Chemical Hydrogen Storage Using Polyhedral Borane Anion Salts

M. Frederick Hawthorne, Satish S. Jalisatgi, and Alexander V. Safronov

University of Missouri - Columbia

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STP 11

Overview

Timeline

- Project start date
  - Fiscal year 2005
- Project end date
  - Fiscal year 2009
- Percent complete 45%

Budget

- Total project funding
  - DOE share $ 1,250,000 (proposed)
  - Contractor share $ 312,000
- Funding received in FY06
  - $ 250,000 (DOE share)
- Funding for FY07
  - $ 250,000 (DOE share)

Barriers

- Barriers addressed
  - System Weight and Volume
  - Efficiency
  - Regeneration Processes
  - By-Product/Spent Material Removal

Partners

- DOE Center of Excellence for Chemical Hydrogen Storage
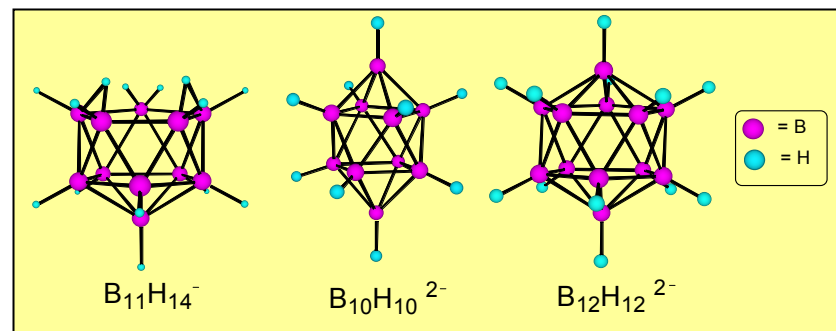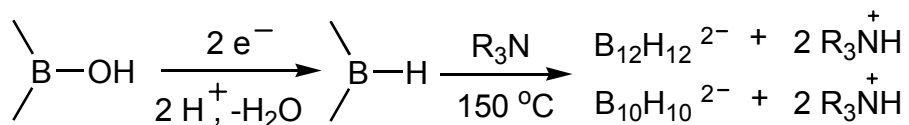 - LANL
  - Penn State

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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 to meet DOE system targets for capacity, efficiency and cost.

- 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.

- Develop BO to BH regeneration process.

Polyhedral Hydridoborates - Electron Reservoirs

The University of Missouri-Columbia (MU) 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.

$$\begin{array}{c}\backslash \\ B-OH \\ /\end{array} \xrightarrow[2\,H^+,\,-H_2O]{2\,e^-} \begin{array}{c}\backslash \\ B-H \\ /\end{array} \xrightarrow[150\,^oC]{R_3N} \begin{array}{l} B_{12}H_{12}{}^{2-} + 2\,R_3\overset{+}{N}H \\ B_{10}H_{10}{}^{2-} + 2\,R_3\overset{+}{N}H \end{array}$$

$B_{11}H_{14}^-$ $B_{10}H_{10}{}^{2-}$ $B_{12}H_{12}{}^{2-}$ ● = B   ● = H

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°C
- No decomposition on storage in H_2O solution at elevated temperatures

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Approach-Technical Strategy Cont.

System Capacity:

Polyhedral anion 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 $NaB_{11}H_{14}$ can be easily obtained from $NaBH_4$.

System Efficiency and Cost:

