



Effect of Some Dopants on Hydrogen Storage Behaviors of Magnesium Borohydrides

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Abstract: Access to high gravimetric hydrogen content of $\text{Mg}(\text{BH}_4)_2$ is hampered by its thermodynamic stability, which has hindered its utilization as a hydrogen storage material. The destabilizing effects of silicon, carbon, and NaH on $\text{Mg}(\text{BH}_4)_2$ was investigated using TPD (temperature programmed desorption) and XRD. Mechanically milled $\text{Mg}(\text{BH}_4)_2/\text{NaH}$ has a lower onset temperature and desorbs about 6 wt% hydrogen below 350 °C. XRD analysis showed formation of a new phase. The new phase accounts for the change in the hydrogen desorption path of the mixture resulting in the low onset desorption temperature of the mixture containing Si and carbon had no effect on the desorption temperature; they only increased the overall weight of the mixture resulting in a lower amount of hydrogen. XRD analysis also showed the presence of Si and carbon in the as-milled and de-hydrided mixtures. The products of dehydrogenation of $\text{Mg}(\text{BH}_4)_2/\text{CaH}/\text{Si}$ are similar to those of $\text{Mg}(\text{BH}_4)_2/\text{CaH}$ and those of $\text{Mg}(\text{BH}_4)_2/\text{C}$ and they resemble those of $\text{Mg}(\text{BH}_4)_2$.

Key Words: Magnesium borohydride, Desorption, Mechanical milling, Additives.

INTRODUCTION

Complex metal hydrides with high gravimetric hydrogen content such as amides, alanates, and borohydrides are being considered as potential candidates for hydrogen storage [1-6]. Notable among the challenges of using borohydrides as hydrogen storage materials are their high dehydrogenation temperatures, diborane production, poor reversibility, as well as cycle life [6-11]. The study of $\text{Mg}(\text{BH}_4)_2$ as a potential hydrogen storage material is gaining more attention due to its light weight and high gravimetric hydrogen content. Konoplev and Bakulani reported some of its properties in 1971 [12]. Theoretical studies predict $\text{MgB}_{12}\text{H}_{12}$ and MgB_2 to be the only energetically stable and possible decomposition products of $\text{Mg}(\text{BH}_4)_2$ [13]. Thermal analysis showed that most of the hydrogen loss from the decomposition of $\text{Mg}(\text{BH}_4)_2$ occurs between 300 to 400 °C [14]. Decomposition started at 290 °C and about 13 wt% hydrogen was released up to 500 °C with a minimal trace of B_2H_6 . At 290 °C, MgH_2 , MgB_2 , and Mg were observed while at 450 °C and above, Mg, MgB_2 , and an unknown phase were detected.

The effect of ball milling and several additives on the decomposition of $\text{Mg}(\text{BH}_4)_2$ have been investigated [15-29]. Ball milling does not have any effect on the decomposition temperature [15-16]. The sample becomes amorphous during ball milling but is recrystallized to the α -phase after heating to about 150 °C. Li et al. reported the reduction of the onset desorption temperature of $\text{Mg}(\text{BH}_4)_2$ from 262 °C to 88 °C by addition of TiCl_3 [16]. They proposed that the improvement is due to the formation of more stable TiB_2 or less stable MgTi-based borohydride. Badaji et al. also investigated $\text{Mg}(\text{BH}_4)_2$ mechano-chemically alloyed with several metal chlorides [15] and found that combined Nb-Ti additives lowered the onset temperature by up to 125 °C. However, none of the additives were able to improve the reversibility of the material.

There have been reports on studies involving destabilization of $\text{Mg}(\text{BH}_4)_2$ with hydrides, borohydrides, and amides [20-26]. Studies have shown that the system consisting of $\text{Mg}(\text{BH}_4)_2$ and LiBH_4 possess superior hydrogen storage properties to either of the constituents [20-22]. Similarly, Temperature Programmed Desorption, TPD, analyses have shown that the desorption temperature of $\text{Mg}(\text{BH}_4)_2$ can be lowered by ball milling

with $\text{Ca}(\text{BH}_4)_2$ [26]. The resulting mixture absorbed and released hydrogen with a well-defined plateau region in the pressure composition isotherm (PCI). This mixture has also been reported to release hydrogen at a faster rate [27]. In the present study, the effect of NaH, silicon, and carbon on the hydrogen storage properties of $\text{Mg}(\text{BH}_4)_2$ is presented.

