Additive Effects of TiCl_3 on Dehydrogenation Reaction of LiAlH_4

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Recently, LiAlH_4 has attracted attention as one of the most promising hydrogen storage materials, because LiAlH_4 is able to release large amount of hydrogen (7.9 mass% H_2) below 250°C. However, the kinetics of the dehydrogenation reaction of LiAlH_4 is too slow for applications to fuel cell vehicles. To improve the dehydrogenation kinetics, the dopant effect of TiCl_3 has been investigated in this research. Here, LiAlH_4 doped with various ratios (0, 0.1, 0.2, 0.5, 1.0, and 2.0 mol%) of TiCl_3 were prepared by ball milling for 30 min under a 1.0 MPa H_2 atmosphere. The decomposition of LiAlH_4 proceeds via a two-step reaction and the dehydrogenation kinetics of each step were compared to determine the optimum amount of TiCl_3 that would assist the process. With increasing of TiCl_3 amount, the dehydrogenation temperature for both of the reactions decreased. Activation energies decreased with increasing TiCl_3 amount, however the amount of desorbed hydrogen decreased. Considering the kinetics and hydrogen capacity in the both steps, the results suggest that the optimum amount of doped TiCl_3 for the dehydrogenation of LiAlH_4 is around 0.2 mol%. [doi:10.2320/matertrans.MG201415]

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1. Introduction

Some kinds of alanates, MAlH_4 ($\text{M} = \text{Li}, \text{Na}, \text{K}$, etc.), have been considered as candidates for applications in fuel cell vehicles (FCVs) as hydrogen storage materials due to their high hydrogen capacity. Among these, LiAlH_4 has the highest hydrogen capacity (10.5 mass%) among alanates, for example compared with NaAlH_4 (7.4 mass%) and KAlH_4 (5.7 mass%). In 1965, Block and Gray reported that LiAlH_4 can release hydrogen by a three-step reaction as in the following equations, which show the different amounts of the theoretical hydrogen capacity and the reaction temperatures.¹⁾

Further, it was estimated that the enthalpy change (ΔH) of the dehydrogenation reactions (1), (2) and (3) were -10 , $+25$ and $+140$ (kJ/mol H_2), respectively.¹⁾ For applications to FCVs, reactions (1) and (2) are thermodynamically acceptable, however, the kinetics of reactions (1) and (2) are still very slow.²⁾ The dehydrogenation reaction starts at a comparatively high temperature (onset: 170°C, heating rate: 10°C/min). Doping with catalysts such as TiCl_3 has been tried to improve the dehydrogenation kinetics of alanates.^{3–5)} Further, LiAlH_4 has poor reversibility under moderate conditions. Since the enthalpy of the reaction (1) is exothermic, the reverse reaction (hydrogenation reaction) is endothermic, and the hydrogenation reaction cannot proceed spontaneously. To rehydrogenate LiAlH_4 from LiH and Al at room temperature, a hydrogen pressure of 1 GPa is necessary.³⁾ In 2009, Liu *et al.* succeeded in generating LiAlH_4 by agitating LiH , Al , TiCl_3 and dimethyl ether under

a hydrogen pressure of 10 MPa at room temperature.³⁾ However, the catalytic effect of TiCl_3 has not been fully elucidated yet. In this work, we investigate the dehydrogenation kinetics of LiAlH_4 doping with various ratios of TiCl_3 . Then discuss the optimum amount of doped TiCl_3 .

2. Experimental Procedures

Powders of LiAlH_4 and TiCl_3 were purchased from Aldrich, and LiAlH_4 doped with various ratios of TiCl_3 (0, 0.1, 0.2, 0.5, 1.0, and 2.0 mol%) were prepared. Firstly, the powder mixture was loaded in a milling pot, and evacuated for 12 h by using a rotary pump. Then, the powder mixture was ball-milled for 30 min with a rotational speed of 300 rpm under a 1.0 MPa H_2 atmosphere. Here, TiCl_3 was added as a precursor to act as a catalyst after the ball-milling. The samples were labelled as “x mol% TiCl_3 sample”. All samples were handled in a glove box filled with purified Ar gas to minimize contact with oxygen and water vapor.

