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PAPER

Effect of different additives on the hydrogen storage properties of the MgH₂-LiAlH₄ destabilized system

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The hydrogen storage properties of the MgH₂-LiAlH₄ (4 : 1) composite system with and without additives were studied. 5 wt.% of TiF₃, NbF₅, NiF₂, CrF₂, YF₃, TiCl₃·1/3AlCl₃, HfCl₄, LaCl₃, CeCl₃, and NdCl₃, respectively, was added to the MgH₂-LiAlH₄ (4 : 1) mixture, and their catalytic effect was investigated. Temperature programmed desorption results show that addition of metal halides to the MgH₂-LiAlH₄ (4 : 1) composite system improves the onset desorption temperature. The hydrogen desorption properties of metal halide-doped MgH₂-LiAlH₄ (4 : 1) composites were also improved as compared to the undoped MgH₂-LiAlH₄ (4 : 1) composite. Furthermore, the activation energy and the change in enthalpy in the doped and undoped composite were measured by differential scanning calorimetry. In addition, the reaction pathway of the MgH₂-LiAlH₄ (4 : 1) composite system and the mechanisms that work in this composite during the de/re-hydrogenation process were determined by X-ray diffraction.

1. Introduction

As one of the ideal candidates as an energy carrier for both mobile and stationary applications, hydrogen is also considered as a material that can avert adverse effects on the environment and reduce dependence on imported oil for countries without natural resources.¹ There are many approaches to store hydrogen, including high pressure, cryogenics, and chemical compounds that reversibly release H₂ upon heating (solid state storage). Storing hydrogen in solid state form offers several benefits over a pressurized gas or a cryogenic liquid form. Among the solid-state hydrogen storage materials, much work has been focused on MgH₂, due to its high hydrogen capacity (7.6 wt%), with the added advantages of low cost,^{2,3} and superior reversibility.⁴ However, MgH₂ only starts to desorb hydrogen above 300 °C,⁵ and has slow desorption kinetics.⁶ These disadvantages have been overcome by reducing the particle size,⁷ doping with catalysts,^{8–10} and reacting with other metal hydrides (destabilization concept).^{11–16} The destabilization concept has been extensively investigated as an approach aimed at modifying the thermodynamics and kinetics of the hydrogen sorption reaction. Vajo *et al.*¹⁷ destabilised MgH₂ by adding Si. The results indicated that the MgH₂/Si system could be practical

for hydrogen storage at reduced temperature. However, the formation of Mg₂Si would reduce the gravimetric hydrogen density because Si cannot be hydrogenated, so this intermediate phase seems hard to make reversible. Zhang *et al.*¹¹ showed that MgH₂ can be destabilized effectively by LiAlH₄. They found that the reaction enthalpy of the MgH₂-relevant decomposition in MgH₂-LiAlH₄ composites (1 : 1, 1 : 2, and 4 : 1 in mole ratio) was reduced by 31, 27.4, and 15 kJ mol⁻¹ H₂ compared to as-milled pristine MgH₂ (76 kJ mol⁻¹ H₂). According to Zhang *et al.*, the hydrogen desorption is observed to take place in two stages: the first stage is the two-step decomposition of LiAlH₄ as shown in eqn (1) and (2).

During the second stage, the yielded LiH and Al phases decompose the MgH₂ to form Li_{0.92}Mg_{4.08} and Mg₁₇Al₁₂ phases, as shown in eqn (3) and (4).

The hydrogen absorption at 400 °C under 4.0 MPa hydrogen involves two reactions, as shown in eqn (5) and (6).

