

Final Scientific/Technical Report

Project Title: *Kinetic and Mechanistic Studies of B-N Hydrogenation/Dehydrogenation*

Project Period: March 1, 2005 – February 28, 2010

Date of Report: October 31st, 2009

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Award Number: DE-FC36-05GO15057

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Executive Summary

Project Objective:

This project is focused on developing catalysts capable of releasing hydrogen gas from a chemical substrate. The ultimate goal of this project is to then use this system as an on-board source of hydrogen for a fuel-cell powered vehicle. Specific goals include developing a working understanding of the mechanism of dehydrogenation and applying these insights toward developing new catalysts. Rates of dehydrogenation as well as material cost and ease of use are major issues of focus.

Background:

Hydrogen gas (H_2) is an attractive alternative energy carrier, especially for application in the transportation sector. Not only does the use of H_2 in an on-board fuel system produce water as its sole byproduct, thereby eliminating harmful carbon emissions, one can also envision a system in which the H_2 is produced from secure and abundant sources within the country, reducing the political tensions caused by the localization of fossil fuel resources.

Several problems must be overcome before a competent hydrogen based economy can be established. In particular, before the technology can be applied for use in personal transportation the issue of how to store enough hydrogen safely and efficiently on-board a vehicle while allowing it to be delivered quickly and in sufficient quantity to meet the technological requirements of the fuel cell must be addressed. Use of compressed gas or liquefied H_2 is inefficient, and does not meet the gravimetric and volumetric density requirements of an on-board H_2 storage system. As a result, chemical hydrogen storage methods, in which the hydrogen is covalently bound in chemical compounds and released in a subsequent reaction as H_2 gas when needed, are being explored. Materials that have a high weight percent of hydrogen are being investigated, and in particular, ammonia-borane (H_3NBH_3) and related CBN compounds have become the primary candidates for chemical hydrogen storage.

Accomplishments:

The research at UW initially focused on development of catalysts for hydrogen release from ammonia borane. A highly active homogeneous catalyst based on an iridium pincer complex was developed. This catalyst was approximately 2,000 times more active than the best previously reported. The active catalyst under operational conditions was identified and the mechanism was studied. Due to the cost of iridium, analogs using earth abundant cobalt were also explored. The cobalt catalysts exhibited promising initial activity, but catalyst durability was inadequate. Ruthenium catalysts were also studied, and reasonable activity for hydrogen release was observed, but these catalysts were found to be slower than the iridium catalysts. A range of ligand variants were explored for both cobalt and nickel, with similar results.

Due to the difficulty of rehydrogenating the products of hydrogen release from ammonia borane, alternative substrates were pursued which contained carbon, boron and nitrogen in six membered ring structures (CBN compounds). Computational work suggested that multiple dehydrogenation of substrates of this type would be near thermoneutral and possibly reversible. We found that our iridium catalysts would slowly release only one equivalent of hydrogen from model CBN substrates.

Technical Report

Objectives

- Identify materials/systems to meet DOE target goals for gravimetric and volumetric densities of H₂
Amineboranes and other BN compounds have potential for high H₂ storage capacities
- Develop cost-effective metal catalysts for the dehydrogenation of BN hydrogen storage materials
Focus on cheap widely available non-platinum group metals such as cobalt and iron
- Optimize catalysts to meet DOE target goals for H₂ discharging rates from BN materials
- Collaborate with the University of Oregon to develop systems based on novel CBN materials
Will need to identify and investigate catalysts capable of dehydrogenating both B-N and C-C bonds. CBN materials have the potential for direct regeneration

Technical Barriers

This project addresses the following technical barriers from the 3.3.4.2 section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- *System Weight and Volume*
- *System Cost*
- *H₂ Charging/Discharging Rate*
- *Regeneration Processes*

