyhedral borane anion system was able to achieve material system capacity of ~6.5 wt%.
- The hydrolysis follows first-order kinetics with respect to concentration of borane anion as well as concentration of Rh metal catalyst.
- Hydrolysis of $\text{B}_{10}\text{H}_{10}^{2-}$ is faster than $\text{B}_{12}\text{H}_{12}^{2-}$.
- The Rh metal catalyst seems to be a very efficient in the hydrolysis reaction.
- Change of cations accompanying the polyhedral borane ions has no effect on the rate of hydrolysis.
- All polyhedral anion hydrolysis rates are essentially independent of hydrogen ion concentration.

Future research is anticipated to include:

- The work in FY 2007 will focus on improving the system performance by increasing the hydrogen generation rate and reducing the cost of the system.
- Investigate alternative transition metal catalyst formulations, catalyst nanoparticles, zeolite composites, water-soluble Rh catalysts and other solid-supported catalysts to reduce the material system cost and to increase the rate of hydrogen generation.
- Refine kinetic data for polyhedral anion hydrolysis reactions; determine activation energies and explore reaction mechanism.

FY 2007 Publications/Presentations

1. Merit review presented at DOE Chemical Hydrogen Storage Meeting held at Washington D.C., May, 2007.