IV.B.5g Chemical Hydrogen Storage Research at Los Alamos National Laboratory

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Start Date: February 1, 2005
Projected End Date: September 30, 2010

Objectives

- Determine if conversion of B-OH to B-H bonds is possible with sufficient energy efficiency for regeneration of sodium borate obtained from hydrolysis of sodium borohydride.
- Continue to develop catalysts for the controlled release of hydrogen from ammonia-borane (AB) and related amine-borane systems in solutions and slurries.
- Quantify hydrogen released (capacity) and determine kinetics (rates) and mechanisms (pathways) for amine-borane dehydrogenation.
- Characterize BNH_x products from the catalytic dehydrogenation of AB and related amine-boranes obtained from different classes of catalysts.
- Expand upon and simplify previously outlined regeneration scheme for spent AB fuel; demonstrate each of the steps and estimate the efficiency of the process.
- Identify and investigate novel compounds that generate hydrogen-rich fuel-cell feeds by coupling endo- and exothermic reactions.
- Develop methods suitable for analyzing the thermal decomposition of AB and its physical mixtures with metal fluorides (e.g., Mg, Cu, Al, etc.).

- Prepare, characterize and screen candidate metal-AB compounds as high-capacity hydrogen storage materials with potential reversibility (International Partnership for the Hydrogen Economy [IPHE] project with Pacific Northwest National Laboratory [PNNL], the United Kingdom, New Zealand and Singapore).
- Lead and coordinate all Chemical Hydrogen Storage Center of Excellence (CHSCoE) efforts and collaborative projects.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section 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
(C) Efficiency
(R) Regeneration Processes

Technical Targets

LANL is identifying and developing several classes of chemical hydrogen storage materials and systems capable of meeting the 2010 goals for on-board hydrogen storage with the potential to meet the 2015 DOE targets. In Table 1 the reported metrics include the material but do not include tanks, piping, reactors, and ancillary equipment that would make up an operable storage system. Substantial progress has been made toward these DOE targets during FY 2007. Research and development has been primarily directed at obtaining greater capacities and higher rates from viable candidate materials. This year, LANL put additional effort into providing a demonstration of proof-of-principle chemistries for the energy efficient regeneration of spent fuels having a thermodynamic efficiency of greater than 60%. This additional effort resulted in significant progress this year.

TABLE 1. Progress Toward Meeting Technical Targets

Metrics	LANL Brønsted Acid; 20 wt% AB solution, 60°C 18 hr	LANL Ni cat 2% AB, in solvent 80°C	LANL Ru cat, 2% AB in solvent 80°C	LANL Ni, MeAB/AB (neat) 80°C	IPHE Theory
Gravimetric Density (material wt%)	1.7 (vs. 6 wt% 2010 and 9% 2015 DOE targets)	.015 10.8 – calc'd, no solvent (ns)	0.019 13.5 – calc'd, ns	5.7	Measured 7.2 Max. 10 - 11.9 Opt. 8-10.9
Vol. Density (kg-H_2/L material)	0.016 (vs. 0.045 2010 and 0.081 2015 DOE targets)	0.00015 .08 - ns	.00019 .1 - ns	0.06	Measured 0.072
H_2 Flow Rate (g/s per kg material)	18 hrs -- too slow	0.00002 .016 - ns	0.0001 .01 - ns	0.02	Measured 0.02
kg of Material for 0.8 mol/sec	Terminated this approach	70,000 98 - ns	16,000 160 - ns	100	Measured 80

Accomplishments

- Provided ultrapure ionic liquids and modified electrodes to support Penn State University effort on electrochemical regeneration of borate to borohydride.

- Conducted mechanistic studies including kinetic measurements, isotopic labeling, and identification of reaction intermediates to identify metal-catalyzed reaction pathways that maximize the extent of hydrogen release from AB.

- Greatly increased hydrogen storage capacity was using metal-catalyzed dehydrogenations of liquid amine-borane fuels such as AB/methylamine-borane mixtures.