The phase changes and the dehydrogenation kinetics were analyzed by means of X-ray diffraction (XRD), thermogravimetry and differential thermal analysis (TG-DTA) with heating rates of 2, 5, 10, or 20°C/min. For each sample, the activation energies (E_a) of reactions (1) and (2) were estimated by the Kissinger method.^{6,7)} The activation energies of the two reactions are given by the slope fitting the equation: $\ln(b/T_p^2) = (-E_a/RT_p) + \ln(AR/E_a)$ (b = heating rate, T_p = peak temperature of reaction obtained from DTA results, R = gas constant, and A = frequency factor).

3. Results and Discussion

3.1 Dehydrogenation temperature

Figure 1 shows DTA curves of undoped and 2.0 mol% TiCl_3 samples under He flow at a heating rate of 20°C/min. The undoped sample shows three DTA peaks, and the endothermic peak at 170°C corresponds to melting of LiAlH_4 . The exothermic and endothermic peaks at around

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Fig. 1 DTA curves for LiAlH_4 with 0 (undoped) and 2.0 mol% TiCl_3 samples under He flow with a heating rate of $20^\circ\text{C}/\text{min}$.

210 and 255°C correspond to the first and second reactions, respectively. In the DTA curve of the 2.0 mol% TiCl_3 sample there are two peaks at 110 and 150°C . It has already been reported that the first and second endothermic peaks correspond to the decomposition of LiAlH_4 and Li_3AlH_6 , respectively, by Henrietta *et al.*⁸⁾

Figure 2 shows the peak temperatures of the reaction obtained from DTA results under He flow at a heating rate of $20^\circ\text{C}/\text{min}$ as a function of the ratio of TiCl_3 to LiAlH_4 . Both the temperatures of reaction (1) and (2) decrease with increasing amounts of TiCl_3 . The figure shows that doping with a small amount (~ 0.2 mol%) of TiCl_3 can substantially decrease the reaction temperatures in both reactions. However, addition of larger amounts (0.2 – 2 mol%) of TiCl_3 showed no further real decrease in the desorption temperature. It is suggested that the dispersion state of the additive may become saturated. For the undoped (milled only) sample, reactions (1) and (2) occurred at 210 and 255°C , respectively. Then, with 0.1 mol% TiCl_3 of doping, the reactions were observed at 145 and 180°C , that is 65 – 75°C lower than for undoped LiAlH_4 . Further, with doping of 2.0 mol% catalyst, the two peak temperatures of the reactions were 110 and 150°C .

3.2 Amount of desorbed hydrogen

Figure 3 shows the relation between the amount of desorbed hydrogen and the amount of doped TiCl_3 . The weight percentage of desorbed hydrogen is based solely on the weight of LiAlH_4 and not on the combined weights of $\text{LiAlH}_4 + x$ mol% TiCl_3 . The samples were heated up to 280 and 220°C without and with TiCl_3 , respectively. The theoretical maximum value is 7.9 mass%, which means the amount of hydrogen from pure LiAlH_4 . In the case of the

Fig. 2 Peak temperature of the H_2 desorption reactions at a heating rate of $20^\circ\text{C}/\text{min}$ as a function of the ratio of TiCl_3 to LiAlH_4 . R1 (reaction (1)): $\text{LiAlH}_4 \rightarrow 1/3\text{Li}_3\text{AlH}_6 + 2/3\text{Al} + \text{H}_2$, R2 (reaction (2)): $\text{Li}_3\text{AlH}_6 \rightarrow 3\text{LiH} + \text{Al} + 3/2\text{H}_2$.

Fig. 3 Amount of desorbed hydrogen versus the ratio of TiCl_3 to LiAlH_4 .

