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Effect of TiH₂ and Mg₂Ni additives on the hydrogen storage properties of magnesium hydride

S.T. Sabitu, G. Gallo, A.J. Goudy*

Department of Chemistry, Delaware State University, 1200 N. Dupont Highway, Mishoe Science Center 301, Dover, DE 19901, United States

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ABSTRACT

A study was done to determine the effect of TiH₂ and Mg₂Ni additives on the hydrogen sorption behavior of MgH₂. A series of mixtures were made in which MgH₂ was ball milled with various amounts of TiH₂, Mg₂Ni or combinations of both. Temperature programmed desorption (TPD) analysis showed that the addition of increasing amounts of TiH₂ to MgH₂ resulted in a progressive reduction of the onset temperature of MgH₂ by as much as 70 °C for a mixture containing 50 mol% TiH₂. However the hydrogen yield also decreased from a high of 7.5 wt% for pure MgH₂ to a low of 2.4 wt% for the mixture containing 50 mol% TiH₂. The rates of H₂ reaction with MgH₂ increased with increasing amounts of TiH₂. Pressure composition isotherms were also made for each of the mixtures at several temperatures and van't Hoff plots were constructed. The results showed that the enthalpies for hydrogen absorption systematically decreased with increasing amounts of TiH₂, from a high of 76 kJ/mole H₂ for pure MgH₂ to a low of 65 kJ/mole H₂ for a mixture containing 50 mol% TiH2. This indicated that thermodynamic stability can be reduced by TiH₂ additions. When Mg₂Ni was added to these mixtures, the desorption temperatures were reduced dramatically. The addition of 6 or 10 mol% of Mg₂Ni to MgH₂ lowered the onset temperature from 330 to 190 °C with a hydrogen yield of 6 wt%. The addition of both TiH₂ and Mg₂Ni catalysts did not result in any further reduction in the onset temperatures. However, the mixture of both catalysts was more effective at increasing reaction rates than either of them alone.

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1. Introduction

There is great interest in developing suitable materials for hydrogen storage applications. A number of materials ranging from interstitial metal hydrides to complex hydrides such as alanates, borohydrides and imides have been extensively studied [1–7]. Interstitial hydrides such as $LaNi_5H_6$ can absorb hydrogen rapidly and reversibly at moderate temperatures and pressures [8–10] but their low hydrogen-holding capacity limits their potential for hydrogen storage. Complex hydrides such as $LiBH_4$ and $LiNH_2$ have very high hydrogen holding capacities but the release of hydrogen is often accompanied by the release of byproducts such as B_2H_6 and NH_3 .

Magnesium hydride is an attractive material for hydrogen storage because it has a high hydrogen-holding capacity of 7.6 wt% and the release of hydrogen occurs via a simple one-step process with no byproducts [11–13]. However, a major obstacle to its usefulness for hydrogen storage is the high temperature required for it to release hydrogen. Efforts have been made to improve the thermodynamic properties of MgH₂ by using additives to lower the temperature of the hydriding and dehydriding process. One technique that has been used is alloying Mg with other metals. Reilly and Wiswall [14,15] demonstrated that the thermodynamic stability of magnesium hydride can be modified by alloying magnesium with Cu or Ni. They showed that Mg₂Cu and Mg₂Ni alloys formed less stable hydrides with lower reaction temperatures than pure Mg. However, the hydrogen holding capacities of these materials were considerably less than that of MgH₂.

