

IV.A.4 Lightweight Metal Hydrides for Hydrogen Storage

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Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

- Cost: \$3-7/gasoline gallon equivalent at the pump
- Specific energy: 1.5 kWh/kg (4.5 wt% H)
- Energy density: 0.9 kWh/L (0.028 kg/L)

FY 2011 Accomplishments

- We modified the synthetic method of $\text{AlB}_4\text{H}_{11}$. Several grams of $\text{AlB}_4\text{H}_{11}$ were synthesized using the modified method at OSU.
- Both infrared (IR) and pressure-composition-temperature (PCT) tests showed that $\text{AlB}_4\text{H}_{11}$ is partially reversible at relatively mild condition such as 220°C and 100 bar of hydrogen. Differential scanning calorimetry (DSC) measurements also showed that $\text{AlB}_4\text{H}_{11}$ dehydrogenates around 125°C with a broad endothermic peak.
- In collaboration with both Northwestern University and the National Institute of Standards and Testing (NIST), the structure units, a triangle of B_3 and a BH_4 group, were completely identified.
- We modified the synthetic method of $\text{AlB}_6\text{H}_{13}$ (a sister compound to $\text{AlB}_4\text{H}_{11}$) and characterized its properties for potential hydrogen storage applications together with the Oak Ridge National Laboratory (ORNL).
- We recently developed simple and efficient methods for the preparation of both NaB_3H_8 and $\text{NH}_4\text{B}_3\text{H}_8$. They release more hydrogen during hydrolysis under mild condition than the most studied hydrogen storage materials such as NaBH_4 and NH_3BH_3 .
- We developed a new method to prepare $[\text{H}_2\text{B}(\text{NH}_3)_2][\text{B}_3\text{H}_8]$ which has high hydrogen capacity of 18.4 wt%.

Fiscal Year (FY) 2011 Objectives

- Develop a high-capacity lightweight hydride for reversible vehicular hydrogen storage, capable of meeting or exceeding the 2010 DOE/FreedomCAR targets.
- Synthesize and study aluminoborane compounds and other lightweight, high-capacity boron hydrides for hydrogen storage.
- Perform detailed characterization of the decomposition mechanisms, desorbed gaseous species and structures of the synthesized compounds.

Technical Barriers

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

- (D) Durability/Operability
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (E) Charging/Discharging Rates
- (J) Thermal Management

Technical Targets

This project is conducting synthesis and studies of the decomposition mechanism of aluminoborane compounds.



Introduction

The DOE defines on-board hydrogen storage for mobile vehicles as a “Grand Challenge”. It is one of the biggest hurdles to the implementation of hydrogen-powered vehicles. Metal hydrides have the advantages of the highest volumetric density, relatively low working pressure, and reasonable working temperature range. The disadvantage of current reversible hydrides is a significant weight penalty. Metal borohydrides have among the highest gravimetric hydrogen storage capacities with the potential to meet the DOE gravimetric density targets and to offset the system weight penalties. However, desorption temperature, reversibility and formation of gaseous borane compounds during desorption are challenging issues for these materials.

This project attempts to develop a high-capacity lightweight hydride for reversible vehicular hydrogen storage, capable of meeting or exceeding the 2010 DOE/FreedomCAR targets.

Approach

- Explore aluminoborane compounds such as $\text{AlB}_4\text{H}_{11}$ and other high-capacity, lightweight boron hydrides.
- Study the structure and the decomposition mechanisms using multiple techniques such as interrupted PCT tests, nuclear magnetic resonance (NMR), IR, DSC, and residual gas analysis.
- Develop reversibility strategy from detailed mechanistic understanding of the complex desorption processes (such understanding is crucial for reversibility of all borohydrides).
- Synthesize new hydrides and complexes in collaboration with ORNL, Sandia National Laboratories, and NIST.

Results

A modified method for synthesizing aluminoborane, $\text{AlB}_4\text{H}_{11}$, was developed and applied to the preparation of $\text{AlB}_4\text{H}_{11}$ in gram quantities at OSU. Careful measurements were performed on $\text{AlB}_4\text{H}_{11}$ to investigate its properties as a potential hydrogen storage material. Both IR and PCT tests indicate that this compound is partially reversible at relatively mild conditions such as 220°C and 100 bar of hydrogen, which further supports our conclusion of reversibility based on previous NMR observations. Furthermore, DSC measurements show that $\text{AlB}_4\text{H}_{11}$ dehydrogenates around 125°C with a broad endothermic peak, thus it is thermodynamically reversible. Encouraged by these results which suggest that $\text{AlB}_4\text{H}_{11}$ might be a good candidate for reversible vehicular hydrogen storage, we devoted considerable amount of effort to figure out the molecular structure of $\text{AlB}_4\text{H}_{11}$. Structural identification is crucial for understanding the desorption mechanisms and the partial reversibility.

