An Experimental Survey of Additives for Improving Dehydrogenation Properties of Magnesium Hydride

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Abstract: The use of a wide range of additives has been known as an important method for improving hydrogen storage properties of MgH_2 . There is a lack of a standard methodology, however, that can be used to select or compare the effectiveness of different additives. A systematic experimental survey was carried out in this study to compare a wide range of additives including transition metals, transition metal oxides, hydrides, intermetallic compounds, and carbon materials, with respect to their effects on dehydrogenation properties of MgH_2 . MgH_2 with various additives were prepared by using a high-energy-high-pressure planetary ball milling method and characterized by using thermogravimetric analysis (TGA) techniques. The results showed that additives such as Ti and V-based metals, hydride, and certain intermetallic compounds have strong catalytic effects. Additives such as Al, In, Sn, Si showed minor effects on the kinetics of the dehydrogenation of MgH_2 , while exhibiting moderate thermodynamic destabilizing effects. In combination, MgH_2 with both kinetic and thermodynamic additives, such as the MgH_2 -In-TiMn₂ system, exhibited a drastically decreased dehydrogenation temperature.

Keywords: Magnesium hydride, hydrogen storage, kinetics, dehydrogenation temperature

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1. Introduction

Hydrogen is regarded as a future energy carrier for a cleaner environment. Due to the gaseous state of hydrogen, a practical solution for carrying hydrogen is to store it in a solid hydrogen storage material. Magnesium hydride is considered a promising hydrogen storage candidate owing to its high hydrogen storage capacity (up to 7.6 wt.%), reversibility, and low costs.

However, the practical use of MgH_2 is limited by the fact that high temperature (generally above 300 °C) is required to release hydrogen from MgH_2 due to its thermodynamic stability and kinetic barriers.

The thermodynamic stability is one of main reasons impeding the decomposition of MgH_2 at low temperature. For example, the hydrogen equilibrium pressure of MgH_2 at 120 °C is 1.0×10^{-4} bar [1], which is hugely unfavorable for MgH_2 to decompose at such a temperature. Research efforts using additive(s) to thermodynamically destabilize MgH_2 have made some progresses in recent years. In particular, the use of Mg solid solution alloys (Mg-In, [1-3] Mg-Al, [4, 5] Mg-Sn [6] etc.) were demonstrated to be an effective method that could destabilize MgH_2 without significant loss of the hydrogen capacity.

Kinetically, due to a slow diffusion rate of hydrogen in MgH_2 , its decomposition is usually sluggish. To overcome the kinetic barriers, using catalytic additives has been known to be an effective approach. Among previous reports of attempts to improve the kinetics of the dehydrogenation of MgH_2 , the addition of transition metals and their compounds, especially Ti, [7-11] V, [12-14] and Nb_2O_5 showed significant results. [15-18] Other additives, such as non-

transition-metal elements, [1, 19-22] hydride, [8, 11] nitrides, [23, 24] carbides, [23, 25, 26] halides, [27-32] and carbon, [33-36] also showed positive effects, as reported in the literature.

However, although considerable research has been reported in recent decades on using additives to improve the hydrogen storage properties of MgH_2 , [37-39] to date, it is still difficult to assess and compare the effectiveness of different additives because there are considerable discrepancies among different previous research reports, which may be attributed to different methodologies in terms of material preparation and characterization.

Furthermore, there is a constant interest in finding better or optimized catalytic additives. Therefore, a comprehensive study on the effect of additives on MgH_2 is sorely needed for not only gauging the effectiveness of additives but also understanding the underlying mechanisms of their catalytic effects. In this paper, forty-nine MgH_2 -additive materials were synthesized and characterized to compare the effect of those additives on the dehydrogenation properties of MgH_2 . The additives were selected from a wide range of materials including transition metal or other elemental materials, transition metal oxides, transition metal hydrides, transition metal intermetallics, and carbon materials. Since the preparation process and the characterization were maintained throughout these experiments, the results of this work provide analogous data for guiding both experimental and mechanism studies of MgH_2 with additives.