Polyhedral borane applications

- Transition metal catalyst is need to generate hydrogen from $Na_2B_{12}H_{12}$ and $Na_2B_{10}H_{10}$ and will 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 supplying hydrogen to large fixed installations or small and disposable devices when great safety and reliable hydrogen release after prolonged storage times (years) are required.
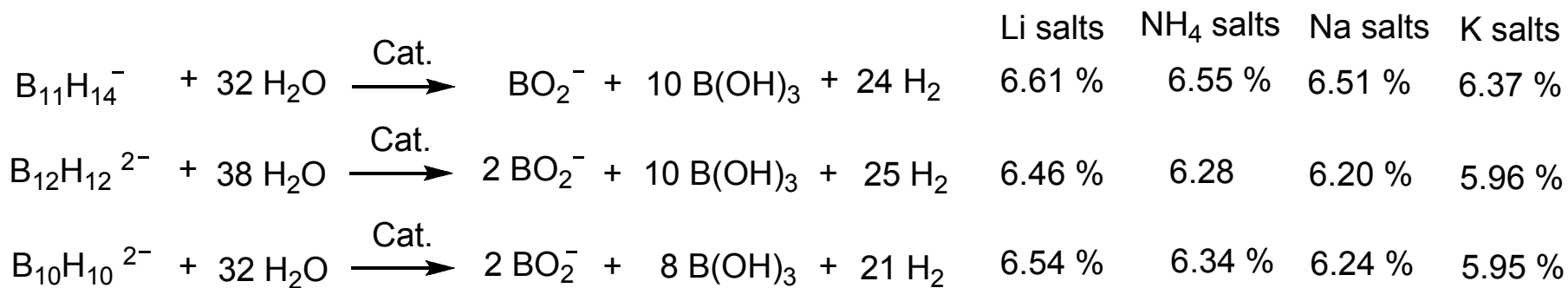
Approach-Technical Strategy
Hydrogen Release

- Material system wt% calculated for material consumed in the reaction vessel.
- DOE targets for system wt. **2005**: 4.5%; **2010**: 6.0%; **2015**: 9.0%

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

					Li salts	NH$_4$ salts	Na salts	K salts
$B_{11}H_{14}^-$ + 32 H_2O $\xrightarrow{Cat.}$ BO_2^- + 10 $B(OH)_3$ + 24 H_2					6.61 %	6.55 %	6.51 %	6.37 %
$B_{12}H_{12}^{2-}$ + 38 H_2O $\xrightarrow{Cat.}$ 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_2O $\xrightarrow{Cat.}$ 2 BO_2^- + 8 $B(OH)_3$ + 21 H_2					6.54 %	6.34 %	6.24 %	5.95 %

- Reaction rates and efficiency can be measured by ^{11}B NMR of the reaction mixtures and by hydrogen evolution as a function of time.

Approach-Technical Strategy
System Variables

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

Technical Accomplishments: Summary

- Identified an active Rh metal catalyst for the hydrolysis of borane anion salts.

- The rate of hydrolysis is first-order with respect to the concentration of borane anion salts and concentration of Rh metal catalyst.

- Hydrogen ion concentration and the identity of the cation accompanying the polyhedral ions has insignificant effect on the rate of hydrogen generation.

Technical Accomplishments:
Search for System for Optimal Capacity, Performance and Cost

- In our search for optimal system for hydrogen generation, we investigated various polyhedral borane anions including $NaB_{11}H_{14}$, $KB_{11}H_{14}$, $(NH_4)_2B_{12}H_{12}$, $K_2B_{12}H_1$, $Cs_2B_{12}H_{12}$, $(NH_4)_2B_{10}H_{10}$ and $K_2B_{10}H_{10}$.

- Transition metal ions, such as cobalt, nickel, palladium and rhodium are known to form catalytically active metal borides in the presence of reactive borane species.

- Transition metals are good first choice catalysts since these could possibly be converted to the respective borides during the hydrolysis reactions.

Technical Accomplishments:
Search for Optimal Catalyst for the Hydrolysis of Polyhedral Borane Anion Salts

- For purposes of initial exploration, Rh, Ni, Co, Pd, Ru, Ir and Pt catalysts of various types were examined for their catalytic activity in the hydrolysis of $NaB_{11}H_{14}$, $(NH_4)_2B_{12}H_{12}$, $K_2B_{12}H_{12}$, $(NH_4)_2B_{10}H_{10}$ and $K_2B_{10}H_{10}$.

- In these preliminary studies, Rh metal was found to be a superior catalyst for the hydrolysis of polyhedral borane anions.

Catalytic Activity of Various Catalysts

Catalyst	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 Rh/Co 1:1 Rh/Co 1:3	Activity Corresponds to Rh Content	Activity Corresponds to Rh Content	Activity Corresponds to Rh Content
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

Hydrolysis of Borane Anions in the Presence of a Rhodium Metal Catalyst

- Of the various transition metal catalysts investigated, only rhodium metal catalyzed the hydrolysis of the generally less reactive $B_{12}H_{12}^{2-}$ and $B_{10}H_{10}^{2-}$ ions. These ions were inert to nickel boride and cobalt boride catalysts.