EXPERIMENTAL

The materials used in this research were obtained from Sigma Aldrich; they were hydrogen storage grade and were hence used without further purification. The $\text{Mg}(\text{BH}_4)_2$ was prepared from MgH_2 and triethylamineborane, as described by Chlopek et al. [14]. All sample handling, weighing, and loading were performed in a Vacuum Atmospheres argon-filled glove box with oxygen and moisture levels below 1 ppm, to prevent contamination from air and moisture. The glove box was vacuum cleaned several times using purified argon gas to remove air and moisture. The mixture of the samples were mechanically mixed for 10 hrs using a SPEX 8000M Mixer Mill that had a stainless steel milling pot, which contained four small and two medium sized stainless steel balls. X-ray powder diffraction, XRD, analysis was used to determine whether new phases were formed by milling the different substances. A Panalytical X'pert Pro MPD Analytical X-ray Diffractometer Model PW 3040 Pro was used for these analyses. The samples were covered with a Kapton film to protect them from air and moisture. Temperature Programmed Desorption, TPD, was done in a gas reaction controller-PCI unit to evaluate the hydrogen desorption properties of each reaction mixture. This apparatus was manufactured by the Advanced Materials Corporation. The unit was fully automated and was controlled by a Lab View-based software program. An in-situ XRD analysis was also carried on the mixture at different temperatures to determine the species that were present during the dehydrogenation of the mixtures.

RESULTS & DISCUSSION

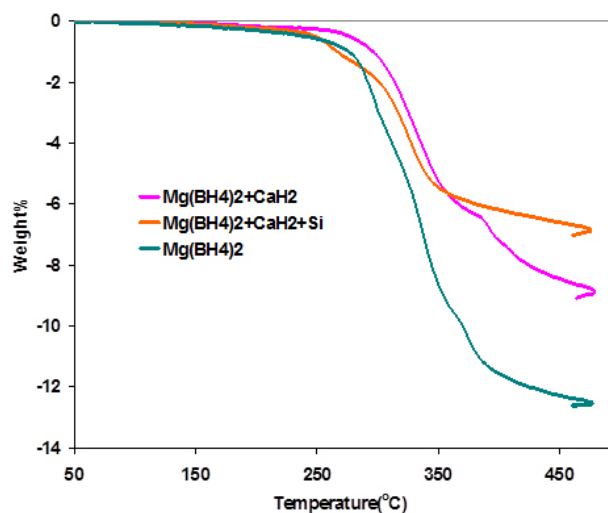
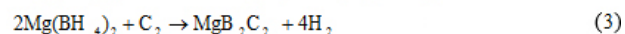
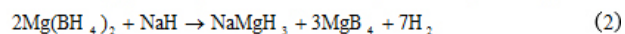
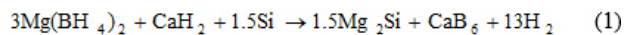


Fig 1: Combined TPD curves of $\text{Mg}(\text{BH}_4)_2/\text{CaH}_2$ and $\text{Mg}(\text{BH}_4)_2/\text{CaH}_2/\text{Si}$ and $\text{Mg}(\text{BH}_4)_2$

The TPD curve of $\text{Mg}(\text{BH}_4)_2/\text{CaH}_2/\text{Si}$ is shown in Fig. 1 along with those of pure $\text{Mg}(\text{BH}_4)_2$ and $\text{Mg}(\text{BH}_4)_2/\text{CaH}_2$. It has been shown that the decomposition temperature of hydrides could be lowered by alloying with silicon [28, 29]. The addition of silicon reduced the onset temperature of the $\text{Mg}(\text{BH}_4)_2/\text{CaH}_2$ mixture, but the overall decomposition temperature is still higher than that of $\text{Mg}(\text{BH}_4)_2$. The silicon also reduced the total amount of hydrogen desorbed by increasing the overall weight of the mixture.

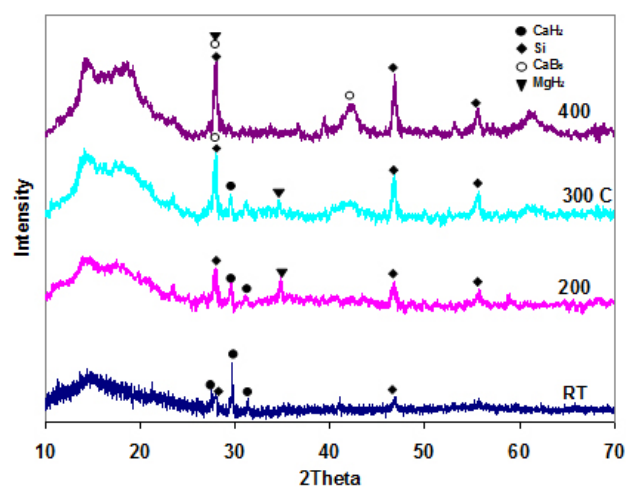


Fig 2: XRD pattern of $\text{Mg}(\text{BH}_4)_2/\text{CaH}_2/\text{Si}$ mixture.