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Recently, Chen *et al.*¹³ confirmed the two-stage nature of the hydrogen desorption in $\text{LiAlH}_4 + x\text{MgH}_2$ ($x = 1, 2.5$, and 4). They found that the two-stage decomposition was similar to what is described by eqn (1), (2), (3), and (4), but from the X-ray diffraction (XRD) pattern, the rehydrogenated composites showed the absence of an Al_3Mg_2 phase, which indicates that $\text{Mg}_{17}\text{Al}_{12}$ is fully transformed into MgH_2 and Al as shown in reaction (7):

Chen *et al.* found that eqn (7) could be fully reversible without formation of Mg_2Al_3 if a high pressure of hydrogen (>10 MPa) was applied during the rehydrogenation process. Both articles claimed that the destabilization of MgH_2 by the LiAlH_4 resulted from the formation of $\text{Al}_{12}\text{Mg}_{17}$ and $\text{Li}_{0.92}\text{Mg}_{4.08}$. Although the hydrogen storage properties of MgH_2 were improved after combination with LiAlH_4 , it still doesn't fulfil the requirements for practical application as a suitable hydrogen storage material. Therefore, it is of importance to find a catalyst or additive that can improve the hydrogen storage properties of the MgH_2 - LiAlH_4 composite system.

In this paper we report the hydrogen storage properties of MgH_2 - LiAlH_4 (4 : 1) composite system with additives including 5 wt.% of TiF_3 , NbF_5 , NiF_2 , CrF_2 , YF_3 , $\text{TiCl}_3 \cdot 1/3(\text{AlCl}_3)$, HfCl_4 , LaCl_3 , CeCl_3 , and NdCl_3 , respectively, and investigated the additives' catalytic effects.

2. Experimental details

MgH_2 (hydrogen storage grade), LiAlH_4 ($\geq 95\%$), TiF_3 , NbF_5 (98%), NiF_2 , CrF_2 (98%), YF_3 (99.9%), $\text{TiCl}_3 \cdot 1/3(\text{AlCl}_3)$, and HfCl_4 (98%) were purchased from Sigma Aldrich. LaCl_3 (99.9%), CeCl_3 (99.5%), and NdCl_3 (99.9%) were obtained from Alfa Aesar. Ball milling (BM) of MgH_2 and LiAlH_4 powders in the mole ratio of 4 : 1 was performed in a planetary ball mill (QM-3SP2) for 18 min at the rate of 400 rpm. For simplicity, the mixture of MgH_2 and LiAlH_4 with molar ratio of 4 : 1 will be referred to as MgH_2 - LiAlH_4 composite. 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. 5 wt.% of TiF_3 , NbF_5 , NiF_2 , CrF_2 , YF_3 , $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$, HfCl_4 , LaCl_3 , CeCl_3 , and NdCl_3 was respectively mixed with MgH_2 - LiAlH_4 under the same conditions to investigate their catalytic effects. Pure MgH_2 and LiAlH_4 were also prepared under the same conditions for comparison purposes.

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 °C/min, and samples were heated from room temperature to 450 °C. The re/dehydrogenation kinetics measurements were performed at the desired temperature

with initial hydrogen pressures of 3.0 MPa and 0.001 MPa, respectively.

The phase structures of the samples before and after desorption, as well as after rehydrogenation, were determined by X-ray diffraction (XRD, GBC MMA X-ray diffractometer with Cu K α radiation). Before measurement, a small amount of sample was spread uniformly on the sample holder, which was wrapped with a plastic wrap to prevent oxidation. θ - 2θ scans were carried out over diffraction angles from 25° to 80° with a speed of 2.00°/min.

Differential scanning calorimetry (DSC) analysis of the dehydrogenation process was carried out on a Mettler Toledo TGA/DSC 1. About 2–6 mg of 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 DSC apparatus. An empty alumina crucible was used as the reference material. The samples were heated from room temperature to 500 °C under an argon flow of 30 ml/min, and different heating rates were used.

