

IV.B.1i Solutions for Chemical Hydrogen Storage: Dehydrogenation of B-N Bonds

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Contract Number: DE-FC36-05GO15057

Project Start Date: March 1, 2005
Project End Date: February 28, 2010

Objectives

- Identify materials/systems to meet DOE target goals for gravimetric and volumetric densities of H₂:
 - Amineboranes and other boron-nitrogen (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 carbon-boron-nitrogen (CBN) materials:
 - CBN materials have the potential for direct regeneration. Will need to identify and investigate catalysts capable of dehydrogenating both B-N and C-C bonds.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies

Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost
- (E) Charging/Discharging Rate
- (R) 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

(Note: the specific energy and energy density are the revised DOE 2010 hydrogen storage targets.)

Accomplishments

Identified soluble products of iridium catalyzed dehydrogenation of methylamine borane (MeAB) and ammonia borane (AB)/MeAB mixtures:

- Identified soluble products as mixtures of oligomers of varying chain lengths.
- Observed cross-linked products in the mixed AB/MeAB dehydrogenation reactions containing both (NH₂BH₂) and (CH₃NHBH₂) units.
- Collaborated with the Pacific Northwest National Laboratory (PNNL) to demonstrate an important capability for characterization of liquid spent fuel.
- Successfully extended the highly active (^tBuPOCOP) Ir motif to a first row metal (cobalt).
- Optimized the previously reported cobalt pre-catalyst and targeted more robust ligand motifs.
- Collaborated with the University of Oregon on CBN materials:
 - Transferred synthetic portion of effort to University of Oregon.
 - Began screening CBN materials provided by University of Oregon for dehydrogenation activity with known AB dehydrogenation catalyst.



Introduction

In order for chemical hydrogen storage to be feasible the storage materials must have a high weight percentage of hydrogen. Compounds containing carbon (C), boron (B) and nitrogen (N) are therefore promising. However, the discovery that dehydrogenation of B-N bonds is exothermic means that direct regeneration of spent BN fuel will not be possible. Dehydrogenation of C-C bonds is endothermic and this fact presents a potential opportunity for tuning the thermodynamics of dehydrogenation by mixing carbon, boron and nitrogen in the same material. We are working on developing and testing non-precious group metal (PGM) catalysts for rapid dehydrogenation of B-N and C-C bonds.

Approach

Our approach to meeting the DOE targets is to rationally design non-PGM catalysts for the dehydrogenation of amine borane systems. Through ligand modification we are able to tune the catalyst for increased stability and activity. We are also concerned with the viability of direct regeneration of amine borane materials which determines whether the material might be suitable for on-board regeneration. We have directly measured the enthalpy of dehydrogenation for a variety of amine borane systems and determined that it will not be possible to regenerate them directly by reaction with hydrogen. Collaborations have been initiated with the University of Oregon and University of Alabama to identify and synthesize novel CBN materials. Calculations (University of Alabama) have shown that several cyclic CBN materials have overall thermodynamics of dehydrogenation that are near thermoneutral. The Liu group at the University of Oregon are specialists in synthesizing heterocyclic CBN materials and we are working with them to develop catalysts that are capable of dehydrogenating both B-N and C-C bonds.

Results

Through a newly established collaboration with the Liu group at the University of Oregon we have received and started testing a new CBN heterocycle. Calculations from our collaborators at the University of Alabama suggest that dehydrogenation of CBN heterocycles such as 1,2-azaboracyclohexane will be endothermic and lead to overall thermodynamics near thermoneutral (see Figure 1). Preliminary dehydrogenation studies have been carried out on some of these materials. The first of these cyclic CBN compounds (CBN-1) has been shown to react with the previously successful dehydrogenation catalyst (^tBuPOCOP)IrH₂ (^tBuPOCOP

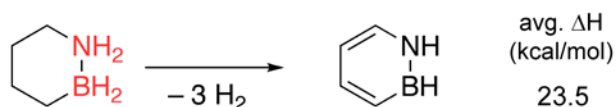


FIGURE 1. Dehydrogenation of 1,2-azaboracyclohexane and calculated enthalpy of reaction.

= [η^3 -1,3-(OP^tBu)₂C₆H₃]). Small amounts of the fully dehydrogenated product (CBN-2) were observed, however, only as a minor product. Additional dehydrogenation reactions will be attempted as the compounds are received from the University of Oregon.

