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Catalytic effect of Ti_5Si_3 on thermal decomposition of Li_3AlH_6

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Abstract Fine Ti_5Si_3 powder has been mechanochemically synthesized from a mixture of elemental Ti and Si powders. When Ti_5Si_3 is added as a catalyst into Li_3AlH_6, it shows a good catalytic ability by reducing the decomposition temperature and improving the decomposition kinetics as well. Although its catalytic effect is not as good as well-known $TiCl_3$, the use of Ti_5Si_3 has a benefit of releasing more hydrogen than $TiCl_3$ during dehydrogenation. This can be explained by that Ti_5Si_3, unlike $TiCl_3$, does not incur any chemical reactions with Li_3AlH_6 and thus remains inert during milling for dispersion.

Introduction

Akali and alkali-earth metal aluminum hydrides (alanates) have attracted much interest as potential hydrogen storage materials for on-board applications, since it was discovered that reversible hydrogen storage and accelerated kinetics in sodium aluminum hydrides ($NaAlH_4$ and Na_3AlH_6) could be achieved by doping with Ti-containing catalysts [1]. Ti-containing catalysts are added into aluminum hydrides usually as chlorides or organometals. According to recent experimental and theoretical investigations [2–7], it is believed that Ti introduced into aluminum hydrides in-situ forms $TiAl_3$, although there is another conjecture that Ti substitutes for metal sites in aluminum hydrides [8–10].

Recently, Balema et al. [2], Resan et al. [11] and the present authors [12] attempted to confirm the catalytic effect of $TiAl_3$ on the thermal decomposition (dehydrogenation) of alkali metal aluminum hydrides such as $NaAlH_4$ and $LiAlH_4$. For example, the present authors [12] was able to reduce the thermal decomposition temperature of Li_3AlH_6 by about 30 °C, by using ultrafine $TiAl_3$ powder as a catalyst, which was synthesized by a mechanochemical reaction. Moreover, $TiAl_3$ catalyst minimized the loss of hydrogen storage capacity in aluminum hydrides, while the addition of titanium chloride inevitably decomposes part of aluminum hydrides and thus forms impotent byproducts such as alkali metal chlorides, which are much more stable than $TiCl_3$. Therefore, there is need to validate the catalytic ability of other Ti compounds that do not react with aluminum hydrides so that it can minimize the loss of hydrogen storage capacity. Actually, Bogdanović et al. [13] demonstrated that the addition of TiN nanoparticles improves the hydrogenation and dehydrogenation kinetics of $NaAlH_4$ with the loss of hydrogen storage capacity less than elemental Ti or organometallic Ti.

The present study aims at synthesizing Ti_5Si_3 powder and validating its catalytic ability in aluminum hydrides. The reason to choose Ti_5Si_3 among various titanium compounds is that Ti_5Si_3 is thermodynamically more stable than $TiAl_3$ in aluminum hydrides and thus it will not change into $TiAl_3$ after being dispersed into aluminum hydrides, as the formation enthalpy of Ti_5Si_3 (–72.4 kJ/g atom) is far more negative than that of $TiAl_3$ (–35.6 kJ/g atom) [14]. The reason to adopt Ti_5Si_3 among various titanium silicides is that Ti_5Si_3 is the thermodynamically most stable [14] and known to be relatively easily prepared [15, 16]. Ti_5Si_3 powder has been synthesized using mechanochemical reactions and dispersed into Li_3AlH_6 through mechanical milling.

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Experimental methods

$TiCl_3$ (99% purity) and Si (99%) powders were purchased from Sigma–Aldrich. Ti (99.98%) and Mg (99.8%) powders were from Sumitomo Titanium and Alfa-Aesar, respectively. A 1 g mixture of Ti and Si with a molar ratio of 5:3 was charged together with seventeen 7.9 mm diameter Cr-steel balls into a tool-steel vial under an Ar atmosphere in a glove box. The ball-to-powder weight ratio (BPR) was approximately 35:1. The mixture was milled in a SPEX 8,000 mill for 4 h. In order to reduce the particle size of the as-synthesized Ti_5Si_3, it was additionally milled for 2 h with 50 wt% NaCl (99.5%, Junsei Chemical) as an inert process agent. NaCl was removed by rinsing the milled powder in distilled water and filtering it.