3. Results and discussion

Fig. 1 displays the TPD performance of the MgH_2 - LiAlH_4 composite system. The as-milled LiAlH_4 and as-milled MgH_2 were also included for comparison purposes. The as-milled MgH_2 starts to release hydrogen at about 330 °C and desorbs about 7.1 wt.% H_2 after 420 °C. Meanwhile, the as-milled LiAlH_4 starts to desorb hydrogen at about 142 °C and about 173 °C for the first and second stage, respectively. For the MgH_2 - LiAlH_4 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 130 to 250 °C, is attributed to the two-step decomposition of LiAlH_4 , as indicated in eqn (1) and (2). The second dehydrogenation stage, starting at about 270 °C and completed at about 360 °C, can be attributed to the MgH_2 -relevant decomposition. These two stages of dehydrogenation are of the same order as reported by Zhang *et al.*¹¹ and Chen *et al.*¹³

In order to investigate the reaction progress and mechanism, XRD measurements were performed on the MgH_2 - LiAlH_4

Fig. 1 TPD curves of the as-milled MgH_2 , the as-milled LiAlH_4 , and the MgH_2 - LiAlH_4 composite.

Fig. 2 XRD patterns of the MgH_2 - LiAlH_4 composite after 18 min ball milling (a), and after dehydrogenation at (b) 250 °C and (c) 400 °C.

composite after dehydrogenation at 250 °C and 400 °C, as shown in Fig. 2. The as-milled MgH_2 - LiAlH_4 is also included in this figure. From Fig. 2(a), it can be seen that MgH_2 and LiAlH_4 phases are present in the as-milled MgH_2 - LiAlH_4 composite. Fig. 2(b) indicates the presence of LiH and Al phases beside the MgH_2 after dehydrogenation at 250 °C. The fact that no LiAlH_4 phase was found indicates that the reactions in eqn (1) and (2) had been completed at this stage. After dehydrogenation at 400 °C, the XRD pattern of Fig. 2(c) reveals that the intermediate phases $\text{Li}_{0.92}\text{Mg}_{4.08}$ and $\text{Al}_{12}\text{Mg}_{17}$ were eventually formed in the composite system besides Mg . These results confirmed that the hydrogen released in the second stage is from the MgH_2 -relevant decomposition through the reactions in eqn (3) and (4), and the decomposition of the excess MgH_2 (Eqn 8), which occurs at a temperature 60 °C lower than the decomposition temperature of the pure as-milled MgH_2 . In this study, it was found that the decomposition temperatures of the first and second stage dehydrogenation are quite similar to what was reported by Zhang *et al.*,¹¹ but slightly higher compared to those reported by Chen *et al.*¹³ This difference may be due to the different duration of the milling process, as Chen *et al.* reported that the sample was ball milled for 10 h, as compared to 18 min in this study.

Fig. 3(a) and (b) shows the influence of catalytic additives on the MgH_2 - LiAlH_4 composite decomposition temperature as measured by temperature-programmed-desorption (TPD). The undoped MgH_2 - LiAlH_4 is also included for comparison. Among the metal fluorides used in this study (Fig. 3(a)), TiF_3 exhibits a strong catalytic influence on MgH_2 - LiAlH_4 decomposition, followed by NiF_2 , CrF_2 , NbF_5 , and YF_3 . The TiF_3 -doped MgH_2 - LiAlH_4 composite sample starts to release hydrogen at about 70 °C and about 180 °C for the first and second stage, respectively, which represents respective reductions of about 60 °C and about 90 °C compared with undoped MgH_2 - LiAlH_4 . Meanwhile, among the metal chloride additives (Fig. 3(b)), $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ shows the best catalytic effect. It seems that the

Fig. 3 TPD curves of (a) the metal fluoride-added MgH_2 - LiAlH_4 and (b) the metal chloride-added MgH_2 - LiAlH_4 composites.

catalytic effect of $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ on the decomposition temperature of MgH_2 - LiAlH_4 composite is similar to that of TiF_3 , in which the decomposition temperature is reduced by about 60 °C and about 90 °C for the first and second stage, respectively, compared with undoped MgH_2 - LiAlH_4 . From the results, one finds also that apart from TiF_3 and $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$, all the other metal halide additives yielded no significant change in the second dehydrogenation stage of the MgH_2 - LiAlH_4 system.

