Solutions for Chemical Hydrogen Storage: Hydrogenation/ Dehydrogenation of B-N Bonds

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Project ID # STP10

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Overview

Timeline

- Start: FY 05
- End: FY 09
- 40% Complete

Budget

- Total project funding
  - $1.1 M DOE share
  - $0.28 M cost share
- Funding received in FY06
  - $200K
- Funding for FY07
  - $200K

Barriers

- System Weight and Volume
- H_2 Charging/Discharging Rate
- System Cost
- Regeneration Processes

Partners

- Pacific Northwest National Laboratory (PNNL)
- Los Alamos National Laboratory (LANL)
- University of Alabama
- University of Arizona

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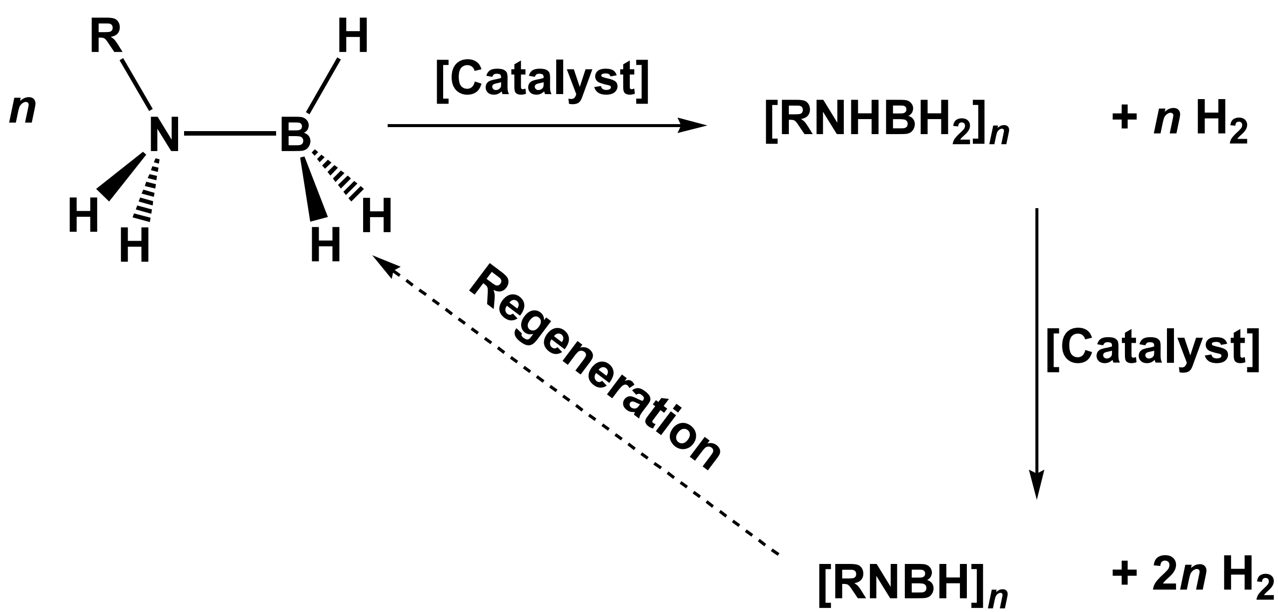
Objectives

- Identify materials/systems to meet DOE target goals for gravimetric and volumetric density of H_2
  - Amineboranes and other BN compounds have potential for high H_2 storage capacities
- Develop catalysts to meet DOE target goals for H_2 charging/discharging rates from BN materials
  - Thermal H_2 release from BN materials is slow and inefficient. Effective catalysts for dehydrogenation/ rehydrogenation will be needed
- Optimize to obtain cost-effective catalysts
  - Scale of project requires inexpensive and widely available system components
- Optimize BN materials for potential in effective regeneration processes
  - Efficient regeneration of spent BN materials is critical

Approach Theme

Develop cost effective and efficient catalysts for the dehydrogenation of BN compounds