- Elemental analysis of the Rh catalyst proved that the catalyst is pure Rh metal having a BET surface area of ~ 55 m^2 / g.

- The majority of the catalyst is monodisperse with a particle size of approximately 240 nm. However, the presence of a few larger particles in the sample makes the average particle size approximately ~ 1um.

- All hydrolysis reactions proceed to completion giving quantitative hydrogen and boric acid production.

Kinetic Data Obtained for Rh Metal-Catalyzed Borane Anion Hydrolysis

- The rates of hydrolysis of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ can be expressed by this differential rate equation:

$$\frac{d[H_2]}{dt} = \underbrace{k\,[\text{Borane anion}]\,[\text{Rh catalyst}]}_{\text{Dominant Term}} + \underbrace{k'\,[H^+]}_{\text{Negligible Term}} \;???$$

- The rate of hydrolysis of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ is first-order with respect to the concentration of borane salts.

- The rate of hydrolysis of borane anions is first-order with respect to the effective Rh metal catalyst surface.

- Change of cations accompanying the polyhderal borane ions has no effect on the rate of hydrolysis.

- All polyhedral anion hydrolysis rates are essentially independent of hydrogen ion concentration.
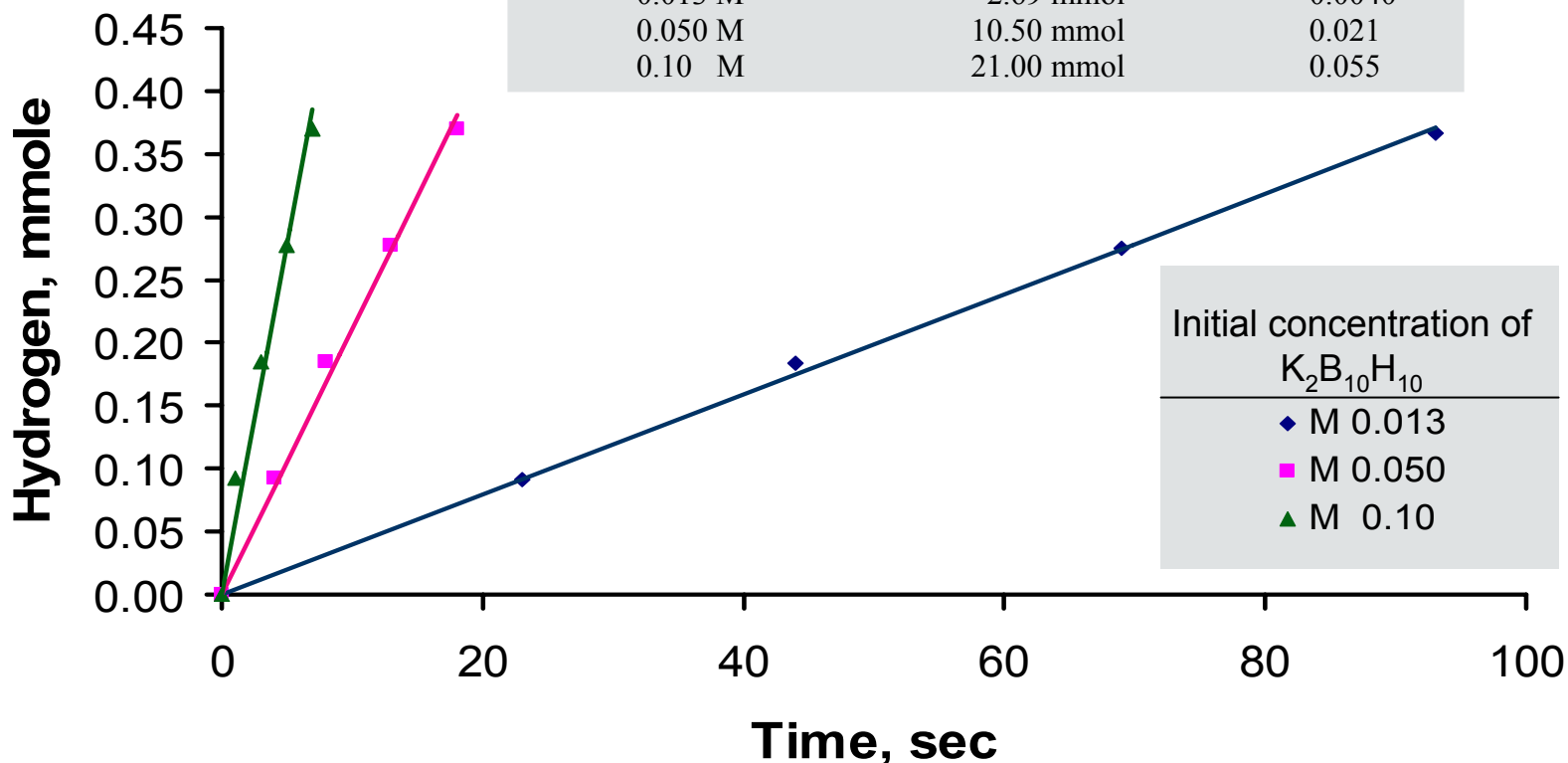
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Representative Kinetic Data: Rh Metal-catalyzed Hydrolysis of $K_2B_{10}H_{10}$

