IV.C.5 HyMARC (Support): PNNL Effort

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Project Start Date: October 1, 2015
Project End Date: Project continuation and direction
determined annually by DOE

Overall Objectives

- Develop a series of advanced characterization tools that allows for rapid advancement and in-depth understanding of next-generation hydrogen storage materials.

- Develop a hydrogen storage material with a total materials-based capacity of >45 g/L above 150 K, that is possible with hydrogen overpressures <100 bar and reversible for multiple cycles.

- Optimize thermal management in hydrogen storage systems by the incorporation of unique phase-change materials.

- Demonstrate the importance of computational methods in developing and understanding of next generation hydrogen storage materials.

- Assist the DOE Hydrogen Materials – Advanced Research Consortium (HyMARC) seedling projects.

Fiscal Year (FY) 2017 Objectives

- Validate concept of enhanced reactivity and selectivity for hydrogen release from tetrahydrofuran (THF) adduct of magnesium borohydride, $Mg(BH_4)_2$.

- Calculate thermodynamic properties of solvated and unsolvated $Mg(BH_4)_2$.

- Resolve the discrepancy for the enthalpy of hydrogen uptake by liquid organic hydrogen carrier (LOHC) triazine.

- Determine the best computational methods required to calculate the binding energy of hydrogen to boron doped carbon.

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

(B) System Cost

(C) Efficiency

(E) Charging/Discharging Rates

(O) Lack of Understanding of Hydrogen Physisorption and Chemisorption

(P) Reproducibility of Performance

Technical Targets

Hydrogen Storage Materials: This project is conducting validation studies of various framework materials, sorbents, hydrides and model compounds. Concurrently, the team also is developing new characterization tools for the rapid enhancement of materials development. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE onboard 2020 automotive hydrogen storage targets.

- 1.5 kWh/kg system (4.5 wt% H_2)

- 1.0 kWh/L system (0.030 kg H_2/L)

- Cost of $10/kWh ($333/kg H_2 stored)

- Operating at ambient temperatures (-40 to 60ºC)

- Onboard efficiency of 90% and minimum hydrogen delivery pressure of 5 bar

- Total refuel time of 5 minutes

FY 2017 Accomplishments

- Validated the concept that Lewis base adducts of $Mg(BH_4)_2$ enhance reactivity and selectivity.

- Calculated thermodynamics (entropy, enthalpy, and free energy) and [11]B nuclear magnetic resonance (NMR) chemical shifts of key intermediates and products

- resulting from hydrogen release from $Mg(BH_4)_2$ and THF adducts of $Mg(BH_4)_2$.

- Determined the enthalpy of hydrogenation of triazine $C_3N_3H_3 + 3H_2 \Leftrightarrow C_3N_3H_9$ (ca. 69 g H_2/L) to resolve the apparent literature discrepancy for hydrogen release from the LOHC.

- Demonstrated capability of time-resolved reaction calorimetry to measure thermodynamics and kinetics for hydrogen uptake by LOHCs. Kinetic measurements are critical for catalyst screening.

- Benchmarked density functional theory (DFT) methods against experiment to determine most promising approach to determine binding energy of hydrogen to boron doped graphene.

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INTRODUCTION

The Hydrogen Storage program supports research and development of technologies to lower the cost of near-term physical storage options and longer-term material-based hydrogen storage approaches. The program conducts R&D of low-pressure, materials-based technologies and innovative approaches to increase the hydrogen storage capacity, reduce cost, and broaden the range of commercial applications for hydrogen. These advanced-material activities focus on development of core capabilities designed to enable the development of novel materials with the potential to store hydrogen near room temperature, at low-to-moderate pressures, and at energy densities greater than either liquid or compressed hydrogen on a systems basis. Key activities include improving the energetics, temperature, and rates of hydrogen release. Advanced concepts include high-capacity metal hydrides, chemical hydrogen storage materials, and hydrogen sorbent materials, as well as novel material synthesis processes. The overarching goal of the Fuel Cell Technologies Office Hydrogen Storage program is to develop and demonstrate viable hydrogen storage technologies for transportation, stationary, portable power, and specialty vehicle applications (e.g., material handling equipment, airport ground support equipment), with a key goal of enabling >300-mile driving range across all light-duty vehicle platforms, without reducing vehicle performance or passenger cargo space.