Technical Targets

Amineboranes are promising substances for chemical hydrogen storage, provided that efficient catalysts can be developed to liberate the stored hydrogen rapidly. This project is working to develop cost effective catalysts for the dehydrogenation of amineboranes. We are also working to develop new mixed CBN materials that have the potential to be directly regenerated. Insights gained from these studies will be applied toward the design of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

Cost: 4 \$/kWh net

Specific energy: 1.5 kWh/kg

Energy density: 0.9 kWh/L

Project Overview

Amineboranes such as H₃NBH₃ (AB) and related BN materials such as CH₃NH₂BH₃ (MeAB) are promising hydrogen storage materials for transportation applications. Thermal hydrogen loss from such materials is too slow to be practical. The main project goal is the development of catalysts for AB dehydrogenation with rates sufficient for on board transportation applications.

Studies with (^tBuPOCOP)IrH₂ (1)

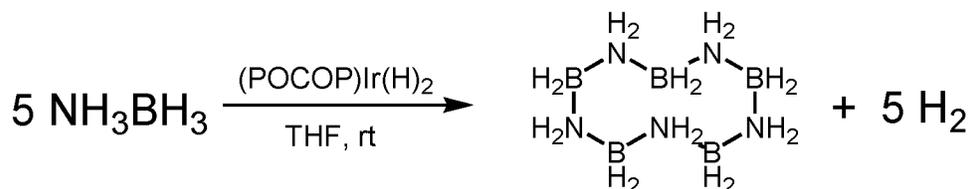
- Characterization of product
 - XRD analysis - comparison to literature
- Thermodynamics of AB dehydrogenation

- DSC measurements at PNNL
- Identification of dormant form of catalyst

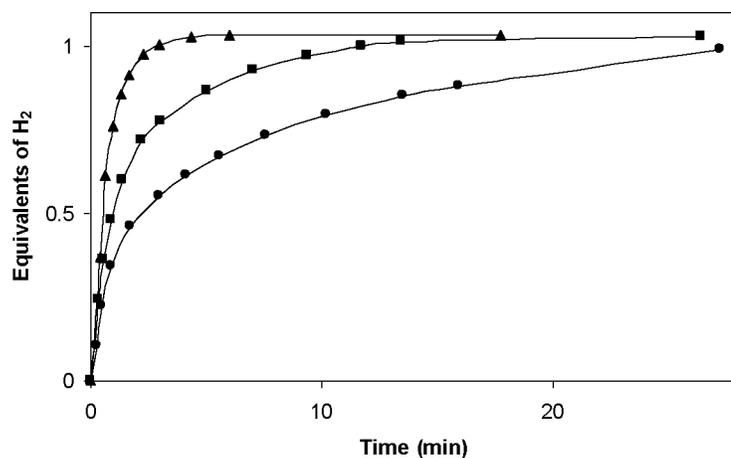
-Dehydrogenation of AB with **1**

- Quantification of H₂ release and kinetic studies

Catalysis of hydrogen release has been extensively studied, with the best results to date achieved using iridium pincer complexes, in particular complex (POCOP)IrH₂(**1**).



Solutions of AB in THF at room temperature in the presence of catalytic amounts of **1** rapidly evolve one equivalent of hydrogen.



Characterization of BN product

The BN containing product has been tentatively identified as a cyclic pentamer (BH₂NH₂)₅, which is very insoluble. This identification is based on comparison with literature data, specifically powder XRD and infrared spectra/

The rapid and clean hydrogen loss reaction has allowed for measurement of the heat of reaction by reaction calorimetry. In THF solution, the reaction is found to be exothermic by 6.7 kcal/mol.

Using the same Ir catalyst, MeAB is also rapidly dehydrogenated. Mixtures of 1:1 MeAB/AB are of interest, since such mixtures are liquid at temperatures slightly above ambient. We find that a MeAB/AB mixture in a very concentrated THF solution is rapidly dehydrogenated in the presence of 0.5% **1**. In a typical experiment, 0.8 g of MeAB/AB gave 500 mL of H₂ in 60 seconds at room temperature. Importantly, the BN containing product of this reaction is soluble, which may be useful in reprocessing.