The identification of the molecular structure of $\text{AlB}_4\text{H}_{11}$ has been difficult because of its polymeric/amorphous nature and its insolubility in major solvents [1]. The former prevents us from determining the structure through X-ray diffraction or neutron diffraction. The latter prevents us from performing solution NMR and mass spectroscopy tests to obtain structural information. The available structural information from solid NMR and IR spectra is insufficient for structural identification. In collaboration with Northwestern University and NIST, we employ both experimental measurements (IR, NMR, and neutron vibration analysis) and theoretical calculations (prototype electrostatic ground state [PEGS] + density functional theory [DFT]) to define the structure of $\text{AlB}_4\text{H}_{11}$.

Even though $\text{AlB}_4\text{H}_{11}$ was synthesized from a benzene solution, it is not soluble in benzene once it is formed. In order to gain more structural information from experiments,

we examine the mother/residual solution by ^{11}B and $^{11}\text{B}\{^1\text{H}\}$ NMR after the precipitation of $\text{AlB}_4\text{H}_{11}$ to determine if trace amount of the polymeric product is retained in the solution. Two boron signals at $\delta -36.7$ and -53.3 ppm observed in solution NMR may be associated with the two signals at $\delta -37.4$ and $\delta -50$ ppm of product in its solid ^{11}B NMR [2]. The process of the reaction between $\text{Al}(\text{BH}_3)_4$ and B_2H_6 is also monitored by ^{11}B and $^{11}\text{B}\{^1\text{H}\}$ NMR with an attempt to find the transformation from starting materials to the product. Several small signals appeared at $\delta -33.5$, -38.2 , -44.7 -52.8 and -53.7 ppm as the reaction proceeds. The peaks at $\delta -38.2$ and -44.7 ppm may be related to dimer or polymer of $\text{HAl}(\text{BH}_4)_n$ ($\delta -38.3$ and $\delta -43.3$ ppm) and the peaks at $\delta -53.7$ ppm may be associated to product ($\delta -50$ ppm in its solid ^{11}B NMR) [3]. So the reaction probably starts with dimerization or polymerization of $\text{Al}(\text{BH}_4)_3$ and then transfers to the product. Though $\text{AlB}_4\text{H}_{11}$ did not dissolve in major solvents, we found that it is soluble in (or reacted with) liquid ammonia without any bubble formation. The ^{11}B NMR spectra of $\text{AlB}_4\text{H}_{11}$ in liquid ammonia clearly show a quintet and a nonet which are assigned to BH_4^- and B_3H_8^- groups (Figure 1). This observation suggests that a B_1 unit and a B_3 unit groups exist in the structure of $\text{AlB}_4\text{H}_{11}$. The neutron vibration spectrum of $\text{AlB}_4\text{H}_{11}$ is recorded in NIST (by Terry Udovic and his co-workers) for comparing with theoretical results.

Based on the available information, six possible structures were predicted through (PEGS + DFT) calculation by Northwestern University (Chris Wolverton, Yongli Wang, and Yongsheng Zhang). Three of these structures (#3, #5, and #6) are more stable than others based on the calculated ground-state energies. It is interesting that all these stable structures contain a B_1

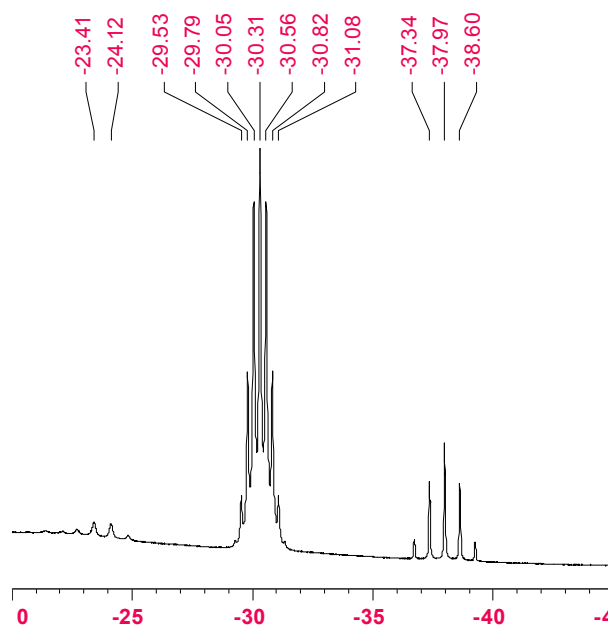


FIGURE 1. ^{11}B NMR Spectrum of $\text{AlB}_4\text{H}_{11}$ in Liquid Ammonia

unit and a B_3 unit which either connected directly (as in structure #3) or separated by Al atom (as in structures #5 and #6). The presence of the B_1 unit and the B_3 unit in these structures is consistent with the experimental observations.