R = H, Me

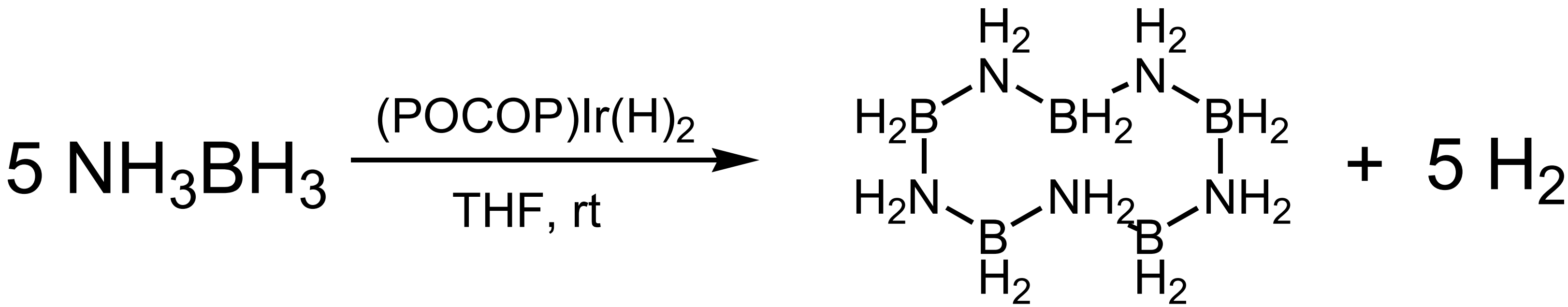
Approach in Detail

- **To develop cost effective catalysts for dehydrogenation of BN compounds**
  - **Understand how previously identified Iridium catalyst (2006 result) dehydrogenates Ammonia Borane (AB) and test its effectiveness for the dehydrogenation of other BN compounds *(weight and volume, H_2 discharge rate)***
  - **Apply knowledge gained from Platinum Group Metal (PGM) catalysts to develop efficient non-PGM catalysts for dehydrogenation of BN compounds (*H_2 discharge rate, system cost*)**
- **To identify BN compounds with high potential for facile regeneration**
  - **Using efficient catalysts (see above), thermodynamics of dehydrogenation/rehydrogenation can be experimentally measured (*regeneration processes*)**

Key Accomplishments for 2007

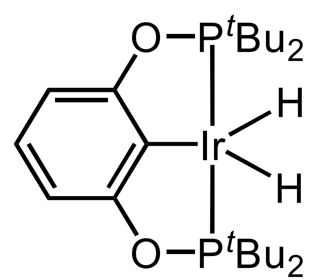
- 2006 Ir catalyst and modified PGM catalysts found to be effective for the dehydrogenation of several different BN materials
- Identified dormant form of 2006 Ir catalyst and conditions for regeneration of the catalyst
- Discovered several non-PGM catalysts for the dehydrogenation of BN materials
- UW catalysts are the fastest PGM and non-PGM catalysts for ammonia borane (AB) dehydrogenation
- Demonstrated a BN system that is within a factor of 10 of 2010 DOE target goals for system gravimetric and volumetric densities of H_2
- Developed a PGM catalyst for the dehydrogenation of a “solvent-free” liquid BN system
- Enthalpy of reaction for the dehydrogenation of AB was experimentally measured

Ir Catalyzed Dehydrogenation of Ammonia Borane (AB)



Insoluble Product

- **Fastest reported transition metal catalyst**
  - **200 fold increase in reaction rate compared to previous best catalyst**
- **Gives single, but insoluble product**
  - **Insolubility presents challenge for further dehydrogenation**



"(POCOP)Ir(H)$_2$"

