

IV.B.4a Chemical Hydrogen Storage Research at Los Alamos National Laboratory

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Objectives

- Determine if conversion of B-OH to B-H bonds is possible with sufficient energy efficiency for regeneration of sodium borate from sodium borohydride hydrolysis.
- Provide a list of hydrogen storage options with potential storage capacities, thermodynamics for hydrogen release and regeneration.
- Develop catalysts for the controlled release of hydrogen from ammonia borane (AB) and related amineboranes in solutions and slurries.
- Determine hydrogen released (capacity), kinetics (rates) and mechanisms (pathways) for amineborane dehydrogenation.
- Characterize products from the catalytic dehydrogenation of ammonia borane (BNH_x) and related amineboranes obtained from different classes of catalysts.
- Conceptualize, develop and demonstrate key steps for regeneration of dehydrogenated AB (i.e. spent storage material).
- Identify compounds and chemical reactions that release hydrogen from organic materials with near thermodynamic neutrality using: a) heteroatom substitution to lower the enthalpy of hydrogen release or b) simultaneous or tandem "coupled reactions" to balance an endothermic hydrogen release with an exothermic reaction step.

- Investigate the effect of nanoscale materials on the hydrogen storage capacity of light elements.
- Lead and coordinate all Center efforts and collaborative projects.

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:

- (B) System Cost
- (A) System Weight and volume
- (K) System Life-Cycle Assessments
- (B) Efficiency
- (R) Regeneration Processes

Technical Targets

LANL's current status on progress towards DOE's technical targets is presented in the Table 1 which reports capacities and rates for the reaction system (i.e. the material and any solvent/catalyst). The reported numbers are not for a complete on-board storage system which would include the storage tank, reactor system, and ancillary components. Although much progress has been made in FY 2006, the systems under investigation are still being optimized for capacity, rate and regeneration efficiency.

Accomplishments

- Identified and assessed potential routes for B-OH reduction.
- Discovered AB dehydrogenation catalysis by Bronsted and Lewis acids where the rates, product distribution, and extent of hydrogen release, depend on relative amounts of AB, acid, and solvent.
- Discovered that N-heterocyclic carbene complexes of transition metals can catalyze hydrogen release from AB to give over 2 equivalents of hydrogen.
- Determined the kinetics of hydrogen release from AB using a set of N-heterocyclic carbene metal complexes and found the fastest rates to be ca 0.06 min⁻¹ in diglyme solution (Ni/Enders carbene complex). Current rates would require 153 g of AB (and ca. 14.6 g Ni catalyst) to provide a hydrogen release rate of 0.02 grams per sec.

TABLE 1. Status of LANL Progress Towards DOE 2010 On-Board Hydrogen Storage Targets

	Gravimetric Capacity (wt%)	Volumetric Capacity (kg/L)	Amount of material to meet H ₂ Flow Rate (g/s/kW)	Regeneration Efficiency
LANL Current AB	2.7 (with solvent, catalyst)	0.02	Needs 153 g AB, 14.6 g Ni	In progress
AB (Theoretical)	13-19%	0.12-0.16	TBD	80%
LANL Coupled Reactions	4.4 (dry)	0.04	Needs 600 g of material	In progress
Current Coupled Reactions (Theoretical)	6.7 (with H ₂ O)	> 0.09	TBD	Up to 90%
LANL Organic Hydride	0.9	0.015	Needs 2 g catalyst	
Organic Hydride (theoretical)	6.9 (ca. 8 possible)	0.062		Up to 90%
DOE 2010 Target (system)	6.0	0.045	0.020	Guidance of 60%

- Developed a conceptual five-step process for regeneration of AB from spent AB.
- Demonstrated three key steps in the five-step AB regeneration process: 1) reduction of a B-X to B-H bond in a chloroboron catecholate compound with a regenerable, tin hydride as well as formation of the metal hydride from decarboxylation of a tin formate, 2) disproportionation of a hydridoboron catecholate to diethylaniline-borane, and 3) conversion of diethylaniline-borane to AB by reaction with ammonia.
- Determined rates and hydrogen storage capacities for magnesium methoxide/magnesium oxide composites (Mg(OCH₃)₂.MgO) which react with water to release hydrogen. Measured capacities to date are about 4.4 wt% out of a theoretical capacity of 6.7% (including water).
- Developed and implemented performance criteria for tracking progress on storage systems investigated by Center R&D efforts that will also assist in down-selection and go/no-go decisions.

