Hydrogenation of Magnesium Nickel Boride for Reversible Hydrogen Storage

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ABSTRACT We report that a ternary magnesium nickel boride (MgNi₂.₅B₂) mixed with LiH and MgH₂ can be hydrogenated reversibly forming LiBH₄ and Mg₂NiH₄ at temperatures below 300 °C. The ternary boride was prepared by sintering a mechanically milled mixture of MgB₂ and Ni precursors at 975 °C under inert atmosphere. Hydrogenation of the ternary, milled with LiH and MgH₂, was performed under 100 to 160 bar H₂ at temperatures up to 350 °C. Analysis using X-ray diffraction, Fourier transform infrared, and ¹¹B magic angle spinning NMR confirmed that the ternary boride was hydrogenated forming borohydride anions. The reaction was reversible with hydrogenation kinetics that improved over three cycles. This work suggests that there may be other ternary or higher order boride phases useful for reversible hydrogen storage.

SECTION Energy Conversion and Storage

Hydrogen is a candidate for the next generation of energy carriers, which are needed to meet the challenges of global warming and finite fossil fuel-based energy resources. Use of hydrogen for transportation applications requires materials that not only store hydrogen at high density but that can operate reversibly at temperatures and pressures below approximately 100 °C and 10 bar, respectively. Among many materials for hydrogen storage, complex hydrides of light metals containing borohydride anions have high hydrogen capacity and, thus, have been studied extensively. However, the thermodynamic and kinetic properties of the borohydrides limit their ability to cycle hydrogen at low temperatures. An example is LiBH₄. Although LiBH₄ has a high enthalpy of formation, ΔHₙ = −194.2 kJ/mol, the formation of LiBH₄ from the elements requires elevated temperatures and pressures, indicating a significant activation energy barrier. Goerrig claimed that direct synthesis can be performed by applying a hydrogen pressure of 150 bar at a temperature of 650 °C to a mixture of elemental lithium and boron. Orimo et al. demonstrated the hydrogenation of decomposed LiBH₄ (i.e., LiH + B and perhaps Li₂B₂H₁₃) at a hydrogen pressure of 350 bar and a temperature of 600 °C. Similarly, Mauron et al. reported that dehydrogenated LiBH₄ could be rehydrogenated at 600 °C with a hydrogen pressure of 155 bar. The reason for the high energy barrier has been suggested to be the general chemical inertness of boron, which may be due to the strong boron–boron bonds in elemental boron (ΔH(B=B) = 560 kJ/mol). As a result of the kinetic barriers, considerable effort has been devoted to the development of materials that can lead to the reversible formation of borohydride anions at lower temperatures. Barkhordarian et al. reported that the kinetic barriers for the formation of LiBH₄, NaBH₄ and Ca(BH₄)₂ are drastically reduced when MgB₂ is used instead of B as the starting material. The authors suggested that the effect is due to the higher reactivity of B in MgB₂ to form [BH₄]⁻ complexes. Similar results were obtained by Vajo et al. who showed that, upon cycling, an LiH/MgB₂ mixture containing TiCl₃ as a catalyst could be hydrogenated at 300 °C. In contrast, several other boride compounds including AlB₂, Ni₂B, B₄C, and ScB₂ appear largely inert. Thus, other than MgB₂, no boride compound has been identified to be readily and reversibly hydrogenated.

In this paper, we report that the ternary boride MgNi₂.₅B₂ mixed with MgH₂ and LiH can be hydrogenated reversibly forming [BH₄]⁻ anions beginning at temperatures below 300 °C.

