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The hydrogen storage properties of destabilized $\text{MgH}_2\text{-AlH}_3$ (2:1) system

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Abstract

Systematic investigations on the hydrogen storage properties of AlH_3 destabilized MgH_2 is investigated. It is found that the $\text{MgH}_2/\text{AlH}_3$ (2:1) composite system showed improved dehydrogenation performance compared with that of as-milled MgH_2 alone. The dehydrogenation process in the $\text{MgH}_2/\text{AlH}_3$ composite can be divided into two stages. During the first dehydrogenation process, AlH_3 decomposed first to produce Al with hydrogen release. In the second dehydrogenation stage, the as-formed Al phase reacts with MgH_2 to form $\text{Mg}_{17}\text{Al}_{12}$ phase at a temperature of about 250 °C, which is about 80 °C lower than the decomposition temperature of as-milled MgH_2 . The second step decomposition enthalpy of the system was determined by differential scanning calorimetry measurements and the enthalpies change to be 45.0 kJ mol⁻¹ H₂, which is smaller than that of MgH_2 alone (75.7 kJ mol⁻¹ H₂). Kissinger analysis indicated that the apparent activation energy, E_A , for the MgH_2 -relevant decomposition in $\text{MgH}_2\text{-AlH}_3$ composite was 94.0 kJ mol⁻¹, which is 68.0 kJ mol⁻¹ less than for as-milled MgH_2 (162.0 kJ mol⁻¹). Rehydrogenation processes show that $\text{Mg}_{17}\text{Al}_{12}$ is fully reversible. It is believed that the formation of the $\text{Al}_{12}\text{Mg}_{17}$ phase during the dehydrogenation process alters the reaction pathway of the $\text{MgH}_2\text{-AlH}_3$ (2:1) composite system and improves its thermodynamic properties accordingly.

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Keywords: Hydrogen storage; Magnesium hydride; Aluminium hydride; Destabilized system

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1. Introduction

Hydrogen is an ideal energy carrier currently under consideration as an alternative fuel for the future, such as in automotive applications. Although hydrogen has a promising, bright future in the energy field, the application of hydrogen requires a safe and efficient storage technology. On the other hand, storage of hydrogen is one of the key challenges in developing the hydrogen economy, especially on-board hydrogen storage in transportation applications. Currently, there are three main on-board hydrogen storage approaches including, specifically: compressed hydrogen gas, cryogenic and liquid hydrogen, as well as solid-state hydrogen storage. Although with the compressed and liquid storage options, hydrogen is easily accessible for use, these storage methods still experience major problems for on-board hydrogen storage in fuel cell vehicles according to U.S. DOE's target, particularly in terms of safety, cost, as well as high volumetric and gravimetric densities [1-3]. Therefore, storing of hydrogen in solid state materials is an alternative to compressed and liquid hydrogen storage.

Due to its large gravimetric density (7.6 wt% H₂), with the added advantages of low cost [4,5] and superior reversibility, MgH₂ show great potential as suitable solid state hydrogen storage materials compared with other metal hydrides and complex hydride such as LaNi [6], LiAlH₄ [7-10], LiBH₄ [11-13], and Mg(BH₄)₂ [14]. Nevertheless, MgH₂ still suffers from both unfavourable thermal stability (76 kJ mol⁻¹ H₂) and slow sorption kinetics. Many studies have been conducted to overcome these problems such as: by reducing the particle size [15]; doping with catalyst [16-26] and reacting with another element (destabilization concept) such as Si [27], Al [4] and Ge [28].

The destabilization concept has been extensively investigated as an approach aimed at modifying the thermodynamics and kinetics of the hydrogen sorption reaction. This approach is aimed at modifying the thermodynamics and kinetics of the hydrogen sorption reaction by combining two or more hydrides [29,30]. Based on this, many MgH₂-alanate destabilized systems have been investigated [31-37]. For example, Zhang et al. [31] showed that the addition of LiAlH₄ has a modest destabilisation effect, reducing the enthalpies of MgH₂-relevant decomposition to 45 kJ mol⁻¹ H₂. They claimed that the formation of Al₁₂Mg₁₇ and Li_{0.92}Mg_{4.08} as a reaction product during the dehydrogenation process alters the reaction pathway of the system. NaAlH₄ has also been studied as a destabilisation agent for MgH₂, as reported in our previous paper [34,36]. The mutual destabilization of MgH₂ and NaAlH₄ in the reactive hydride composite MgH₂-NaAlH₄ is attributed to the formation of intermediate compounds, namely, NaMgH₃ and Mg₁₇Al₁₂.