Studies involving MeAB

-Dehydrogenation of MeAB with **1**

-Quantification of H₂ release and kinetic studies

Rates of dehydrogenation of MeAB catalyzed by **1** are very similar to that observed for AB, but the products are soluble. Using ESI-MS and GPC analysis, the products have been identified as oligomers and polymers of MeAB

Using DSC measurements at PNNL, the reaction enthalpy for MeAB dehydrogenation has been measured to be *ca.* -6.5 kcal/mol.

Mixed AB/MeAB system studies

Dehydrogenation of 1:1 AB/MeAB mixture with **1** gives copolymers, as shown by GPC, mass spectroscopy and NMR spectroscopy. The ratio of AB:MeAB can be adjusted.

CBN material studies

-Dehydrogenation catalyzed by **1**

-Quantification of H₂ release

-Qualitative description of product

We investigated the cyclic amine borane 1,2-azaborinane as a potential hydrogen storage material (Figure 1). Our collaborators at the University of Alabama have performed calculations suggesting that this material has the potential to be directly regenerated after dehydrogenation. While we were able to synthesize the direct precursor to the desired product, the final transformation step has proved to be difficult and has not yet been achieved. Ultimately, a collaboration with the Liu Group provided us with these types of CBN compounds.

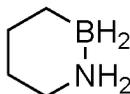


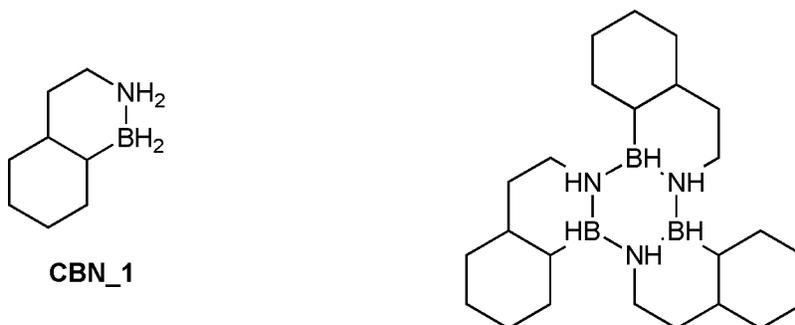
Figure 1. 1,2-azaborinane

Treatment of **CBN_1** with the iridium catalyst results in slow release of 1 equivalent of hydrogen. We have tentatively identified the primary product of dehydrogenation as a trimeric species (Figure 1). ESI-MS analysis of the product mixtures reveal fragments corresponding to molecular weights below that expected for trimer. To this point we have not been able to directly observe the mass peak for trimer. It is believed that this species is fragmenting in the mass spectrometer.

We have found that the same trimeric dehydrogenation product can be prepared by heating a sample of **CBN_1** in THF solution. We are currently attempting to grow crystals of the product of this reaction in order to unequivocally determine the identity of the initial product of dehydrogenation.

One major obstacle for utilization of CBN materials as a class of hydrogen storage compounds is the need to dehydrogenate both BN and CC bonds within the same material. Utilization of the (¹BuPOCOP)IrH₂ complex for this is a logical choice as this complex is known to be competent at

dehydrogenation of CC bonds. To this end we have been exploring the reaction of (^tBuPOCOP)IrH₂ with **CBN_1** at higher temperatures in order to promote further dehydrogenation. Initial studies have given no evidence for CC bond dehydrogenation. Future studies with this system will continue with varied reaction conditions to attempt to promote CC bond dehydrogenation. Other potential catalysts will also be screened as discussed below.



Model CBN compound **CBN_1** and proposed product of dehydrogenation

Non-PGM metal catalysts

Synthesis of (POCOP)CoH₂ shows that the complex is a dihydrogen complex, not a dihydride as for iridium. This Co complex is a catalyst precursor for AB dehydrogenation. Initial rates are promising, but catalyst lifetime is poor.