Simulation of the neutron vibration spectra for structures #5 and #6 has been performed by NIST for comparing with the experimental vibration spectra of AlB_4H_{11} . Figure 2 shows that even though some agreements are observable, the overall agreement is less than ideal, indicating that both structures #5 and #6 need further refinement to reflect the correct structure of AlB_4H_{11} . It is worthwhile mentioning that even for well-defined structures from single crystal data, the simulated and experimental neutron vibration spectra do not match perfectly for many compounds.

The ^{27}Al NMR of AlB_4H_{11} in liquid ammonia shows two Al signals which are inconsistent with structures #5 or #6 because that Al has an identical chemical environment in structure #5 or structure #6. With this new observation, the structure of AlB_4H_{11} is simulated again using PEGS+DFT by inputting only B_3H_7 and BH_4 units and Al atoms. It is surprising that the energy of the modified structure is at least 40 KJ/mol lower than that of structures #5 and #6.

After spending tremendous efforts by OSU, Northwestern University, and NIST on this collaborative research, the structure units are completely identified. The

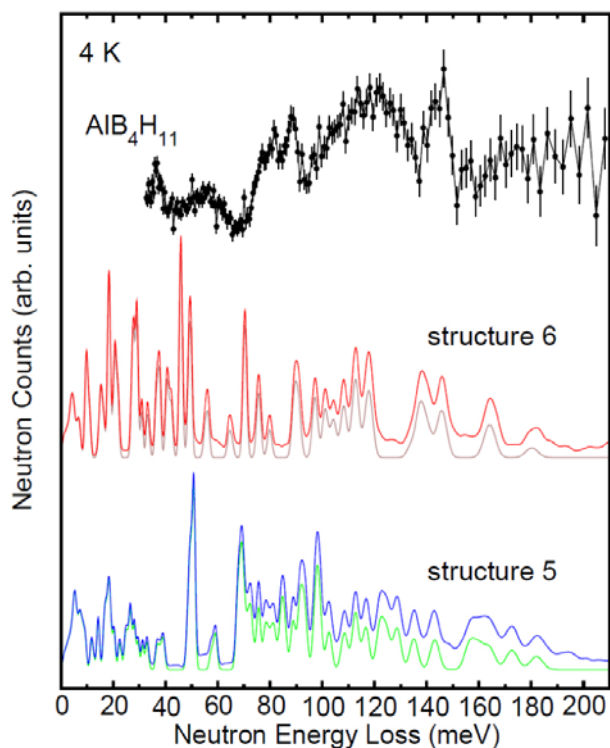
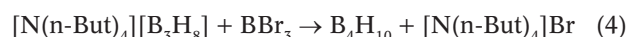
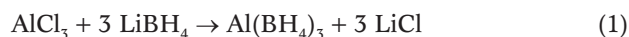


FIGURE 2. The Neutron Vibration Spectrum of AlB_4H_{11} and Simulated Vibration Spectra of Structures #5 and #6 predicted by the Northwestern University

structure of AlB_4H_{11} consists of B_3H_7 units and BH_4 unit that are separated by Al atoms (Figure 3). Only a slight uncertainty still exists in terms of the exact arrangement of these structure units. The structural information will help us to understand the desorption mechanisms and partial reversibility of AlB_4H_{11} .

With the experience of preparing AlB_4H_{11} , we have successfully synthesized AlB_6H_{13} , another aluminoborane compound, through the reaction between $Al(BH_4)_3$ and B_4H_{10} . Since the starting materials are not commercially available, considerable efforts are devoted to the preparation of the precursors [4]. Overall, the process includes five reactions (reactions 1 to 5):



However, preliminary characterization of its properties as a potential storage material, in collaboration with ORNL, shows a very discouraging result: a large amount of borane complexes were observed during desorption, which discourages further study of this compound for hydrogen storage.