Effect of Borane Anion Concentration on the Initial Rate of Hydrolysis of $K_2B_{10}H_{10}$

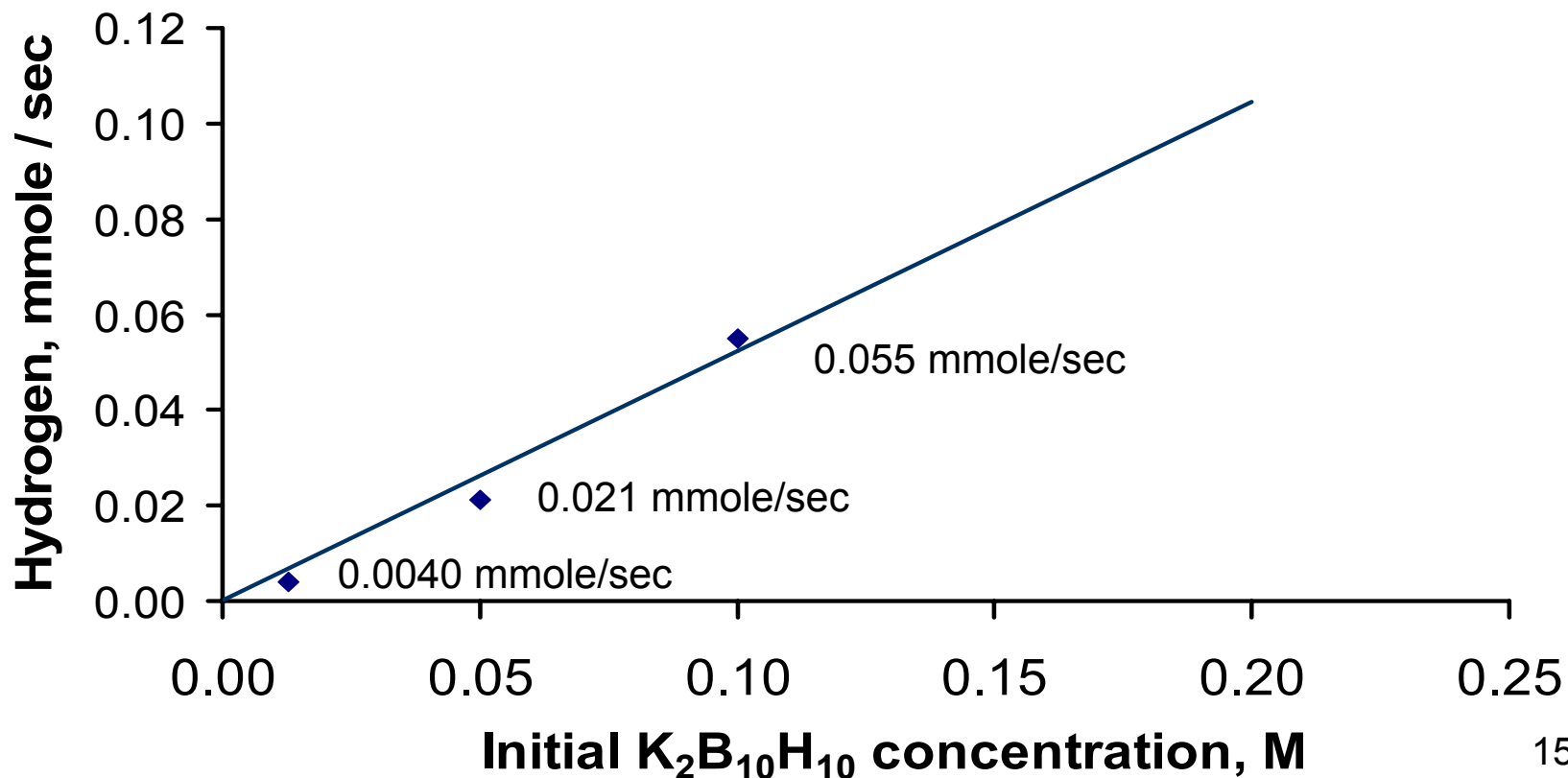Reaction conditions: 5 mol% Rh catalyst at 80 ºC. The plot shows the initial 5% of hydrogen generation data.