We have also revisited the previously reported Co complex (Figure 2). This complex is a precursor to a species that is our fastest first-row metal catalyst for AB dehydrogenation. Again, we found that initial catalyst activity is promising, but catalyst lifetime is unacceptably short.

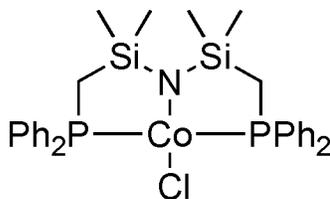
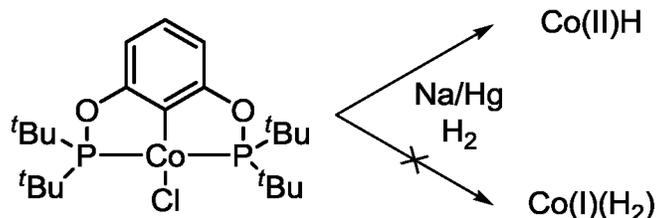


Figure 2. Co Complex

We are also working on developing a Co system analogous to the highly successful Ir complex using the (^tBuPOCOP) ligand system. The Co(II) halogen complex has been obtained and well characterized. Unfortunately this complex does not catalyze H₂ release from BN materials without the addition of water as a promoter. Preliminary tests show that the product of *in situ* reduction of this complex is an effective catalyst, eliminating the previously observed induction period. Further efforts have been carried out to isolate the reduction product. Material

isolated from the reduction of (^tBuPOCOP)CoX under H₂ gas is characterized as the Co(II)H complex, *not* as a Co(I) complex as desired (Scheme 1).



Scheme 1. Reduction of (^tBuPOCOP)CoCl in the presence of H₂ gives Co(II)H, not Co(I)(H₂).

In contrast to the Co(II) halide complexes, Co(II)H is reactive with AB, forming the previously reported “pentamer” as well as cycloborazane and other boron containing products (observed in ¹¹B NMR). The Co(II) hydride is consumed, although it is not known what form the Co containing product takes. Further studies on this particular system will be limited given the poor potential for the desired type of activity.

Conclusions

Effective iridium catalysts for rapid dehydrogenation of amine boranes have been developed. Efforts to extend these observations to non-PGM metals were not successful. Calorimetric measurements indicate that dehydrogenation of ammonia borane is quite exothermic. Studies on CBN materials gave slow release of only one equivalent of hydrogen.

Publications and Presentations

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“New catalysts for dehydrogenation of amine boranes” D. Michael Heinekey, Denise Mery, Melanie C. Denney, Karen I. Goldberg, Brandon L. Dietrich, Nathan A. Bennette, and Travis Hebden, 234th ACS National Meeting, Boston, August 2007, Abstract Fuel 136.

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“A convenient one pot synthesis of di t-butylphosphinic chloride” Daniel F. Brayton, Karen I. Goldberg, Werner Kaminsky and D. M. Heinekey. *Phosphorus, Sulfur, and Silicon and the Related Elements*, **2008**, *183*, 2534-2540

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“Dehydrogenation catalysts for BN and CBN hydrogen storage materials” D. Michael Heinekey, Travis J. Hebden, Steven L. Matthews, Karen I. Goldberg, Brandon L. Dietrich, and Anthony J. St. John. 238th ACS National Meeting, Washington, DC, August 2009, Abstract Fuel 296.

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“Preparation of a Dihydrogen Complex of Cobalt.” Travis J. Hebden, Anthony J. St. John, Dmitry G. Gusev, Werner Kaminsky, Karen I. Goldberg, D. Michael Heinekey. *Angewandte Chemie*, **2011**, *50*, 1873-1876.

“Pincer Complexes as Catalysts for Amine Borane Dehydrogenation ” Anthony J. St. John, Karen I. Goldberg and D. Michael Heinekey. *Topics in Organometallic Chemistry*, **2013**, *40*, 271-288. (Invited review article).