2. Experimental

In order to quantitatively characterize the dehydrogenation behavior, two temperature points, namely calculated on-set dehydrogenation temperature ($T_{\text{on-set}}$) and calculated end dehydrogenation temperature (T_{end}) were determined based on TGA curves. As illustrated in Figure 1, the point of $T_{\text{on-set}}$ was determined by the intersection of the extension line of the high plateau (the horizontal part of the curve before the dehydrogenation reaction) and the tangent of the half-dehydrided point (the mid-point in Figure 1). The point of T_{end} was determined by the intersection of the extension line of the low plateau (the horizontal part of the curve after the dehydrogenation reaction) and the tangent of the half-dehydriding point.

All the material handling was carried out in a glove-box filled with circulating purified argon (99.999%), which contained less than 1ppm water vapor and oxygen. The sources of the raw materials used in this work, along with some notes on processing, can be found in supplementary information. Three grams of the mixtures of MgH_2 and additives in various molar ratio were milled using a custom-made ultrahigh-energy-high-pressure (UHEHP) planetary ball milling machine under a 150 bar hydrogen pressure. The ball-to-powder ratio was 20:1 by volume and the milling was carried out for 4 hours at room temperature. Dehydrogenation experiments were conducted by the use of a thermal gravimetric analyzer (Shimadzu, TGA50) in which approximately 15 mg samples were heated under 50 ml/min flowing argon to 400 °C at a heating rate of 5 °C/min. The TGA instrument was placed inside the glove-box during testing.

3. Results and discussion

Figure 2 summarizes the key results of all MgH_2 -additive samples that were prepared and tested in this work. The additives were classified into groups as: transition metals and their compounds (oxides and hydride), intermetallic compounds, III-B and IV-B group elements, and carbon materials. In addition, MgH_2 with LiH as an additive, and three other compositions with binary-additives (combining two additives together) i.e., $\text{MgH}_2\text{-TiH}_2\text{-Ni}$, $\text{MgH}_2\text{-TiH}_2\text{-Nb}_2\text{O}_5$, and $\text{MgH}_2\text{-In-TiMn}_2$, were synthesized and characterized. The dehydrogenation temperatures of as-milled pure MgH_2 were also given as a baseline for comparison. The effectiveness of additives was evaluated by comparing their $T_{\text{on-set}}$ and T_{end} to those of the as-milled MgH_2 sample without any additives (see the lines in Figure 2).

Transition metals and their hydrides and oxides The most effective additives in this study were found in the IV-A and V-A groups. The elements from VII-A (Mn), VIII-A (Fe, Co, Ni) groups had moderate catalytic effects. For the VI A group, metal Cr presented a moderate improvement; however Mo, Mo oxides, and W oxides seemed to have no effect. Yttrium (III-A group) and Yttrium oxide showed no improvement to the kinetics. For the catalysts in metallic form, Ti exhibited the lowest $T_{\text{on-set}}$, followed by V, Mn, Zr, Nb, Fe, Ni, Cr, and Co.

It was seen that the light elements such as Ti, V, and their compounds were more effective than heavier metals (Zr, Nb, Ta) in the same groups. Another interesting observation was that the metals of Ti, Zr, V, showed stronger catalytic effect than their hydrides and oxides. However, for Nb and Ta metals and compounds, the oxides performed better than their hydrides or the pure metals.

Intermetallic compounds A set of intermetallic compounds as additives was also examined. It was found that the compounds containing Ti and/or V (TiMn₂, TiNb_{0.2}, TiFe, TiAl, Ti₃Al, TiVMn, TiNi, VTiCr) [7] exhibited relatively low T_{on-set} and T_{end}. It was noted that some of the compounds, such as TiMn₂, TiFe, TiVMn, and VTiCr, were themselves hydride-forming materials with very good reaction kinetics with hydrogen. [40] LaNi₅, which is another well-known alloy for hydrogen storage, showed moderate improvement on the dehydrogenation of MgH₂. However, the AlLi compound, which contains no transition metal, showed limited effect on the dehydrogenation.