- Demonstrated that benzenedithiol, one of several thiol-containing reagents screened for their digestion ability, could digest the spent AB fuel polyborazlyene for AB regeneration.

- Determined that B-S bonds are most easily reduced with mild reducing agents screening model digestion products against various reducing agents.

- Used theory support from the University of Alabama (Alabama) to estimate energy efficiency of new sulfur-based AB regeneration scheme.

- Designed and fabricated high throughput batch screening reactors and installed hydrogen quantification equipment, including mass spectrometry for transient analyses and gas chromatography for steady-state analyses.

- Modified materials characterization equipment for high-pressure (0–81 atm) applications in support of regeneration processes (i.e., hydrogenation reactions).

- Performed vibrational spectroscopy analysis experiments on mixtures of magnesium fluoride (MgF_2) and AB as a function of temperature using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS).

- Initiated work on IPHE project: prepared and characterized new stable M-B-N-H compounds that release hydrogen without volatile co-products and have potential for reversibility.

✧   ✧   ✧   ✧   ✧

Introduction

Chemical hydrogen storage involves storing hydrogen in compounds and materials so that an on-board reaction can be used to release hydrogen. The resulting spent fuel is regenerated off-board. In addition to the importance of on-board storage capacity and hydrogen release rates, the energy efficiency of the regeneration of spent fuel is a key contributor to the overall energy efficiency of the fuel cycle. Chemical hydrogen storage provides a diversity of options and could also be used for hydrogen delivery where it offers the opportunity for a liquid or solid fuel infrastructure with the potential for eliminating direct hydrogen handling by the consumer. Researchers at LANL are advancing a number of integrated projects involving the development of materials, catalysts, catalytic processes, and new concepts for hydrogen release and regeneration of spent fuels, as well as the development of engineering feasibility of the processes. In addition, LANL hydrogen storage research benefits from productive interactions with theory collaborators at Alabama, PNNL, and LANL.

Approach

LANL contributes to collaborative experimental projects in all three tiers of CHSCoE's efforts, primarily through investigations of the fundamental chemistry and reactivity, experimental evaluation of the limits of capacity, release rates, and regeneration efficiencies, as well as development of new chemistry and catalytic processes and optimization of promising systems. In

Tier 1 work, LANL continues to work 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. In Tier 2, the bulk of the work at LANL in FY 2007 focused on increasing hydrogen storage capacity and release rate for AB and on identifying an energy efficient AB regeneration scheme. The hydrogen release 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. Alabama and PNNL have provided key information on the energetics of products and potential reaction intermediates. LANL's work with solutions and liquid formulations of AB complements the solid-state AB chemistry being conducted at PNNL. The AB regeneration work has been coordinated with Penn, PNNL, and UC Davis, in conjunction with theoretical guidance from Alabama. Within Tier 3, two high-throughput batch reactor well plates (each containing 25 wells) were designed and fabricated to expedite the discovery of novel catalysts and hydrogen storage materials. LANL is also developing solution routes to metal-AB compounds that have the potential for reversibility.

Results

Amine-Borane Dehydrogenation

In FY 2006, several classes of homogeneous catalysts were identified for dehydrogenation of AB, including strong Lewis and Brønsted acids and metal complexes. Working with Alabama, we showed that the mechanism of acid-catalyzed dehydrogenation applies also to thermolysis of AB in the solid state (PNNL work) and ionic liquids (Penn). Limitations of reaction rates and product distribution (borazine formation) caused us to terminate further work in this area during FY 2007.