Attempts have also been made to lower the reaction temperature of MgH₂ by ball milling it with various additives such as metal oxides and transition metals [16–20]. For example, Hanada et al. [16] used Nb₂O₅, prepared by ball milling under a hydrogen atmosphere, to act as a catalyst and found that approximately 6 wt% hydrogen could be desorbed from MgH₂ in the 200–250 °C range. Oelerich et al. [17] used a variety of metal oxides (e.g. Nb₂O₅, Fe₃O₄, V₂O₅, Mn₂O₃, Cr₂O₃, TiO₂, Sc₂O₃, Al₂O₃, CuO, and SiO₂) to improve reaction rates of MgH₂ and found that as little as 0.2 mol% was sufficient to provide fast sorption kinetics. Huot et al. [18] ball milled a mixture of Mg and Ni under hydrogen atmosphere and found that the presence of Ni lowered the onset temperature for desorption of hydrogen from MgH₂ from 440.7 to 225.4 °C. However, the presence of Mg₂Ni slowed the decomposition kinetics of MgH₂. Liang

^{*} Corresponding author. Tel.: +1 302 857 6534; fax: +1 302 857 6539. *E-mail address:* agoudy@desu.edu (A.J. Goudy).

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et al. [19] studied the catalytic effect of transition metals (e.g. Ti, V, Mn, Fe and Ni) on hydrogen sorption by MgH₂. They found that the formation enthalpy of MgH₂ was not altered by milling with transition metals. In another study, Liang et al. [20] studied the hydrogen storage properties of $Mg_{1.9}Ti_{0.1}Ni$, made by mechanical alloying, and found that it absorbs more than 3 wt% H₂ in 2000 s at 423 K. This material showed better kinetics than ball milled Mg₂Ni and cast Mg₂Ni.

In this work, an attempt has been made to compare the hydrogen sorption behavior of MgH_2 ball milled with TiH_2 , Mg_2Ni or a mixture of both. The results would lead to a better understanding of the role that thermodynamic stability has on reaction temperatures and rates.

2. Experimental details

The starting materials used in this research were obtained from Sigma-Aldrich. The MgH₂ powder was hydrogen storage grade and according to the analysis provided by the supplier, the total amount of trace metal contaminants was less than 0.09%. The major contaminants were Ca = 199.0 ppm, Al = 157.8 ppm, Mn = 126.6 ppm, Fe = 126.2 ppm and K = 109.7 ppm. All other contaminants were less than 70 ppm. The TiH₂ powder was 99.98% pure. All sample handling, weighing and loading were performed in a Vacuum Atmospheres argon-filled glove box to prevent contamination from air and moisture. The glove box was capable of achieving less than 1 ppm oxygen and moisture. Prior to analysis, each sample mixture was milled for up to 10 h in a SPEX 8000M Mixer/Mill that contained an argon-filled stainless steel milling pot with four small stainless steel balls. The ball-to-powder ratio in the pot was 5:1. X-ray powder diffraction analysis was used to determine whether new phases were formed from milling the different substances. A Panalytical X'pert Pro MPD Analytical X-ray Diffractometer Model PW 3040 Pro was used for this analysis. The samples were covered with a Mylar film to keep them from air and moisture. Pressure composition isotherm (PCI) analyses and temperature programmed desorption (TPD) were used to evaluate the hydrogen desorption properties of each reaction mixture. These analyses were done in a gas reaction controller-PCI unit. This stainless steel apparatus was manufactured by the Advanced Materials Corporation in Pittsburgh, PA. The unit was fully automated and was controlled by a Lab View-based software program. The amount of hydrogen absorbed or released from samples was determined by monitoring the pressure changes in a 50 cm³ calibrated volume. The pressure was measured by Heise HPO pressure transducers that had an accuracy of $\pm 0.05\%$ of full scale, a repeatability of $\pm 0.005\%$ of full scale and a resolution of $\pm 0.01\%$ of full scale. The temperature was controlled to ± 0.1 °C with an Omega CN616 Series temperature controller. This unit accepted signals from a CN616TC1 thermocouple. The thermocouple was inside of a stainless steel reactor with its tip in contact with the center of the sample bed. PCI analyses were done on freshly ball milled materials and no activation procedure was necessary. The MgH₂ was found to absorb and release hydrogen reversibly under the conditions used and it was stable when subjected to repeated cycling. The TPD analyses were done on freshly ball milled materials. The wt% hydrogen released during the runs was determined by the software based on the pressure rise in the calibrated volume at constant temperature. Scans were done in the 30-450 °C range at a temperature ramp of 4 deg/min. Absorption rate measurements were also carried out in the gas reaction controller. In each run, the sample was fully evacuated and hydrogen was allowed to flow from the calibrated volume into the stainless steel sample reactor. The initial pressure was set at 100 atm and the reaction rate was determined by measuring the rate of pressure decrease in the calibrated volume. High purity hydrogen gas of 99.999% purity was used throughout the analyses.