Following on from this idea, in this study, the hydrogen storage performance of the MgH₂ - AlH₃ destabilized system (molar ratio: 2:1) is investigated. To the best of the author's knowledge, so far, there have been few reports on the hydrogen storage properties of MgH₂/AlH₃ mixed system [38-40]. In general, Liu et al. [38,40] show that the addition of AlH₃ destabilized MgH₂, further improves the hydrogenation properties of MgH₂. The authors reported that the apparent activation of energy for the dehydriding of MgH₂ is reduced from 174.6 kJ mol⁻¹ for as-milled MgH₂ to 138.1 kJ mol⁻¹ for MgH₂ mixed with AlH₃ and this is responsible for the improvement in the dehydriding kinetics of MgH₂. Meanwhile, Iosub et al. [39] studied an effort to thermodynamically stabilize the AlH₃ by MgH₂ and reported that the effect of alane stabilization (i.e., the increase in the desorption enthalpy) by partial substitution of Mg for Al was not observed. However, neither of the articles reported the thermodynamics properties (enthalpy change) of the MgH₂ in the MgH₂/AlH₃ system. It is well-known that thermodynamic destabilization is achieved when the mixed hydrides react and form a new intermediate that may facilitate thermodynamics and kinetics properties of hydrogen release and uptake. Accordingly, in this paper, the author focused on investigating thermodynamics and kinetics properties of the MgH₂/AlH₃ composite system. It is envisaged that this study will be helpful in improving the properties of Mg-Al-H systems.

2. Experimental details

MgH₂ (hydrogen storage grade) was purchased from Sigma Aldrich. Ball milling of MgH₂ and AlH₃ powders in the mole ratio of 2 : 1 was performed in a planetary ball mill (NQM-0.4) for 1 h at the rate of 400 rpm. Handling of the samples was conducted in an MBraun Unilab glove box filled with high purity Ar atmosphere. Samples were put into a sealed stainless steel vial together with hardened stainless steel balls. The ratio of the weight of balls to the weight of powder was 30 : 1. For comparison purposes, pristine MgH₂ and AlH₃ were also milled for 1 h.

The temperature programmed desorption (TPD) and re/dehydrogenation kinetics experiments were performed in a Sieverts-type pressure-composition-temperature (PCT) apparatus (Advanced Materials Corporation). The sample was loaded into a sample vessel in the glove box. For the TPD experiment, all the samples were heated in a vacuum chamber, and the amount of desorbed hydrogen was measured to determine the lowest decomposition temperature. The heating rate for the TPD experiment was $5\text{ }^{\circ}\text{C min}^{-1}$, and samples were heated from room temperature to $450\text{ }^{\circ}\text{C}$. The re/de-hydrogenation kinetics measurements were performed at the desired temperature with initial hydrogen pressures of 3.0 MPa and 0.001 MPa , respectively.

XRD analysis was performed using a Rigaku MiniFlex II diffractometer with $\text{Cu K}\alpha$ radiation. θ - 2θ scans were carried out over diffraction angles from 25° to 80° with a speed of $2.00\text{ }^{\circ}\text{ min}^{-1}$. Before the measurement, a small amount of sample was spread uniformly on the sample holder, which was wrapped with plastic wrap to prevent oxidation. Thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) of the dehydrogenation process was carried out on a Mettler Toledo TGA/DSC 1. The sample was loaded into an alumina crucible in the glove box. The crucible was then placed in a sealed glass bottle in order to prevent oxidation during transportation from the glove box to the TGA/DSC apparatus. An empty alumina crucible was used for reference. The samples were heated from room temperature to $500\text{ }^{\circ}\text{C}$ under an argon flow of 30 ml min^{-1} , and different heating rates were used.

