

## IV.C.7 Novel Carbon(C)-Boron(B)-Nitrogen(N)-Containing H<sub>2</sub> Storage Materials

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Contract Number: DE-EE0005658

Project Start Date: March 5, 2012  
Project End Date: August 14, 2015

### Overall Objectives

- Develop new carbon-boron-nitrogen (CBN)-based chemical hydrogen storage materials that have the potential to meet the DOE technical targets for vehicular and non-automotive applications

### Fiscal Year (FY) 2015 Objectives

- Synthesize a liquid CBN hydrogen storage material with thermal stability that satisfies DOE specifications (no spontaneous decomposition below 60°C)
- Develop a catalytic system for H<sub>2</sub> release from the carbonaceous component of CBN materials
- Continue computational and experimental studies of the mechanism of H<sub>2</sub> release from CBN materials

### Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

- (A) System Weight and Volume
- (C) Efficiency
- (E) Charging/Discharging Rates

### Technical Targets

This project is developing and characterizing new CBN materials for hydrogen storage. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2020 hydrogen storage system targets:

- Specific energy: 1.8 kWh/kg (5.5 wt%)
- Energy density: 1.3 kWh/L (4.0 vol%)

### FY 2015 Accomplishments

- Measured the kinetics of the release of the first equivalent of H<sub>2</sub> from Compound B using ReactIR; the reaction order, activation energy, pre-exponential factor, and enthalpy and entropy of activation were all experimentally determined to corroborate the results of computational modeling of the BN dehydrogenation process
- Applied density functional theory calculations to develop a mechanism for the initial H<sub>2</sub> release from B consistent with the above kinetic data; such mechanistic understanding will aid in identifying the geometric and electronic elements which govern the thermal stability of CBN materials
- Measured the kinetics of the release of two equivalents of H<sub>2</sub> from Compound J using a gas burette; the activation energy and pre-exponential factor for each loss of H<sub>2</sub> was estimated based on these results and used in subsequent COMSOL modeling (*vide infra*)
- Achieved dehydrogenation from the carbonaceous component of a CBN material using a Pd/C catalyst in a gas flow micro-reactor to facilitate reaction kinetics analysis
- Experimentally determined the activation energy, pre-exponential factor, and enthalpy and entropy of activation for carbonaceous dehydrogenation for comparison with all-carbon analogues and use in COMSOL modeling (*vide infra*)
- Applied combined experimental and computational results for both BN and CC dehydrogenation to modeling a coupled exothermic-endothermic H<sub>2</sub> release system in a theoretical reactor using COMSOL to assess the benefits of such coupling

- Developed new approaches to predict melting points and stabilities (resonance stabilization energies) to more efficiently identify new molecular structures for stable liquid CBN materials



## INTRODUCTION

Approaches to store H<sub>2</sub> in chemical bonds provide a means for attaining high energy densities. Molecular complexes containing protic and hydridic hydrogen such as ammonia borane (AB) provide between 8 wt% to 16 wt% H<sub>2</sub> at acceptable temperatures in a kinetically controlled decomposition. AB shows promise to meet a number of important technological targets such as high volumetric and gravimetric density of H<sub>2</sub>, fast kinetics, thermal stability, facile synthesis at large scale and safe handling under atmospheric conditions. Some of the challenges involving AB include volatile impurities (e.g., ammonia, diborane, borazine) and the economics of spent fuel regeneration [1–4].

This project is developing hydrogen storage materials that contain the element carbon in addition to boron and nitrogen. The inclusion of carbon can be advantageous for developing chemical H<sub>2</sub> storage materials that are structurally well defined (thus have good potential to be liquid phase to use current infrastructure), exhibit thermodynamic properties conducive to reversibility, and demonstrate good storage capacities.