Previous work by the University of Washington showed that some metal catalysts afforded cyclic aminoborane polymers such as $(H_2NBH_2)_5$ (cyclopentaborazane, CPB) and only a single equivalent of hydrogen. Previous LANL work with nickel carbene (Ni-NHC) catalysts, in contrast, showed greater than two equivalents of hydrogen released with formation of borazine and linked borazines. In FY 2007, we conducted mechanistic and theory studies (with Alabama and PNNL) to understand the factors distinguishing the two catalytic reaction pathways to maximize hydrogen release. Kinetics and isotopic labeling studies showed that reaction of AB with the Ni-NHC complex affords hydrogen and aminoborane, H_2NBH_2, in the rate-determining step (Figure 1). If the aminoborane product remains bound to the metal center, a metal-mediated ring expansion process affords CPB, while if aminoborane is ejected from the metal center, it is rapidly trapped by AB to form an observable intermediate, the B-N analog of ethylcyclobutane. The latter is then converted directly to borazine in a metal-catalyzed process. As a result of this mechanistic understanding, we are now working with PNNL to clarify the electronic catalyst requirements to maximize rate (reducing activation barrier for initial hydrogen release from AB) and extent of hydrogen release (identify factors that discourage aminoborane binding to metal center).

With the tools in hand to design a superior catalyst, we turned to increasing the system storage capacity by replacing the unproductive reaction solvent. Taking a lead from a Japanese patent held by Nippon Oil, we worked with the University of Northern Arizona, the University of Washington, and PNNL to investigate mixed amine-borane liquid fuels that liquefy AB and provide an additional source of hydrogen. In Equation 1, for example, a liquid equimolar mixture of AB and methylamine-borane (MeAB) can theoretically yield 10.5 wt% hydrogen assuming two equivalents released from each substrate and excluding the mass of the catalyst.
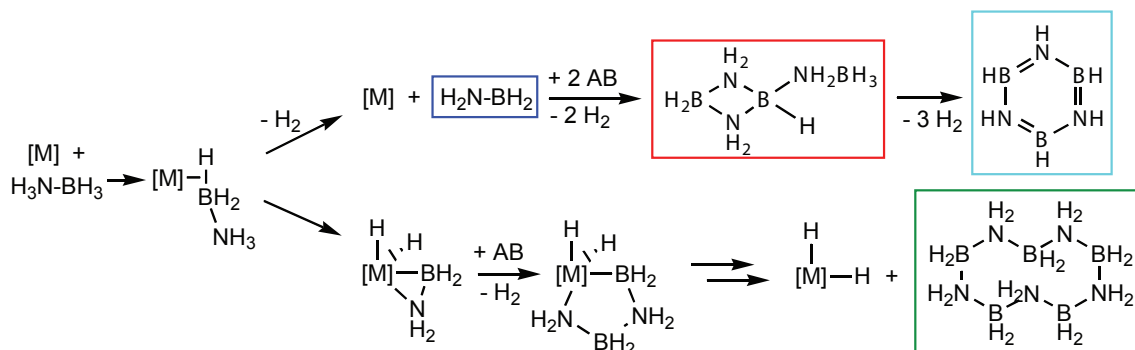

FIGURE 1. Reaction Pathways for Metal-Catalyzed Dehydrogenation of Ammonia-Borane

$$H_3NBH_3 + MeH_2NBH_3 \rightarrow 1/3\ (HNBH)_3 + 1/3\ (MeNBH)_3 + 4\ H_2 \quad (1)$$

Initial studies using our Ni carbene catalyst are promising although complications arising from the volatility of MeAB need to be mitigated.

Regeneration

Substantial progress was made at LANL in FY 2007 toward optimizing the energy efficient regeneration of AB from spent fuel. In FY 2006, a regeneration scheme was presented by LANL. The strategy included *digestion* of spent fuel using alcohols, followed by *reduction* using a mild reducing agent, resulting in *disproportionation* and formation of AB by reintroduction of ammonia (*ammoniation*). In FY 2007, a number of digesting and reducing agents were assessed in order to identify the best candidates for energy efficient regeneration. Reactions of several reducing agents with a wide variety of BXYZ species indicated that thiol-derived digestion products were the most promising for reduction with mild agents such as silanes and tin hydrides (Table 2). Potential thiol and dithiol digestion agents were evaluated theoretically by Alabama. Digestion using benzenedithiol was shown to be slightly exothermic and experimental work indicated successful conversion of polyborazylene (PB) to new products that were identified by independent synthesis (Figure 2). The reducing agent tributyltin hydride (Bu_3Sn-H) can readily reduce $(C_6H_4S_2)_3B_2(NH_3)_2$ (**A**) to $(C_6H_4S_2)$B-H(NH_3) (**B**) in a high yielding reaction, and trimethoxysilane [$(MeO)_3Si$-H] is capable of further reducing $(C_6H_4S_2)$B-H(NH_3) (**B**) to a BH_2-containing product still being fully characterized.