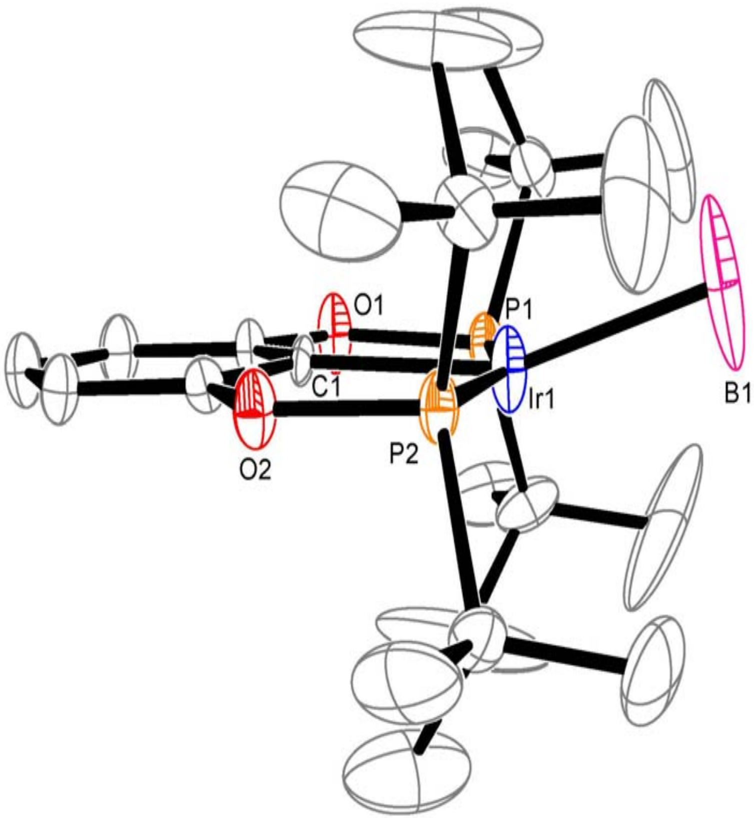
✓ **Dehydrogenation occurs very rapidly, but insoluble product allows generation of only one equivalent of H_2 which limits weight %**

Denney, M. C.; *et al.*, *J. Am. Chem. Soc.*, **2006**, 128(37), 12048-12049

Characterization of Dormant Catalyst and Subsequent Regeneration

- Slowing rates upon continued addition of BN substrate indicate catalyst deactivation

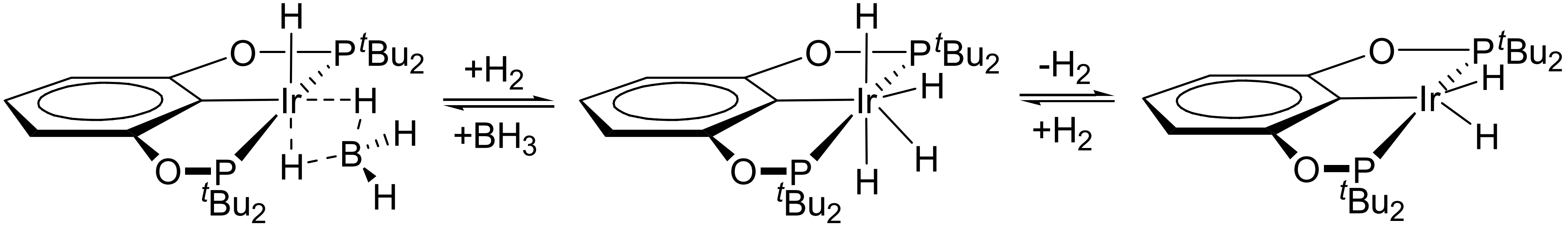
- The dormant catalyst has been characterized by X-ray crystallography and ^{1}H NMR spectroscopy



✓ **The deactivated form of the catalyst is a single, well-characterized species**

Regeneration of Active Catalyst

- Investigations of the reactivity of the dormant form of the catalyst — reaction with H_2 (30 psi) results in loss of BH_3 and regeneration of Ir hydride complexes



✓ **Active Ir catalyst can be regenerated under moderate H_2 pressure from dormant form**

Ir Catalyzed Dehydrogenation of Other BN Systems

- **Dehydrogenation of Methylamine Borane (MeAB)**

$$n\,MeNH_2BH_3 \xrightarrow[\text{THF, rt}]{(POCOP)Ir(H)_2} [MeNHBH_2]_n + n\,H_2$$