The powder X-ray diffraction (XRD) spectrum of MgNi₂.₅B₂, synthesized from MgB₂ + Ni, indicates that the product has the same structure as MgNi₂.₅B₂ in the ICDD database (SI Figure 1, Supporting Information). Samples with overall compositions of MgB₂ + xNi (x = 0.5, 0.75, 1.0, 2.0, 3.0) were also prepared. Several Mg–Ni–B ternary phases, such as Mg₆Ni₂B₄, Mg₅Ni₃B₂, and MgNiB, have been reported in previous studies related to the superconducting material MgB₂. The previous research results indicate that these ternary borides belong to a hexagonal crystal structure with similar lattice constants. In our work, we found identical

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Thus, it appears that single-phase ternary alloys, MgNi$_x$ compositions with MgB$_2$ were observed in any of the compositions. On the other hand, $^{11}$B magic angle spinning (MAS) NMR measurements (SI Figure 2) show that there are two boron species for the compositions with $x = 0.5, 0.75, 1.0$, with NMR shifts of 98 ppm and 142 ppm, respectively. The species at 98 ppm is identified to be MgB$_2$.

$^{2}$ As shown in SI Figure 2, with increasing Ni content, the B species at 98 ppm decreases and disappears at approximately $x = 2$, while the species at 142 ppm increases and shifts to slightly higher field for $x > 2$. This suggests that the boron content in the ternary phase has increased with each cycle.

There are two boron resonances observed at 98 ppm and 145 ppm, indicating that all of the boron is present in the form of MgB$_2$, with $x$ between approximately 1.5–2 and ~3, being possible.

The MgNi$_{2.5}$B$_2$/LiH/MgH$_2$ hydride system contains ideally MgNi$_2$B$_2$ and Mg$_2$NiH$_4$. The infrared absorption at 275 cm$^{-1}$ corresponds to MgH$_2$, while significantly more hydrogenation was observed at 3225, 2291, and 2387 cm$^{-1}$, which is reported to be Mg$_2$NiH$_4$.$^{11}$ Meanwhile, the peak at 1126 cm$^{-1}$ corresponds to a BH$_4^-$ deformation, and the three peaks at about 2225, 2291, and 2387 cm$^{-1}$ can be assigned to B–H (terminal) stretching.$^{18}$ The spectra in Figure 2d was obtained after hydrogenation at 50 °C.

To determine whether hydrogenation proceeded according to the reaction above, the products were examined using Fourier transform infrared (FTIR). Figure 2 shows FTIR spectra of the mixture before and after hydrogenation. Compared with a Mg$_2$NiH$_4$ standard (Figure 2a), a LiBH$_4$ standard (Figure 2b), and the milled MgNi$_{2.5}$B$_2$/LiH/MgH$_2$ mixture (Figure 2c), the hydrogenated sample (Figure 2d) clearly contains Mg$_2$NiH$_4$ and LiBH$_4$. The infrared absorption at ~1645 cm$^{-1}$ is reported to be the infrared absorption for bulk Mg$_2$NiH$_4$. However, the peak at 1126 cm$^{-1}$ corresponds to a BH$_4^-$ deformation, and the three peaks at about 2225, 2291, and 2387 cm$^{-1}$ can be assigned to B–H (terminal) stretching. The spectra in Figure 2d was obtained after hydrogenation at 350 °C. However, we have observed the formation of [BH$_4^-$] anions at temperatures as low as 250 °C, while significantly more hydrogenation was observed at 275 °C (SI Figure 3). The FTIR spectrum of the dehydrogenated sample (Figure 2e) shows that the LiBH$_4$ and Mg$_2$NiH$_4$ have reacted completely.

To investigate the nature of the boron species during cycling, we performed $^{11}$B NMR measurements. Figure 3a shows that the as-prepared sample has a single B resonance at 145 ppm, indicating that all of the boron is present in the form of the ternary boride as also shown in SI Figure 2e. After hydrogenation, two boron resonances are observed at 145 ppm and ~41 ppm, respectively. The boron species ~41 ppm corresponds to LiBH$_4$ as reported previously.$^6$ The resonance at 145 ppm indicates that the hydrogenation reaction did not proceed to completion, consistent with the hydrogen uptake measurements. To establish unequivocally that the ternary boride was hydrogenating, we performed NMR analysis using MgB$_2$ as an internal standard to quantify the ternary and LiBH$_4$ resonances. The spectra are shown in SI Figure 4. Using calibration curves of the ternary MgNi$_{2.5}$B$_2$ and MgB$_2$ resonances and separately the LiBH$_4$ and MgB$_2$ resonances, molar ratios were determined from the peak area of the resonances (a detailed explanation is given in SI Figure 4).
The composition of the MgNi$_{2.5}$B$_2$/LiH/MgH$_2$ system was also studied using XRD (SI Figure 5). After hydrogenation, diffraction peaks occur for Mg$_2$NiH$_4$ and LiBH$_4$. There are also diffraction peaks for unreacted MgH$_2$ and the ternary boride phase. However, the composition of the remaining ternary boride phase may differ from the original composition because, as discussed above, identical diffraction patterns were found for ternary borides with a range of Ni concentrations. The unreacted ternary boride may act as seeds for the further growth of the ternary boride phase during dehydrogenation, thereby reducing the reaction temperature.

