COMPUTATIONAL STUDIES OF BORON/NITROGEN AND ALUMINUM/NITROGEN COMPOUNDS FOR CHEMICAL HYDROGEN STORAGE

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Introduction

The DOE Office of Energy Efficiency and Renewable Energy have recently proposed a Grand Challenge for on-board Hydrogen Storage in response to the Presidents 2003 State of the Union Address.[1] To meet the target of the long-term DOE volumetric (0.09 kg H_2/kg) and energy density (3.0 kWh/kg) targets further development and understanding of hydrogen storage materials will require substantial new research effort.

Much work thus far has focused three systems to store hydrogen for potential on-board applications, metal hydride storage involving the reversible uptake and release of H_2 from $Na^+AlH_4^-$,[2] chemical hydrogen storage involving the irreversible hydrolysis of $Na^+BH_4^-$ → H_2 + borate[3] and storage on carbon materials involving physi- and chemi-sorption of hydrogen on single walled carbon nanotubes.[4] None of these current systems are likely to meet the long-term DOE goals system making a strong argument for the discovery of new storage possibilities. In this paper we discuss our computational approaches to screen for potential new hydrogen storage materials. Our hope is to find a material that is a solid, high weight percent hydrogen, and reversibly releases (or uptakes) hydrogen under moderate conditions. The thermodynamics of the ideal material would be thermoneutral for hydrogen release.

We start with an analysis of the current most studied hydrogen storage material, the complex hydride $NaAlH_4$. Since this material only stores hydrogen on the anionic site only, AlH_4^-, a dramatic improvement in capacity is envisioned if hydrogen is stored on both the cationic and anionic sites. Another improvement is feasible with the substitution of B (FW=10.8) for Al (FW=27). NH_4^+, BH_4^-, and AlH_4^- are known building blocks of ionic solids, which are isoelectronic with Na^+, F^-, and Cl^-, respectively. Ionic solids built of NH_4^+ and XH_4^- (X=B, Al) are expected to be insulating and dense (to meet the density requirements) and both Boron and Nitrogen are light elements (to meet the volumetric requirements). Furthermore, several of the NH_xBH_x series of compounds are reported to be both *water and air stable*[5] as opposed to many of the complex hydrides currently under investigation.

Given these favorable specifics we undertook a computational approach to investigate the potential of amine boranes as potential solid hydrogen storage materials.[6] These materials are quite attractive from both volumetric and gravimetric considerations, for example NH_4BH_4 and NH_3BH_3, store 0.24 kg H_2/kg and 0.19 kg H_2/kg respectively! The storage capacity is well above any currently studied material. The optimum decomposition reaction is NH_4BH_4 → BN + $4H_2$, outlined in a stepwise process below, eqs 1-4. Even if only two of the four steps proved feasible H_2 storage capacities greater than 0.12 kg H_2/kg could be realized.[7]

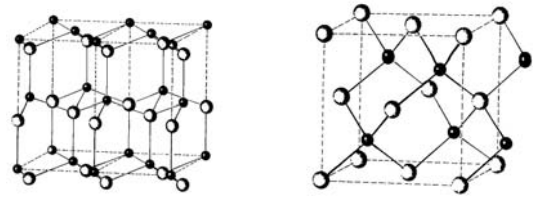
$$NH_4BH_4 \rightarrow NH_3BH_3 + H_2 \quad (1)$$
$$NH_3BH_3 \rightarrow NH_2BH_2 + H_2 \quad (2)$$
$$NH_2BH_2 \rightarrow NHBH + H_2 \quad (3)$$
$$NHBH \rightarrow NB + H_2 \quad (4)$$

Methods

Computational studies have been performed for (i) isolated NH_4^+, BH_4^-, and AlH_4^- species and (ii) solids NH_4BH_4, NH_3BH_3, NH_4AlH_4, BN, and AlN. For molecular clusters and complexes we have used highly correlated electronic structure methods (coupled cluster level of theory with single, double, and non-perturbative triple excitations, Green's function (propagator) methods, etc.) and augmented correlation-consistent basis sets, as implemented in the NWChem code[8]. For solids, we used density functional theory with gradient-corrected exchange functionals (PW91, as implemented in the VASP code[9]). Periodic boundary conditions were assumed for the solids and static optimizations have been completed. The sodium chloride, cesium chloride, zinc blende, and wurtzite structures of NH_4AH_4 (A=B, Al) were explored. The hexagonal planar, zinc blende, and wurzite structures have been optimized for BN and the wurzite and zinc blende for AlN.

Results and Discussion

Relative stability of solid phase materials. Our computational results allow several thermodynamic comparisons to be drawn between the NH_4BH_4 (**1**) and NH_4AlH_4 (**2**) as potential chemical hydrogen storage materials. The first noticeable characteristic difference is the in thermodynamic stability between the zinc blende and wurzite crystalline structures for the two species (Figure 1). In the case of NH_4BH_4 the zinc blende phase was found the more stable then the wurzite phase by 0.23 eV per BN unit. The density of the zinc blende structure is 0.554 g/cm^3. The opposite was found for the case of NH_4AlH_4 where the wurzite phase was found to be more stable than zinc blende by0.12 eV per AlN unit. The density of the wurzite structure is 0.663 g/cm^3. The most stable phase of BN is hexagonal graphite-like, rather than cubic (zinc blende) or hexagonal (wurtzite). This unique feature will be important for the hydrogen mobility in the reloading/releasing cycles. Knowledge of these phase compositions will be important for the hydrogen mobility in the reloading/releasing cycles.



