ChemComm

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Reversible dehydrogenation of magnesium borohydride to magnesium triborane in the solid state under moderate conditions†‡

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Received 25th August 2010, Accepted 28th October 2010
DOI: 10.1039/c0cc03461d

Thermal decomposition of magnesium borohydride, $Mg(BH_4)_2$, in the solid state was studied by a combination of PCT, TGA/MS and NMR spectroscopy. Dehydrogenation of $Mg(BH_4)_2$ at 200 °C *en vacuo* results in the highly selective formation of magnesium triborane, $Mg(B_3H_8)_2$. This process is reversible at 250 °C under 120 atm H_2. Dehydrogenation at higher temperature, > 300 °C under a constant argon flow of 1 atm, produces a complex mixture of polyborane species. A borohydride condensation mechanism involving metal hydride formation is proposed.

Group I and II borohydrides have among the highest theoretical hydrogen storage capacities of all known compounds. Thus the utilization of these materials as hydrogen carriers in practical applications of polymer electrolyte membrane fuel cells is a tantalizing possibility which has prompted recent studies of their reversible dehydrogenation.[1–14] In order to optimize the efficiency of borohydrides as hydrogen storage materials, the identification and quantification of key intermediates in the solid state decomposition is needed. Insight into the reaction mechanisms will permit a rational evaluation of the full potential of reversible hydrogen storage. Recent reports suggest that dodecaborane, $[B_{12}H_{12}]^{2-}$, may be a significant product of the dehydrogenation.[10–12,14]

Observations of dodecaborane in borohydride chemistry were extensively published in the 1960's by the groups of Hawthorne, Gaines, Muetterties, Schaeffer, Shore and others.[15–18] In these early solution phase studies, either MBH_4 or a polyborane (*e.g.*, MB_3H_8) react with diborane to form the corresponding dodecaborane in high yields. However, studies of the dehydrogenation of MBH_4 in the solid state indicate that diborane is produced as only a minor side product.[19] Thus an alternative pathway for the formation of $[B_{12}H_{12}]^{2-}$ apparently operates in the solid state. Additionally, the fully reversible dehydrogenation of MgB_2 to $Mg(BH_4)_2$ was recently accomplished under high pressure.[13] It is not clear from the results of this study whether $Mg[B_{12}H_{12}]$ is an intermediate in the reaction pathway that operates under these conditions. Clearly, there is a need for further elucidation of the reaction pathways whereby $Mg(BH_4)_2$ undergoes reversible dehydrogenation in the solid state. To this end, we have investigated the thermal decomposition of $Mg(BH_4)_2$ and found that the initial step of this process, the formation of $Mg(B_3H_8)_2$, can be reversed under mild conditions. Furthermore, our studies offer general guidelines for rational approaches to reversible hydrogen storage in borohydride materials.

The dehydrogenation of $Mg(BH_4)_2$ (prepared by the method of Chlopek *et al.*[8]) was followed by thermal gravimetric analysis over a set of isothermal temperatures (300, 350, and 400 °C) at various reaction times. The study was conducted under constant flow of 1 atm of argon gas with the concomitant analysis of the volatile gas species by mass spectroscopy (TGA/MS). Over this temperature range, a decrease of 6–10 mass% from the $Mg(BH_4)_2$ sample was observed with H_2 as the only volatile species detected by MS. At the end of each TPD experiment, the residual decomposition products were dissolved in aqueous media for analysis by solution phase NMR spectroscopy. Unlike the stable closo-boranes, arachno- and nido-boranes hydrolyze in aqueous media to form boric acid.[20–23] Fig. 1 shows representative $^{11}B[H]$ NMR spectra from samples heated to 300, 350 and 400 °C. Four major resonances are observed in each spectra; boric acid at 5 ppm, $[B_{12}H_{12}]^{2-}$ at −15.6 ppm, $[B_{10}H_{10}]^{2-}$ at −29.2 ppm and $[B_3H_8]^{-}$ at −31 ppm.