3. Results and discussion

Fig. 1 exhibits the thermal desorption performances of the as-milled AlH_3 , the as-milled MgH_2 , and the MgH_2 - AlH_3 composite. The as-milled AlH_3 starts to desorb hydrogen at around $125\text{ }^{\circ}\text{C}$ and about $10.0\text{ wt.}\%$ of hydrogen is released according to the following reaction:

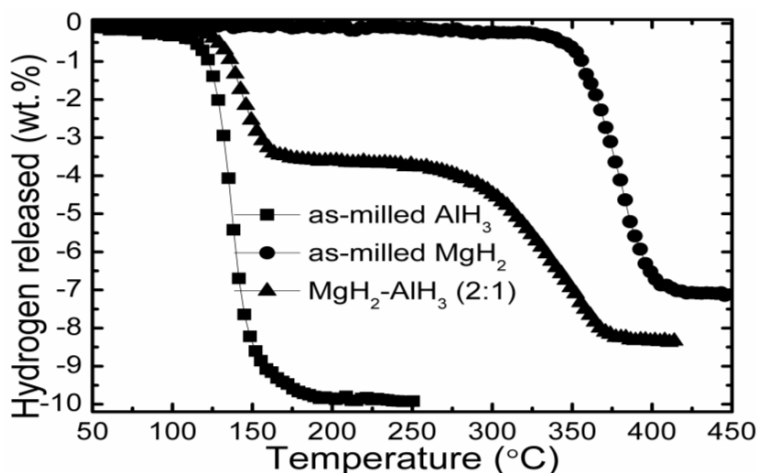


Fig. 1. Thermal desorption performances patterns for the dehydrogenation of as-milled AlH_3 , as-milled MgH_2 , and the MgH_2 - AlH_3 composite.

Meanwhile, the as-milled MgH_2 starts to release hydrogen at about $330\text{ }^{\circ}\text{C}$ and desorbs about $7.1\text{ wt.}\%$ H_2 after $420\text{ }^{\circ}\text{C}$ (Eqn 2).



For the MgH_2 - AlH_3 composite, there are two significant stages of dehydrogenation that occur during the heating process. The first stage, which takes place within the temperature range from 125 to $200\text{ }^{\circ}\text{C}$, is attributed to the decomposition of AlH_3 , as indicated in eqn (1). The second dehydrogenation stage, starting at about $250\text{ }^{\circ}\text{C}$ and completed at about $400\text{ }^{\circ}\text{C}$, can be attributed to the MgH_2 -relevant decomposition with reduced dehydrogenation

temperatures compared to the milled MgH_2 .

In order to investigate the reaction progress and mechanism, XRD measurements were performed on the MgH_2 - AlH_3 composite after being milled and after dehydrogenation at 200 °C and 400 °C, as shown in Fig. 2. From the results in Fig. 2(a), it can be seen that MgH_2 and AlH_3 phases are detected in the as-milled MgH_2 - AlH_3 composite. Fig. 2(b) shows the XRD pattern of the MgH_2 - AlH_3 composite after dehydrogenation at 200 °C. Clearly, the pattern indicates the presence of Al besides the MgH_2 . The fact that no AlH_3 phase was found indicates that the Eq. (1) reaction was completed at this stage. After dehydrogenation at 400 °C, the XRD pattern of Fig. 2(c) reveals that the intermediate phases $\text{Al}_{12}\text{Mg}_{17}$ were eventually formed in the composite system. These results confirmed that the hydrogen released in the second stage is from the MgH_2 -relevant decomposition through the reactions in Eq. (3). This process occurs at a temperature 80 °C lower than the decomposition temperature of the pure as-milled MgH_2 .

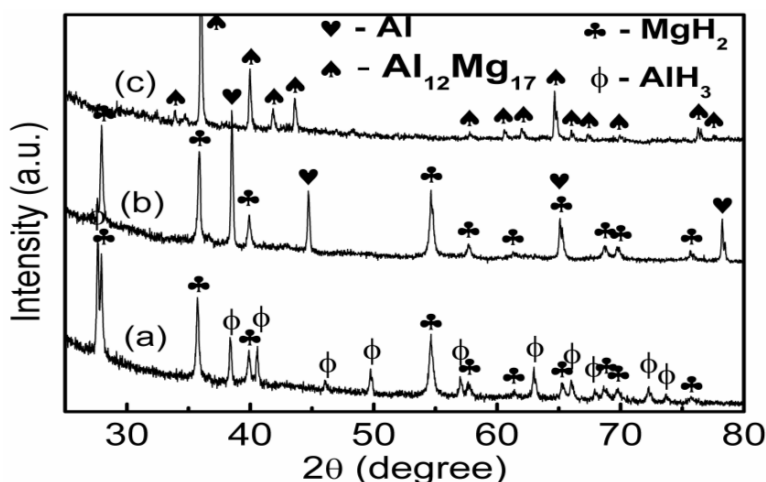


Fig. 2. X-ray diffraction patterns of the 1MgH_2 - AlH_3 composite (a) after milling, and after dehydrogenation at (b) 200 °C and (c) 400 °C.