3. Results and discussion

A series of MgH₂–TiH₂ mixtures containing various amounts of TiH₂ ranging from 4 to 50 mol% were studied to determine the effect of TiH₂ on the hydrogen sorption properties of MgH₂. After each mixture was ball milled for 10 h, XRD measurements were used to determine if any alloying had taken place. Fig. 1 contains XRD patterns for MgH₂, TiH₂ and a mixture containing MgH₂ + 4 mol% of TiH₂. Scan (c) was done on the mixture before ball milling and scan (d) was done on the same mixture after ball milling. A comparison of the patterns in scans (c) and (d) shows the disappearance and emergence of some of the Mg and Ti reflections between 25° and 75°. This indicates that some alloying of the Mg and Ti had most likely taken place. It is also evident that the diffraction peaks for the major phase, MgH₂, in the ball milled mixture are broader as the result of smaller particle size. This type of behavior was also



Fig. 1. X-ray diffraction patterns for MgH_2 , TiH_2 and MgH_2 + 4 mol% TiH_2 .

observed by Shang et al. [21] who did a study on MgH₂ mechanically alloyed with various transition metals. Fig. 2 contains XRD patterns for mixtures of MgH₂ with different mole percentages of TiH₂ (i.e. 4, 10, and 50). The diffraction patterns show a progressive decline in the peak corresponding to MgH₂ in the region of 54° as the mol% of TiH₂ in the mixture increases. There is also the emergence of prominent TiH₂ peaks in the regions of 60° and 70° as the amount of TiH₂ in the reaction mixture increases. This is a further indication that a new phase was starting to form.

Temperature programmed desorption measurements were done on a series of MgH₂ mixtures containing 0, 4, 10, and 50 mol% TiH₂ in order to determine the effect of TiH₂ on the hydrogen desorption properties of MgH₂. The profiles in Fig. 3 show the effect of various mole fractions of TiH₂ on the hydrogen desorption temperatures of MgH₂. In the case of pure MgH₂, the onset temperature was about 330 °C. This temperature systematically decreased to 250 °C as the relative amount of TiH₂ in the mixture increased to 50 mol[%]. The plots also show that as the mol[%] of TiH₂ increases the amount of H₂ released decreases from a high of about 7.5 wt% for pure MgH₂ to a low of about 2.4 wt% for the mixture containing 50 mol% TiH₂. This reduction in hydrogen weight percentage is most likely due to the fact that TiH₂ does not release its hydrogen in the temperature range used in this study. Temperatures in excess of the 450 °C used in these experiments must be reached before TiH₂ begins to release hydrogen. Thus, there is an increasing weight penalty that occurs as the percentage of TiH₂ in the mixture increases.



Fig. 2. X-ray diffraction patterns for several MgH_2 -Ti H_2 mixtures. All mixtures were ball milled for 10 h.



Fig. 3. TPD profiles for MgH₂ and several TiH₂-MgH₂ mixtures.