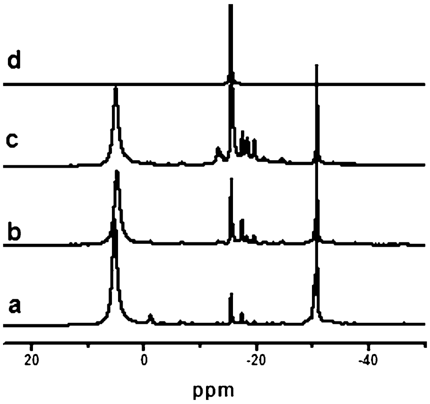

Fig. 1 Solution $^{11}B\{H\}$ NMR of products resulting from dehydrogenated $Mg(BH_4)_2$ dissolved in aqueous solutions showing various species formed during dehydrogenation and hydrolysis. (a) $Mg(BH_4)_2$ heated to 300 °C for 12 h, (b) $Mg(BH_4)_2$ heated to 350 °C for 6 h, (c) $Mg(BH_4)_2$ heated to 400 °C for 2 h, (d) $MgB_{12}H_{12}$.

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† Electronic supplementary information (ESI) available: Proposed mechanism for polyhedral borane formation and experimental details for instrumental analysis and sample preparation. See DOI: 10.1039/c0cc03461d

‡ This article is part of a ChemComm 'Hydrogen' web-based themed issue.

Table 1 Major products (mol%) formed in decomposition of $Mg(BH_4)_2$ determined from ^{11}B NMR of the hydrolyzed material. Mass loss from TGA: at 300 °C, 12 h (5.9%); at 350 °C, 6 h (6.9%); 400 °C, 2 h (8.5%). Chemical shifts are reported relative to $BF_3{\cdot}OEt_2$ at 0 ppm

δ/ppm	Species	300 °C	350 °C	400 °C
5	$B(OH)_4^-$	86	87	83
−15.2	$(B_{12}H_{12})^{2-}$	0.4	1.5	4.5
−29.2	$(B_{10}H_{10})^{2-}$	0.8	0.2	0.0
−30.3	$(B_3H_8)^-$	12.6	9.0	6.5

The results of these studies are summarized in Table 1. The finding that boric acid is the major species observed in the ^{11}B NMR suggests that the major production of unstable polyborane species and thus $Mg(BH_4)_2$ decomposition yields a mixture of poly-borane structures ranging from the triborane anion to the dodecaborane dianion. In addition to the unstable polyborane species a small amount of the stable dodecaborane $[B_{12}H_{12}]^{2-}$ is observed. However, the yield, which ranges from 0.4 mol% to 4.5 mol%, is significantly less than the theoretical yield assuming complete conversion of $Mg(BH_4)_2$ to magnesium dodecaborane approximately 16.6 mol% $(B_{12}H_{12})^{2-}$ (8.0 wt% H_2). It is also notable that a significant concentration of the triborane is present, especially at lower temperatures. This indicates that the first step in the decomposition of $Mg(BH_4)_2$ involves the formation of a meta-stable triborane species, $Mg(B_3H_8)_2$. To verify this conclusion, we investigated the slow dehydrogenation of $Mg(BH_4)_2$ *en vacuo* at 200 °C over a 5 week period. Solid state and solution ^{11}B NMR spectra (solution NMR seen in Fig. 2a) of the dehydrogenated product showed that there is much higher selectivity for the production of $Mg(B_3H_8)_2$ at this lower temperature.