Fig. 3 illustrates the TGA/DSC results of the MgH_2 - AlH_3 composite. For the DSC curve, the first endothermic peak at 160 °C corresponds to the decomposition of AlH_3 (eqn (1)); while the second endothermic peak at about 380 °C is assigned to the decomposition of MgH_2 (eqn (3)). The two endothermic processes in the DSC curve agree well with the two dehydrogenation stages shown by the TGA curve. Fig. 4 presents the comparison of DSC traces of the MgH_2 - AlH_3 composite and the as-milled MgH_2 . Compared to the as-milled MgH_2 , the temperature of the MgH_2 -relevant decomposition in the MgH_2 - AlH_3 composite is clearly decreased. It starts to release hydrogen at about 315 °C, 80 °C below the temperature for the as-milled MgH_2 (395 °C). This decrease in the hydrogen release temperature is correlated with the results observed in the PCT measurement (Fig. 1).

As discussed in the introduction section, we expect that the adding of AlH_3 will affect the thermodynamics properties of MgH_2 (the reaction enthalpy of the MgH_2 decomposition). To determine the enthalpy (ΔH_{dec}) of MgH_2 decomposition, the DSC curves were analysed by STARE software. The hydrogen desorption enthalpy was obtained from the integrated peak areas. From Fig. 4, for the as-milled MgH_2 , the hydrogen desorption enthalpy can be calculated as $75.7 \text{ kJ mol}^{-1} \text{ H}_2$. This value is almost the same as the theoretical value ($76.0 \text{ kJ mol}^{-1} \text{ H}_2$). The reaction enthalpies of the MgH_2 - AlH_3 composite were determined by the same methods. For the MgH_2 - AlH_3 composite, the enthalpy change calculated from the second endothermic peak of DSC curves is $45.0 \text{ kJ mol}^{-1} \text{ H}_2$, which is lower than the overall decomposition enthalpy of as-milled pure MgH_2 ($75.7 \text{ kJ mol}^{-1} \text{ H}_2$). This result indicates that the presence of AlH_3 destabilizes MgH_2 .

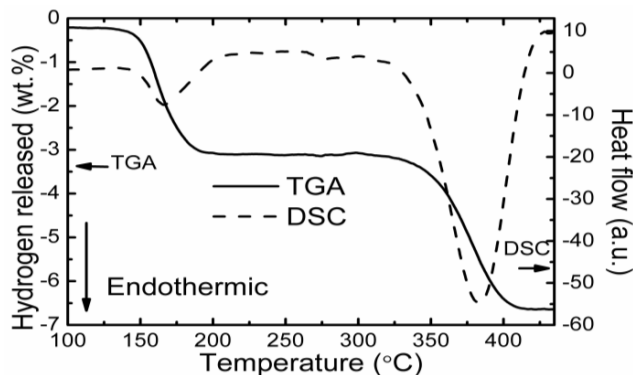


Fig. 3. TGA and DSC traces of the $\text{MgH}_2\text{-AlH}_3$ composite. Heating rate: $10\text{ }^\circ\text{C min}^{-1}$, argon flow: 30 ml min^{-1} .

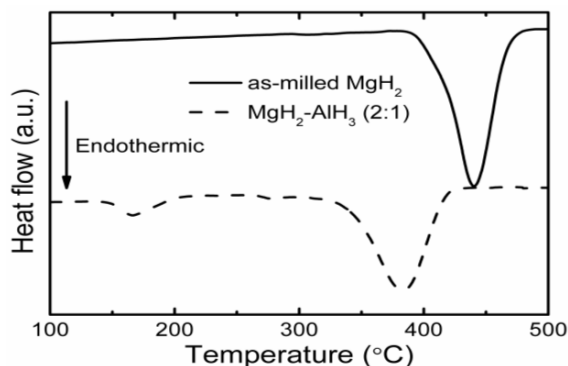


Fig. 4. DSC traces of the as-milled and the $\text{MgH}_2\text{-AlH}_3$ composite. Heating rate: $10\text{ }^\circ\text{C min}^{-1}$, argon flow: 30 ml min^{-1} .