0.2 mol% TiCl_3 sample, the amount of desorbed hydrogen is 7.5 mass% and the largest value in all samples. The amount of desorbed hydrogen dramatically decreases when the amount of doped TiCl_3 exceeds 0.5 mol%. This may be because of two reasons: one is decomposition of LiAlH_4 occurred during the ball milling, and the other is decomposition of LiAlH_4 because of the reaction between LiAlH_4 and TiCl_3 to generate LiCl . Therefore, to verify phase changes after ball milling, XRD experiment was also carried out.

Figure 4 shows the XRD patterns of samples after the ball milling. Here, the intensity ratio of the highest Al peak to LiAlH_4 becomes much larger with doping above 1.0 mol% TiCl_3 . This agrees well with the results in Fig. 3, suggests that LiAlH_4 is liable to decompose during ball milling when doping with a large amount of catalyst.

3.3 Activation energy

Figure 5 shows activation energies estimated by the Kissinger method for both reactions (1) and (2) for all the samples. In reaction (1), the activation energies decreased and

Fig. 4 X-ray diffraction patterns of LiAlH_4 doped with 0–2.0 mol% TiCl_3 .

Fig. 5 Activation energy of H_2 desorption reactions as a function of the ratio of TiCl_3 to LiAlH_4 . R1: $\text{LiAlH}_4 \rightarrow 1/3\text{Li}_3\text{AlH}_6 + 2/3\text{Al} + \text{H}_2$, R2: $\text{Li}_3\text{AlH}_6 \rightarrow 3\text{LiH} + \text{Al} + 3/2\text{H}_2$.

were saturated by doping of more TiCl_3 . This may be one of the reasons why LiAlH_4 decomposed during ball milling even at room temperature. In reaction (2), it is confirmed that the activation energies decrease by doping 0.1 and 0.2 mol% TiCl_3 , while they increase when doping more than 0.5 mol% TiCl_3 . From these results it may be concluded that LiAlH_4 with 0.2 mol% TiCl_3 has the minimum activation energy.

Considering the relationship between the dehydrogenation temperature and activation energy, when doping large amounts (more than 0.5 mol%) of catalyst, the dehydrogenation temperatures of reaction (2) decrease, while the activation energies increase. The following assumption including the reaction frequency could be an explanation for this phenomenon: Increasing the frequency factor of the dehydrogenation reaction leads to decreased dehydrogenation temperatures while the activation energies increase, as the

rate constant k can be expressed as $k = Ae^{-E/RT}$.⁶⁾ A higher reaction frequency is equivalent to nano-scale origins of dehydrogenation reactions such as Ti–Al agglomerates spreading more widely. However, the dispersion state may become saturated by doping large amount of catalyst as discussed in 3.1.

Liu *et al.* reported that more complex Ti–Al alloys are formed with increasing dehydrogenation and rehydrogenation cycling.⁹⁾ On the basis of that study, $\text{Ti}_x\text{Al}_{1-x}$ is produced by ball milling and then the x value may increase and more complex $\text{Ti}_x\text{Al}_{1-x}$ form during reaction (1). Complex $\text{Ti}_x\text{Al}_{1-x}$ may have a negative effect on the dehydrogenation process as a function of the x value. Then $\text{Ti}_x\text{Al}_{1-x}$ is more likely to be formed with increasing amounts of TiCl_3 . As a result, the activation energy increases with the increased the amount of catalyst in reaction (2).

In short, when the amount of TiCl_3 in LiAlH_4 increases, nano-scale originations of reactions are located widely, on the other hand, more negative agglomerates of Ti–Al alloy which is produced during reaction (1) is then present in reaction (2). However, further experiments including microstructural observations are required to investigate the reasons in more detail.

4. Conclusions

This paper reports three results about the optimum amount of TiCl_3 doping of LiAlH_4 as follows:

- (1) Activation energies of reaction (1) are almost saturated from 0.2 mol%.
- (2) Activation energies of reaction (2) have the minimum value with a 0.2 mol% TiCl_3 sample.
- (3) The amount of desorbed hydrogen is the highest with the 0.2 mol% TiCl_3 sample.

From the above results we may conclude that the most effective amount of TiCl_3 doping to LiAlH_4 is 0.2 mol%.

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