Fig. 4(a) and (b) compares the isothermal dehydrogenation kinetics of MgH_2 - LiAlH_4 composite with and without metal halides at 320 °C. The dehydrogenation of MgH_2 was also examined for comparison under the same conditions. At 320 °C, the pure MgH_2 releases about 3.4 wt.% hydrogen after 60 min. Mixed with LiAlH_4 , the dehydrogenation kinetics of MgH_2 was improved. The composite releases about 4.6 wt.% hydrogen after 40 min of dehydrogenation. With the addition of 5 wt.% metal halide, the results show that all the metal halides improved the dehydrogenation kinetics of MgH_2 - LiAlH_4 compared with undoped MgH_2 - LiAlH_4 . The titanium based metal halide-added MgH_2 - LiAlH_4 showed the best improvement, so that saturation of the dehydrogenation process for the TiF_3 -added MgH_2 - LiAlH_4 sample can be achieved within 10 min, and within 20 min for the $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ -added MgH_2 - LiAlH_4 sample.

Fig. 4 Isothermal dehydrogenation kinetics at 320 °C of (a) the metal fluoride-added MgH₂-LiAlH₄ and (b) the metal chloride-added MgH₂-LiAlH₄ composites.

Fig. 5 presents the DSC traces of the MgH₂-LiAlH₄ composite and the as-milled MgH₂, which is also shown for comparison purposes. For the MgH₂-LiAlH₄ composite, the first exothermic peak at 140 °C is due to the presence of surface hydroxyl impurities in the LiAlH₄ powder, as reported in our previous papers,^{18–20} and the first endothermic peak at 170 °C corresponds to the melting of LiAlH₄.²¹ The second exothermic peak at 180 °C corresponds to the decomposition of liquid LiAlH₄ (first step decomposition, eqn (1)), and the second endothermic peak at 225 °C is assigned to the decomposition of Li₃AlH₆ (second step decomposition, eqn (2)). The last endothermic peak at about 365 °C is due to the decomposition of MgH₂, which occurs at a temperature 55 °C lower than that of the pure as-milled MgH₂ (peak at about 420 °C). This decrease in the hydrogen release temperature is correlated with the results observed in the PCT measurement (Fig. 1).

Fig. 6 and 7 show the DSC curves for all metal halide-added MgH₂-LiAlH₄ samples. Apart from the YF₃-added MgH₂-LiAlH₄ sample, the number of thermal events in all the metal halide-added MgH₂-LiAlH₄ samples is quite different from what occurs in the undoped MgH₂-LiAlH₄. These metal halide-doped

Fig. 5 DSC traces of the MgH₂-LiAlH₄ composite and the as-milled MgH₂.

Fig. 6 DSC traces of (a) the undoped MgH₂-LiAlH₄ and the MgH₂-LiAlH₄ with added (b) TiF₃, (c) NbF₅, (d) NiF₂, (e) CrF₂, and (f) YF₃.

Fig. 7 DSC traces of (a) the undoped MgH₂-LiAlH₄ and the MgH₂-LiAlH₄ with added (b) TiCl₃·1/3AlCl₃, (c) HfCl₄, (d) LaCl₃, (e) CeCl₃, and (f) NdCl₃.

Fig. 8 DSC traces of the as-milled MgH_2 and the $\text{MgH}_2\text{-LiAlH}_4$ at different heating rates. The inset plot is the Kissinger's analysis for as-milled MgH_2 and $\text{MgH}_2\text{-LiAlH}_4$ composite.