To investigate more boron-containing lightweight hydrides for hydrogen storage, we focus on a type of boron compounds with a formula of $M_xB_3H_8$, which may be less stable than M_xBH_4 and thus may be easier for dehydrogenation and rehydrogenation. We first developed a simple and efficient route to unsolvated NaB_3H_8 [5], and investigated its hydrogen release properties. Pyrolysis test results are discouraging since large amount of gaseous species were observed, indicating that this compound is not suitable for on-board reversible hydrogen storage. It is

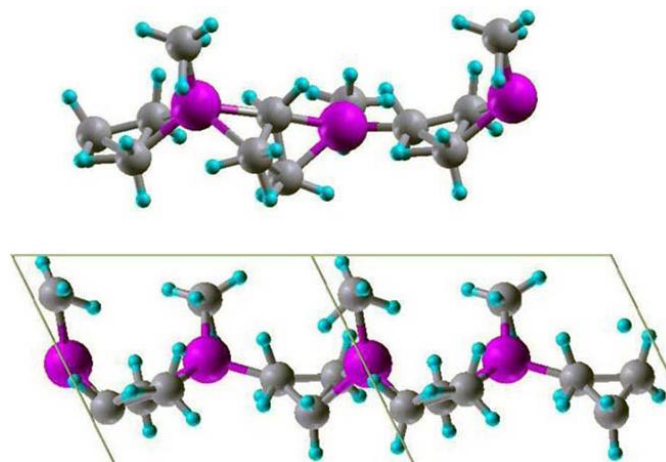


FIGURE 3. Two different lowest energy structures for AlB_4H_{11} . They have the same B_3H_7 and BH_4 structure units but slightly different arrangements.

found that NaB_3H_8 is highly soluble in water. Quantitative measurements of hydrogen released using a Toepler pump and gas buret showed that upon adding 14 mmol water to 1 mmol NaB_3H_8 with Pt/C (1 mol % Pt), a near theoretical value of 8.85 mol hydrogen is released in 20 mins via hydrolysis. Therefore, this system has a high theoretical hydrogen weight percent [$\text{wt}\% = \text{H}_2 / (\text{NaB}_3\text{H}_8 + \text{H}_2\text{O})$] of 10.5 wt%. It is also observed that NaB_3H_8 is significantly more stable in water (distilled water is used in the study) than NaBH_4 . The fairly stable aqueous NaB_3H_8 solution without additives can be a good candidate for certain applications where hydrogen is consumed continuously. In this regard, NaB_3H_8 has advantages over the most studied hydrogen storage materials such as NaBH_4 and NH_3BH_3 via hydrolysis [6].

We have also successfully developed a simple and high-yield synthesis of $\text{NH}_4\text{B}_3\text{H}_8$ through a metathesis reaction between unsolvated NaB_3H_8 and NH_4Cl [7]. The crystal structure shows weak $\text{N}-\text{H}^{\delta+} \cdots \text{H}^{\delta-}-\text{B}$ interaction in $\text{NH}_4\text{B}_3\text{H}_8$, which is different from the close $\text{N}-\text{H}^{\delta+} \cdots \text{H}^{\delta-}-\text{B}$ contacts observed in $\text{NH}_3\text{B}_3\text{H}_7$ and NH_3BH_3 . $\text{NH}_4\text{B}_3\text{H}_8$ has a high hydrogen content of 20.5 wt%. Thermal decomposition analysis shows that 10 wt% hydrogen is released below 160°C, but with appreciable amounts of borane complexes. Therefore, $\text{NH}_4\text{B}_3\text{H}_8$ is unlikely a candidate for hydrogen storage through thermal decomposition.

Hydrolytic studies have shown that upon adding catalysts, $\text{NH}_4\text{B}_3\text{H}_8$ rapidly releases pure H_2 [7]. For an aqueous solution with a 1:18 molar ratio of $\text{NH}_4\text{B}_3\text{H}_8$ to H_2O , which represents a system density of 4.6 wt% H (water weight included), the commercially available 10 wt% Pt/C catalyst (1 mol% Pt) shows the best catalytic activity, with complete hydrolysis in less than 30 min (Figure 4). Lower-cost transition metal catalysts were also explored in our study and fairly good catalytic activity was observed for CoCl_2 . With 4 mol% loading of CoCl_2 , full hydrolysis was complete in about 100 min. A black powder appeared instantly when CoCl_2 was brought into contact with an aqueous $\text{NH}_4\text{B}_3\text{H}_8$ solution, suggesting the formation of cobalt boride as found during the hydrolysis of NaBH_4 . The ^{11}B NMR spectrum of the catalyzed hydrolysis solution of $\text{NH}_4\text{B}_3\text{H}_8$ and H_2O (1: 18 ratio) reveals one broad peak centered at 16 ppm which is likely associated with $\text{B}_3\text{O}_3(\text{OH})_4^-$ and $\text{B}_5\text{O}_6(\text{OH})_4^-$, along with another sharp peak situated at around 0 ppm that is also due to $\text{B}_5\text{O}_6(\text{OH})_4^-$. Similar products were also formed during the hydrolysis of $\text{NH}_3\text{B}_3\text{H}_7$.