To optimize the efficiency of AB regeneration, it may be desirable to recover residual B-H bonds prior to digestion (as methods for releasing hydrogen from AB currently achieve ca. 2 to 2.5 equivalents of H_2, there are still B-H units remaining in the spent fuel).

We found that PB reacts with liquid ammonia at room temperature in a few hours to extract residual B-H as AB. In conjunction with Alabama, an analysis of the above thiol-based regeneration strategy using Equation 2 was completed (Figure 3). If significant residual B-H bonds can be recovered through the ammonia extraction method described above, the first term in the denominator can be reduced, thereby further increasing the efficiency.

$$\frac{(\text{Equiv. } H_2 \text{ stored})(57.8)}{(\text{Equiv. } H_2 \text{ used})(57.8) + \sum(\Delta H_{endo}) - (\%\ \text{heat recovery})\sum(-\Delta H_{exo})} = efficiency \quad (2)$$

Preparation of Metal-AB salts as Potentially Reversible Hydrogen Storage Materials

Tier 3 work on coupling endo- and exothermic reactions was postponed in FY 2007 in order to install instrumentation for rapid throughput hydrogen quantification (below) and characterization of new solid metal-AB materials. We are currently exploring two routes to the latter: reactions of metal hydrides
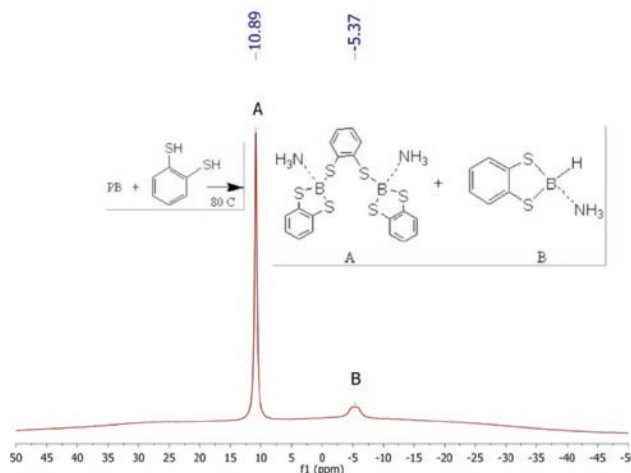

FIGURE 2. B-11 Nuclear Magnetic Resonance Spectrum of Digestion of Polyborazylene Using 1,2-Benzenedithiol
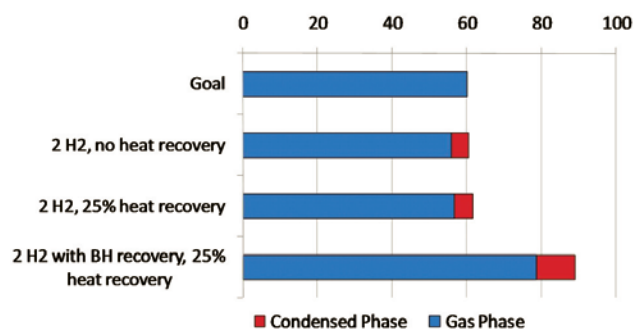
TABLE 2. Reactions of Reducing Agents with BXYZ Species that Model Digestion Products

(Entries in gray were reported in FY 2006. Y = reduction occurred; N = reduction did not occur.)