NH_4BH_4 (**1**) (zinc blende) NH_4AlH_4 (**2**) (wurzite)

Figure 1. Thermodynamically stable phase of NH_4BH_4 (ammonium borohydride) is zinc blende. Thermodynamically stable phase of NH_4AlH_4 (ammonium aluminum hydride) is wurzite phase. Hydrogen atoms are not shown in structure for simplicity.

Relative energetics of decomposition pathways. Initial computational results on the solid materials show the reaction energetics are neither extremely exothermic nor too endothermic for loss of hydrogen for NH_4BH_4(solid). These results are promising because it strongly suggests that reversal uptake of hydrogen is feasible under moderate conditions. Furthermore, it is predicted by theory that hydrogen elimination, eq 5, is more favorable, than N-B bond scission, eq 6. Hydrogen elimination is exothermic by less than 0.3 eV/BN unit whereas B-N bond scission is predicted to be

endothermic by 1.1 eV. Similar results are predicted for hydrogen loss from NH_4AlH_4, eq 7, more favorable than N-Al bond scission, eq 8. However, in the case of NH_4AlH_4 hydrogen loss is far more exothermic, 1.07 ev per AlN unit compared to the endothermic Al-N bond scission of 0.7 eV. This is an interesting result that may have implications on regeneration of the hydrogen storage materials. If the reaction is too exothermic it likely require greater effort to regenerate the material. Alternatively, the system may still be reversible if the end product is NH_xAlH_x (x=1-3) rather than AlN.

$$NH_4BH_4(s) \rightarrow BN(s) + 4H_2(g) \quad (5)$$
$$NH_4BH_4(s) \rightarrow NH_3(g) + \tfrac{1}{2} B_2H_6(g) + H_2(g) \quad (6)$$
$$NH_4AlH_4(s) \rightarrow AlN(s) + 4H_2(g) \quad (7)$$
$$NH_4AlH_4(s) \rightarrow NH_3(g) + AlH_3(g) + H_2(g) \quad (8)$$

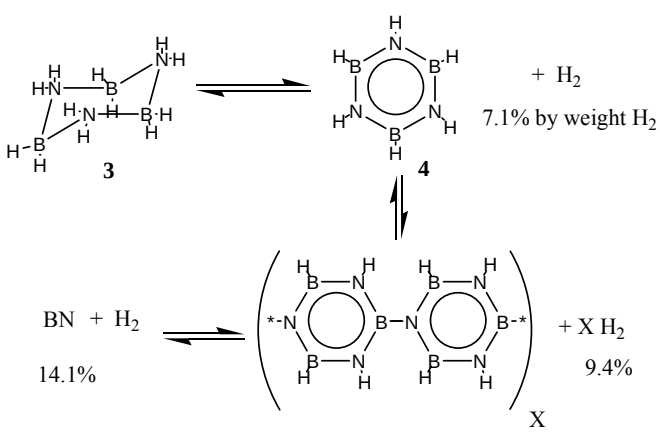
A more detailed investigation of the step-wise loss of hydrogen from NH_4BH_4 reveals some intriguing features in Scheme 1. The release of hydrogen from NH_4BH_4 proceeds through intermediate steps, forming linear polymers[10] and hydrogen gas with specific thermodynamic characteristics (ΔE in kcal/mol).

Scheme 1.

$$NH_4BH_4(s) \rightarrow NH_3BH_3(s) + H_2(g) \quad \Delta E = -2.3$$
$$NH_3BH_3(s) \rightarrow NH_2BH_2(poly) + H_2(g) \quad \Delta E = 8.8$$
$$NH_2BH_2(poly) \rightarrow NHBH(poly) + H_2(g) \quad \Delta E = -3.2$$
$$NHBH(poly) \rightarrow BN(s) + H_2(g) \quad \Delta E = -9.2$$

Alternatively, cyclic polymer structures, starting with perhydroborazine, **3**, as shown in Scheme 1, could be involved in the decomposition pathways of amine borane. Sneddon and coworkers[11] report that at moderate temperatures borazine, **4**, undergoes a dehydropolymerization to yield hydrogen and a borazine polymer. At higher temperatures the polymer undergoes further dehydrogenation to yield a polyborazylene (BN) polymer. This observations merit further study to investigate the feasibility of reversible hydrogen storage.

Scheme 2.



Conclusions

Computational methods offer an attractive approach to screen new potential chemical hydrogen storage materials. Two potential systems were examined in this study, hydrogen releases from NH_xBH_x (amine/ammonium borohydrides) and NH_xAlH_x (amine/ammonium alanates). Both materials could potentially meet the long term DOE requirements for volumetric and energy density requirements. Theoretical calculations predict that hydrogen loss is the thermodynamically favored pathway over B-N or Al-N bond scission. However, the loss of hydrogen from the NH_xBH_x series of compounds is predicted to be less exothermic than hydrogen loss from the NH_xAlH_x series of compounds. This could be an important observation to enhance the economic considerations for recycle.

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