Soluble Product

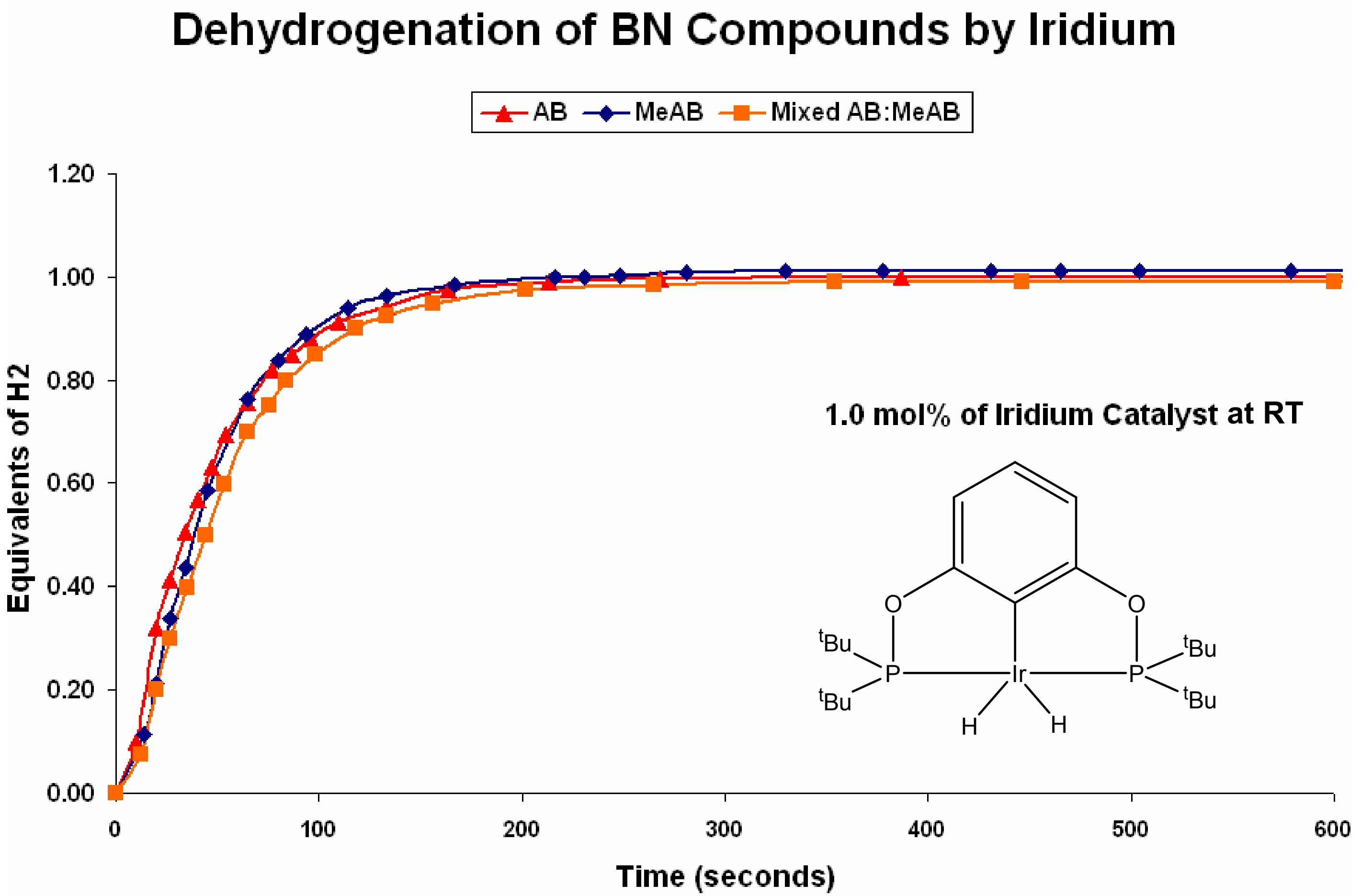
- **Dehydrogenation of a 1:1 mixture of AB and MeAB**

$$NH_3BH_3 + MeNH_2BH_3 \xrightarrow[\text{THF, rt}]{(POCOP)Ir(H)_2} [(NH_2BH_2)(MeNHBH_2)]_n + 2\,H_2$$

