CHEMICAL HYDROGEN STORAGE IN NANO-STRUCTURED MATERIALS. CONTROL OF HYDROGEN RELEASE AND REACTIVITY FROM AMMONIA BORANE COMPLEXES.

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Introduction

The DOE has recently issued a Grand Challenge in Hydrogen Storage to compliment existing programs on Hydrogen Production and Fuel Cell development.[1] In response to this challenge we have initiated a program that uses a combination of experimental and computational approaches to investigate the potential of NH_xBH_x (x=1-4) as chemical hydrogen storage materials for on-board hydrogen storage. Our initial computational results suggest that the step-wise process is not greatly exothermic.[2] If true, these materials may provide great hope for a reversible hydrogen storage material with high volumetric and gravimetric density for on-board storage.[3] The optimum thermal decomposition reaction $NH_4BH_4 \rightarrow BN + 4H_2$, occurs by a four-step process and provides a theoretical yield of 24 wt% hydrogen far exceeding DOE's most ambitious goals. Even if two of the four steps prove feasible H_2 capacities of greater than 12 weight % would be realized. In this present work we have focused our experimental efforts on ammonia-borane [NH_3BH_3]. In the solid state ammonia-borane (AB) undergoes a rapid dehydropolymerization reaction upon melting at 115 ˚C to yield polyammonia-borane [$(NH_2BH_2)_n$], an inorganic analog of polyethylene, + H_2.[4] In a subsequent step the $(NH_2BH_2)_n$ decomposes to [$(NHBH)_2$], an inorganic analog of polyacetylene, + H_2 at 170 ˚C.[5] An undesirable side reaction, formation of the cyclic borazine $(NHBH)_3$, an inorganic analog of benzene, has also been observed to form from the bulk material at the higher temperatures. Borazine is an undesirable side product due to its high vapor pressure. Given the stringent requirements of hydrogen purity for fuel cell applications it will be important to minimize side reactions. One of the major goals of this work was to use the nanometer diameter pores of mesoporous templates to control the selectivity of the hydrogen release pathways from ammonia-borane and polyammonia-borane.

Experimental

Ammonia borane was purchased from Aldrich (90% tech) and purified by recrystallization from diethyl ether followed by a wash with ethanol to remove polymeric and borate impurities to yield >99% pure NH_3BH_3 by ^{11}B NMR. Analyses were performed using a Netzsch STA 409 TGA/DSC and a Pfeiffer QMS300 MS or a Setaram C80 Calorimeter. In the Netzsch equipment a heated fused silica capillary (200 ˚C) was used to transfer the off gas from the TGA to the MS. The MS uses a standard electron impact ionization detector. The MS scanning rate was 12 seconds for a range of 1 to 100 amu. A thermal ramp of 5 ˚C/min from room temperature to 250 ˚C using an argon flow of 100 cc/min was used in our analysis.

Results and Discussion

Preparation of mesoporous templated ammonia-borane. Mesoporous silica templates have extremely high surface area and a highly ordered pore structure by virtue of surfactant templated synthetic process.[6] The material used in this work, SBA-15, prepared according to literature procedures for another project, was characterized and found to have average particle 100-200 μm, surface area 1000 m^2/g, pore diameter 3 nm. A sample of 50 mg of the SBA-15 was exposed to a 300 μL methanolic solution containing 50 mg of AB. Given the porous nature of the material we expected capillary action to fill the internal channels of the mesoporous template. The 'wet' SBA-15 was dried under vacuum to produce a sample with an internal coating of ammonia-borane (ca. 1:1 wt% AB to SBA-15). Comparison of SEM images of the material before and after coating with AB showed very similar features as shown in Figure 1. We expected to visually observe clumping of the solid AB on the template if we were not successful in our attempt to coat the internal channels. An EDM scan of the 1:1 mixture of AB:SBA-15 sample also produced very little signal from N and B and we again would have expected a greater signal if the AB was not efficiently deposited within the core structures of the SBA-15. Given these negative observations we assumed that we had a sample of SBA-15 mesoporous template with internal pores coated with monomeric ammonia-borane.

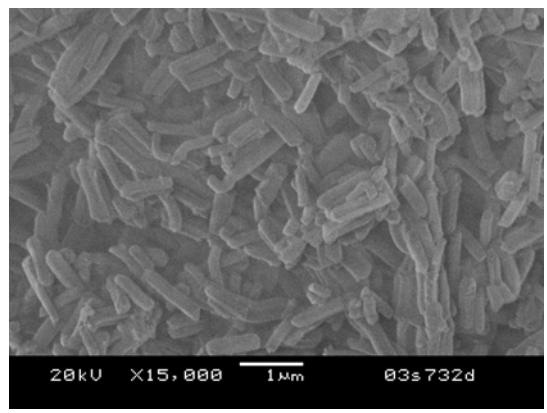

Figure 1. SEM image of 1:1 Mixture of AB:SBA-15. We could observe no difference in the image before or after AB was added. The EDM scan showed no evidence for either Boron or Nitrogen. These observations lead us to assume that the AB was deposited as a thin layer within the mesoporous template.