The phase constitution and morphology of the synthesized powders were characterized by X-ray diffraction (XRD) using Bruker D8 Advanced with CuKα radiation and scanning electron microscopy (SEM) using FEI XL-30 FEG.

Li_3AlH_6 was mechanochemically synthesized as follows: A 5 g mixture of $LiAlH_4$ (95%, Sigma–Aldrich) and LiH (95%, Sigma–Aldrich) with a molar ratio of 1:2 was charged together with ten 15 mm and thirty 10 mm diameter zirconia balls into a 250 ml silicon nitride bowl under an Ar atmosphere in a glove box. The BPR was approximately 37:1. The mixture was milled in a Fritsch P4 planetary mill at 350 rpm for 4 h 30 min.

In order to confirm the catalytic effect of Ti_5Si_3 on the thermal decomposition of Li_3AlH_6, 12 wt% Ti_5Si_3 was dispersed into Li_3AlH_6 by milling in a SPEX 8,000 mill for 30 min. About 12 wt% (5 mol%) $TiCl_3$ was also dispersed into Li_3AlH_6 for comparison. The decomposition behavior of Li_3AlH_6 with and without catalysts was analyzed by differential scanning calorimetry (DSC) using NETZSCH DSC 204 and thermogravimetry (TG) using NETZSCH TG 209 coupled with NETZSCH QMS 403C (mass spectrometer). The heating rate was 2 °C/min and flow rate of Ar (99.9999%) gas was 50 ml/min for both DSC and TG measurments. The decomposition kinetics was volumetrically measured with 0.5 g of samples by a Sievert type apparatus.

Results and discussion

Figure 1 shows an XRD pattern of the Ti and Si mixture milled for 4 h. Ti_5Si_3 is identified as a major phase and trace of $TiSi_2$ is also observed. This result is consistent with those of Yen et al. [15] and Kudaka et al. [16] who synthesized Ti_5Si_3 from mixtures of elemental powders by mechanochemical synthesis, although our XRD peaks are much broader than theirs, which indicates that our Ti_5Si_3 has a smaller crystallite size. The average crystallite size of Ti_5Si_3 calculated by the Scherrer formula, for the (222) peak that does not overlap other peaks, is about 12 nm.

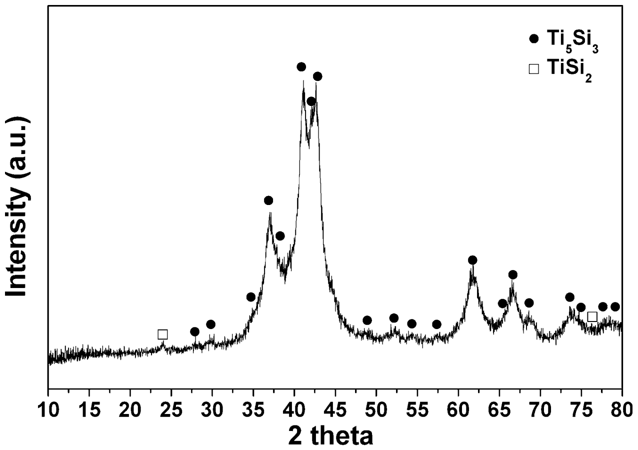

Fig. 1 XRD patterns of Ti and Si mixture milled for 4 h

Figure 2 shows SEM micrographs of Ti_5Si_3 powders. The particle size of the as-synthesized Ti_5Si_3 powder is