From the results of the XRD studies shown in Fig. 2, it is clear that the silicon did not form any alloy with CaH_2 . It only remains in the mixture throughout the dehydrogenation reaction. The expected product of dehydrogenation of this mixture, Mg_2Si according to equation 1, as predicted by Alapati et al. [30] and Ozolin et al. [31] is conspicuously absent in the XRD pattern. The products of the dehydrogenation are also similar to those of the mixture involving only $\text{Mg}(\text{BH}_4)_2$ and CaH_2 (i.e., MgH_2 and CaB_6 shown in Fig. 3).

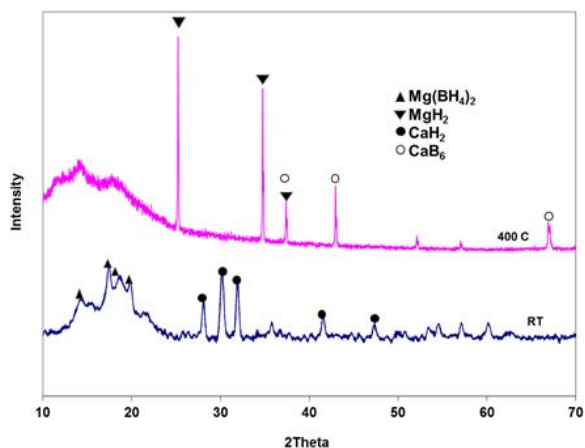


Fig 3: XRD pattern of $\text{Mg}(\text{BH}_4)_2/\text{CaH}_2$ mixture.

In Fig. 4, the TPD curve of $\text{Mg}(\text{BH}_4)_2/\text{NaH}$ shows a big reduction in the onset temperature of $\text{Mg}(\text{BH}_4)_2$, releasing about 6 wt% of hydrogen below 350 °C. This shows that NaH is better at destabilizing the $\text{Mg}(\text{BH}_4)_2$ than either CaH_2 or a mixture of CaH_2 and NaH.

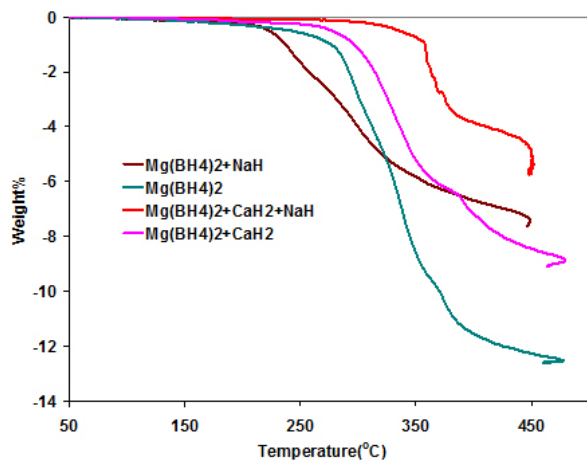


Fig 4: Combined TPD curves of $\text{Mg}(\text{BH}_4)_2$, $\text{Mg}(\text{BH}_4)_2/\text{NaH}$, $\text{Mg}(\text{BH}_4)_2/\text{CaH}_2/\text{NaH}$, and $\text{Mg}(\text{BH}_4)_2/\text{CaH}_2$.

In the XRD analysis of the $\text{Mg}(\text{BH}_4)_2/\text{NaH}$ shown in Fig. 5, neither the peaks of $\text{Mg}(\text{BH}_4)_2$ nor NaH were present in the as-milled sample at room temperature. This suggests that a new species might have been formed during ball milling. The appearance of some new peaks, which become persistent even after heating to 300°C, indicates the presence of a new phase.

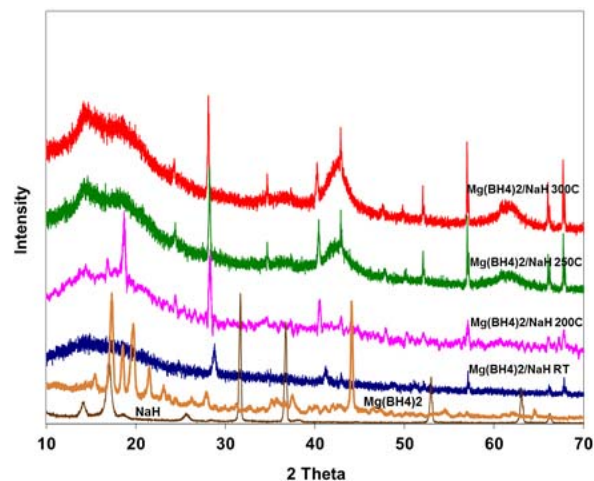


Fig 5: XRD pattern of $\text{Mg}(\text{BH}_4)_2/\text{NaH}$ mixture.

