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### Controlled Hydrogen Release From Ammonia Borane Using Mesoporous Scaffolds

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Hydrogen storage on chemical hydrogen storage materials may provide an attractive new opportunity to meet and exceed the goals of the recent DOE Grand Challenge in Hydrogen Storage for on-board fuel cell applications. We have been investigating the feasibility of using ammonia borane ( $\text{NH}_3\text{BH}_3$ ), and polyammonia borane  $(-\text{NH}_2\text{BH}_2)_n$  as reversible hydrogen storage materials. This family of molecules is promising given capacity for high volumetric storage densities, ca. >12 wt % hydrogen, and recent computational results that suggest hydrogen uptake and release is near thermoneutral. Ammonia borane (AB) is a stable solid at room temperature that requires heating to release the  $\text{H}_2$ . AB decomposes upon melting at 114 °C with the vigorous bubbling of  $\text{H}_2$  gas. Alternatively the hydrogen from AB can be released from the solid material at temperatures below 100 °C, albeit at significantly lower rates. Thermal decomposition of  $\text{NH}_3\text{BH}_3$  at temperatures below 100 °C yields  $\text{H}_2$  and a complex polyaminoborane-like  $(-\text{NH}_2\text{BH}_2)_n$  material (PAB). The solid phase thermal reaction involves a bimolecular dehydrocoupling reaction to yield a new B-N bond, i.e.,  $\text{HNB-H} \rightarrow \text{HNBH}$  to yield  $\text{HNB-NBH}$  in contrast to our observations of the catalytic pathway involves the intramolecular abstraction of H-H from a single H-NB-H molecule to yield N=B intermediate. At temperatures above 150 °C the PAB decomposes to yield a second equivalent of  $\text{H}_2$ , concurrent with formation of a polyiminoborane-like  $(-\text{NHBH})_n$  material (PIB) and borazine  $c-(\text{NHBH})_3$ . The latter is a volatile inorganic analog of benzene, which is highly undesirable in the  $\text{H}_2$  feed. While AB exceeds volumetric and gravimetric density targets for a hydrogen storage material, three additional physical obstacles must be overcome: (i) increasing the rates of  $\text{H}_2$  release at temperatures below 80 °C, (ii) preventing borazine formation and (iii) demonstrating the potential for reversibility. There are reports that nano-phase metal hydrides show enhanced kinetics for reversible hydrogen storage relative to the bulk materials. However, after a few hydriding/dehydriding cycles the kinetic enhancement is diminished for some materials as they lose nano-phase structure. We suggest that a rigid nano-phase scaffold loaded with a hydrogen-rich material, may provide an attractive option to preserve the nano-scale dimensions through several hydriding/dehydriding cycles. To demonstrate the effect of a nano-phase scaffold on hydrogen release we use a high-surface area mesoporous silica, loaded with AB as a model system. The work presented in this symposium will highlight our success in lower the temperature of hydrogen release from ammonia borane (<80 °C) and to minimize the formation of borazine from polyammonia borane decomposition using mesoporous silica templates (SBA-15). Three notable observations are described in this work: (i) increased rates of  $\text{H}_2$  release, (ii) modifications of the non-volatile polymeric products that change the thermodynamics of hydrogen release and (iii) minimized formation of borazine.