Soluble Product

✓ **Ir catalyzed dehydrogenation of substituted and mixed BN systems yields *soluble* products and thus provides potential for further dehydrogenation to release more than one equivalent of H_2**

Versatility of Iridium Catalyst



✓ **Ir catalyst promotes release of H_2 from different BN systems at similar rates allowing for potential development of mixed BN materials for hydrogen storage applications**

Approaching DOE Goals

- **Reaction Conditions**
  - High concentration mixture of NH_3BH_3 (AB) and $MeNH_2BH_3$ (MeAB) at RT (~800 mg of total amine borane)
  - 0.5 mol% Ir catalyst
- **Results**
  - Produces 0.500 L of H_2 (1 equiv.) in ~60 s
  - System (solvent, catalyst, etc…) generates 0.4 wt% H_2

	Concentrated AB/MeAB Mixture	DOE 2010 Target
Gravimetric Density (wt% H_2)	0.4%	6.0%
Volumetric Density (kg H_2/L)	0.005	0.045

✓ **Unoptimized system is within a factor of 10 of several DOE goals**

"Solvent-Free" Mixed AB:MeAB Dehydrogenation

- Center partners determined that 1:1 mixture of AB and MeAB forms a liquid at 60 °C
  - Absence of solvent increases the wt% of H_2 for the system
- Knowledge gained from Ir system was used by UW to identify a PGM catalyst* that can dehydrogenate the liquid AB/MeAB mixture
  - Preliminary results
    - 0.25 equivalents of H_2 released in ~10 minutes
    - Up to 1.25 equivalents of H_2 released in ~16 hours

✓ **Dehydrogenation of AB/MeAB mixtures with no solvent can lead to systems with very high gravimetric density (potentially 11.0 wt%)**

*Catalysts not identified because information is proprietary

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Development of non-PGM Catalyst

- **Benefits of non-PGM catalysts over PGM group catalysts: price and availability**

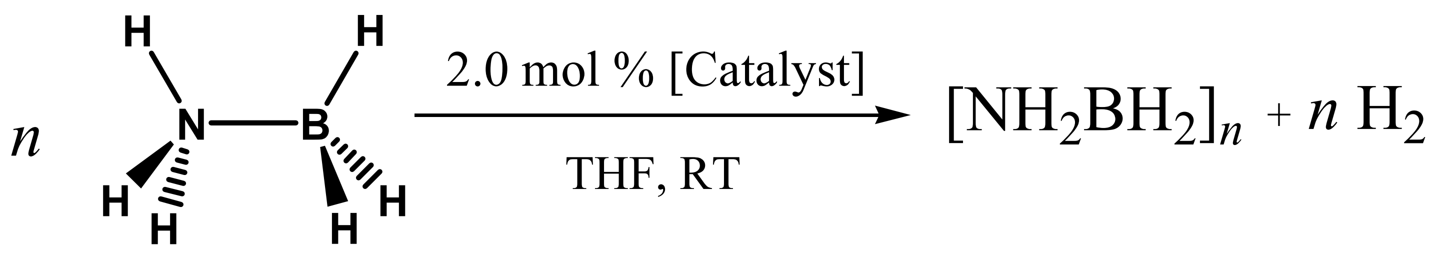
  (e.g. Co versus Ir)