$K_2B_{10}H_{10}$ Concentration	100% Hydrogen Yield	Observed Rate mmole H_2 / sec
0.013 M	2.69 mmol	0.0040
0.050 M	10.50 mmol	0.021
0.10　M	21.00 mmol	0.055

Initial concentration of $K_2B_{10}H_{10}$
- ◆ M 0.013
- ■ M 0.050
- ▲ M 0.10

Initial Rate of Hydrogen Generation with Respect to Concentration of $K_2B_{10}H_{10}$
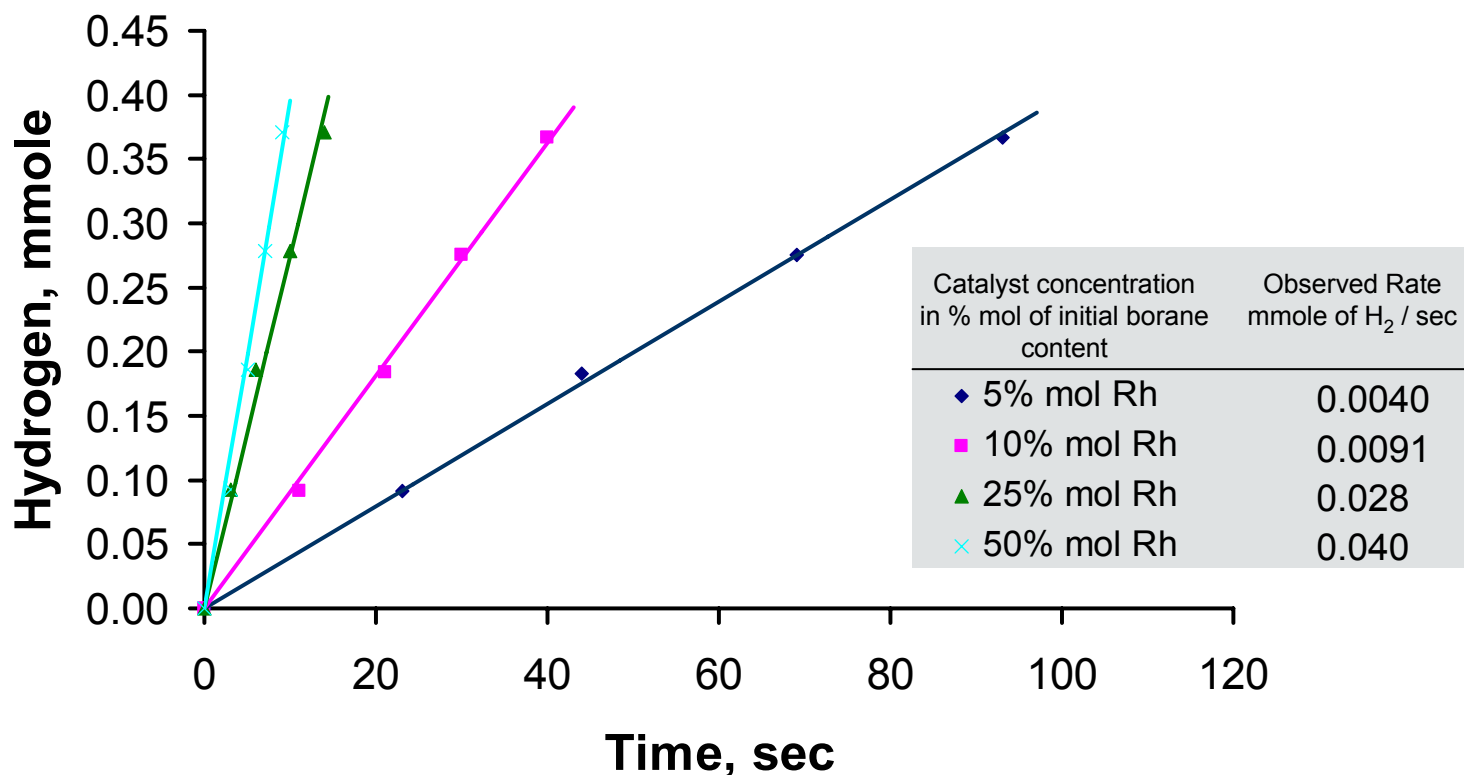
- Determination of initial rates was carried out by linear approximation of first ~ 5% of kinetic data observed.
- Reaction conditions: 5 mol% Rh metal catalyst at 80 ºC