Compound	X	Y	Z	NaH/LAH	$HSiR_3$	$HSnR_3$
BBr_3	Br	Br	Br	Y	--	Y
BCl_3	Cl	Cl	Cl	Y	Y	Y
$BHCl_2.SMe_2$	H	Cl	Cl	Y	Y	Y
$BH_2Cl.SMe_2$	H	H	Cl	Y	Y	Y
ClBCat	Cat	Cl	--	Y	--	fast
Bu_2BOTf	OTf	Bu	Bu	Y	Y	Y
$B_3N_3Cl_3H_9$	Cl	NHR	H	Y	N	Y
$BF_3.OEt_2$	F	F	F	Y	slow	slow
$B(SPh)_3$	SPh	SPh	SPh	Y	slow	Y
HB(phenylenediamine)	NHR	NHR	H	N?/other	N	N
$B(OC_6F_5)_3$	OC_6F_5	OC_6F_5	OC_6F_5	fast	N	N
$(C_6F_5)OBCat$	Cat	OC_6F_5	--	--	N	N
HBCat	Cat	H		--	slow	slow
B_2Cat_3	Cat	Bcat	--	--	slow	slow
$B(OMe)_3$	OMe	OMe	OMe	Y	N	N

FIGURE 3. Efficiency Assessment of Dithiol-Based AB Regeneration Schemes

and fluorides with AB; and reactions of the $(H_3BNH_2)^-$ anion with metal halide precursors. Initial calculations of the relative hydrogen storage capacities of metal fluoride/ammonia-borane composites indicate that any system containing greater than 2 equivalents of AB gives acceptable initial hydrogen capacities (Table 3).

TABLE 3. Theoretical Hydrogen Storage Capacities of Metal Fluoride-AB Composites

| | Equivalents of BH3NH3 | | | |
	1	2	3	4
MgF_2	6.5	9.7	11.6	12.9
AlF_3	5.2	8.2	10.2	11.5
CaF_2	5.5	8.6	10.5	11.9
ScF_3	4.5	7.3	9.2	10.6
TiF_4	4.4	7.2	9.1	10.5
VF_3	5.0	7.9	9.9	11.3
CrF_2	5.0	7.9	9.9	11.3
MnF_2	4.8	7.7	9.7	11.1
FeF_3	4.2	6.9	8.7	10.1
CoF_3	4.1	6.7	8.6	10.0
NiF_2	4.7	7.5	9.5	10.9
CuF_2	4.5	7.3	9.2	10.6
ZnF_2	4.5	7.3	9.2	10.6

The possibility of mixed compositions such as MgF_2:TiF_4:6 BH_3NH_3 give us access to a large range of potential high-capacity hydrogen storage materials. Preliminary thermal reactions of MgF_2, CaF_2 and ZnF_2 with 2 equivalents of AB at 70°C showed significant gas evolution and consumption of both starting materials via powder X-ray diffraction analysis. Hydrogen quantification and further characterization of the products is in progress, along with hydrogen uptake measurements to test reversibility.

As part of the IPHE collaboration, we have used solution syntheses to prepare $NaNH_2BH_3$ and $Ca(NH_2BH_3)_2$, in which a new covalent bond between the nitrogen of AB anion and the main group element has been formed (Equations 3-5). These new compounds have significantly different thermal properties than solid AB. For example, hydrogen loss from $Ca(NH_2BH_3)_2$ occurs over a wider temperature range and is less exothermic than that of AB.