APPROACH

This national laboratory collaboration brings together internationally recognized leaders in hydrogen storage materials characterization and development at National Renewable Energy Laboratory, PNNL, Lawrence Berkeley National Laboratory, and the National Institute of Standards and Technology, as the HyMARC support team (also known as the Hydrogen Storage Characterization and Optimization Research Effort [HySCORE]). This collaboration is predicated on a synergistic approach to further validate hydrogen storage concepts and develop the key core capabilities necessary for accurate evaluation of hydrogen storage materials capacity, kinetics, and sorption/desorption physio-chemical processes. The overall approach involves collaborative experimental and modeling efforts. We are validating concepts and utilizing core capabilities to rapidly define, model, synthesize, and characterize the appropriate materials necessary for achieving the 2020 Hydrogen Storage goals set forth by DOE. The approach is multifaceted to mitigate risk and ensure success as we bridge the gap between physisorption and chemisorption to provide the basis for a new generation of hydrogen storage materials technologies.

Specifically in this project, PNNL is developing advanced characterization capabilities to provide critical approaches to validate theories and test concepts proposed in the development of new details into the chemical and physical properties of hydrogen storage materials. Variable pressure (1–200 bar) and temperature (298–473 K) in situ multi-nuclear solid state magic angle spinning NMR is being developed to identify key intermediates in the release and uptake of hydrogen in complex metal hydrides to validate claims that additives control selectivity and enhance reversibility. Low temperature (down to 5 K) solid state ^{1}H NMR is being developed to measure the enthalpy of adsorption of hydrogen in high surface area adsorbent materials and to assist in the validation of the concept that more than one hydrogen molecule can bind to a metal site on a high surface amorphous material. Variable pressure (1–100 bar) and temperature (250–350 K) multi-nuclear liquid NMR is available to measure key intermediates. Variable pressure (1–20 bar) and temperature (298–353 K) reaction calorimetry is available to measure kinetics and enthalpies of hydrogen uptake in liquid and solid stores to benchmark and validate computational predictions of binding enthalpies in liquid carriers.

Our work in FY 2017 included efforts to develop state-of-the-art characterization techniques for hydrogen storage materials including calorimetry and in situ NMR spectroscopy. Through a theoretical and experimental interaction, we focused on (i) the validation of key intermediates formed during release of hydrogen from solid state complex hydrides (i.e., magnesium borohydride, $Mg(BH_4)_2$); (ii) determination of the thermodynamics of H_2 uptake and release from liquid carriers (i.e., triazine and diazine); and (iii) characterization of computational approaches to gain insight into the binding energies of hydrogen in boron and nitrogen doped carbons. In addition, we were able to assist a number of HyMARC seedling projects in their characterization efforts using NMR, X-ray diffraction, and transmission electron microscopy.

RESULTS

I. Validation of Key Intermediates Formed during Release of H_2 from Solid State Complex Hydrides. Using Lewis basic adducts complexed to alkali and alkaline metal borohydrides has the potential to open new dimensions in chemical materials space to be explored by the research community. Sub-stoichiometric quantities of THF to $Mg(BH_4)_2$, e.g., $Mg(BH_4)_2 \cdot 0.67$ THF (5.6 wt% hydrogen) enhances the rate of H_2 release and selectively yields products that fall in the desirable thermodynamic range for reversible storage.

We used NMR spectroscopy to compare and contrast the products formed upon hydrogen release from a series of Lewis base adducts of $Mg(BH_4)_2$. This work validated the claim that THF enhances reactivity and selectivity for $MgB_{10}H_{10}$ formation. Additives that drive the reaction towards $B_{10}H_{10}$ are highly desired as regeneration of $Mg(BH_4)_2$ from the closoborane $MgB_{10}H_{10}$ is thermodynamically more favorable than regeneration from $MgB_{12}H_{12}$. The experimental studies suggest that a low temperature phase change to make a more mobile phase of borohydride enhances kinetics while thermodynamics, i.e., destabilization of the closoborane products, drive the reaction selectivity (Figure 1).