Another amine borane compound, $(\text{NH}_3)_2\text{BH}_2\text{B}_3\text{H}_8$, with high hydrogen capacity of 18.4 wt%, has attracted little attention as a potential hydrogen storage material, probably because of its unavailability. The procedure reported before is through the reaction between ammonia and tetraborane, which is highly volatile and flammable [8,9]. Inspired by recent success in developing safe and efficient methods for synthesizing unsolvated NaB_3H_8 and $\text{NH}_4\text{B}_3\text{H}_8$, we developed a new method for synthesizing $(\text{NH}_3)_2\text{BH}_2\text{B}_3\text{H}_8$

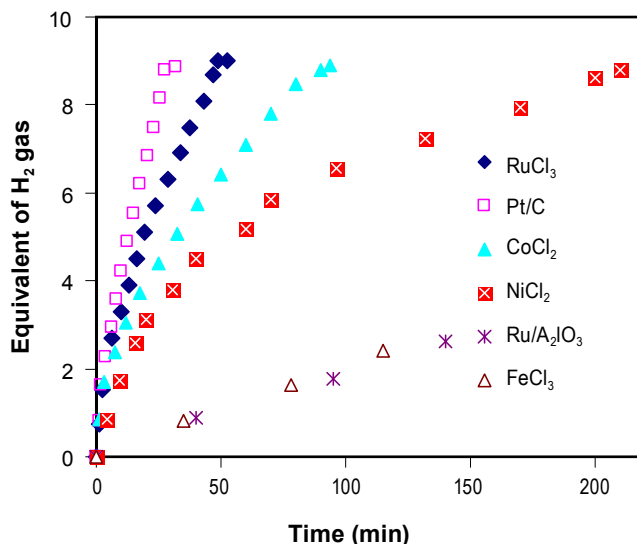


FIGURE 4. Hydrogen evolution at room temperature from an aqueous $\text{NH}_4\text{B}_3\text{H}_8$ solution (molar ratio of $\text{NH}_4\text{B}_3\text{H}_8:\text{H}_2\text{O}$ being 1:18) containing 10 wt% Pt/C (1 mol% Pt); 5 wt% Ru/ Al_2O_3 (1 mol% Ru), RuCl_3 (1 mol% Ru), CoCl_2 (4 mol% Co), NiCl_2 (4 mol% Ni) and FeCl_3 (4 mol% Fe). Molar ratios are referenced to $\text{NH}_4\text{B}_3\text{H}_8$.

via a metathesis reaction. The method includes three steps (reactions 6, 7, and 8):



All three reactions are carried out in liquid ammonia. After the second step (reaction 7), $(\text{NH}_3)_2\text{BH}_2\text{Cl}$ is isolated from the tetrahydrofuran (THF) solution after removal of liquid ammonia. The desired $(\text{NH}_3)_2\text{BH}_2\text{B}_3\text{H}_8$ is extracted using THF. Overall, the new method is more efficient. The ^{11}B NMR spectrum of $(\text{NH}_3)_2\text{BH}_2\text{B}_3\text{H}_8$ in THF shows a triplet and a nonet corresponding to BH_2^+ and B_3H_8^- group. Crystal structure of an adduct with crown ether, $(\text{NH}_3)_2\text{BH}_2\text{B}_3\text{H}_8 \cdot 18\text{-crown-6}$ has been determined in which one ammonia molecule orients toward the crown ether to form three $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds between the hydrogen atoms of the ammonia and the oxygen atoms of the ether. Further characterization of its desorption products and mechanism is in progress.

Conclusions and Future Directions

- In collaboration with Northwestern University and NIST, we have now identified the structure units in polymeric/amorphous $\text{AlB}_4\text{H}_{11}$. The structure consists of B_3H_7 and BH_4 groups linked to a polymer chain via Al atoms.
- $\text{AlB}_6\text{H}_{13}$ (a sister compound to $\text{AlB}_4\text{H}_{11}$) was synthesized and characterized for potential hydrogen storage, and was found not a viable hydrogen storage material.