Previously we have reported the dehydrogenation of AB, MeAB, and mixed AB/MeAB using the catalyst (^tBuPOCOP)IrH₂ [1]. The product of AB dehydrogenation was found to be consistent with the reported cyclic pentamer, [NH₂BH₂]₅ [2]. Further characterization of the soluble products of MeAB and mixed AB/MeAB dehydrogenation systems by electrospray-ionization mass spectrometry (ESI-MS) and gel permeation chromatography (in collaboration with PNNL) has now revealed that the soluble products of both MeAB and 1:1 AB/MeAB appear to be mixtures of oligomers [3]. In the case of MeAB dehydrogenation, the isotopic distribution patterns observed by ESI-MS are consistent with both cyclic oligomers of the form [CH₃NHBH₂]_n and linear oligomers of the form [CH₃NH₂BH₃]_x[CH₃NHBH₂]_n[NH₂CH₃]_y. The majority of the oligomers appear to be in the 600-800 molecular weight (MW) range, although this distribution is likely concentration dependent. The ESI-MS of the 1:1 AB/MeAB dehydrogenation product shows a similar distribution of cyclic and linear oligomers, consistent with the formulas [NH₂BH₂]_x[MeNHBH₂]_y and [NH₂BH₂]_x[MeNHBH₂]_y[H₂]_z, respectively. All of the observed distribution patterns can be described without x or y differing by more than 3, consistent with previous observation that AB and MeAB appear to react in an approximate 1:1 ratio.

We have also previously reported that dehydrogenation of 2:1 and 5:1 AB/MeAB mixtures results in both soluble and insoluble products. The ESI-MS characterization of the soluble products supports earlier observations that the reaction between AB and MeAB still approximates a 1:1 ratio in these reactions but shifts the distribution of oligomers, as identical isotopic distribution patterns are seen in the ESI-MS spectra but shift towards lower MW oligomers. The insoluble products of these reactions have also been characterized by infrared spectroscopy and are consistent with the previously reported pentamer.

Development of 1st row transition metal catalysts is imperative to reducing costs of H₂ storage. The successful Ir catalyst utilizes a phosphorus-carbon-phosphorus (P-C-P) type pincer ligand which has been

employed for the analogous Co complexes. Direct analogues to the active Ir species ($(t^{\text{Bu}}\text{POCOP})\text{IrH}_2$ and $(t^{\text{Bu}}\text{POCOP})\text{IrH}_4$) have been obtained using Co. These complexes are only stable at low temperatures. At room temperature and above, these complexes decompose to the thermally stable $(t^{\text{Bu}}\text{POCOP})\text{Co}(\text{H})$ complex for which there is no Ir analogue. This form does not have adequate catalytic activity for AB dehydrogenation.

We have been studying the previously reported Co complex Co_1 in order to better understand and characterize the catalytically active species. Rapid dehydrogenation is observed with the addition of Co_1 to a tetrahydrofuran solution of AB. Under modest catalyst loadings (2.0 mol% Co) one equivalent of H_2 can be released in less than 4 minutes (see Figure 2). Notably however, there is an irreproducible induction period during which time Co_1 is converted to the highly active species. Studies to isolate and/or synthesize this highly active species have been unsuccessful, likely due to the instability of the species.

In order to circumvent the problem of catalyst instability we have targeted and synthesized more robust analogs of this successful system. In the interim a publication has appeared from a German research group with a similar P-N-P aliphatic pincer complex of ruthenium that is very active for AB dehydrogenation. The ligand of their study and the ligand we have prepared are closely related and so we expect to produce competent catalysts. We are currently synthesizing Fe and Co complexes with these more robust P-N-P ligands. This same ruthenium complex has also shown potential for dehydrogenation of B-H, N-H and C-H bonds.

Conclusions and Future Directions

Products from the dehydrogenation of AB, MeAB, and mixed AB/MeAB using the catalyst $(t^{\text{Bu}}\text{POCOP})$

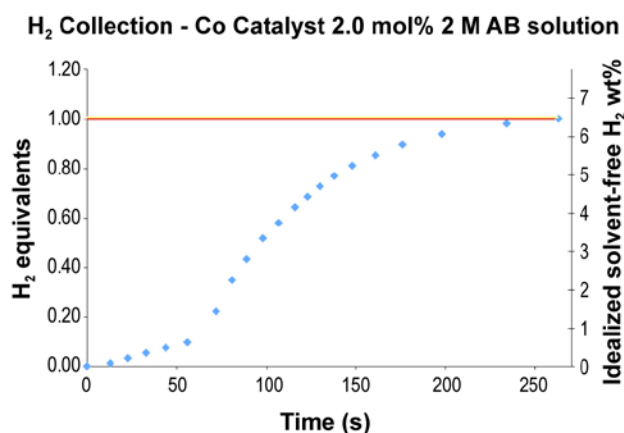


FIGURE 2. H_2 collection graph at 30°C for dehydrogenation of AB with 2 mol% Co_1. The idealized solvent free wt% of the system is depicted on the right hand axis.