Approach

LANL's overall approach has been to contribute to collaborative experimental projects in all three tiers of the Center's efforts, primarily through investigations of the fundamental chemistry and reactivity, experimental evaluation of the limits for capacity, release rates, and regeneration efficiencies, as well as development of new chemistry and catalytic processes and optimization of promising systems. LANL has collaborated extensively with the experimental, theoretical and engineering assessment components of the Center. For Tier 1 work, LANL works closely with Rohm and Haas (ROH), Millennium Cell (MCEL) and Penn State University (PSU) to evaluate past data on, and experimentally determine the potential for, electrochemical and chemical reduction of B-OH bonds to B-H bonds. The bulk of the work at LANL in FY 2006 focused on the two key aspects of ammonia borane (AB) chemistry for Tier 2: catalytic dehydrogenation and development of regeneration concepts. Our approach to AB dehydrogenation has centered on studies of homogeneous catalysts in solution to determine rates and identify key intermediates and products. We are focusing on electron-rich ligands in order to enable the use of non-precious transition metals. The focus in FY 2006 has been on understanding the chemistry rather than maximizing the storage capacity. This work has been coordinated with the University of Washington, the University of Pennsylvania (Penn), and Intematix Corporation, the latter two of which are investigating heterogeneous catalysis. The University of Alabama and the Pacific Northwest National Laboratory (PNNL) have been vital in providing key information on the energetics of products and potential reaction intermediates. This solution work complements the focus on solid-state AB chemistry at PNNL.

Due to the rapid development of promising results on catalytic dehydrogenation at LANL and within the Center, we accelerated our efforts on the conceptualization, demonstration and development of processes for regenerating AB from spent dehydrogenated material. In FY 2006, this work was largely done at LANL in collaboration with Penn, but we anticipate significant collaborations with UC Davis, Alabama, and PNNL in FY 2007 due to the importance of regeneration for chemical hydrogen storage systems.

Organic molecules are capable of storing significant amounts of hydrogen in C-H bonds and offer potential advantages as storage materials (e.g. liquid storage materials); however, the dehydrogenation reactions are typically rather endothermic and would thus require impractically high temperatures (>150°C). We have

taken two general approaches to reducing the energy requirements for dehydrogenation: 1) employing heteroatom substitution, particularly for 1,1-elimination reactions, and 2) investigating methods for mechanistically coupling endothermic hydrogen release reactions with other exothermic reactions.

Results

Our initial experimental forays into electrochemical reduction of borane compounds to generate B-H bonds have not proven fruitful. ROH, PSU, MCEL and LANL have identified some potential routes for reduction based on proprietary ROH data which will be investigated largely at PSU in the future. As part of the assessment task, LANL contributed significantly to the Center effort to pull together a spreadsheet of chemical storage options based on storage capacity and thermodynamics.

The bulk of our work in FY 2006 focused on ammonia-borane dehydrogenation and regeneration of spent AB, primarily due to the high hydrogen storage capacity of this system and a number of promising preliminary results. We discovered that strong Lewis and Bronsted acids promote hydrogen release even at room temperature to afford $[\text{BH}_2\text{NH}_2]_n$ oligomers; however, intermediates build up that reduce the hydrogen yield. At low acid concentrations these intermediates are formed at much lower concentrations and linked borazines are obtained at 80°C indicating release of greater than two equivalents of hydrogen. Concentrated ammonia-borane solutions thus react faster and afford more hydrogen than solid AB at 80°C.

