Enhancement of hydrogen desorption kinetics in magnesium hydride by doping with lithium metatitanate

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ABSTRACT

Lithium metatitanate (Li_2TiO_3) doped magnesium hydride (MgH_2) has been investigated in this paper. Desorption properties of the sample with catalyst are compared to the pure MgH_2. Particularly, MgH_2 doped with 5 mol % Li_2TiO_3 started to desorb hydrogen at 170 °C with a peak temperature at 211 °C, which is 100 °C and 80 °C lower than that of the as-milled MgH_2. The reversibility and cyclability of sample with catalyst have also been investigated. Compared with the raw material, the desorption activation energy was reduced from 113 kJ/mol to 84 kJ/mol. Furthermore, the catalytic mechanism was discussed according to the experimental results.

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1. Introduction

Nowadays, the consumption of fossil fuels, such as oil, natural gas, and coal, has been dramatically increased year by year. The environment problem include air pollution, global warming and resource exhaustion, changes to be a hotspot in recent year [1–3]. To solve these essential issues, a sustainable and clean energy system should be developed in current modern society. Hydrogen, with the great advantages of a high gravimetric energy density, zero-CO_2-emissions, and light weight, has been widely considered a promising alternative energy carrier to the current energy predicament. So far, many metal hydrides such as LaNi and TiCrV have been developed for practical use. However, the capacity for these materials are too low for practical storage of hydrogen [4–6]. Therefore, there is a demand to develop light metal hydrides.

MgH_2 as a light metal hydride has advantages of a high hydrogen capacity (7.6 wt%), a high volumetric density (110 kgm^{-3}) and abundance with low cost, as well as its good reversibility. Therefore, MgH_2 has been investigated as one of the most practical materials for on-board storage [7–11]. However, its sluggish de/hydrogenation kinetics and thermodynamic stability limit practical utilization. Various investigations have been made to overcome these problems by adding catalysts. Especially in the last years, research has focused on the addition of transition metal compounds as a catalyst. Some recent studies have further illustrated the catalytic behavior of transition metal compounds [12–21]. Barkhordarian et al. have evaluated the hydrogenation properties of MgH_2-transition metal composite powders [14]. Furthermore, some of the researchers have reported that Ti compounds catalyzed the absorption/desorption properties of MgH_2 [12,18,20,22,23]. For instance, Hanada et al. studied the valence state of Ti compounds that were added to MgH_2 [23]. Recently, we reported that the dehydrogenation kinetics of the MgH_2 system can be enhanced by the addition of lithium titanate ($LiTi_2O_4$) [24]. Supported by the previous research, Ti compounds has shown a good catalytic effect on improving the desorption properties of MgH_2, however the

catalytic mechanism could not be clarified due to the instability of Ti compounds after high-energy ball-milling. With the aim of optimizing property of catalyst, it is needed to find an ideal material with better stability, high efficiency, longer cycling life and reasonable cost. More recently, we studied the catalytic effect of Li_2TiO_3 in lithium alanate (LiAlH$_4$) [25] and lithium amide/hydride systems (LiNH$_2$/LiH) [26]. This material was stable after high-energy ball-milling with high efficiency during cycling. Herein, Li_2TiO_3 is introduced to MgH$_2$ system, which is expected to improve the dehydrogenation performance.

2. Experimental method

To synthesize Li_2TiO_3, a two-step process was adopted as described below. In the first stage, Li_2CO_3 (99.997%, Sigma-Aldrich) and TiO$_2$ (99%, Sigma-Aldrich) were mixed homogeneously by a ball-milling equipment (Fritsch P7). Second, the as-collected mixture was calcined in air at 900 °C for 24 h and sintered at 900 °C for 8 h in a Muffle Furnace (MF410 Yamato). Finally, Li_2TiO_3 pebbles were synthesized by the solid-state reaction in equation (1).

$$Li_2CO_3 + TiO_2 \rightarrow Li_2TiO_3 + CO_2 \qquad (1)$$
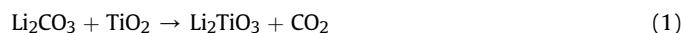
The composites were prepared by ball-milling of as-received MgH$_2$ (98%, Alfa Aesar) and the fabricated Li_2TiO_3 as catalyst. The stoichiometric amount of additive to MgH$_2$ were 1 mol% and 5 mol%, respectively. In the ball-milling process, the mixture was brought into a Cr steel pot (SKD-11) with 20 steel balls (7 mm, SUJ-2) and milled at 400 rpm for 20 h under a hydrogen (99.9999% purity) pressure of 1 MPa at room temperature. The ball-to-powder ratio was 100:1. The milling was interrupted every 30 min for 15 min to prevent frictional heat during the milling process. In addition, pure MgH$_2$ without catalyst was also ball-milled in the same way as a reference sample. A glovebox filled with purified argon (99.9999%) was used for all the materials to keep the water vapor and oxygen levels below 0.5 ppm. The purification system could protect samples from hydroxide formation and/or oxidation.