- Simple and efficient methods for the preparation of both NaB_3H_8 and $\text{NH}_4\text{B}_3\text{H}_8$ were developed. These compounds were found unsuitable for reversible hydrogen storage, but showed good properties via hydrolysis.
- We developed a new method to prepare $[\text{H}_2\text{B}(\text{NH}_3)_2][\text{B}_3\text{H}_8]$ which has high hydrogen capacity of 18.4 wt%.
- As the program/project is drawn to completion, we will do our best in completing the analysis and reporting.

FY 2011 Publications/Presentations

1. T.B. Yisgedu, X. Chen, H.K. Lingam, Z. Huang, S. Maharrey, R. Beherns, S.G. Shore, and J.-C. Zhao, "Synthesis, Structural Characterization, and Thermal Decomposition Study of $\text{Mg}(\text{H}_2\text{O})_6\text{B}_{10}\text{H}_{10}\cdot 4\text{H}_2\text{O}$ ", *J. Phys. Chem. C.*, 115, 11793-11802 (2011).
2. Z. Huang, X. Chen, T. Yisgedu, J.-C. Zhao, and S.G. Shore, "High-Capacity Hydrogen Release through Hydrolysis of NaB_3H_8 ", *Inter. J. Hydrogen Energy*, 36, 7038-7042 (2011).
3. Z. Huang, X. Chen, T. Yisgedu, E.A. Meyer, S.G. Shore, and J.-C. Zhao, "Ammonium Octahydrotriborate ($\text{NH}_4\text{B}_3\text{H}_8$): New Synthesis, Structure and Hydrogen Storage Properties", *Inorg. Chem.*, 58, 3738-3742 (2011).
4. D.T. Shane, L.H. Rayhel, Z. Huang, J.-C. Zhao, X. Tang, V. Stavila, M.S. Conradi, "A Comprehensive NMR Study of Magnesium Borohydride", *J. Phys. Chem. C.*, 115, 3172-3177 (2011).
5. Z. Huang, G. King, X. Chen, J. Hoy, T. Yisgedu, H.K. Lingam, S.G. Shore, P.M. Woodward, and J.-C. Zhao, "A Simple and Efficient Way to Synthesize Unsolvated Sodium Octahydrotriborate", *Inorg. Chem. (Comm.)*, vol. 49, pp. 8185-8187 (2010).
6. X. Chen, J.-C. Zhao, and S.G. Shore, "Facile Synthesis of Aminodiborane and Inorganic Butane Analogue $\text{NH}_3\text{BH}_2\text{NH}_2\text{BH}_3$ ", *J. Am. Chem. Soc. (Comm.)*, 132, 10658-10659 (2010).
5. "Dihydrogen Bond Effects in Amine Borane Chemistry" (INOR-1001), X. Chen*, J.-C. Zhao, S.G. Shore, Abstracts of Papers, 241st ACS National Meeting & Exposition, Anaheim, CA, March 27-31, 2011.
6. "Aluminoboranes and Boron Compounds for Hydrogen Storage", J.-C. Zhao*, X. Chen, Z. Huang, T. Yisgedu, H.K. Lingman, B. Billet, S.G. Shore, (Oral presentation) TMS Annual Meeting, San Diego, California, February 27 to March 3, 2011.
7. "Lightweight Metal Hydrides for Hydrogen Storage", J.-C. Zhao*, X. Chen, Z. Huang, H. K. Lingam, T. Yisgedu, B. Billet, and S.G. Shore, (Oral presentation) International Energy Agency (IEA) Task 22 Hydrogen Storage Experts' Meeting, Fremantle/Perth, Australia, January 17-20, 2011.
8. "Lightweight Metal Hydrides for Hydrogen Storage", J.-C. Zhao*, X. Chen, Z. Huang, H.K. Lingam, T. Yisgedu, B. Billet, and S.G. Shore, (Oral presentation) US Department of Energy Hydrogen Storage Tech Team Meeting, USCAR, Southfield, MI, November 18th, 2010.
9. "Borohydrides, Aluminoboranes and Boron-Cage Compounds for Hydrogen Storage", J.-C. Zhao*, X. Chen, Z. Huang, H. K. Lingam, T. Yisgedu, B. Billet, and S.G. Shore, (Keynote lecture), First International Conference on Materials for Energy, Karlsruhe, Germany, July 4-8, 2010.

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