The improvement of the decomposition temperature and sorption kinetic is related to the energy barrier for H_2 release from MgH_2 . In the present study, the activation energy for decomposition of the MgH_2 was reduced by adding AlH_3 . To calculate the activation energy required for the MgH_2 -relevant decomposition, the Kissinger analysis [41] was used. The Kissinger analysis is based on differential scanning calorimetry (DSC) analysis of decomposition or formation processes. The endo- or exothermic peak positions related to these reactions are related to the heating rate. The apparent activation energy, E_A , can be obtained from the following equation:

$$\ln[\beta/T_p^2] = -E_A/RT_p + A \quad (4)$$

where β is the heating rate, T_p is the peak temperature in the DSC curve, R is the gas constant, and A is a linear constant. Thus, the activation energy, E_A , can be obtained from the slope in a plot of $\ln[\beta/T_p^2]$ versus $1000/T_p$. Fig. 5 shows DSC traces for the as-milled MgH_2 and $\text{MgH}_2\text{-AlH}_3$ composite at different heating rates ($\beta = 10, 15,$ and $20\text{ }^\circ\text{C min}^{-1}$, respectively). Obviously, both of the $\ln k$ versus $1/T$ plots exhibit good linearity as shown in Fig. 6. The value of E_A is calculated to be 162.0 and 94.0 kJ mol^{-1} for the as-milled MgH_2 and $\text{MgH}_2\text{-AlH}_3$ composite. This result suggests that the mixing of AlH_3 decreases the kinetic barrier for the dehydrogenation from commercial MgH_2 .

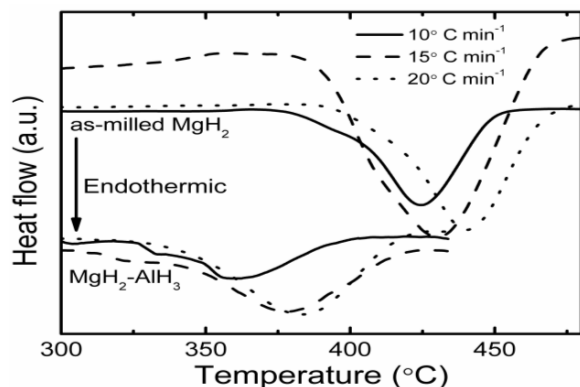


Fig. 5. DSC traces at different heating rates for the as-milled MgH_2 and the $\text{MgH}_2\text{-AlH}_3$ composite.

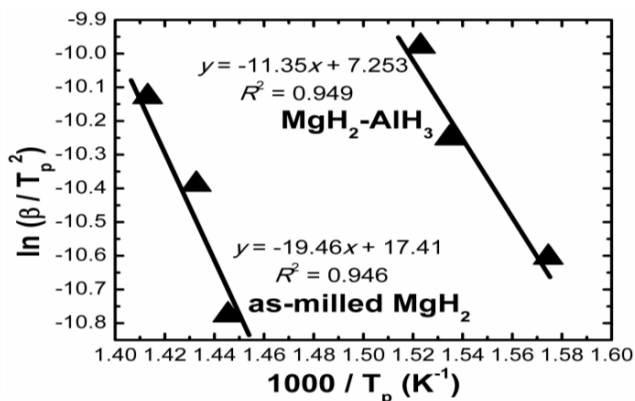


Fig. 6. The Kissinger's plot of the dehydrogenation for the $\text{MgH}_2\text{-AlH}_3$ composite as compared with the as-milled MgH_2 .

Fig. 7 shows the isothermal dehydrogenating kinetics measurements at 320 °C after a rehydrogenation process under ~3 MPa of H₂ at 300 °C for the MgH₂-AlH₃ composite. For comparison, the as-milled MgH₂ is also included in this figure. As can be seen, pure MgH₂ releases about 2.0 wt.% hydrogen after 30 min. Milled with AlH₃, the dehydrogenation kinetics of MgH₂ was improved, after which the MgH₂-AlH₃ composite released about 4.9 wt.% hydrogen after 30 min of dehydrogenation. This result indicates that the MgH₂-relevant dehydrogenation kinetics is significantly improved after combining with AlH₃.