Next, we probed the reversibility of the dehydrogenation of the $Mg(BH_4)_2$ to the borane species. Our initial re-hydrogenation attempts were carried out on the mixture of boranes obtained from the dehydrogenations conducted at ≥ 300 °C. The experiments were carried out at 250 °C under 120 atm of H_2. ^{11}B NMR analysis consistently indicated that only $Mg(B_3H_8)_2$ undergoes hydrogenation to $Mg(BH_4)_2$ under these conditions. This finding was confirmed by experiments conducted with samples containing only $Mg(B_3H_8)_2$ obtained through the low temperature dehydrogenation. As seen in Fig. 2b, nearly complete conversion of the triborane back to $Mg(BH_4)_2$ occurred at 250 °C under 120 atm of H_2 after 48 h. This result is especially noteworthy as it is the first example of the *reversible*, solid-state dehydrogenation of a borohydride occuring at temperatures below 350 °C. However, it is also noted that the hydrogen cycling capactity associated with the reaction seen below in eqn (1) is only 2.5 wt%.

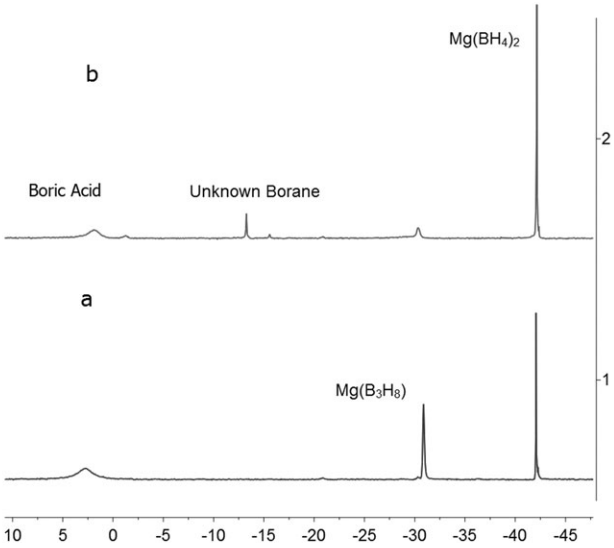


Fig. 2 $^{11}B\{^1H\}$ spectra of: (a) $Mg(BH_4)_2$ following solid-state dehydrogenation at 200 °C for 5 weeks and (b) re-hydrogenation under 120 atm of H_2 at 250 °C for 48 h.

$$3Mg(BH_4)_2 \Leftrightarrow Mg(B_3H_8)_2 + 2MgH_2 + 2H_2 \qquad (1)$$

Our results provide a number of other insights into the solid-state dehydrogenation pathways of solid $Mg(BH_4)_2$, eqn (2). It has previously been shown that triborane is readily formed when BH_4 reacts with diborane in solution. This transformation proceeds through the thermally unstable B_2H_7 species which disproportionates to form B_3H_8 and BH_4, as seen in eqn (2) through (5).[24] However, diborane formation, eqn (5),

$$Mg(BH_4)_2 \Leftrightarrow Mg(B_nH_{n+2})_2 + Mg(B_{12}H_{12}) + 2H_2 \qquad (2)$$

$$2MBH_4 + B_2H_6 \Leftrightarrow 2MB_2H_7 + H_2 \qquad (3)$$

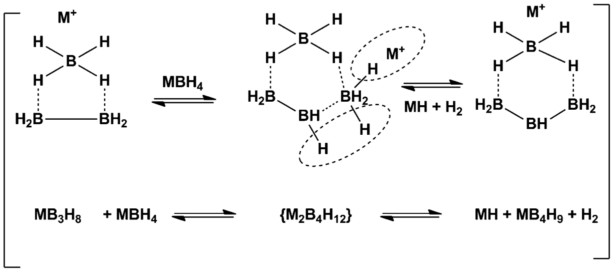
$$2MB_2H_7 \Leftrightarrow MB_3H_8 + MBH_4 \qquad (4)$$

$$2MBH_4 \Leftrightarrow 2MH + B_2H_6 \qquad (5)$$

is not observed to occur during the solid-state dehydrogenation of magnesium borohydride at 200 °C. It may be that under these conditions diborane is formed but reacts so rapidly with the magnesium borohydride at high temperatures that is trapped in place and can diffuse through the solid.