We discovered that iron and nickel phosphine complexes can catalyze dehydrogenation but they are slow and short-lived presumably due to the formation of inactive metal borides. On the other hand, metal complexes containing N-heterocyclic carbene ligands were found to be long-lived catalysts that afford linked borazines without significant build-up of $[\text{BH}_2\text{NH}_2]_n$ intermediates, as determined by in situ nuclear magnetic resonance (NMR) studies. The fastest rates observed to date (Figure 1) are ca. 0.06 min^{-1} in diglyme solution (Ni/Enders carbene complex) which would require 153 g of AB (and ca. 14.6 g Ni catalyst) to provide a hydrogen release rate of 0.02 grams per second.

In the area of regeneration of spent AB, we have conceptualized a five-step process for regeneration that involves digestion, activation, reduction, disproportionation and ligand exchange. In FY 2006, we demonstrated the net reduction of the B-Cl bond in catechol chloroborane (ClBCat) to a B-H bond mediated by a tin hydride. The latter could be regenerated by decarboxylation of the tin formate obtained by reaction of formate (itself generable from the hydrogenation of carbon dioxide) with the corresponding tin hydride (Figure 2). Diethylaniline was found to drive the

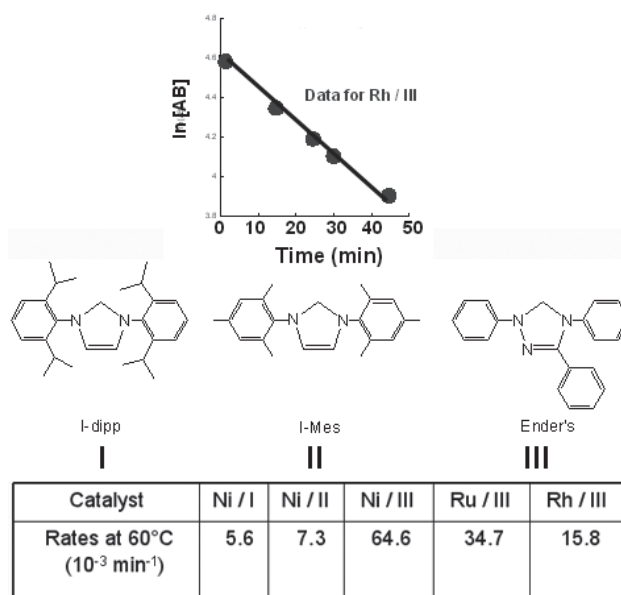


FIGURE 1. Relative Rates of Ammonia Borane Dehydrogenation Using Metal Carbene Complexes

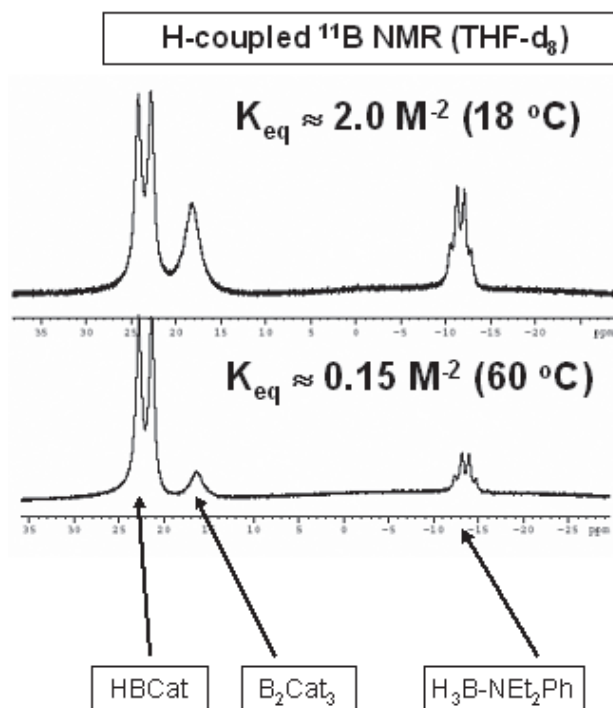


FIGURE 2. Tin Hydride Reduction of Catechol Chloroborane

disproportionation of HBCat to (diethylaniline)- BH_3 (Figure 3) which reacts quantitatively with ammonia to make AB. It is proposed that the B_2Cat_3 co-product could be recycled (i.e. activated, then reduced).