IrH_2 have been positively identified. The fast Ir catalyst has provided us with mechanistic insight valuable to extending this reactivity to complexes with lower overall cost. We were successful in creating direct analogues of this system with Co; however, the accessibility of a thermally stable +2 oxidation state precludes its usefulness as a dehydrogenation catalyst. Other Co catalysts bearing pincer-type P-N-P ligands have been identified with impressive AB dehydrogenation activity. These catalysts have variable induction periods and poor catalyst lifetimes. We are currently working toward understanding and circumventing these shortcomings. We have also investigated dehydrogenation of novel CBN materials using $(t^{\text{Bu}}\text{POCOP})\text{IrH}_2$. These compounds are dehydrogenated substoichiometrically, making identification of new catalysts necessary for this application. We have identified promising leads for complexes of less expensive metals for catalytic dehydrogenation reactions and will test these materials in CBN dehydrogenation reactions.

FY 2009 Publications/Presentations

- Sigma Borane Complexes of Iridium: Synthesis and Structural Characterization.* Travis J. Hebden, Melanie C. Denney, Vincent Pons, Paula M. B. Picolli, Thomas F. Koetzle, Arthur J. Schultz, Werner Kaminsky, K.I. Goldberg, and D. M. Heinekey, *J. Am. Chem. Soc.* **2008**, *130*, 10812.
- A Convenient One Pot Synthesis of di(t-butyl) phosphinic chloride.* Daniel F. Brayton, Karen I. Goldberg, Werner Kaminsky and D. Michael Heinekey. *Phosphorus, Sulfur, and Silicon and the Related Elements*, **2008**, *183(10)*, 2534.
- Iridium Catalyzed Dehydrogenation of Substituted Amine-Boranes: Kinetics, Thermodynamics and Implications for Hydrogen Storage.* Brandon L. Dietrich, Karen I. Goldberg, D. Michael Heinekey, Tom Autrey, John Linehan, *Inorganic Chemistry* **2008**, *47(19)*, 8583.
- Dihydrogen Complexes of Co Supported by Pincer Ligands.* Travis J. Hebden, Karen I. Goldberg, D. Michael Heinekey, Dmitri G. Gusev. Presented at the Inorganic Chemistry Gordon Conference, June 2009.
- Structural Investigations of Ir Pincer Complexes Relevant to Catalytic H_2 Release from the Chemical Hydrogen Storage Material H_3NBH_3 .* Travis J. Hebden, Karen I. Goldberg, D. Michael Heinekey, Karsten Krogh-Jespersen, Alan S. Goldman, Thomas J. Emge, John A. Cowan, Arthur J. Schultz. Presented at the 238th ACS National Meeting, Washington, D.C., August 2009.
- Dehydrogenation Catalysts for BN and CBN Hydrogen Storage Materials.* D. Michael Heinekey, Travis J. Hebden, Steven L. Matthews, Karen I. Goldberg, Brandon L. Dietrich, Anthony J. St. John. Presented at the 238th ACS National Meeting, Washington, D.C., August 2009.

**7. Solutions for Chemical Hydrogen Storage:
Hydrogenation/Dehydrogenation of B-N Bonds.**
Anthony J. St. John, Brandon L. Dietrich,
Travis J. Hebden, Steven L. Matthews, Karen I. Goldberg,
D. Michael Heinekey. Presented at the DOE Hydrogen
Program Annual Review Washington D.C., June 2008.

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2. Bøddeker, K.W.; Shore, S.G.; Bunting, R.K. *J. Am. Chem. Soc.* **1966**, *88*, 4396.
3. Dietrich, B.L.; Goldberg, K.I.; Heinekey, D.M.; Autrey, T.; Linehan, J.C. *Inorg. Chem.* **2008**, *47*, 8583.