The desorption properties of the composites were measured by Thermogravimetry and Differential Thermal Analysis (TG-DTA) equipment (Hitachi Bruker TAPS3000S) combined with Thermal Gas Desorption Mass Spectrometry (TDMS, Netzsch) at a heating rate of 5 °C/min to 400 °C under dynamic helium with a purge rate of 300 ml/min. The sample was placed in an aluminum sample-holder during TG-DTA measurement. The phase characterization of each sample was performed using X-ray diffraction (XRD, PAN-alytical, X'Pert-Pro with Cu Kα radiation, λ = 0.15418 nm), operating at 40 kV and 40 mA in the angular range from 10° to 80° (2θ) at a step size of 0.0167°. The samples were put in glass sample holders and covered with Kapton to isolate any possible contact between the sample and air during XRD experiments. The X-ray photo-electron spectroscopy (XPS; Thermo Fisher Scientific, ESCALAB 250Xi, Al-Kα = 1486.6 eV) technique was used to understand the surface state of the catalyst. The binding energy was calibrated using C-C binding energy at 284.4 eV in order to compare the binding energies with the data from the literature. A base pressure is 7.0×10^{-10} mbar in the measuring chamber and the accelerating voltage is 15.6 kV to generate X-ray.

The activation energy (Ea) of dehydrogenation can be evaluated by the Kissinger method [27] through the mass spectra data measured at different heating rates, i.e. 5 °C/min, 10 °C/min, 15 °C/min, and 20 °C/min, separately. It is according to the following equation which is derived from the Arrhenius equation:

$$\ln\left(\beta/T_p^2\right) = -E_a/RT_p + \ln(AR/E_a) \qquad (2)$$

where β is the heating rate, T_p is the peak temperatures of desorption given by the result of TDMS, R is the gas constant and A is the pre-exponential factor which can be extracted from the intercept of the Kissinger curve.

The hydrogen sorption properties i.e thermodynamics and kinetics were evaluated by the conventional pressure-composition-isotherm (PCI) and rate measurements using a Sieverts' type apparatus (Suzuki Shokan Co.) following the procedures described elsewhere [28]. 0.1 g of the as-milled sample was loaded into a steel reactor and dehydrogenated for 6 h at 200 °C in dynamic vacuum. PCI measurements were performed in pressure range of 0.001−2 MPa at 250, 275, 300 and 350 °C. The absorption kinetics was carried out at hydrogen pressure of 2.5 MPa at different temperature ranging from room temperature to 300 °C (purity: 99.9999%).

The thermodynamic properties were evaluated by using the Van't Hoff equation, which is expressed as functions of the equilibrium pressures observed by PCI measurements.

$$\ln(p_{H_2}/p_0) = -\Delta H/RT + \Delta S/R,$$

Where p_{H2}, ΔH, and ΔS are the hydrogen equilibrium pressure, enthalpy, and entropy change, respectively.

3. Results and discussions

To investigate the catalytic effect of Li_2TiO_3, the desorption properties of the as-milled MgH$_2$ with/without catalyst were measured by TG-DTA. As-milled MgH$_2$ as a reference sample was reported previously [24]. The hydrogen desorption for as milled MgH$_2$ sample without any catalyst was started at ~270 °C, with two endothermic peaks at 290 °C and 345 °C, respectively. The weight loss of 5.1 wt % was much less than the theoretical value of 7.6 wt %, which could be due to poor desorption kinetics as well as equipment working condition, i.e. partial oxidation of the sample during handling. Fig. 1 a and b shows the desorption properties of MgH$_2$-1mol%Li$_2$TiO$_3$ and MgH$_2$-5mol%Li$_2$TiO$_3$, respectively. In the case of sample with 1 mol % Li_2TiO_3 (Fig. 1a), the single peak temperature decreased to 230 °C. The dehydrogenation onset temperature downshifted to 200 °C according to the DTA curve. A weight loss of 6.9 wt % was achieved from the TG curve compared with the theoretical value. This difference was related to the impurities in the original sample, i.e. Mg (Fig. 5). This downward trend was more visible after adding 5 mol% Li_2TiO_3 (Fig. 1b). For instance, the onset and peak temperature downshifted to 170 °C and 211 °C, respectively. This obvious temperature reduction illustrated the significant catalytic effect of Li_2TiO_3. Additionally, the shoulder in the DTA curve is present for both Mg hydride sample and 5mol% Li_2TiO_3 doped sample and could be due to active/non-active sites in the sample during inhomogeneous mingling and/or the formation of γ-MgH$_2$ after long-time ball-milling [29,30]. For instance, some powder of MgH$_2$ sometimes would adhere to the wall of the ball-milling tank during mechanical milling. It would make the particle size of the whole sample be inhomogeneous which would form active/non-active sites in the sample.

In this study, a brief comparison including the famous catalyst Nb$_2$O$_5$ [31,32] and previously reported catalyst LiTi$_2$O$_4$ [24] are listed in Table 1. The peak temperature is almost same for 1 mol% Li_2TiO_3 doped sample and 1 mol% Nb$_2$O$_5$ doped sample, which is lower than 1 mol% LiTi$_2$O$_4$ doped sample and the as-received sample. The desorption kinetics has been accelerated obviously by increasing