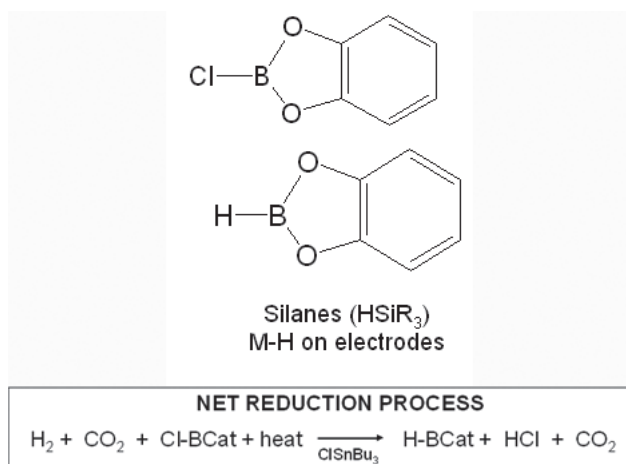


FIGURE 3. Amine-Promoted Disproportionation of Catecholborane

In FY 2005 we discovered that dihydrobenzimidazoles could act as “organic hydrides” and react with acids (including water) to exothermically release hydrogen [1]. This work was completed in FY 2006. While these specific compounds are not being pursued further due to their low hydrogen storage capacities, we are still exploring with Alabama combinations of reactions to enable high capacity storage in organics based on 1,1-elimination (and subsequent reactions) of heteroatom-containing organics, partly based on the mechanisms we uncovered in our earlier work. Our studies on simultaneous or tandem “coupled reactions” to balance an endothermic hydrogen release with an exothermic reaction has led to the development of magnesium methoxide/magnesium oxide composites $\text{Mg}(\text{OCH}_3)_2 \cdot \text{MgO}$ which react with water to release hydrogen (Figure 4).

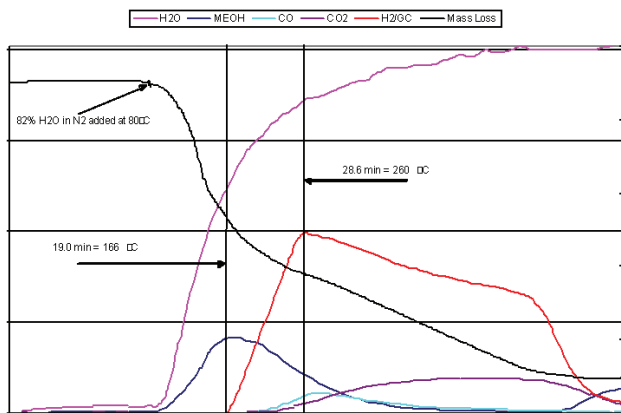
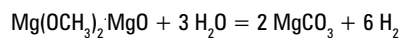


FIGURE 4. TGA of Hydrogen Release from Magnesium Methoxide/Magnesium Oxide Composite



Rates were determined at 260°C. Further work is required to better mechanistically couple the hydrogen release reaction with the carbonation of magnesium oxide to lower the reaction temperature.