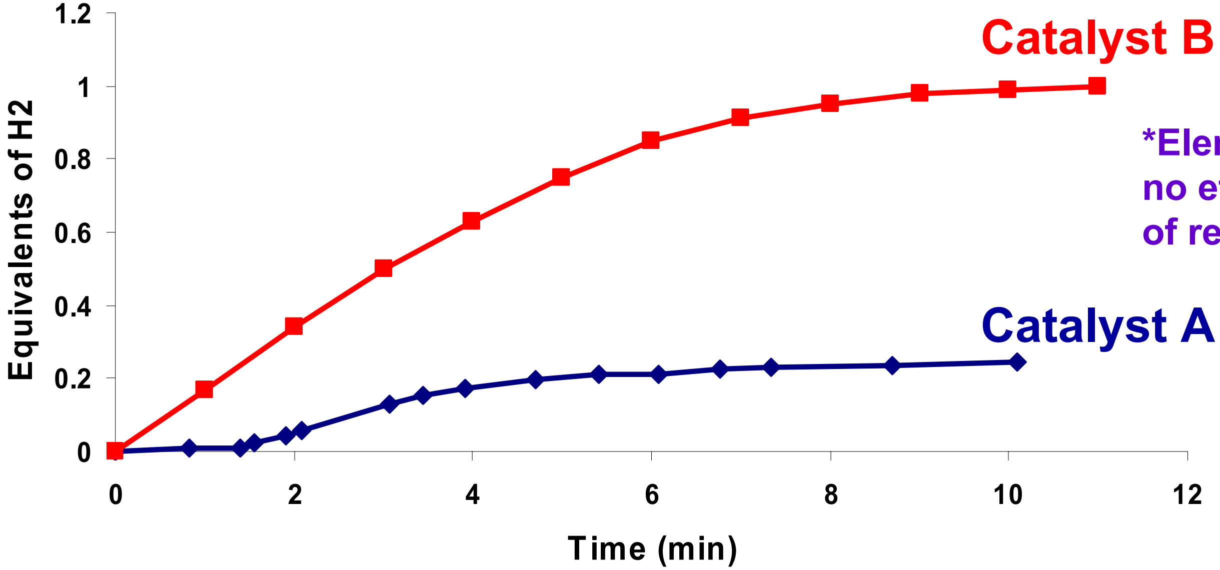
  - **Cobalt is much cheaper than Iridium**
    - **Ir market price ~ $14,000 / kg**
    - **Co market price ~ $32 / kg**
  - **Cobalt is more abundant than Iridium[1]**
    - **Abundance of Ir in earth's crust – 1 µg / kg**
    - **Abundance of Co in earth's crust – 2.5 mg / kg**
- **Knowledge from PGM catalysts allowed identification of several non-PGM catalysts that dehydrogenate BN compounds**

✓ **Information gained from studying PGM catalysts can be applied towards the development of inexpensive non-PGM catalysts**

1) *CRC Handbook of Chemistry and Physics,* Internet Version 2007, (87th Edition)

Homogeneous* Ammonia Borane Dehydrogenation Catalyzed by Cobalt Complexes





*Elemental Hg has no effect on rate of reaction

- ✓ **Homogeneous cobalt catalysts show high activity for AB dehydrogenation**
- ✓ **Fastest known base metal catalyst for AB dehydrogenation**

Catalysts not identified because information is proprietary

Enthalpy Measurements

- **DSC Calorimetry at PNNL in collaboration with Center Investigators Autrey and Linehan**

ΔH (kcal·mol⁻¹)

$$5\ NH_3BH_3\ (solv) \xrightarrow[THF]{Ir\ catalyst} (BH_2NH_2)_5\ (s) + 5\ H_2\ (g) \qquad -6.7 \pm 0.6$$

- **Previous Experimental Work by Baumann, Baitalow and Hoffman[1]**

$$x\ NH_3BH_3\ (s) \xrightarrow[\Delta]{} (BH_2NH_2)_x\ (s) + x\ H_2\ (g) \qquad -5.2 \pm 0.6$$

- **Theoretical Calculations by Center Investigators Dixon and Gutowski[2]**

$$NH_3BH_3\ (g) \longrightarrow BH_2NH_2\ (g) + H_2\ (g) \qquad -5.1$$

✓ **Ir catalyst allowed measurement of enthalpy for AB dehydrogenation**

✓ **Results imply that direct rehydrogenation of spent AB will not be possible and alternate regeneration routes are required**