III-B and IV-B groups The elements in the group of post-transition metals were generally less effective than the transition metals, with two notable exceptions. The addition of Sn significantly reduced the T_{on-set} to 250.1 °C and the addition of Al reduced the T_{on-set} and the T_{end} by approximately 30 °C. It has been reported that the addition of III-B and IV-B group elements including Al, In, Si, and Sn can destabilize MgH₂ thermodynamically [1, 2, 4, 6, 22, 41, 42] The destabilization reaction can be given generally as: $\text{MgH}_2 + x\text{A} \rightarrow \text{MgA}_x + \text{H}_2$. The results of this study suggest that the destabilizing of MgH₂ by these III-B and IV-B elements do not necessarily result in an improvement of the kinetics of the dehydrogenation of MgH₂. For example, the addition of indium was able to thermodynamically destabilize MgH₂ significantly, while significant reduction of the dehydrogenation temperature was only observed when indium was used in combination with another additive, such as TiMn₂. [1]

Carbon and LiH Carbon materials that were tested in this work, regardless of the form of those carbon materials (micrometer-sized graphite, nanometer-sized carbon nanotube carbon, or mesoporous graphite), showed no improvement to the dehydrogenation kinetics. These results are consistent with previous reports. [35, 43, 44] It should be pointed out, however, that there have been intense efforts recently on using carbon materials as additives for tailoring the hydrogen storage properties of MgH_2 . It was reported that carbon could offer various advantages including improving cyclic stability, [36] and enhancing the thermal conductivity of the hydride. [45-47] Moreover, LiH as a dopant was also tested in the present work; however, it showed no improvement on the dehydrogenation, which corresponded to a recent report for LiH doped MgH_2 . [48]

Binary-additives The effects of binary-additives were studied by simultaneously milling MgH_2 with two additives. It can be seen that the addition of indium and TiMn_2 drastically decreased the $T_{\text{on-set}}$ and the T_{end} to 174.2 °C and 234.2 °C, respectively. This is because of a synergetic effect of indium that provided thermodynamic destabilization and TiMn_2 that has been proven as a strong kinetics enhancer. More detailed results and discussions on the thermodynamic destabilization of MgH_2 by indium have been reported by the present authors elsewhere. [1] However, the binary-additives such as MgH_2 -5% TiH_2 -1% Nb_2O_5 and MgH_2 -5% TiH_2 -5% Ni, did not show significant improvements compared to those with similar mono-additives such as MgH_2 -5% TiH_2 , MgH_2 -5% Ni and MgH_2 -1% Nb_2O_5 . It can be inferred that the catalytic mechanisms of various transition metals and transition metal compounds are very similar to each other, if not exactly the same. Therefore, adding another catalyst into the system is probably similar to increasing the amount of catalyst, which is discussed in the next section.

Content of additives In order to examine the effect of the relative content of additives on the dehydrogenation behavior of MgH_2 , three samples with the addition of 1, 3 and 5 mol% of Nb_2O_5 were prepared and their TGA weight loss analysis are shown in Figure 3. Figure 3 shows that the dehydrogenation reaction of MgH_2 -5 mol% Nb_2O_5 occurred at a temperature that is approximately 10 °C lower compared to the sample with 1 mol% Nb_2O_5 . As expected, the total weight loss (i.e. hydrogen capacity of the systems) decreased when more Nb_2O_5 additive was added to the MgH_2 . Also, the result showed that the $T_{\text{on-set}}$ and the T_{end} decreased from 238.6 °C to 220.6 °C, and 285.6 °C to 266.2 °C, respectively, as more Nb_2O_5 was added. It was found that the $T_{\text{on-set}}$, and particularly the T_{end} , were also affected by the amount of hydrogen that was released from the system. Despite that, the comparison of the pure MgH_2 (see Figure 1) and MgH_2 - Nb_2O_5 systems showed that 1 percentage of Nb_2O_5 doping caused a significant reduction of dehydrogenation temperature (e.g. $T_{\text{on-set}}$ is 323.5 °C for the as-milled MgH_2 and 238.6 °C for MgH_2 -1 mol% Nb_2O_5). This result indicated that increasing the quantity of the additive from 1 to 5 mol% did not provide significant further benefits, while it significantly reduced the hydrogen capacity of the material. A similar trend was also reported by Choi et al., [9] in which the change of on-set dehydrogenation temperature of MgH_2 - TiH_2 system was studied, varying the TiH_2 content from 2 mol% to 20 mol%.