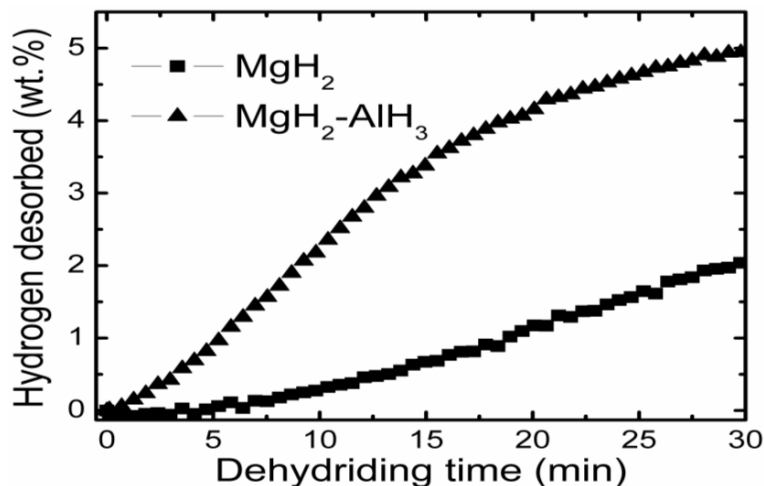


Fig. 7. Isothermal desorption kinetics curves for the as-milled MgH₂ and the MgH₂-AlH₃ composite at 320 °C under vacuum.

In order to investigate the reversibility of the MgH₂-AlH₃ composite, the rehydrogenation of the dehydrogenated samples was performed under ~5 MPa of H₂ at 350 °C. Fig. 8 exhibits the isothermal rehydrogenation kinetics of the MgH₂-AlH₃ composite. The MgH₂-AlH₃ composite achieves 80% of its maximum absorption capacity within 60 min.

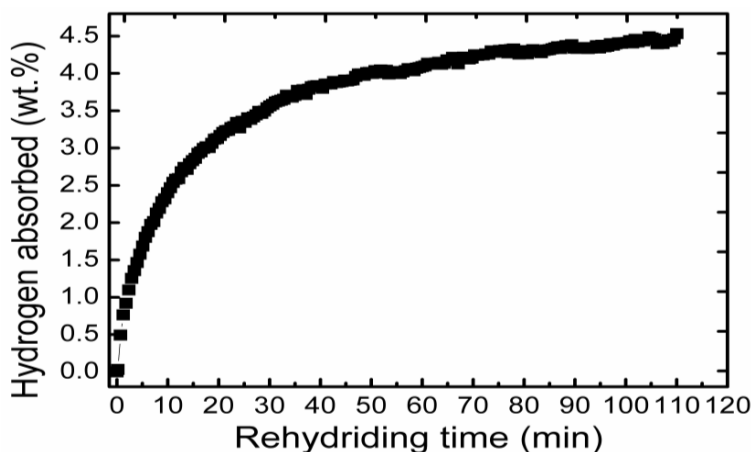
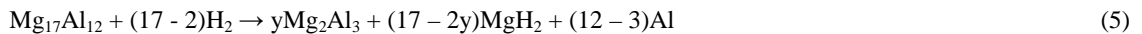


Fig. 8. Isothermal absorption kinetics measurement of the MgH₂-AlH₃ composite at 350 °C under 5 MPa hydrogen pressure.

In order to determine the rehydrogenation products, XRD measurements were carried out on the rehydrogenated MgH₂-AlH₃ sample. Fig. 7 displays the XRD patterns of the MgH₂-AlH₃ composite after rehydrogenation under ~3 MPa of H₂ at 350 °C. From the pattern, it can be seen that the peaks correspond to MgH₂, and Al, along with a small peak for Al₃Mg₂ that appears after rehydrogenation. A small amount of MgO was also detected in the

dehydrogenation spectra due to slight oxygen contamination. The fact that no AlH_3 peak was detected confirms that reaction (1) is irreversible under moderate conditions. After rehydrogenation, the $\text{Mg}_{17}\text{Al}_{12}$ peaks disappear, and peaks of MgH_2 , Al, and small peaks of Al_3Mg_2 appear. This indicates that $\text{Mg}_{17}\text{Al}_{12}$ can be dissociated into Mg_2Al_3 , MgH_2 , and Al (Eq. (5)) as reported by previous studies [31,32,42,43].