$\text{MgH}_2\text{-LiAlH}_4$ samples showed one exothermic peak and two endothermic peaks. The exothermic peak and the first endothermic peak correspond to the decomposition of LiAlH_4 and Li_3AlH_4 , respectively. These results show that LiAlH_4 decomposes without melting under the catalytic effects of TiF_3 , NiF_2 , CrF_2 , NbF_5 , $\text{TiCl}_3\cdot 1/3\text{AlCl}_3$, HfCl_4 , LaCl_3 , CeCl_3 , and NdCl_3 , agreeing well with the results on the 0.5 h ball-milled 4 mol% TiF_3 -doped LiAlH_4 reported by Liu *et al.*²² and our previously reported NbF_5 -doped LiAlH_4 .¹⁸ For all metal halide-added $\text{MgH}_2\text{-LiAlH}_4$ samples, the second endothermic event, corresponding to the decomposition of MgH_2 , is similar to what occurs in the undoped $\text{LiAlH}_4\text{-MgH}_2$ sample. However, the broad peak in the TiF_3 and $\text{TiCl}_3\cdot 1/3\text{AlCl}_3$ -added $\text{MgH}_2\text{-LiAlH}_4$ composites indicates faster dehydrogenation kinetics.

We obtained the activation energy required for the MgH_2 -relevant decomposition using the Kissinger equation,²³ which is usually utilized in thermal analysis as follows:

$$\ln[\beta/T_p^2] = -E_A/RT_p + A \quad (9)$$

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. 8 shows DSC traces for the as-milled MgH_2 and $\text{MgH}_2\text{-LiAlH}_4$ composite at different heating rates ($\beta = 10, 15$, and $20^\circ\text{C min}^{-1}$, respectively). From a Kissinger plot of the DSC data (inset of Fig. 8) the apparent activation energy for the MgH_2 -relevant decomposition in the $\text{MgH}_2\text{-LiAlH}_4$ composite is found to be 126 kJ/mol, which is

much lower than the activation energy of the decomposition of as-milled MgH_2 (162 kJ/mol). This reduction indicates that the apparent activation energy for decomposition of hydrogen from MgH_2 was reduced by adding LiAlH_4 . Table 1 shows the apparent activation energy measured by the Kissinger method for selected metal halide-added $\text{MgH}_2\text{-LiAlH}_4$ and undoped $\text{MgH}_2\text{-LiAlH}_4$ composites, as well as for as-milled MgH_2 . The table shows that, titanium-based metal halides, TiF_3 and $\text{TiCl}_3\cdot 1/3\text{AlCl}_3$, exhibit the best additives in reducing the activation energy for H-desorption in the $\text{MgH}_2\text{-LiAlH}_4$ composites. The apparent activation energies calculated were found to be 83 and 98 kJ/mol for the hydride decomposition of TiF_3 and $\text{TiCl}_3\cdot 1/3\text{AlCl}_3$ -added $\text{MgH}_2\text{-LiAlH}_4$ composites, respectively.

To determine the enthalpy (ΔH_{dec}) of MgH_2 decomposition, the DSC curves were analysed by STARE software. From the integrated peak areas, the hydrogen desorption enthalpy was obtained. 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 ($76 \text{ kJ mol}^{-1} \text{ H}_2$). By the same methods, the reaction enthalpies of the $\text{MgH}_2\text{-LiAlH}_4$ composite and the metal halide-added $\text{MgH}_2\text{-LiAlH}_4$ samples were determined. The enthalpy changes for selected samples are listed in Table 1. For the $\text{MgH}_2\text{-LiAlH}_4$ composite, the enthalpy change calculated from the DSC curves is $61 \text{ kJ mol}^{-1} \text{ H}_2$, which is lower than the overall decomposition enthalpy of pure MgH_2 ($75.7 \text{ kJ mol}^{-1} \text{ H}_2$). This result indicates that the presence of LiAlH_4 destabilizes MgH_2 . The enthalpy change in the $\text{MgH}_2\text{-LiAlH}_4$ composite system is similar to that reported by Zhang *et al.*¹¹ ($61 \text{ kJ mol}^{-1} \text{ H}_2$). After the addition of metal halide, the enthalpy of hydrogen desorption from $\text{MgH}_2\text{-LiAlH}_4$ was similar to that of undoped $\text{MgH}_2\text{-LiAlH}_4$. Although the enthalpy reaction of these metal halide-doped $\text{MgH}_2\text{-LiAlH}_4$ composites remains unchanged, the destabilized complex hydride composites, $\text{MgH}_2\text{-LiAlH}_4$ -5 wt.% metal halides, have better hydrogen storage behaviour with improved hydrogen desorption and faster desorption kinetics.