Computational studies were undertaken to gain insight into the enhanced selectivity. Solid-state DFT calculations were performed to determine thermodynamics of complex borohydride species that may be observed on the reversible reaction pathway during the release of hydrogen from $Mg(BH_4)_2$. We calculated the thermodynamic energies, ΔH and ΔG (at 300 K), for the conversion of $Mg(BH_4)_2$ to
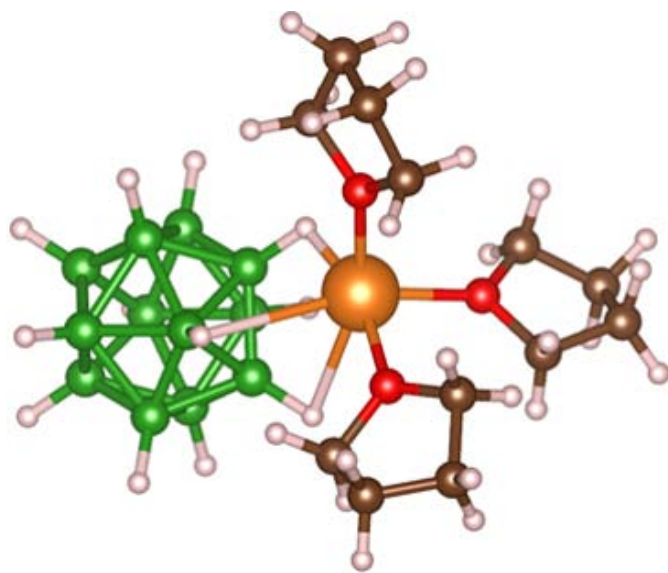
$Mg(B_3H_8)_2$, $Mg_3(B_3H_6)_2$, $MgB_{10}H_{10}$, $Mg(B_{11}H_{14})_2$, MgB_2H_6, MgB_2 and $MgB_{12}H_{12}$ to gain insight into the reaction pathways leading to the release of H_2. Using combination of experiment and theory, we have used a combination of vibrational spectroscopy (infrared and Raman) and NMR chemical shift calculations for these borohydride clusters in order to predict unknown observable intermediates in release of H_2 from $Mg(BH_4)_2$. Figure 1 shows the structure of $MgB_{12}H_{12} \cdot 3$ THF determined from PXRD that was used to calculate the destabilization of the closoborane.

II. Determination of the Thermodynamics of H_2 Uptake and Release from Liquid Organic Hydrogen Carriers. Our work focused on calculating the reaction energy for addition of three H_2 molecules to $C_3N_3H_3$ (ca. 69 g H_2/L). The work suggested four different configurations for the product state $C_3N_3H_9$, differing in the orientation of the hydrogen atoms attached to nitrogen atoms, relative to the plane of the ring. The structures of the four product states are denoted in Figure 2 as ip0 to ip3. All stable structures were confirmed by absence of imaginary frequencies in the vibrational analysis of the hessian, calculated in the framework of the rigid rotor-harmonic oscillator approximation. Table 1 compares the enthalpy of H_2 addition of a stable isomer with a calculated enthalpy of 43 kJ/mol H_2 in agreement with the low end of reported enthalpies, whereas ip2 and ip3 are

ip0

ip1

ip2

ip3
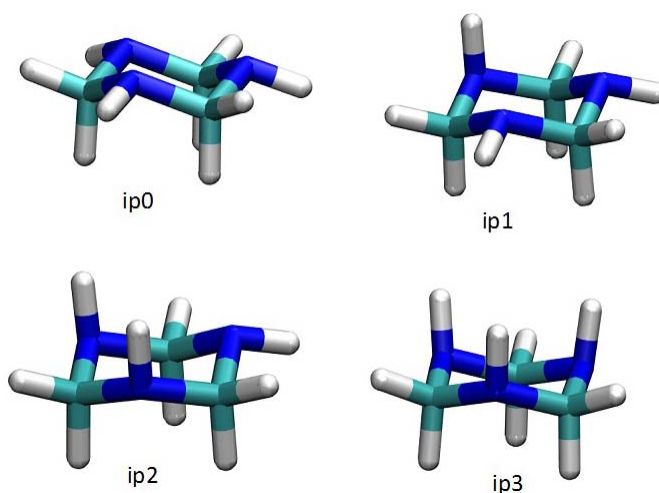
FIGURE 2. Structural isomers of reduced triazine. Absolute energies are shown in Table 1.