If higher hydrogenation pressure were applied, Mg_2Al_3 would subsequently be transformed into MgH_2 and Al, as shown in Eq. (6) [44]:



In this study, Mg_2Al_3 was barely able to transform into MgH_2 and Al due to the lower hydrogenation pressure applied (3 MPa). This phenomenon is similar to that reported by Zhang et al. [31] for the $\text{MgH}_2\text{-LiAlH}_4$ (4:1) composite, in which their sample was rehydrogenated under 4 MPa. For comparison, Chen et al. [32] reported that no Mg_2Al_3 phase was detected from their $\text{MgH}_2\text{-LiAlH}_4$ (4:1) composite sample after rehydrogenation at 350 °C and under 10 MPa; implying that reaction (6) occurred when the higher hydrogen pressure was applied.

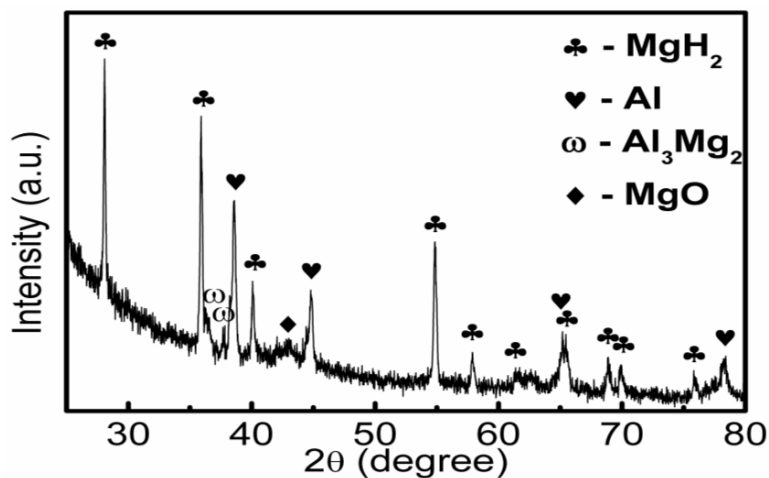


Fig. 9. X-ray diffraction patterns of the $\text{MgH}_2\text{-AlH}_3$ composite after rehydrogenation at 350 °C under 5 MPa hydrogen pressure.

The effect of in situ formed Al from the self-decomposition of AlH_3 is believed to be the primary reason for the improved hydrogen release from the $\text{MgH}_2\text{-AlH}_3$ (2:1) system compared to the unary MgH_2 . The formation of $\text{Al}_{12}\text{Mg}_{17}$ phase due to the reaction between Al and MgH_2 during the dehydrogenation process alters the reaction pathway of the $\text{MgH}_2\text{-AlH}_3$ (2:1) composite system and improves its thermodynamic properties. Moreover, it is speculated that the higher dispersion of Al species increases the close contact and shortens the diffusion path between the reacting phases and thus enhances the dehydrogenation of MgH_2 . In order to improve the hydrogen storage properties of the $\text{MgH}_2\text{-AlH}_3$ composite system, further experiments are currently underway by the introduction of a different type of catalyst to the system.

4. Conclusion

A metal hydride-alanate composite system, $\text{MgH}_2/\text{AlH}_3$ (2:1) was prepared by ball milling, and the hydrogen storage properties and reaction mechanisms were investigated systematically. Upon dehydrogenation, AlH_3 decomposed first to form Al with hydrogen release at below 250 °C. Subsequently, as-formed Al reacts with MgH_2 to produce $\text{Mg}_{17}\text{Al}_{12}$ and hydrogen, respectively, at 250 °C, in which this temperature is about 80 °C lower than the

decomposition temperature for as-milled MgH_2 . DSC measurements indicate the enthalpy change in the decomposition of MgH_2 to be $45 \text{ kJ mol}^{-1} \text{ H}_2$, which is smaller than that of MgH_2 alone ($75.7 \text{ kJ mol}^{-1} \text{ H}_2$). The Kissinger plots for different heating rates in DSC show that the apparent activation energy, E_A , for decomposition of MgH_2 in the $\text{MgH}_2\text{-AlH}_3$ composite is reduced to 94.0 kJ mol^{-1} . It is believed that the formation of intermediate compounds upon dehydrogenation, $\text{Mg}_{17}\text{Al}_{12}$, which change the thermodynamics of the reactions through altering the de/rehydrogenation pathway, plays a critical role in the enhancement of dehydrogenation in the $\text{MgH}_2\text{-AlH}_3$ composite.

Acknowledgements

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