In order to investigate the reversibility of $\text{MgH}_2\text{-LiAlH}_4$ composite and metal halide-added $\text{MgH}_2\text{-LiAlH}_4$, the rehydrogenation of the dehydrogenated samples was performed under $\sim 3 \text{ MPa}$ of H_2 at 320°C . The MgH_2 system was also examined for comparison. However, the rehydrogenation measurements revealed that the $\text{MgH}_2\text{-LiAlH}_4$ (4 : 1) composite did not show any improvement in kinetics compared with the MgH_2 , as shown in Fig. 9. After 5 min, about 5.0 wt.% hydrogen was absorbed for the MgH_2 while the $\text{MgH}_2\text{-LiAlH}_4$ composite just absorbed about 3.6 wt.% hydrogen after the same time. With addition of the titanium-based metal halides, the $\text{MgH}_2\text{-LiAlH}_4$ samples also did not show any improvement. Both the TiF_3 and $\text{TiCl}_3\cdot 1/3\text{AlCl}_3$ -added $\text{MgH}_2\text{-LiAlH}_4$ sample absorbed just about 3.3 wt.% hydrogen after 5 min rehydrogenation.

Table 1 The apparent activation energy and the enthalpy changes for as-milled MgH_2 , $\text{MgH}_2\text{-LiAlH}_4$ composite, and selected metal halide-added $\text{MgH}_2\text{-LiAlH}_4$

	Non-catalysed		4MgH ₂ -LiAlH ₄ catalysed with metal halide					
	As-milled MgH ₂	4MgH ₂ -LiAlH ₄	TiF ₃	NbF ₅	NiF ₂	TiCl ₃ ·1/3AlCl ₃	HfCl ₄	LaCl ₃
Activation energy (kJ/mol)	162	126	83	110	120	98	106	123
Enthalpy (kJmol ⁻¹ H ₂)	76	61	59	62	63	60	62	64

Fig. 9 Isothermal rehydrogenation kinetics of the MgH_2 , the $\text{MgH}_2\text{-LiAlH}_4$ composite and the titanium-based metal halide-added $\text{MgH}_2\text{-LiAlH}_4$ at 320 °C and under 3 Mpa.

In order to determine the rehydrogenation products, XRD measurements were carried out on the rehydrogenated undoped $\text{MgH}_2\text{-LiAlH}_4$ sample, as shown in Fig. 10. From the pattern, it can be seen that the peaks correspond to MgH_2 , Al, and LiH, along with a small peak for Al_3Mg_2 that appears after rehydrogenation. The disappearance of the $\text{Al}_{12}\text{Mg}_{17}$ and $\text{Li}_{0.92}\text{Mg}_{4.08}$ peaks and the appearance of an Al_3Mg_2 peak in the rehydrogenated sample confirm that reactions (5) and (6) have occurred during the rehydrogenation process.

To understand the possible mechanism behind the metal halide effects on the enhancement of $\text{MgH}_2\text{-LiAlH}_4$ composite, X-ray diffraction analysis was carried out on the $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ - and TiF_3 -added $\text{MgH}_2\text{-LiAlH}_4$ composite. Fig. 11(a) and (b) shows the XRD patterns of the $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ and TiF_3 -added $\text{MgH}_2\text{-LiAlH}_4$ composites after 18 min ball milling and after dehydrogenation at 400 °C. For both samples, after 18 min ball milling, MgH_2 phases are detected along with small peaks of LiAlH_4 , Li_3AlH_6 , and Al (with Li_3AlH_6 and Al peaks

Fig. 10 XRD patterns of the undoped $\text{MgH}_2\text{-LiAlH}_4$ composite after rehydrogenation at 320 °C and under 3 MPa.