4. Conclusion

In summary, forty-nine MgH_2 -additive compositions were examined based on the dehydrogenation temperature of MgH_2 through the use of TGA analysis. Additives with strong

catalytic effects were found to be Ti-based, V-based metals, hydride, as well as some intermetallic compounds. Elements such as Al, In, Ge, Sn, Si did not show significant improvement of the kinetic rates of the dehydrogenation of MgH_2 . Moreover, the dehydrogenation temperature was further reduced by combining TiMn_2 , a kinetic additive, and indium, a thermodynamic destabilizer.

Acknowledgements

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Figure captions:

Figure 1. Determination of calculated on-set temperature ($T_{\text{on-set}}$) and calculated end temperature (T_{end}) based on TGA dehydrogenation curve of as-milled MgH_2 .

Figure 2. Effect of various additives on dehydrogenation temperature of MgH_2 . The percentage of the additives to MgH_2 was in molar ratio (mol%).

Figure 3. Effect of varying amounts of additive on the TGA dehydrogenation behavior of MgH_2 .

Supplementary Information: An Experimental Survey of Additives for Improving Dehydrogenation Properties of Magnesium Hydride

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Table 1. Raw materials for this study.

Materials	Supplier (Part No.)	Remarks
MgH ₂	Sigma-Aldrich (683043)	Pulverized by hydriding-dehydriding cycle, denoted as TiMn ₂ Sintered
Ti _{0.98} Zr _{0.02} V _{0.43} Fe _{0.09} Cr _{0.05} Mn _{1.5} alloy	Sigma-Aldrich (685941)	
TiNb _{0.2} alloy	Custom making	
TiFe alloy	Alfa Aesar (43500)	
TiAl alloy	Alfa Aesar (88393)	
Ti ₃ Al alloy	Alfa Aesar (43101)	Pulverized by hydriding-dehydriding cycle, denoted as TiVMn
TiV _{0.62} Mn _{1.5} alloy	GfE, Hydralloy C	
TiNi alloy	Alfa Aesar (88384)	
V _{0.75} Ti _{0.05} Cr _{0.2} alloy	Custom making	
LaNi ₅ alloy	Sigma-Aldrich (685933)	
AlLi alloy	Sigma-Aldrich (426490)	Arc-melted, pulverized by hydriding denoted as VTiCr
LiH	Alfa Aesar (41596)	
Y	Sigma-Aldrich (261327)	
Y ₂ O ₅	Sigma-Aldrich (205168)	
Ti	Sigma-Aldrich (268496)	
TiH ₂	Sigma-Aldrich (209279)	Hydrided V metal powder
Zr	Alfa Aesar (00847)	
ZrH ₂	Alfa Aesar (89484)	
ZrO ₂	Sigma-Aldrich (544760)	
V	Alfa Aesar (12234)	
VH	Custom making	Hydrided Nb metal powder
V ₂ O ₃	Alfa Aesar (43377)	
Nb	Sigma-Aldrich (262722)	
NbH	Custom making	
Nb ₂ O ₅	Sigma-Aldrich (203920)	
Ta	Sigma-Aldrich (262846)	
Ta ₂ O ₅	Sigma-Aldrich (204536)	
Cr	Alfa Aesar (10148)	
Mo	Alfa Aesar (10030)	
MoO ₂	Sigma-Aldrich (234761)	
MoO ₃	Sigma-Aldrich (711209)	
WO ₃	Sigma-Aldrich (550086)	
Mn	Sigma-Aldrich (266132)	
Fe	Alfa Aesar (10214)	
Co	Alfa Aesar (10453)	
Ni	Alfa Aesar (43214)	
Al	Alfa Aesar (43891)	
Ge	Alfa Aesar (10190)	
In	Alfa Aesar (11024)	
Sn	Alfa Aesar (10397)	
Si	Alfa Aesar (12681)	
Pb	Alfa Aesar (10223)	
Sb	Alfa Aesar (10099)	
Graphite	Alfa Aesar (40798)	
Carbon nanotube	Alfa Aesar (44945)	
Mesoporous Carbon	Sigma-Aldrich (699624)	