Calorimetric and mass spectroscopy studies of ammonia-borane , thermolysis in mesoporous silica templates. In order to test our hypothesis that the yield of borazine [*c*-$(NHBH)_3$], an inorganic analog of benzene, would be reduced when the AB was heated as a 1:1 weight mixture, we undertook differential scanning calorimetry (DSC) experiments to compare the neat bulk material to our 1:1 AB:SBA-15 sample prepared as described above. It is likely that hydrogen formation occurs by an intermolecular dimerization pathway as shown in equation 1,[7] however a two-step mechanism can not be completely ruled out, eqs 2 and 3.

(1) $2\ NH_3BH_3 \rightarrow NH_3BH_2\text{-}NH_2BH_3 + H_2$

(2) $NH_3BH_3 \rightarrow NH_2{=}BH_2 + 2H_2$

(3) $2NH_2{=}BH_2 \rightarrow NH_3BH_2\text{-}NH_2BH_3$

If reaction 1 is the mechanistic pathway then it follows that the dimer would form oligomers through subsequent bimolecular dehydopolymerization pathways. Each step that forms a new B-N bond also forms hydrogen, eqs 4 and 5.

(4) $NH_3BH_3 + NH_3BH_2\text{-}NH_2BH_3$
$\rightarrow NH_3BH_2\text{-}NH_2BH_2\text{-}NH_2BH_3 + H_2$
(5) $NH_3BH_3 + NH_3BH_2NH_2BH_2\text{-}NH_2BH_3$
$\rightarrow NH_3BH_2\text{-}NH_2BH_2\text{-}NH_2BH_2\text{-}NH_2BH_3 + H_2$

As the temperature approaches 170 ˚C additional hydrogen is released, eqs, 6 and 7. However, a competing side reaction is cyclization to form borazine, eq 8.[8]

(6) $(NH_3BH_2NH_2BH_2\text{-}NH_2BH_3)_n$
$\rightarrow (NH_3BH_2NH_2BH{=}NHBH_3)_n + H_2$
(7) $(NH_3BH_2NH_2BH{=}NHBH_3)_n$
$\rightarrow (NH_3BH{=}NHBH{=}NHBH_3)_n + H_2$
(8) $(NH_3BH{=}NHBH{=}NHBH_3)_n \rightarrow$ borazine + H_2

Under optimum conditions we want to minimize cyclization, reaction (8) and optimize further dehydrogentation, i.e., reactions (6 and 7). We expected that if the AB was coated on the inside of the mesoporous silica template that the template would minimize borazine formation by controlling linear polymer growth and minimizing cyclization. To test this hypothesis DSC experiments were preformed with both the neat AB and the 1:1 mixture of AB:SBA-15. Two results are notable. First, as hoped, borazine formation appears to have been substantially reduced when AB is heated as the 1:1 composite with SBA-15. It is below the detection limits of our mass detector. Even when the flow rate of argon is reduced to 40 cc/minute we did not detect borazine, though hydrogen release was still observed at ca. 170 ˚C, temperature corresponding to borazine formation in the neat AB. Second, a surprising result, the observation that hydrogen is released in the initial step, eq 1, at a significantly lower temperature when the AB is heated as the 1:1 composite with SBA-15! This result is illustrated in Figures 2. This novel finding is especially attractive given that a

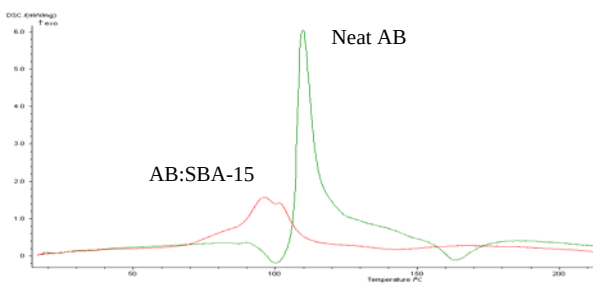

Figure 2. Comparison of DSC scan (temperature vs power) of neat AB (green line) and 1:1 AB:SBA-15 mixture (red line). Ramp rate 5 ˚C/min from room temperature to 250 ˚C. The peak of the exotherm is 110 ˚C for neat AB and 96 ˚C for the mixture.

fundamental requirement for on-board storage is the release of H_2 at temperatures below 100 ˚C. In the 1:1 AB:SBA-15 sample hydrogen is released at 96 ˚C compared to the 110 ˚C for the neat AB sample.

Conclusions

In this paper we present the results of our efforts using the mesoporous silicate template (SBA-15) to control the chemistry of dehydropolymerization of ammonia-borane (AB) to yield gaseous hydrogen. Thermolysis of AB in the SBA-15 template shows two profound effects different than observed in the bulk thermal reaction: (i) hydrogen is released from AB at significantly lower temperatures (well below 100 ˚C) and (ii) contrary to observations that borazine is formed in bulk AB thermolysis, no borazine is detected in AB thermolysis in the mesoporous template.

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