## APPROACH

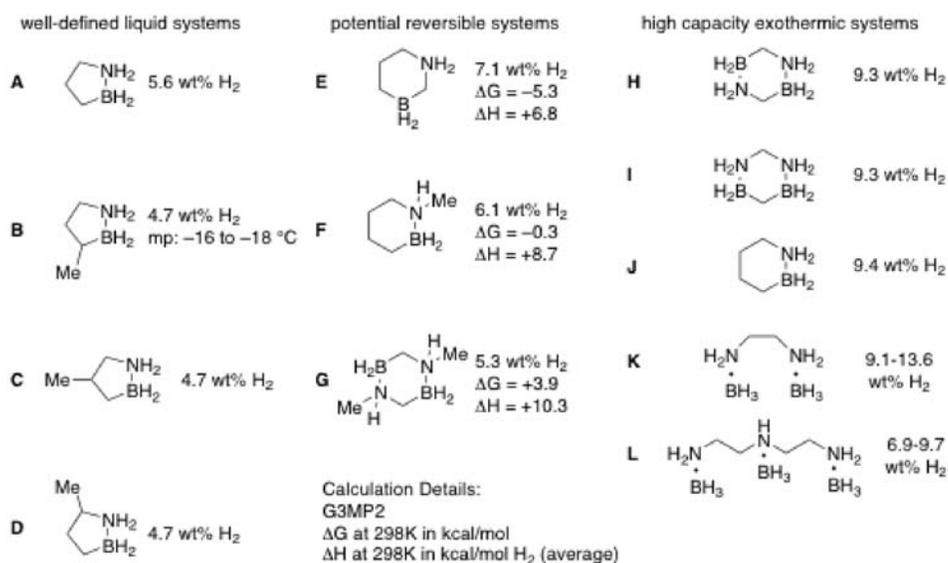
This project will develop new CBN H<sub>2</sub> storage materials that have the potential to meet the DOE targets for motive and non-motive applications. Specifically, we will be focusing on three basic systems (1) liquid phase systems that release H<sub>2</sub> in a well defined and high yield fashion, minimizing the formation of NH<sub>3</sub> and B<sub>3</sub>N<sub>3</sub>H<sub>6</sub>; (2) reversible storage systems that could potentially be regenerated onboard; and (3) high H<sub>2</sub>-content storage systems that can be used in slurries and regenerated off-board (Figure 1). Computational chemistry studies will help direct our research. Finally, we will demonstrate the developed material as a fuel in a fuel cell device. These new materials will be prepared and characterized by our interdisciplinary team comprised of Boston College, The University of Alabama, Pacific Northwest National Laboratory, and Protonex Technology Corporation (Southborough, Massachusetts, a small business fuel cell manufacturer).

## RESULTS

### Mechanistic Studies of Compound B BN-Hydrogen Release

A kinetics analysis of the thermal decomposition of Compound B in tetraglyme was performed using ReactIR. Specifically, the evolution of the first equivalent of H<sub>2</sub> from B was measured by monitoring the disappearance of a peak unique to the starting material at 1,600 cm<sup>-1</sup>.

The reaction order of the initial loss of H<sub>2</sub> from B was determined by the initial rates method; by varying the initial concentration of B between 0.56 M and 1.28 M, the



**FIGURE 1.** Selected synthetic targets and their potential storage capacities and predicted thermodynamic parameters

reaction was found to be second order in B. The temperature of the reaction was also varied between 100°C and 160°C to perform Arrhenius and Eyring analyses. The former yielded an activation energy ( $E_a$ ) of 15.7 kcal·mol<sup>-1</sup> and a pre-exponential factor ( $A$ ) of  $4.98 \times 10^5$  M<sup>-1</sup>·s<sup>-1</sup>, while the latter revealed an enthalpy of activation ( $\Delta H^\ddagger$ ) of +14.9 kcal·mol<sup>-1</sup> and an entropy of activation ( $\Delta S^\ddagger$ ) of -35.0 cal·mol<sup>-1</sup>·K<sup>-1</sup>.