Representative Kinetic Data:
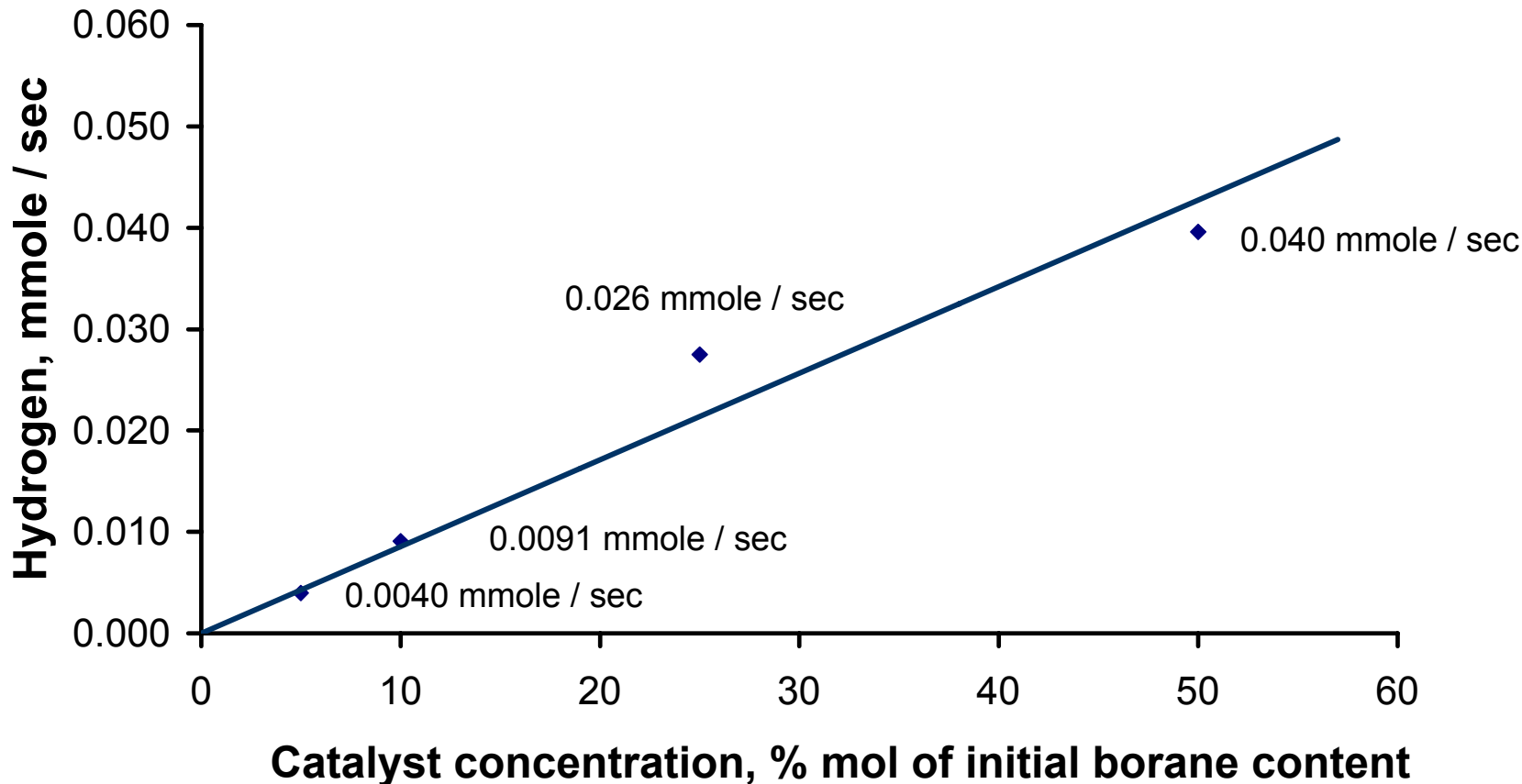# Effect of Rh Metal Catalyst Added on the Hydrolysis of $K_2B_{10}H_{10}$