Since adding large amounts of TiH₂ to MgH₂ to lower reaction temperatures is accompanied by an excessive weight penalty, it was desirable to test another material to see if similar temperature lowering could be achieved with less weight penalty. Since nickel is known to be a good hydrogenation catalyst, the Ni-containing alloy, Mg₂Ni, was studied to determine if it would be more effective at lowering the reaction temperature. A mixture containing 10 mol% Mg₂Ni in MgH₂ was made by ball milling and the TPD curve is shown in Fig. 4. It can be seen that the onset temperature for the mixture containing 10 mol% Mg₂Ni is 195 °C, which is 55° lower than that for the mixture containing 50 mol% TiH₂, shown in Fig. 3. Just as importantly, the weight penalty is significantly lower than the mixture containing 50 mol% TiH₂. This mixture releases about 6.3 wt% H₂, which is considerably better than the 2.4 wt% that was observed in the case of the 50 mol% TiH₂ mixture. Based on this, it appears that Mg₂Ni is a more effective catalyst than TiH₂. In order to determine if a combination of both catalysts might yield even better results, another mixture containing 4 mol% TiH₂ and 6 mol% Mg₂Ni, a total of 10 mol% catalyst, was also studied. The curves in Fig. 4 show that the mixed catalyst causes about the same temperature lowering as the mixture containing 10 mol% Mg₂Ni. Thus, in this case, the presence of TiH₂ does not produce any significant improvement in the results.

Since Mg_2Ni has such a large effect on the onset temperature for hydrogen desorption from MgH_2 , a TPD profile was done on sample of pure Mg_2NiH_4 to determine if it might have an even lower onset temperature than the MgH_2-Mg_2Ni mixtures. Surprisingly, the TPD curves in Fig. 4 for hydrogen desorption from the MgH_2-Mg_2Ni mixtures all show a lower onset temperatures than the Mg_2NiH_4 , which has an onset temperature of 245 °C. In addition,



Fig. 4. TPD profiles for pure MgH_2 , pure Mg_2NiH_4 , and several mixtures containing various amounts of TiH₂ and/or Mg_2Ni .



Fig. 5. Absorption isotherms for MgH₂ and several TiH₂-MgH₂ mixtures.



Fig. 6. Van't Hoff absorption plots for MgH₂ and several TiH₂-MgH₂ mixtures.

since Mg₂NiH₄ releases only 4.45 wt% hydrogen, its hydrogen storage potential is very limited. It is interesting to note that a similar phenomenon was also observed in the MgH₂ mixtures containing TiH₂. The TiH₂ is stable up to temperatures in excess of 500 °C. But when it is ball milled with MgH₂, the new phase releases hydrogen at a temperature which is lower than that of either constituent.

Since TiH₂ and Mg₂Ni are both able to lower reaction temperature of MgH₂, it was also of interest to determine their effect on the thermodynamic stability of MgH₂. Reilly and Wiswall [15] had already established that Mg₂NiH₄ had a lower stability than MgH₂ and thus it was expected that incorporating TiH₂ might produce a similar effect. Pressure-composition-isotherms were constructed for the MgH₂-TiH₂ mixtures shown in Fig. 3. Fig. 5 shows the absorption isotherms for these mixtures at 350 °C. It is evident from the curves that the plateau pressure increases with increasing TiH₂ content. It is also evident that the hydrogen-holding capacity decreases as the TiH₂ content increases. This was also observed in the TPD profiles. Pressure composition isotherms were constructed for each mixture at several temperatures and thus it was possible to construct the van't Hoff plots shown in Fig. 6. The value of ΔH for each mixture could be determined from the slopes of these plots. Table 1 gives the values of ΔH for each mixture. It is evident that

Table 1
Thermodynamic parameters obtained for pure MgH_2 and MgH_2 -TiH ₂ mixtures

Composition	Onset temp. (°C)	wt%	P_m (at 350 °C)	ΔH (kJ/mol)
MgH ₂	346	7.50	7.49	76.0
MgH ₂ + 4 mol% TiH ₂	276	7.60	7.79	75.1
MgH ₂ + 10 mol% TiH ₂	265	6.25	8.81	72.2
MgH ₂ + 50 mol% TiH ₂	250	2.40	12.93	65.2