The results of our solid-state studies also clearly show that at higher temperatures, > 300 °C, triborane decomposes with the release of hydrogen forming higher arachno-borane species $[B_nH_{n+5}]^-$ as well as the closo-borane species, deca-, $[B_{10}H_{10}]^{2-}$, and dodecaborane $[B_{12}H_{12}]^{2-}$ and possibly nido boranes $[B_nH_{n+3}]^-$ ($3 < n < 12$). As summarized in Scheme 1 and Fig. S1 (ESI†), we suggest a sequential BH condensation pathway involving a build-up of the increasing higher B_nH_{n+x} species. A B–H insertion into a growing polyborane, in concert with the formation of hydrogen and the corresponding metal hydride, is similar to the related decomposition pathways suggested for metal amidoboranes.[25,26]

The stability of the corresponding metal hydride formed in the decomposition of borohydride may explain in part the observed reversibility for some borohydrides and the irreversibility of others. The thermodynamics of the reaction, H_2 desorption or



Scheme 1 Metal ion assisted BH condensation pathway.

H_2 absorption, depends on the stability of the metal hydride in addition to the stability of the polyborane intermediate. Thus the formation of a more stable metal hydride (*e.g.*, LiH compared to MgH_2) will make the thermodynamics for the reverse reaction less favorable. Further, an explanation for the *partial* reversibility in borohydride materials may be explained by the yield of dodecaborane formed in the decomposition reaction. Once $MgB_{12}H_{12}$ is formed it is more difficult to regenerate borohydride. That is, hydrogen addition to the arachnopolyborane species, observed as boric acid after hydrolysis of the decomposed borohydride, is kinetically accessible whereas hydrogen addition to the thermodynamically stable closoborane species is kinetically inaccessible. However, if the borohydride reaction is cycled a limited number of times eventually the thermodynamically stable $[B_{12}H_{12}]^{2-}$ species will be formed in greater yields with each cycle.[27]

Finally, the results of this mechanistic study provide an alternate explanation for the observed onset temperature for dehydrogenation of a specific borohydride.[28] If the rate limiting step for the dehydrogenation of a metal borohydride is disproportionation to form borane and the corresponding metal hydride (eqn (5)), then the onset temperature for dehydrogenation can be predicted based upon the barrier for the disproportionation reaction.

In summary, the initial borane species produced in the solid state dehydrogenation of $Mg(BH_4)_2$ under the conditions we have studied is $Mg(B_3H_8)_2$. This conversion has been shown to be reversible at moderate temperature and pressure thus providing the first example of direct hydrogen cycling of a borohydride under moderate conditions. Although the 2.5 wt% cycling capacity does not meet current on-board storage targets,[29] our results provide key experimental evidence that practical hydrogen storage based on a boron hydride is plausible. Heating to higher temperatures results in a series of B–H condensation reactions leading to a complex mixture of polyboranes. Given the nature of the reaction pathways discussed in this work, it is recommended that the stability of the corresponding metal hydride (as well as the polyborane) be considered in the design and development of borohydrides for reversible hydrogen storage. Additionally, the effect of back H_2 pressure on the dehydrogenation reaction pathway should be the topic of further investigation.

We wish to thank Professor Fred Hawthorne, Drs Martin O. Jones and Ewa Ronnebro for useful discussion. This work was supported by the US Department of Energy (DOE), Office of Energy Efficency and Renewable Energy, and was performed in part at EMSL, a national scientific user facility sponsored by the DOE Office of Biological and Environmental Research located at the Pacific Northwest National Laboratory (PNNL). PNNL is operated by Battelle for the DOE.

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27 For example, after 2 h of heating at 400 °C under constant flow of 1 atm of argon approximately 30% of the theoretical yield of $[B_{12}H_{12}]^{-2}$ is formed. Up to *ca.* 70% of the material can be rehydrogenated back to BH_4. However, after a second dehydrogenation cycle another 30% yield of $[B_{12}H_{12}]^{-2}$ will be formed and only *ca.* 50% (70% of the original 70%) will be recycled. The reversible capacity will continue to decrease with each cycle.

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