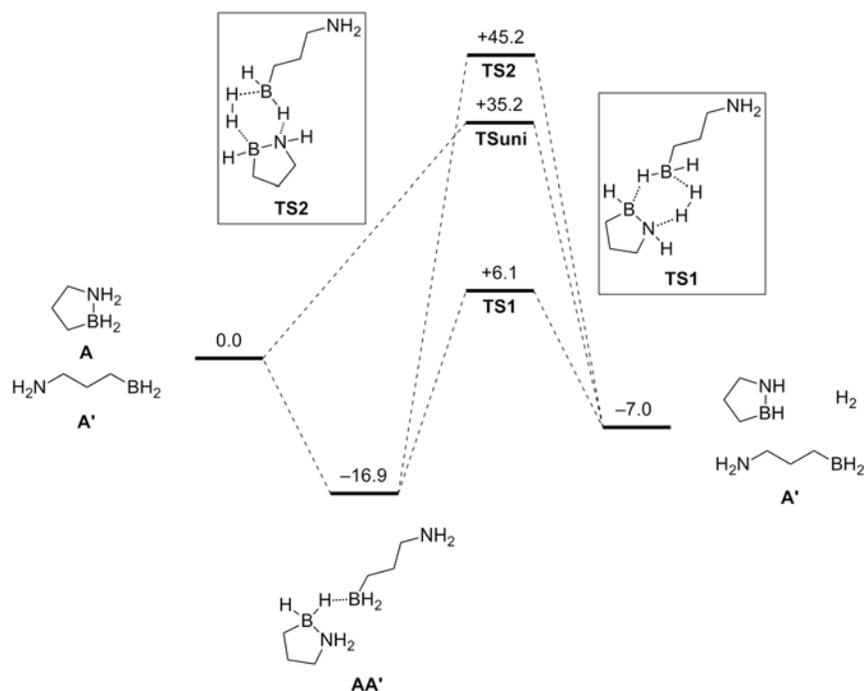
The mechanism of the thermal decomposition of B was also explored computationally at the B3LYP/DZVP2 level of density functional theory followed by higher level correlated molecular orbital theory calculations. To simplify the calculations, the de-methyl form of B, i.e., Compound A, was used for the actual modeling. Evidence of a bimolecular process (*vide supra*) directed investigation toward a system involving two molecules of A wherein one is ring-opened (A') through heterolytic dissociation of the B–N bond (Figure 2). Interaction between the BH<sub>2</sub> units of A and A' results in formation of a complex (AA') 16.9 kcal·mol<sup>-1</sup> lower in energy than the separated species. The lowest energy transition state (TS1) for loss of H<sub>2</sub> from AA' involves the BH<sub>2</sub> unit of A transferring a hydride to the BH<sub>2</sub> group of A', while a proton from the NH<sub>2</sub> group of A interacts with another hydride of the A' BH<sub>2</sub> to form H<sub>2</sub>. The barrier to this transition state from AA' was calculated as 23.0 kcal·mol<sup>-1</sup>, significantly less than that required for unimolecular decomposition from the separate species (TSuni, 35.2 kcal·mol<sup>-1</sup>). These results are highly reminiscent of those previously reported by Dixon for the BH<sub>3</sub>-catalyzed decomposition of ammonia borane [5].

## Kinetic Studies of Compound J BN-Hydrogen Release

A kinetic analysis of the loss of two equivalents of H<sub>2</sub> from Compound J catalyzed by Pd/C at 80°C, 100°C, and 120°C was performed using a gas burette. The measured rates of H<sub>2</sub> evolution were treated as originating from a pair of first-order reactions occurring in series and were fitted to an appropriate theoretical model. From this model, the activation energy and pre-exponential factor for release of the first and second equivalents of H<sub>2</sub> were estimated as 19.0 kcal·mol<sup>-1</sup> and  $8.04 \times 10^8$  s<sup>-1</sup> and 39.7 kcal·mol<sup>-1</sup> and  $3.53 \times 10^{19}$  s<sup>-1</sup>, respectively.

## Dehydrogenation of the Carbonaceous Component of a BN-Heterocycle

The acceptorless dehydrogenation of the carbonaceous component of a model BN-heterocycle, 1,2-dimethyl-1,2-BN-cyclohexene (X), was achieved using a Pd/C catalyst in a gas-flow micro-reactor. In-line quantitative mass spectrometry showed the reaction proceeded to consistently generate H<sub>2</sub> and the aromatized product X' in a 2:1 ratio, in accordance with the expected stoichiometry for complete CC dehydrogenation (Figure 3). Varying the reaction temperature from 170°C to 190°C enabled Arrhenius and Eyring analyses; for comparison, these analyses were also performed for the dehydrogenation of the related all-carbon species cyclohexene and cyclohexane. As shown in Table 1, the  $E_a$  and  $\Delta H^\ddagger$  values for dehydrogenation of X are similar to those of cyclohexene,



**FIGURE 2.** Potential energy surface in kcal·mol<sup>-1</sup> (B3LYP/DZVP2, 298 K) for a bimolecular mechanism of elimination of first equivalent of H<sub>2</sub> from A