$$NaH \;+\; H_3NBH_3 \;\rightarrow\; Na(NH_2BH_3) \qquad (3)$$

$$CaH_2 \;+\; 2\,H_3NBH_3 \;\rightarrow\; Ca(THF)_2(NH_2BH_3)_2 \qquad (4)$$

$$Ca(THF)_2(NH_2BH_3)_2 \;\rightarrow\; Ca(NH_2BH_3)_2 \;+\; 2\,THF \qquad (5)$$

Design, Construction, and Implementation of New Analytical Instrumentation

We have recently modified existing materials characterization equipment (i.e., tapered element oscillating microbalance - TEOM - and DRIFTS vibrational spectroscopy coupled to a micro-gas chromatograph and mass spectrometer) to perform experiments at elevated pressures (i.e., 1–81 atm) for both dehydrogenation and rehydrogenation (Figure 4A). In order to facilitate the identification of viable hydrogen storage materials, two high throughput batch screening instruments were designed and fabricated (Figure 4B). Each batch reactor is capable of screening 25 samples, thus allowing for rapid screening (i.e., 50 samples) of potential hydrogen storage material. Samples that show promise will be analyzed using our kinetics reactor system. These reactors were designed for precise control of kinetic variables (i.e., temperature, pressure, and reactant flow rates). The range of operating pressures and temperature are 1 atm to 81 atm, and 25°C to 1,000°C. The reactors can be operated in either integral or differential mode. Additional features include the ability to perform gas-gas, gas-solid, liquid-liquid, liquid-solid, and gas-liquid experiments, thus giving us the capability to investigate a wide range of hydrogen storage materials.
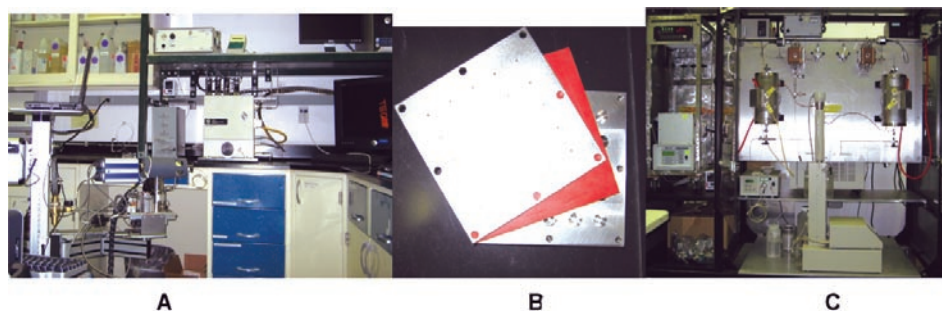

FIGURE 4. (A) Material Characterization System Equipped with Mass Spectrometer, Micro-GC, Gas Phase IR, and TEOM (Equipped for High Pressure Applications); (B) High-Throughput Batch Reactors for Screening Hydrogen Storage Materials; (C) High-Pressure Reactors for Kinetic Studies on Candidate Hydrogen Storage Materials

Conclusions and Future Directions

- Identified key factors needed to optimize extent and rate of hydrogen release from AB through catalyst design.

- Further increased hydrogen storage capacity using metal catalysts in mixed amine-borane liquid fuels.

- Identified new dithiol-based AB regeneration scheme and performed initial energy efficiency assessment.

- Prepared new high-capacity metal-AB hydrogen storage materials with potential for reversibility.

- Designed, and installed new analytical instrumentation for detailed kinetics and thermodynamic studies of hydrogenation and dehydrogenation reactions.

In FY 2008, we will:

- Optimize catalyst performance for hydrogen release from liquid amine-borane fuels and further examine properties of the latter (thermal and chemical stability, solubility, etc.).

- Expand amine-borane dehydrogenation catalyst design to include heterogeneous and single-site molecular variants.

- Optimize reaction conditions for dithiol-based AB regeneration process to maximize energy efficiency and process simplicity.

- Work with IPHE partners to identify and characterize new M-B-N-H hydrogen storage compounds as potentially reversible, high-capacity hydrogen storage materials.

- Use new analytical instrumentation to rapidly assess new catalysts and reaction kinetics for hydrogenation and dehydrogenation, determine quality of hydrogen stream, and continue work on coupled endo- and exothermic reactions.

- Use bread-boarding approach to refine engineering assessment for on-board hydrogen release and off-board regeneration.

- Coordinate partner efforts to make best use of resources.

Special Recognitions & Awards/Patents Issued

Special Recognition

1. *Angewandte Chemie* paper was selected by reviewers as a Very Important Paper and featured on the journal cover.

2. *Journal of the American Chemical Society* paper was featured as a Research Concentrate in the premier US trade magazine *Chemical and Engineering News*.