Fig. 6 contains the TPD curve of the $\text{Mg}(\text{BH}_4)_2/\text{C}$ system alongside that of pure $\text{Mg}(\text{BH}_4)_2$. It can be deduced from the curve that the presence of carbon does not affect the desorption temperature of the mixture. However, the amount of hydrogen released was reduced and this can be ascribed to the physical presence of carbon adding to the overall weight of the mixture. Further evidence from the XRD analyses shows that carbon is just passive in the mixture.

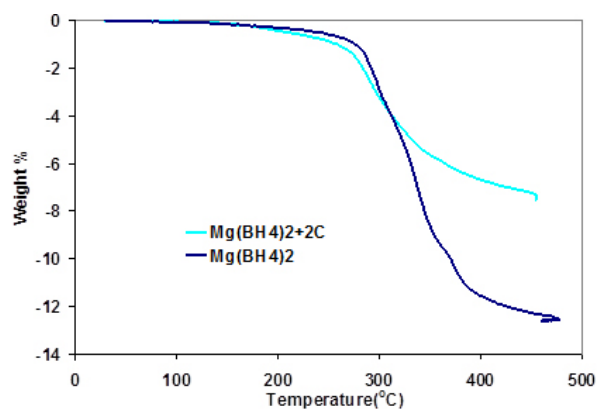


Fig 6: Combined TPD curves of $\text{Mg}(\text{BH}_4)_2/\text{C}$ and pure $\text{Mg}(\text{BH}_4)_2$.

In Fig. 7, the major peaks of carbon were persistent throughout the analysis. No peak for the expected product of dehydrogenation (MgB_2C_2) according to equation 2 was detected. MgB_2 is the only species identified as the product after dehydrogenation.

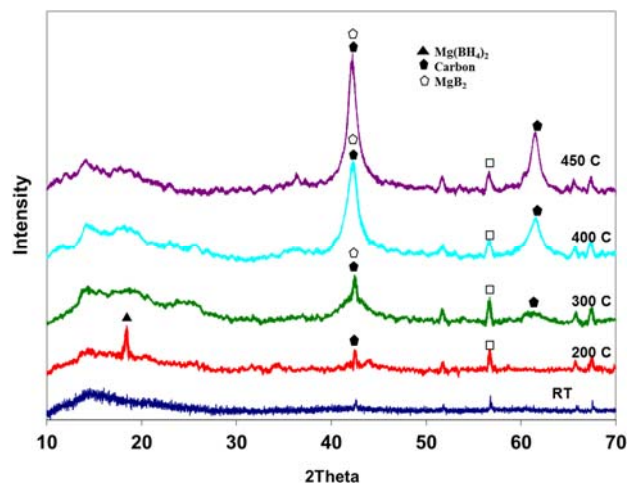


Fig 7: XRD pattern of $\text{Mg}(\text{BH}_4)_2/\text{C}$ mixture

The TPD curves of the rehydrogenated samples are shown in Fig 8. All the mixtures released just about 1 wt% hydrogen in the second dehydrogenation cycle, showing that reversibility of these mixtures are very poor. Attempts to obtain the isotherms for the mixtures were unsuccessful as no clear plateau region was observed, also indicating that their reversibility is poor.

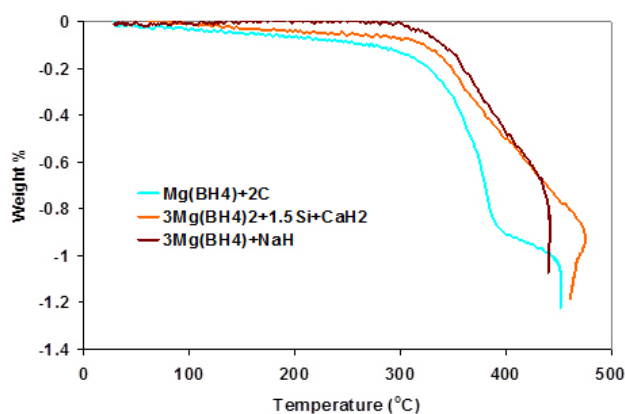


Fig 8: TPD curves of Rehydrogenated Magnesium Borohydride Mixtures.

CONCLUSION

The results from this study have shown the effects of various additives on the dehydrogenation of borohydrides. Of all the various ball milled mixtures of

$\text{Mg}(\text{BH}_4)_2$ and additives, NaH is the only one that effectively lowers the desorption temperature of $\text{Mg}(\text{BH}_4)_2$. This may be due to the formation of new borohydride species during ball-milling of the mixture. Other additives did not have any effect on the desorption temperatures, but rather reduced the amount of hydrogen released due to their physical presence increasing overall weight of the mixture. The mixtures also showed poor reversibility, releasing much lower amounts of hydrogen in the second dehydrogenation.

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