Boron–Nitrogen Compounds

DOI: 10.1002/anie.201103830

Advances with Ammonia-Borane: Improved Recycling and Use as a Precursor to Atomically Thin BN Films**

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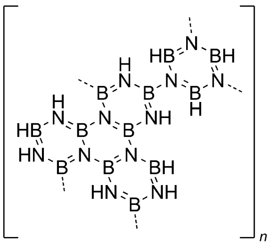
ammonia-borane · boranes · boron nitride · hydrogen storage · hydrogenation

Amine-boranes, exemplified by ammonia-borane (AB), $H_3N{\cdot}BH_3$, represent some of the simplest and best-known inorganic molecules. Over the past decade these compounds have attracted considerable attention as portable hydrogen storage materials, due in the main part to their high gravimetric hydrogen contents (ca. 20% by weight for AB).[1] This has motivated the development of new synthetic methods for convenient hydrogen release, and a variety of highly active catalysts that function under mild conditions are now known. These procedures have recently been adapted to allow the preparation of new polymeric materials. For example, polyaminoboranes, $(RNH\text{-}BH_2)_n$, have been prepared by catalytic dehydrogenation of primary amine-boranes, such as $MeNH_2{\cdot}BH_3$.[2] Amine-boranes have also been widely used as reducing agents, including for the preparation of metal nanoparticles, and in hydrogen-transfer reactions involving organic substrates.[3] Moreover, as a consequence of the expanded interest in hydrogen release, the field of amine-borane coordination chemistry is now under active development.[4] Discoveries in this new area promise improved fundamental understanding of the activation and transformation of these fascinating molecules at transition-metal centers, processes that appear central to both their dehydrogenation and polymerization chemistries.

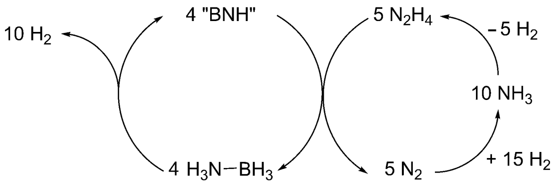
The dehydrogenation of AB[1] may be viewed in terms of three distinct exergonic steps, each associated with the loss of one equivalent of hydrogen. The challenge with developing AB as a practical hydrogen-storage material therefore lies not only in the liberation of hydrogen but also in the regeneration of the spent fuel. Furthermore, this problem becomes particularly acute if the reaction proceeds with complete dehydrogenation to form boron nitride, which is thermodynamically very stable.

In practice, the near-ambient-temperature routes to dehydrogenate AB do not result in the formation of boron nitride but yield a spent fuel whose precise nature depends on the method of hydrogen release. Polyborazylene (BNH_x ($0 < x < 2$), Scheme 1) functions as a model for such species, as it contains the fused borazine rings and B–H and N–H bonds that should be common to any dehydrogenated material. A viable synthetic route to convert polyborazylene back to AB would therefore have important implications for the feasibility of using the latter for hydrogen storage.



Scheme 1. Proposed structure of polyborazylene.

An impressive recent advance by Gordon and co-workers describes the successful conversion of polyborazylene to AB upon treatment with hydrazine in liquid ammonia.[5] Polyborazylene was found to react with hydrazine at room temperature to afford predominantly hydrazine-borane. Exchange of the hydrazine in this compound for ammonia, however, could not be achieved at this temperature owing to the greater thermodynamic stability of the hydrazine adduct. Heating to 60 °C was therefore employed to cleave the B–N bond and afford AB by combination of the liberated borane with ammonia from the surrounding medium. All volatiles including the hydrazine were then removed to prevent any appreciable reverse reaction. Combining these two steps in a one-pot process enabled polyborazylene to be converted to ammonia-borane at 40 °C and in 92% yield, with the hydrazine so liberated from the initially formed adduct being available to perform further reductions. The ideal reaction can be formulated for BNH (Scheme 2), although practically



Scheme 2. Overall reaction scheme for the conversion of polyborazylene ("BNH") to AB and recovery of the liberated nitrogen.

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[**] I.M. thanks the EPSRC and ERC for funding.

a slight excess of hydrazine was employed to account for varying degrees of cross-linking in the polyborazylene. This process has other attributes that potentially help take AB a step forward as a practical hydrogen-storage material. For example, the reductant is already reasonably inexpensive and is of low molar mass, thereby minimizing transportation costs to regeneration sites. In addition, the nitrogen formed as a by-product of the regeneration step may be converted back to ammonia, further reducing the emissions of the process.

Although the complete dehydrogenation of AB to boron nitride is disadvantageous with respect to recycling the material, such approaches are highly attractive in materials science. In particular, the dehydrogenation of AB has received attention as a convenient route to 2D boron–nitrogen thin films. Hexagonal boron nitride (*h*-BN) is a layered material structurally similar to graphite, but with complementary electronic properties. Whereas single layers of graphite (graphene) have zero band gap, *h*-BN is a wide-band-gap semiconductor with promising applications in UV lasing and as a dielectric.[6] Monolayer *h*-BN, also known as "white graphene", has recently been isolated from bulk samples by micromechanical cleavage and ultrasonication. As a result of its flat structure and small lattice mismatch with graphene, it has potential as a 2D dielectric substrate for graphene-based electronics.[7] However, the formation of large-area films of controlled thickness represents a challenge.

h-BN nanosheets were first prepared by chemical vapor deposition (CVD) using liquid borazine ($(\mathrm{(HN{-}BH)_3})$) as the precursor.[8] In recent advances reported by Lou, Ajayan, and co-workers, easily handled AB has been successfully used as a solid CVD precursor to atomic layers of *h*-BN.[9–11] Continuous and uniform *h*-BN films consisting of multiple layers over large areas were prepared that could be subsequently transferred to various substrates.[9] During growth, the AB was first sublimed and thereby transferred to a high-temperature zone for decomposition. The deposition was performed at 1000 °C on a copper surface where the AB supplies both the boron and nitrogen to the metallic substrate. The copper is believed to catalyze the dehydrogenation of AB, thus affording surface-bound species that can diffuse prior to growth of the *h*-BN films.

Hybrid (*h*-BNC) films that consist of separated graphene and BN domains have been prepared by a similar CVD approach that utilized methane and AB as precursors.[10] The resulting films were uniform and continuous and could be transferred onto different substrates for further characterization and device fabrication. It was possible to readily control their electrical properties from insulating to highly conducting by tuning the carbon concentration. A field-effect transistor was also fabricated from the *h*-BNC film, which displayed characteristics similar to that of CVD-grown graphene. In a further advance, growth of large-area graphene/*h*-BN stacks, consisting of a few layers of graphene and *h*-BN, was achieved in a two-step CVD process using *n*-hexane and AB (Figure 1).[11]

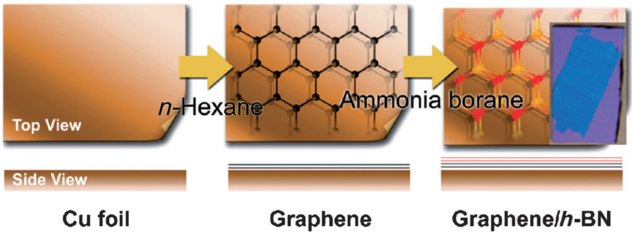

Figure 1. Schematic representation of the preparation of a graphene/*h*-BN stacked film with (inset) photograph of the resulting material (reprinted with permission from reference [11], Copyright 2011 American Chemical Society).

The recent advances in AB regeneration and its use as a precursor to BN materials are expected to lead to yet further interest in AB chemistry.

Received: June 6, 2011

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