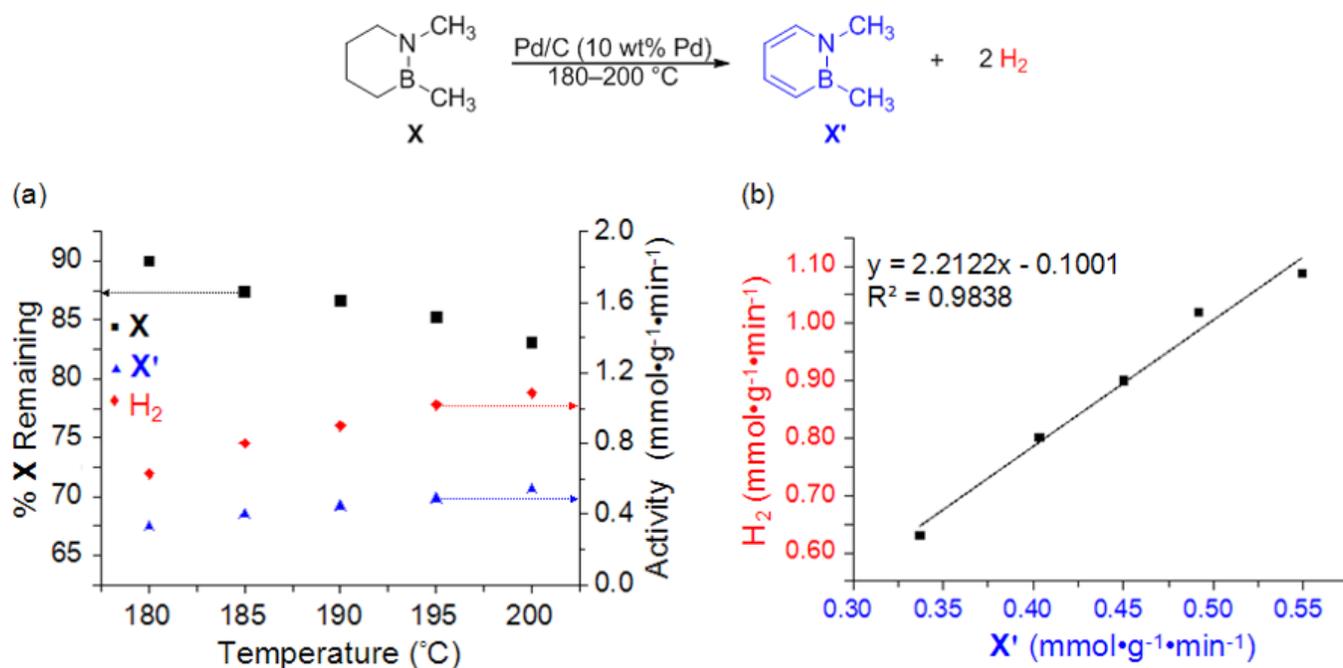


FIGURE 3. (a) Percent unreacted X (left) and rates of H<sub>2</sub> and X' formation normalized by mass catalyst (right); (b) comparison of H<sub>2</sub> and X' evolution rates

TABLE 1. Measured Activation Parameters for Dehydrogenation of X, Cyclohexane, and Cyclohexene

Reaction <sup>a</sup>	E <sub>a</sub> (kcal mol <sup>-1</sup> )	log <sub>10</sub> (A)	ΔH <sup>‡</sup> (kcal mol <sup>-1</sup> )	ΔS <sup>‡</sup> (cal mol <sup>-1</sup> K <sup>-1</sup> )
<chem>CN(C)C1CCCCC1B(C)C &gt;&gt; CN(C)C1=CC=CC=C1B(C)C + 2H2</chem>	+10.3±0.3	2.2±0.2	+9.4±0.3	-51.6±1.0
<chem>C1CCCCC1 &gt;&gt; C1=CC=CC=C1 + 3H2</chem>	+12.9±0.1	3.1±0.4	+12.0±0.1	-47.0±1.8
<chem>C1=CCCC=C1 &gt;&gt; C1=CC=CC=C1 + 2H2</chem>	+10.9±0.2	5.6±0.2	+10.2±0.2	-35.5±1.0

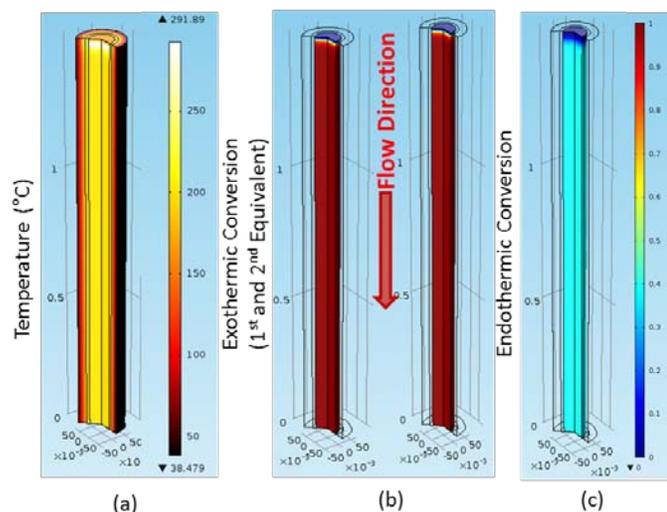
<sup>a</sup> Conditions: 50 mL/min Ar carrier gas, 10 wt% Pd/C; substrate injection rates (mmol·s<sup>-1</sup>): X (1.04×10<sup>-4</sup>), cyclohexane (1.03×10<sup>-4</sup>), cyclohexene (1.10×10<sup>-4</sup>); hydrogen evolution rates measured at 5°C increments over temperature range indicated: X (170–190°C), cyclohexane (170–190°C), cyclohexene (70–110°C). All reactions repeated in triplicate.