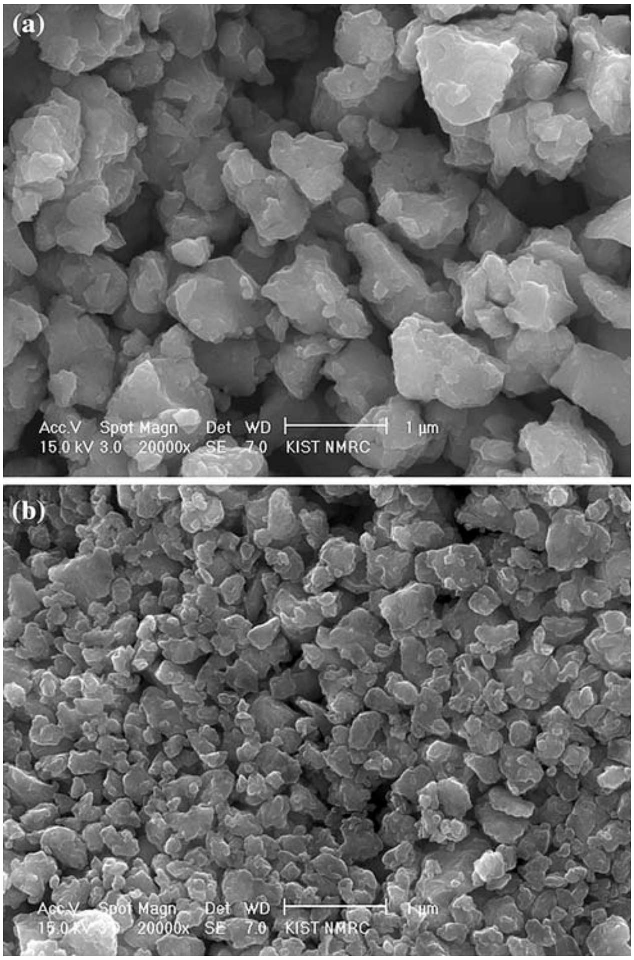

Fig. 2 SEM micrographs of Ti_5Si_3 (**a**) synthesized from Ti and Si and (**b**) milled additionally with NaCl after the synthesis

around 1 μm (Fig. 2a), although it shows wide particle size distribution. However, it is found that the particle size has been significantly reduced to a few hundred nanometers after only 2 h of additional milling with NaCl (Fig. 2b). On the whole, both Ti_5Si_3 powders exhibit irregular shape with hard agglomerates, as powders prepared through mechanical milling usually do.

XRD patterns of Li_3AlH_6 catalyzed with Ti_5Si_3 and $TiCl_3$ are presented in Fig. 3. Ti_5Si_3 remains stable in Li_3AlH_6 indicating no reaction with Li_3AlH_6 (Fig. 3a). It is, therefore, expected that Ti_5Si_3 would not incur the significant loss of the hydrogen storage capacity of Li_3AlH_6. On the other hand, $TiCl_3$ reacts with Li_3AlH_6 to form LiCl, as shown in Fig. 3b. $TiCl_3$ is believed to form nanocrystalline $TiAl_3$ as claimed by Graetz et al. [4] based on the high-energy X-ray absorption analysis, although the formation of $TiAl_3$ is not quite clear in the present XRD pattern due to the overlap of its XRD peaks with those of Li_3AlH_6.

Figure 4 shows DSC curves of Li_3AlH_6 with and without catalysts. Each DSC curve has one sharp endothermic peak attributed to the following decomposition reaction:

$$Li_3AlH_6 \rightarrow 3LiH + Al + \frac{3}{2}H_2 \quad (1)$$

Li_3AlH_6 without catalyst starts to decompose releasing H_2 gas at about 190 °C and the peak temperature is about 210 °C. On the other hand, the decomposition of Li_3AlH_6 with Ti_5Si_3 starts at about 160 °C and exhibits the peak at about 190 °C. This decrease in decomposition temperature is similar to those of Li_3AlH_6 with $TiAl_3$ catalyst in our previous investigation [12]. Both coarse and fine Ti_5Si_3 catalysts show a similar decomposition behavior, implying that the particle size of Ti_5Si_3 is unlikely to produce a big difference in catalytic effect in this particle size range (0.1–1 μm). Although Ti_5Si_3 shows a good catalytic ability, it is not as good as $TiCl_3$ which decreases the decomposition starting temperature down to about 130 °C, as shown in Fig. 4. The actual equilibrium temperature for reaction (1) might lie below 130 °C, because DSC scans with a heating rate.