Fig. 7. Reaction rate plots for MgH₂ and several TiH₂-MgH₂ mixtures.

the values of ΔH systematically decrease from a high of 76 kJ/mol for pure MgH₂ to a low of 65 kJ/mol for the mixture containing 50 mol% TiH₂. This indicates that the thermodynamic stability of MgH₂ mixtures decreases with increasing TiH₂ content. This finding is somewhat different than that reported by Liang et al. [19]. They studied the catalytic effect of transition metals on hydrogen sorption by MgH₂ and found that the formation enthalpy of MgH₂ was not altered by milling with transition metals.

In addition to lowering reaction temperatures, it is also important to have fast reaction rates. Huot et al. [20] reported that adding Mg₂Ni to MgH₂ actually decreases reaction rates. Therefore a series of experiments were done in order to determine the effect of additives on the reaction rates of H₂ with magnesium. Fig. 7 contains plots of reacted fraction versus time for the uptake of hydrogen by the MgH₂–TiH₂ for mixtures containing 0, 4, 10, and 20 mol% TiH₂. In these experiments the pressure in the reaction chamber was initially set to 100 atm. Then the pressure decrease in the constant volume system was monitored as the sample mixture absorbed hydrogen. It can be seen that reaction rates increase with increasing percentage of TiH₂ in each mixture. The reaction rates of hydrogen in mixtures containing both TiH₂ and Mg₂Ni were also measured. Fig. 8 contains the rate curves for mixtures containing 10 mol% TiH₂, 10 mol% Mg₂Ni, or a mixed catalyst containing 4 mol% TiH₂ + 6 mol% Mg₂Ni. From the curves it is evident that the Mg₂Ni is more effective than TiH₂ in increasing reaction rate. This is somewhat different than the findings of Huot et al. who reported a decrease in reaction rates of desorption reactions. It is also evident that the mixed catalyst is more effective than the individual catalysts at increasing



Fig. 8. Reaction rate plots for mixtures containing $90\,mol\%~MgH_2$ and $10\,mol\%$ of TiH_2 or Mg_2Ni or both.

Table 2

Reacted fractions obtained for pure MgH₂ and mixtures containing MgH₂, TiH₂ and/or Mg₂Ni after 1000 s of reaction time. All reactions were done at 350 $^{\circ}$ C.

Composition	Reacted $fraction_{(1000)}$
MgH ₂	0.138
MgH ₂ + 4 mol% TiH ₂	0.185
MgH ₂ + 10 mol% TiH ₂	0.229
MgH ₂ + 20 mol% TiH ₂	0.522
MgH ₂ + 10 mol% Mg ₂ Ni	0.430
$MgH_2 + 4 mol\% TiH_2 + 6 mol Mg_2Ni$	0.551

reaction rates. This is significant because it indicates that using an appropriate mixture of catalysts is a promising way to make MgH₂ a suitable material for hydrogen storage purposes. These findings are in agreement with those of Lu et al. [22]. They studied the hydrogen storage behavior of MgH₂ mechanically alloyed with Ti and Ni catalysts and found that a combination of Ti and Ni is more effective catalyst for increasing reaction rates than Ti or Ni alone (Table 2).

4. Conclusions

This research has shown that TiH_2 and Mg_2Ni are both effective catalysts for lowering the reaction temperature of MgH_2 and increasing reaction rates, with Mg_2Ni being the more effective of the two. The research has also shown that a mixed catalyst is better at increasing reaction rates than a single catalyst. This indicates that an optimum amount of two or more catalysts is the most promising way to make MgH_2 a suitable material for hydrogen storage purposes. The research has also demonstrated that the enthalpy for the reaction of hydrogen with MgH_2 decreases with the addition of TiH_2 . Thus it appears that the thermodynamic stability and reaction rates can be affected by ball milling MgH_2 with TiH_2 .

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