Patents

1. "Acid Catalyzed Amine-Borane Dehydrogenation," US patent application filed June, 2006.

2. "Base Metal-Catalyzed Dehydrogenation of Amine-Boranes," US patent application filed September, 2006.

3. "Metal Carbene Complex-Catalyzed Dehydrogenation of Amine-Boranes," provisional US patent application filed August, 2006.

4. "Energy-Efficient Synthesis of Boranes," US patent application filed January, 2007. "Composition and Method for Storing and Releasing Hydrogen," US patent application filed January, 2007.

FY 2007 Publications/Presentations

1. Stephens, F. H.; Baker, R. T.; Matus, M. H.; Grant, D. J.; Dixon, D. A., "Acid-initiated Dehydrogenation of Ammonia-Borane for Hydrogen Storage," *Angewndte Chemie Internatioanl. Edition*, **2007**, *46*, 746.

2. Keaton, R. J.; Blacquiere, J. M.; Baker, R. T., "Base Metal Catalyzed Dehydrogenation of Ammonia-Borane for Chemical Hydrogen Storage," *Journal of the American Chemical Society*, **2007**, 129, 1844-1845.

3. Stephens, F. H.; Pons, V.; Baker, R. T., "Ammonia-Borane: The Hydrogen Source Par Excellence?" *J. Chem. Soc., Dalton Trans*., **2007**, 2613-2626.

4. Stephens, F. H.; Baker, R. T.; Matus, M. H.; Grant, D. J.; Dixon, D. A., "Acid-Catalyzed Dehydro-Oligomerization of Ammonia-Borane," *232nd American Chemical Society Meeting*, **2006**, FUEL-130.

5. Keaton, R. J.; Blacquiere, J. M.; Baker, R. T. "Dehydrogenation of Amine-Boranes for Chemical Hydrogen Storage, *232nd American Chemical Society Meeting*, **2006**, FUEL-166.

6. R. T. Baker and W. Tumas, "Chemical Hydrogen Storage for Automotive Applications," presentation at Hydrogen Economy 2006, Portland, OR, August, 2006.

7. R. T. Baker, "Catalyzed Dehydrogenation of Ammonia-Borane for Transportation Applications," presentation at 15th International Symposium on Homogeneous Catalysis, Sun City, South Africa, August, 2006.

8. F. H. Stephens, "Catalysts for the Production of Hydrogen from Ammonia-Borane," presentation at Advanced Research Workshop on Hydrogen Storage Materials, *EVS-22*, Yokohama, Japan, October, 2006.

9. R. T. Baker, "Towards a Sustainable Transportation Fuel: Catalyzed Hydrogen Release from Ammonia-Borane," presentation at Renewable Energy Gordon Research Conference, Ventura, CA, January, 2007.

10. R. T. Baker, "Mechanistic Studies of Amine-Borane Dehydrogenation," presentation at Inorganic Reaction Mechanisms Gordon Research Conference, Ventura, CA, February, 2007.

11. R. T. Baker, "Catalyzed Dehydrogenation of Ammonia-Borane for Transportation Applications," presentation at Argonne National Laboratory, April, 2007.

12. R. T. Baker, "Catalyzed Dehydrogenation of Ammonia-Borane for Transportation Applications," presentation at Northwestern University, June, 2007.

13. R. T. Baker et al., "Acid-Initiated Dehydrogenation of Ammonia-Borane for Hydrogen Storage," poster at Royal Society Main Group Chemistry Discussion, London, UK, June, 2006.

14. R. T. Baker et al., "Amine-Boranes for Chemical Hydrogen Storage: Controlling Rate and Degree of Hydrogen Release with Homogeneous Catalysis," poster at 37th *International Coordination Chemistry Conference*, Capetown, South Africa, August, 2006.

15. F. H. Stephens et al., "Acid-Initiated Dehydrogenation of Ammonia-Borane for Hydrogen Storage," poster at Renewable Energy Gordon Research Conference, Ventura, CA, January, 2007.