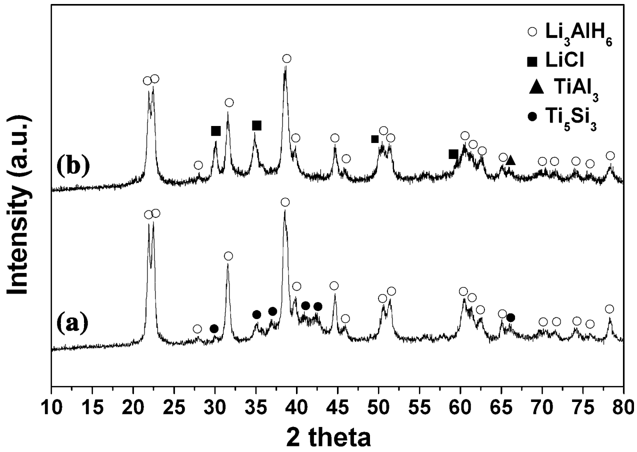

Fig. 3 XRD patterns of Li_3AlH_6 catalyzed with (**a**) 12 wt% Ti_5Si_3 and (**b**) 12 wt% $TiCl_3$

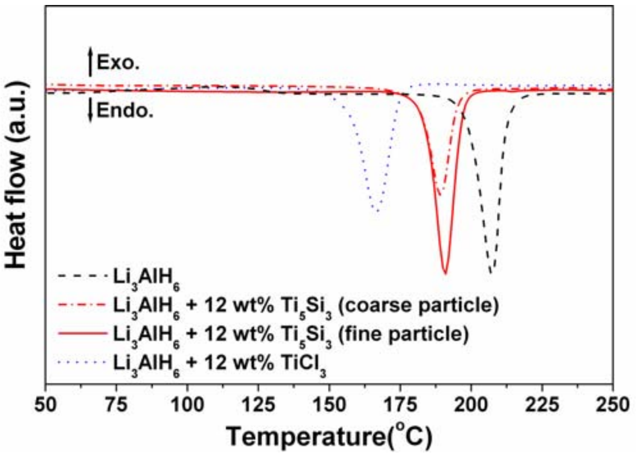

Fig. 4 DSC curves of Li_3AlH_6 with and without catalyst

As shown in Fig. 5, the measured TG curves show the decomposition temperature ranges consistent with the DSC curves. Li_3AlH_6 without catalyst releases about 4.8 wt% H_2 during thermal decomposition, which is lower than the theoretical hydrogen storage capacity (5.6 wt%) due to the low purity of raw materials and the partial decomposition of Li_3AlH_6 during mechanochemical preparation. It should be noted that Li_3AlH_6 catalyzed with Ti_5Si_3 releases larger amount of hydrogen (4.5 wt%) than $TiCl_3$ (4.0 wt%) as expected. Therefore, it will be favorable to add Ti_5Si_3 instead of $TiCl_3$ into aluminum hydrides in order to minimize the loss in hydrogen storage capacity. No gas is detected during thermal decomposition by mass spectrometry, except for H_2.