Conclusions and Future Directions

LANL made significant progress on several fronts in FY 2006 along with our Center partners. We concluded that a number of catalytic systems could affect the release of more than one equivalent of hydrogen from AB and that regeneration of spent AB was possible. We also developed two promising leads in heteroatom-containing organics. While we anticipate that further discoveries at LANL and other partners' laboratories will dictate the level of effort on some of the proposed areas for future work we anticipate future collaborative work in the following areas:

- Determine if B-O to B-H is possible through indirect electrochemical reduction or chemical reduction with thermally regenerable hydrides and/or metals.
- Increase the capacity and rates of AB dehydrogenation by catalyst development studies including mechanistic studies, optimization, solvent effects and minimization of the amount of required solvent.
- Use engineering assessment to identify key parameters for solution catalysis.
- Reduce number of steps by determining most suitable digestion agents for spent AB regeneration process.
- Develop and demonstrate more energy efficient metal hydrides for the reduction to B-H and C-H bonds.
- Develop new chemistry for non-boron-based storage system with > 6-7 material wt% based on results from LANL and Alabama.
- Determine how to better mechanistically couple endothermic and exothermic reactions to lower the temperature and increase the rate of dehydrogenation from heteroatom-substituted organics.
- Quantify the effect of nanoscale light elements on hydrogen capacity and thermodynamics.

FY 2006 Publications/Presentations

1. D. E. Schwarz, T. M. Cameron, P. J. Hay, B. L. Scott, W. Tumas, and D. L. Thorn, “Hydrogen evolution from organic hydrides.” *Chemical Communications*, 2005, (47), 5919- 5921.
2. F. H. Stephens, R. T. Baker, D. J. Grant, M. Hernandez-Matus, and D. A. Dixon, “Acid-initiated dehydrogenation of ammonia-borane,” submitted.

3. R. T. Baker and F. H. Stephens, "Acid-initiated dehydrogenation of ammonia-borane," Canadian National Chemistry Conference, Halifax, May 2006.
4. R. T. Baker, "Amine-Boranes for Chemical Hydrogen Storage," Purdue Energy Center Hydrogen initiative Symposium, April 2006.
5. R. T. Baker, "Amine-Boranes for Chemical Hydrogen Storage," Singapore National Chemistry Conference, December 2005.
6. W. Tumas, "Hydrogen Storage for Fuel Cell Vehicles: Challenges and Recent Developments," FC Expo invited plenary, Tokyo, January 2006.
7. W. Tumas, "Hydrogen Storage for Fuel Cell Vehicles: Challenges and Recent Developments," invited seminars at AIST/Osaka and NEDO/Tokyo, February 2006.
8. D. L. Thorn, D. E. Schwarz, J. Webb, T. M. Cameron, P. J. Hay, B. L. Scott, and W. Tumas, "Chemical hydrogen storage using organic materials," MRS Spring Meeting, San Francisco, CA, April 2006.
9. W. Tumas et al. Presentation and poster at DOE Hydrogen annual review, May 2006.
10. R. J. Keaton, J. Blacquiere and R. T. Baker, "Dehydrogenation of amine-boranes for chemical hydrogen storage," Fall National Meeting of the American Chemical Society, Washington, D.C., August 2005.
11. F. H. Stephens, R. T. Baker, D. J. Grant, M. Hernandez-Matus, and D. A. Dixon, "Acid-initiated dehydrogenation of ammonia-borane," Fall National Meeting of the American Chemical Society, Washington, D.C., August 2005.
12. Six university seminars on storage center work during the fiscal year.

Special Recognitions & Awards/Patents Issued

1. Composition and method for storing and releasing hydrogen, patent filed.
2. Energy efficient synthesis of boranes, provisional patent filed.
3. Method and system for hydrogen evolution and storage, provisional patent filed.
4. Base metal dehydrogenation of amineboranes, provisional patent filed.
5. Acid-catalyzed dehydrogenation of amineboranes, patent filed.
6. Transition metal carbene complexes for amineborane dehydrogenation catalysis, provisional patent filed.

References

1. D. Schwarz et al. "Hydrogen evolution from organic hydrides," *Chemical Communications*, 2005, (47), 5919-5921.