Fig. 11 XRD patterns of the $\text{MgH}_2\text{-LiAlH}_4$ with addition of (a) 5 wt% $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ and (b) 5 wt.% TiF_3 , after 18 min ball milling and after dehydrogenation at 400 °C.

overlapping in the XRD pattern). As compared with the peaks of LiAlH_4 in the undoped $\text{MgH}_2\text{-LiAlH}_4$ sample (Fig. 2(a)), the diffraction peaks of LiAlH_4 in the $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ and TiF_3 -added $\text{MgH}_2\text{-LiAlH}_4$ samples become weaker. The appearance of Li_3AlH_6 and Al indicates that LiAlH_4 has already partly decomposed into Li_3AlH_6 and Al (eqn (1)) after 18 min ball milling in the presence of $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ or TiF_3 . After dehydrogenation at 400 °C, as compared with the undoped $\text{MgH}_2\text{-LiAlH}_4$ sample (Fig. 2(c)), the new phases Al_3Ti , LiCl, and LiF were formed. The formation of Al_3Ti and LiCl (Fig. 11(a)), and Al_3Ti and LiF (Fig. 11(b)) may be due to the reaction of LiAlH_4 with $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ or TiF_3 during the ball milling or the dehydrogenation process. According to Resan *et al.*²⁴ and Balema *et al.*²⁵, doping LiAlH_4 with Al_3Ti improved the dehydrogenation behaviour. Meanwhile, a study by Yin *et al.*²⁶ revealed that it was the F that actively played the catalytic role in enhancement of $\text{NaAlH}_4\text{-TiF}_3$ system. We assume that the catalytic effect of TiF_3 on the dehydrogenation process of LiAlH_4 could be similar to its effect on NaAlH_4 , as investigated by Liu *et al.*²² Furthermore, according to,^{27–29} the catalytic effect of a Ti-containing phase and the active function of the F anion

have also been proved to be significant in improving the hydrogen sorption properties of MgH_2 . Therefore, Al_3Ti and LiF are believed to act as the actual catalysts in the $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ and TiF_3 -added MgH_2 - LiAlH_4 composites, which may promote the interaction of LiAlH_4 and MgH_2 , and accelerate the hydrogen desorption process of the MgH_2 - LiAlH_4 composite system.

4. Conclusion

In the present study, the hydrogen storage properties of the MgH_2 - LiAlH_4 (4 : 1) composite system with and without additives were investigated. It was found that the destabilization of MgH_2 by the LiAlH_4 resulted from the formation of $\text{Al}_{12}\text{Mg}_{17}$ and $\text{Li}_{0.92}\text{Mg}_{4.08}$ during the dehydrogenation process, furthermore improves the dehydrogenation properties of MgH_2 . The dehydrogenation process in the MgH_2 - LiAlH_4 composite can be divided into two stages: the first stage is the two-step decomposition of LiAlH_4 . In the second stage, the yielded LiH and Al phases decompose the MgH_2 to form $\text{Li}_{0.92}\text{Mg}_{4.08}$ and $\text{Al}_{12}\text{Mg}_{17}$ phases accompanied with the self-decomposition of the excessive MgH_2 . Among the additives examined, the titanium-based metal halides, TiF_3 and $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$, exhibit the best improvement in reducing the dehydrogenation temperature and enhancing the dehydrogenation rate. From the Kissinger plot, the activation energy for H-desorption is reduced from 126 kJ/mol for MgH_2 - LiAlH_4 composite to 83 kJ/mol and 98 kJ/mol after addition of TiF_3 and $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$, respectively. DSC measurements indicate that the enthalpy change in the MgH_2 - LiAlH_4 composite system was unaffected by the addition of metal halides. It is believed that the formation of Ti-containing and F-containing species during the ball milling or the dehydrogenation process may be actually responsible for the catalytic effects and thus further improve the dehydrogenation of the TiF_3 and $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ -added MgH_2 - LiAlH_4 composite system.

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