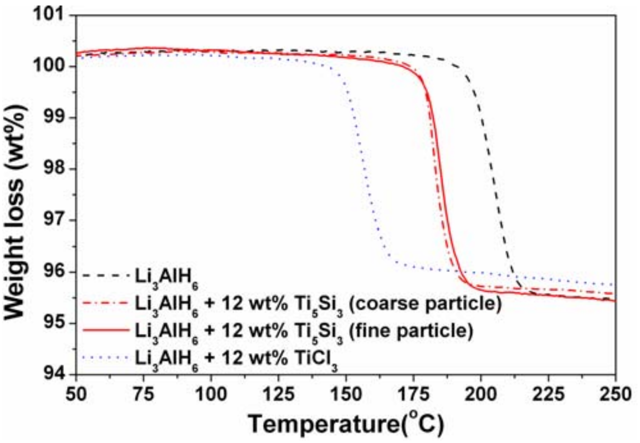

Fig. 5 TG curves of Li_3AlH_6 with and without catalyst

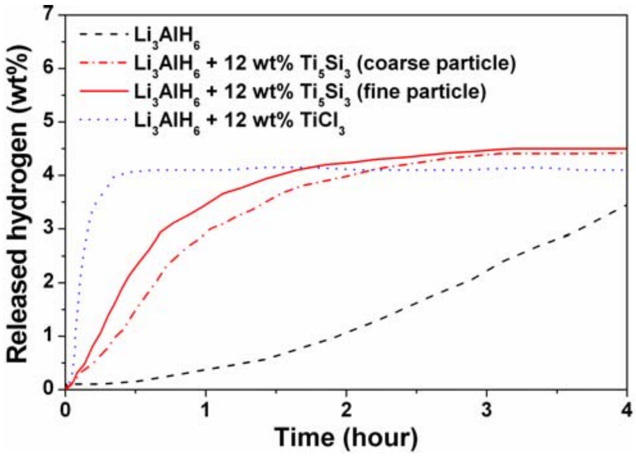

Fig. 6 Amount of hydrogen released during thermal decomposition of Li_3AlH_6 with and without catalysts at 150 °C as a function of time

The decomposition kinetics of Li_3AlH_6 with and without catalyst at 150 °C is shown in Fig. 6. Without catalyst, Li_3AlH_6 shows quite slow decomposition kinetics, releasing about 3.4 wt% hydrogen at most in 4 h. It is found that the addition of both coarse and fine Ti_5Si_3 catalysts significantly improve the decomposition kinetics, although fine Ti_5Si_3 powder gives slightly faster kinetics. The amount of released hydrogen of Li_3AlH_6 catalyzed with Ti_5Si_3 exceeds that of Li_3AlH_6 catalyzed with $TiCl_3$ in about 2 h and is saturated to about 4.5 wt% in about 3 h. Li_3AlH_6 catalyzed with $TiCl_3$ releases only about 4.0 wt% hydrogen, although it shows much faster kinetics. Sandrock et al. [17] showed that the minimum amount of $TiCl_3$ required for enhanced dehydrogenation kinetics of alanate is about 6 wt%. Comparing theoretical hydrogen capacities of Li_3AlH_6 with 12 wt% Ti_5Si_3 and 6 wt % $TiCl_3$, the addition of Ti_5Si_3 is still slightly more favorable than that of $TiCl_3$ in terms of hydrogen storage capacity.

In this study, the effect of the particle size of Ti_5Si_3 on the catalytic efficiency in a 0.1–1 µm range is not large. However, the catalytic effect of Ti_5Si_3 nanoparticles below 0.1 µm needs to be investigated further, since it is known that the size of the active catalytic species in $NaAlH_4$ with $TiCl_3$ is only a few nanometers [4].

Conclusions

Fine Ti_5Si_3 powder has been prepared from a mixture of elemental Ti and Si powders by mechanochemical synthesis. The addition of Ti_5Si_3 as a catalyst decreases the decomposition temperature of Li_3AlH_6 by about 30 °C and significantly improves the decomposition kinetics. The particle size of Ti_5Si_3 does not seem to produce a big difference in the catalytic effect, at least, in the range between 0.1 µm and 1 µm, although the addition of fine Ti_5Si_3 powder shows slightly faster kinetics. It is also confirmed that $TiCl_3$ is more effective in reducing the decomposition temperature and improving the decomposition kinetics of Li_3AlH_6. Nevertheless, it is clearly demonstrated that the use of Ti_5Si_3 as a catalyst is more favorable than $TiCl_3$ in terms of hydrogen storage capacity.

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