1) *Thermochim. Acta*, **2000**, *343*, 19 2) *J. Phys. Chem. A*, **2005**, *109*, 5129-5135

Future Work

- Mechanistic study of dehydrogenation of BN systems with current catalysts
  - Optimization and further catalyst development will be assisted by understanding the catalyst mode of action
  - Better catalysts will lead to higher H_2 discharge rates
- Development of efficient non-PGM catalysts for the dehydrogenation of BN materials
  - Continue to use knowledge gained from PGM catalysts to design non-PGM catalysts
  - Non-PGM catalysts will lower system costs
- Increase amount of H_2 released from BN materials
  - Increase solubility of first BN dehydrogenation product to allow further dehydrogenation
  - Pursue tandem catalysts for first and second dehydrogenation reactions (in collaboration with LANL)
  - Further dehydrogenation needed to meet DOE weight and volume targets

Future Work

- Development of catalysts for liquid phase "solvent-free" BN systems
  - New catalysts for solvent-free BN systems are being developed
  - Liquid BN materials can meet DOE weight and volume targets
- Identify/develop new BN materials* that have the potential for direct rehydrogenation of spent fuel
  - New systems have been proposed and computational studies are being carried out (in collaboration with PNNL and University of Alabama)
  - Thermodynamic (enthalpy) measurements using our fast PGM and non-PGM catalysts allow experimental assessment of the potential of different BN materials (in collaboration with PNNL)
  - Will impact regeneration processes

*Compounds not identified because information is proprietary

Collaborations with Center Partners

- Pacific Northwest National Lab (PNNL)
  - DSC calorimetry experiments (enthalpy measurements)
  - Computations on thermodynamics of dehydrogenation of new BN materials
- Los Alamos National Lab (LANL)
  - Regular exchange of catalyst and system information (e.g. Liquid AB/MeAB mixture conditions)
  - Tandem catalysis experiments
- University of Alabama
  - Theoretical calculations of thermodynamics for AB dehydrogenation/rehydrogenation
  - Theoretical calculations on new BN materials
- University of Arizona
  - Have provided UW with AB and MeAB materials

Project Summary

- **Relevance**
  - BN compounds have significant potential as hydrogen storage materials which can meet DOE goals
- **Approach**
  - Develop catalysts for dehydrogenation of BN systems
  - Investigate different BN materials and systems
  - Optimize systems to meet DOE weight and volume, H_2 discharge rate, and system cost targets
- **Accomplishments**
  - Developed the fastest PGM and non-PGM catalysts reported to date for the dehydrogenation of BN compounds at mild conditions
  - Determined thermodynamic data relevant to the potential regeneration of BN compounds by direct rehydrogenation
- **Collaboration**
  - Collaborations with groups at PNNL, LANL, University of Alabama, and University of Arizona
- **Future Work**
  - Acquire and utilize mechanistic information concerning the dehydrogenation of BN compounds with current catalyst systems to guide optimization of new systems
  - Develop catalysts for the dehydrogenation of liquid “solvent-free” BN systems
  - Investigate new BN materials which may have the potential for regeneration by direct rehydrogenation

Project Summary Table

Barrier	FY 2006 Results*	FY 2007 Results: High Concentration AB/MeAB Mixture	FY 2007 Results: Solvent-Free System	DOE 2010 Target
Gravimetric Density (wt% H_2)	0.001 %	0.4%	11.0%**	6.0%
Volumetric Density (kg H_2/L)	0.0009	0.005	Density of AB/MeAB Liquid (TBD)	0.045
Charging / Discharging Rate (System volume required to meet target rate for an 80 kW stack)	81 L	24 L***	TBD	Minimum Full Flow Rate of 0.02 (g/s)/kW = 0.80 mol H_2/sec for an 80 kW stack

* Based on dilute AB solution in THF with 1.0 mol% catalyst

** Theoretical potential with release of 2 equivalents of H_2

*** Conservative value based on the average rate over entire reaction time