TABLE 1. Thermodynamics for the reaction $C_3N_3H_3 + 3H_2 \rightarrow C_3N_3H_9$ (in kJ/mol per H_2)

	ΔE	E+zpc	ΔH	TΔS	ΔG
ip0	-70.7	-35.1	-43.1	-35.6	-7.5
ip1	-79.5	-43.5	-51.0	-35.6	-15.5
ip2	-84.5	-48.1	-55.6	-35.6	-20.1
ip3	-85.8	-49.0	-56.9	-36.4	-20.5

FIGURE 1. Structure of THF adduct of $MgB_{12}H_{12}$ showing the attachment of THF molecules to the magnesium cation.

the most stable isomers with a calculated enthalpy of ca. 56 kJ/mol H_2 in agreement with the high end of reported enthalpies.

The least stable isomer, ip0, could be formed at the surface of a heterogeneous catalyst if all the H_2 was added to one side. If the barrier for inversion of the ring at the nitrogen center is sufficiently high it could be possible to form the unstable isomer and then release the H_2 in a cyclic reaction at temperatures less than 80°C. To gain insight into the inversion barrier we calculated the transition state energy for inversion of one isomer to another. These studies showed that the barrier for inversion is sufficiently low that the most thermodynamically stable isomer will form even at room temperature.

We demonstrated the utility of reaction calorimetry to measure the enthalpy of H_2 uptake by LOHCs. This approach provides an opportunity to benchmark computational methods to determine the optimum approach to predict the enthalpies of hydrogen release from new LOHCs. In addition, the time-dependence of the heat release provides critical insight into kinetics and the ability to compare different catalyst materials to optimize efficiency in LOHCs.

For triazine, with a T_c of 110°C and 69 g H_2/L, additional catalyst work is warranted. The product perhydrotriazine is not stable with Pd/C but further catalysis development work was outside the scope of funded project. NMR is valuable to monitor stability and products formed while reaction

calorimetry is valuable to compare rates of H_2 uptake and release for both heterogeneous and homogeneous catalysis.

III. Evaluation of Computational Approaches to Predict Binding Energies of H_2 to Boron and Nitrogen Doped Carbons. Our research focused on the evaluation of different DFT methods to gain insight into the effects of boron and nitrogen doping on the H_2 interaction (physisorption) with carbon (graphene). We used two models as representative classes of molecular systems (coronene) and extended systems (graphene) (Figure 3). Evaluation of molecular systems allows us to rapidly and systematically study the electronic and steric effects of heteroatoms (boron or nitrogen). The accuracy of theoretical calculations, as determined by agreement with experimental benchmarks, depends on the various functionals used in performing DFT calculations. We also compared correlations between molecular and extended systems. Our key findings are summarized below:

- The B3LYP functional with DFT-D3 Grimme's dispersion correction provides the best agreement with experiment for known published values.

- Calculations show an enhancement of H_2 physisorption by ca. 22%, i.e., 6.2–7.6 kJ/mol H_2 for sp2 hybridized B in $BC_{23}H_{13}$ (around 2.7% of B doping).