- Reaction conditions: 13 mM (0.025 g) of $K_2B_{10}H_{10}$ in presence of Rh metal catalyst at 80 ºC; 100% hydrogen yield = 2.69 mmole
- The plot shows the initial 5% of hydrogen generation data.

Catalyst concentration in % mol of initial borane content	Observed Rate mmole of H_2 / sec
◆ 5% mol Rh	0.0040
■ 10% mol Rh	0.0091
▲ 25% mol Rh	0.028
✕ 50% mol Rh	0.040

Dependence of Initial Rates of Hydrogen Generation on Effective Added Rh Catalyst

Reaction conditions: 13 mM (0.025 g) of $K_2B_{10}H_{10}$ in presence of Rh metal catalyst at 80 °C.

Plot of Hydrogen, mmole / sec (y-axis, 0.000 to 0.060) versus Catalyst concentration, % mol of initial borane content (x-axis, 0 to 60).

Data points labeled:
- 0.0040 mmole / sec
- 0.0091 mmole / sec
- 0.026 mmole / sec
- 0.040 mmole / sec

Future Work

- The work in year '07 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 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.

Collaboration and Partners

- Electrochemical studies of reversible electron (hydrogen) storage mediated by electrochemical reactions of polyhedral borane anions and their derivatives (Penn State University) will be supported by MU as follows:

  - Through MU and Penn State consultation, promising candidate polyhedral borane derivatives will be identified for electrochemical studies at Penn State for BO to BH regeneration process.
  - Feasible polyhedral borane derivatives will be supplied to Penn State for study following their synthesis at MU.

- Polyhedral borane derivatives sought by the DOE Chemical Hydrogen Storage Center of Excellence for reversible hydrogen uptake and release will be supplied by MU.

Overall Result Summary

- Capacity
  - The polyhedral borane anion system was able to achieve material system capacity of ~ 6.5 wt% (0.056 g H_2 released / g laboratory vessel contents)

- Efficiency
  - Number of other transition metal catalysts were investigated and are being perused for the hydrolysis of polyhedral borane anions.
  - In our preliminary investigations, Rh metal catalyst was found to be best catalyst for the hydrolysis of polyhedral borane anions.
  - The hydrolysis of $B_{10}H_{10}^{2-}$ is faster than $B_{12}H_{12}^{2-}$ anions.

Overall Result Summary:
Quantitative Performance Metrics:

Hydrolysis of 13mM $K_2B_{10}H_{10}$ with 50% mol of Rh catalyst at 80 ºC

DOE TARGET	Metrics	2010 Center Goal
System Gravimetric Capacity (6 wt%)	0.056 g H_2 released/g laboratory vessel contents "in laboratory vessel" [$K_2B_{10}H_{10}$+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	0.083 kg H_2/L laboratory vessel contents "in laboratory vessel" [$K_2B_{10}H_{10}$+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)	1821 ml laboratory reactor required for 0.80 mole H_2/sec	Reactor volume Amount of catalyst