The hydrogenation behavior of pure MgNi$_{2.5}$B$_2$ and MgNi$_{2.5}$B$_2$/LiH and MgNi$_{2.5}$B$_2$/MgH$_2$ mixtures was also investigated. Upon treatment with 100 bar H$_2$ at 350 °C for ~24 h, no signature of [BH$_4$]$^-$ formation was detected using FTIR from pure MgNi$_{2.5}$B$_2$ (SI Figure 6c). However, clear signatures from trace amounts of [BH$_4$]$^-$ formation were detected from MgNi$_{2.5}$B$_2$/LiH (SI Figure 6a) and MgNi$_{2.5}$B$_2$/MgH$_2$ (SI Figure 6b) mixtures. The FTIR signatures were reversible, although the extent of hydrogenation was too low to measure volumetrically. These results indicate that MgNi$_{2.5}$B$_2$ has some activity for formation of Mg(BH$_4$)$_2$, which has, thus far, only been observed under extremely high pressures (~900 bar) when MgB$_2$ alone was used.$^{19}$

In summary, we have shown that a ternary magnesium nickel boride together with MgH$_2$ and LiH can be hydrogenated reversibly forming LiBH$_4$ and Mg$_2$NiH$_4$ at temperatures below ~300 °C. The hydrogen capacity is low (~1 wt %) and the cycling temperature is still much greater than 100 °C. Nevertheless, the reactivity of this ternary boride may lead to identification of other ternary or higher order borides with sufficient reactivity to enable utilization of the high hydrogen capacity in [BH$_4$]$^-$ anions while operating under the conditions required for future hydrogen fuel cell powered vehicles.

The MgNi$_{2.5}$B$_2$ sample was prepared from a 1:2.5 molar ratio mixture of MgB$_2$ powder and Ni powder. All material handling was performed in an argon filled glovebox with <1 ppm oxygen and water concentrations. Specifically, in a typical synthesis, 0.54 g of MgB$_2$ (Aldrich) was mixed with 1.71 g of Ni metal powder (Aldrich 99.99%, <150 μm). This mixture was then milled for 60 min in an agate milling vessel with 20 silicon nitride milling balls 7 mm in diameter using a Frisch P6 planetary mill operated at 400 rpm for 1 h. The mixture was then placed in a stainless steel tube, which was sealed with Swagelok caps on both ends. The tube was heated at 975 °C for 24 h (the ramp up time from room temp to 975 °C was 4 h). The same procedure was used to prepare samples with overall compositions of MgB$_2$ + xNi (x = 0.5, 0.75, 1.0, 2.0, 3.0). Samples for hydrogenation were prepared by milling mixtures of LiH (97 %, Fluka), MgH$_2$ (Geltset), and MgNi$_{2.5}$B$_2$ in 2:4:1 molar ratios in an 80 cm$^3$ hardened-steel milling vessel with 30 Cr-steel milling balls 7 mm in diameter as described above. After milling, the mixtures were hydrogenated in a volumetric gas apparatus, which is described in detail elsewhere.$^{20}$ The hydrogenation treatment consisted of exposing the mixture to an initial H$_2$ pressure of 160 bar, heating at 2 °C/min to 300 °C, holding the temperature constant for 2 h, and then heating to 350 °C.

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SUPPORTING INFORMATION AVAILABLE Additional experimental details and SI Figures 1–6. This material is available free of charge via the Internet at http://pubs.acs.org.

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