and lower than those of cyclohexane by approximately 2.6 kcal·mol<sup>-1</sup>. Conversely, the pre-exponential factor (log<sub>10</sub>(A)) for X is lower than that of either cyclohexene or cyclohexane and the ΔS<sup>‡</sup> value is also more negative; this is indicative of a more entropically demanding rate-determining step for the dehydrogenation of X compared to that of the all-carbon compounds.

### Modeling Coupled Exothermic-Endothermic Hydrogen Release

The experimentally derived kinetic parameters for BN dehydrogenation of J and CC dehydrogenation of X (*vide supra*) were combined with computationally derived

enthalpies of reaction for both processes to facilitate COMSOL Multiphysics<sup>®</sup> modeling of potentially coupled exothermic-endothermic H<sub>2</sub> release from a single CBN material (Figure 4). The reaction was modeled in the liquid phase in a plug flow reactor and accounted for heat and mass transfer with both axial and radial heat conductance. As shown in Table 2, the model predicted that maximum conversion resulting from BN (100%) and CC (39%) dehydrogenation occurred within the first 4% of the length of the reactor. Additionally, in the absence of endothermic CC dehydrogenation, the maximum reactor temperature was significantly higher than in the combined exothermic-endothermic case (364°C vs. 292°C,



**FIGURE 4.** Temperature (a), exothermic reaction conversion (b), and endothermic reaction conversion (c) estimates from the COMSOL model for the coupled exothermic-endothermic dehydrogenation of a single CBN material

**TABLE 2.** Modeling Results of Thermodynamically Coupled Reactions of a Single CBN Material

Active Reactions	Exothermic Conversion	Endothermic Conversion	Maximum Reactor Temperature
Exothermic and Endothermic	100%	39%	292°C
Exothermic only	100%	–	364°C
Endothermic only	–	5.6%	160°C
Exothermic and Endothermic w/o equilibrium constraints	100%	74%	292°C

respectively). Conversely, in the absence of exothermic BN dehydrogenation, the maximum reactor temperature was significantly lower (160°C), and also conversion from CC dehydrogenation was greatly reduced (5.6%). By eliminating the equilibrium constraints of the reversible CC dehydrogenation reaction, the endothermic conversion can be nearly doubled in the coupled reactions. This result indicates that most of the limitations of reaction coupling of these materials result from the reaction equilibrium rather than balancing the reaction heat and kinetics.

## CONCLUSIONS

This year we performed kinetics analyses of the initial H<sub>2</sub> release from B, the release of two equivalents H<sub>2</sub> from J, and the dehydrogenation of the carbonaceous component of X. The results obtained from the study of B aided in the development of a plausible mechanism for the reaction using

electronic structure calculations. The kinetic parameters determined for J and X were used in the COMSOL modeling of coupled exothermic-endothermic H<sub>2</sub> release from a single CBN material. The end of FY 2015 marks the conclusion of this project.

## FY 2015 PUBLICATIONS/PRESENTATIONS

1. G. Chen, L.N. Zakharov, M.E. Bowden, A.J. Karkamkar, S.M. Whittemore, E.B. Garner III, T.C. Mikulas, D.A. Dixon, T. Autrey, S.-Y. Liu. “Bis-BN Cyclohexane: A Remarkably Kinetically Stable Chemical Hydrogen Storage Material,” *J. Am. Chem. Soc.* **2015**, *137*, 134.
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3. “Novel Carbon(C)-Boron(B)-Nitrogen(N)-Containing H<sub>2</sub> Storage Materials,” Washington DC, DOE Annual Merit Review, June 10, 2015.
4. Mark Bowden, Tom Autrey, Shih-Yuan Liu, Sean Whittemore, Kriston Brooks, “Liquid Carbon-Boron-Nitrogen (CBN) Hydrogen Storage Materials,” presented at the January 2015 Expert Meeting of Task 32 IEA Hydrogen Implementation Agreement, January 18–22, 2015, Chamonix, France.

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