- Non-planarity of the coronene surface results in increase in the binding energy of H_2 physisorption.
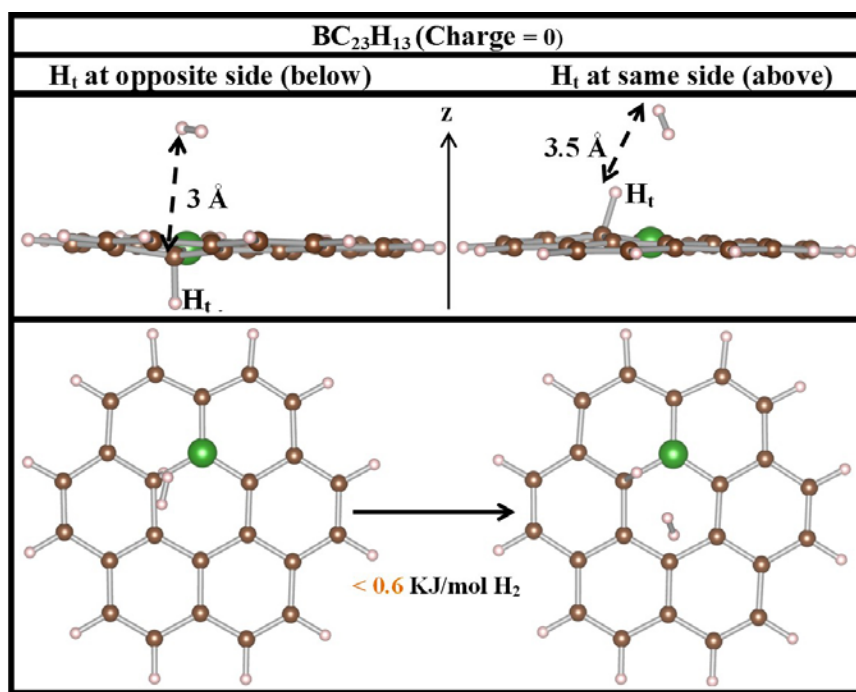
FIGURE 3. H_2 is stabilized near the defect created by insertion of boron into coronene $BC_{23}H_{12}$; however, there is little difference in the binding energy of H_2 approaching from above or below the plane of the coronene ring.

- The steric hindrance pushes the H_2 molecule towards the C atoms with ≤ 0 charge.

- Site of physisorption is a function of non-planarity, steric hindrances and charge distribution.

- Binding energies are dependent on site of physisorption and charge delocalization which in turn is governed by atomic arrangements of dopants and the corresponding defects.

CONCLUSIONS AND UPCOMING ACTIVITIES

We have validated the claim that THF adducts of $Mg(BH_4)_2$ enhance reactivity and selectivity for hydrogen release to yield closodecaborane as the major hydrogen release product. Experimental studies suggest the enhanced reactivity, i.e., hydrogen release at temperature below 180°C, is due in part to a phase change to a mobile complex. Calculations support that the THF adduct destabilizes the products in greater magnitude than the starting materials. This is a positive result that leads to new materials classes of complex hydrides that can reversibly store hydrogen with greater efficiency. Going forward we will test the hypothesis that solvates enable regeneration of $Mg(BH_4)_2$ from the closoboranes.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Excellent Poster award for Marina Chong. 11th International Symposium on Hydrogen Energy.

FY 2017 PUBLICATIONS/PRESENTATIONS

1. Solvent-coordinated Compounds Formed from Magnesium Hydroborates and Tetrahydrofuran. Mark Bowden, Marina Chong, Phuong Nguyen, Sunil Shrestha, Bojana Ginovska, Iffat Nayyar, Abhi Karkamkar, Craig Jensen, and Tom Autrey. 11th International Symposium on Hydrogen Energy.

2. Hydrogen storage characterization and optimization research effort. 11th International Symposium on Hydrogen Energy. HyScore. Iffat Nayyar, Marina Chong, Abhi Karkamkar, Mark Bowden, Bojana Ginovska, Adrian Houghton, Phuong Nguyen, Sunil Shrestha, Craig Jensen, Tom Gennett, and Tom Autrey. 11th International Symposium on Hydrogen Energy.

3. A New Role for Solvents: from Undesirable Residue to Useful Additive (at least, in the dehydrogenation of $Mg(BH_4)_2$). Marina Chong, Phuong Nguyen, Sunil Shrestha, Mark Bowden, Abhi Karkamkar, Tom Autrey, and Craig Jensen. 11th International Symposium on Hydrogen Energy.

4. High Capacity Hydrogen Cycling between Magnesium Borohydride and Magnesium Boranes under Moderate Conditions. Marina Chong, Junzhi Wang, Phuong Nguyen, Motoaki Matsuo, Mark Bowden, Tom Autrey, Shin-ichi Orimo, and Craig M. Jensen. MH 2016.