Remarkable Improvement of Hydrogen Sorption Kinetics in Magnesium Catalyzed with Nb_2O_5

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Abstract

Kinetics of hydrogen absorption and desorption reactions was investigated on the MgH_2 composite doped with 1 mol% Nb_2O_5 as a catalyst by ballmilling. The composite after dehydrogenation at 200 °C absorbed gaseous hydrogen of ~ 4.5 mass% even at room temperature under lower pressure than 1 MPa within 15 sec and finally its capacity reached more than 5 mass%. On the other hand, the catalyzed MgH_2 after rehydrogenation desorbed ~6 mass% hydrogen at 160 ºC under purified He flow, which followed the first order reaction. From the Kissinger plot, the activation energy for hydrogen desorption was estimated to be ~71 kJ/molH_2, indicating the product was significantly activated due to the catalytic effect of Nb_2O_5.

Keywords: hydrogen storage materials[A]; high energy ballmilling[B]; thermal analysis[D]

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1. Introduction

Magnesium hydride MgH_2 has been considered as one of attractive hydrogen storage (H-storage) materials because it possesses a high hydrogen capacity of 7.6 mass% and abundant resources. However, the reaction speed of hydrogen absorption and desorption is too low, and it needs a high temperature than 300 ºC for the hydrogen desorption to take place at 0.1 MPa hydrogen. Recently, some Mg or MgH_2 composites with a small amount of transition metals prepared by ballmilling have been studied to improve the kinetics of hydrogen absorption/desorption reactions without reducing the high hydrogen capacity [1-4]. Furthermore, the H-storage properties of MgH_2 with a small amount of transition metal oxides as a catalyst have been also examined [5-9]. Especially, Barkhordarian et al. have claimed that Nb_2O_5 revealed the best catalytic effect on the H-storage properties among the oxide catalysts in their trials [10-11]. According to their reports, MgH_2 catalyzed with 0.5 mol% Nb_2O_5, which was prepared by ballmilling for 100 h, desorbs almost all the hydrogen gas within 90 sec under a vacuum condition at 300 ºC, after that, the dehydrogenated product absorbs up to ~7 mass% hydrogen within 60 sec under a hydrogen atmosphere of 0.84 MPa.

Similarly, we have prepared the MgH_2 composites with a small amount of some transition metals and metal oxides by the ballmilling method and studied the H-storage properties[12-14]. Among these additives, we clarified that the 1 mol% Nb_2O_5-catalyzed MgH_2 exhibited the most superior H-desorption properties. The product desorbed ~6 mass% hydrogen in the temperature range from 200 to 250 ºC at the heating rate of 5 ºC/min under purified helium flow atmosphere with zero hydrogen partial pressure. Furthermore, the product after rehydrogenation at 200 ºC desorbed ~6 mass% hydrogen at lower peak temperature by 50 ºC than that just after ballmilling treatment. To understand the mechanism of the metal oxides catalyst, we examined the chemical bonding state of Nb_2O_5 doped in mechanically milled MgH_2 by XAFS measurement. The results showed that Nb_2O_5 was partially reduced by MgH_2 during mechanically milling, so that the niobium in which the valence is less than 5+, could act as a catalyst for the H-desorption [15]. And, it seems that only the surface of the additive Nb_2O_5 which exists on the surface of MgH_2 powder are reduced, leading to catalytic effect of the hydrogen absorbing/desorbing reactions like recombination of H.

In this work, we investigated the kinetics of hydrogen absorption and desorption reactions for MgH_2 catalyzed with the 1 mol% Nb_2O_5 by ballmilling in details and observed significant improvement of the kinetics.

2. Experimental procedures

Magnesium hydride MgH_2 powder (the purity is 90 mass%, 9 mass% is unreacted Mg and the rest of 1 mass% are impurities; the size of several tens of micrometers) and niobium oxide Nb_2O_5 with mesoporous of 3.2 nm size (99.5 % purity) were purchased from Sigma-Aldrich. First of all, the mixture of 300 mg MgH_2 and 1 mol% Nb_2O_5 were put into a Cr steel vessel (30 cm^3 inner volume) together with 20 steel balls (7 mm in diameter). After the vessel was evacuated below $1x10^{-4}$ Pa for 12 h, highly pure hydrogen gas (7 N) of 1.0 MPa was introduced into it. Then, the mixture was mechanically milled for 20 h at 400 rpm using a planetary ballmilling apparatus (Fritsch P7). The samples before and after ballmilling were always handled in a glovebox filled with purified Ar gas so as to minimize the oxidation on the samples. To synthesize dehydrogenated and rehydrogenated states of the catalyzed MgH_2, the ballmilled product was dehydrogenated under a high vacuum condition for 8 h at 200 °C (catalyzed Mg) and rehydrogenated under a pure hydrogen gas of 1 MPa for 8 h at 200 °C (catalyzed MgH_2).

The H-desorption properties of the products were examined by a specially designed equipment which is composed of thermal desorption mass spectroscopy (TDMS) (Anelva M-QA200TS) and thermogravimetry (TG) (Rigaku TG8120) in the heating process with the several rates from 1 to 20 ºC/min under a highly pure helium gas (6 N) flow with zero partial pressure of hydrogen. The equipment is installed in the other glovebox filled with purified Ar gas. Therefore, the measurements of TDMS and TG were performed without exposing the samples to air.

For examining the H-absorption properties, about 100 mg of the product was loaded into a sample cell and was kept at 3 different programmed temperatures of room temperature (~20 °C), 150 and 250 °C under a high vacuum. After reaching the programmed temperatures, the valve, which combines a hydrogen reservoir tank with the sample cell, is quickly opened and the corresponding variations of pressure and temperature were monitored. Total amount of the H-absorption were independently estimated from the weight loss by TG method with increasing temperature up to 400 ºC.

3. Results and Discussion

Figure 1 shows the H-absorption behaviors at 3 different temperatures of room temperature RT (~20 ºC), 150 and 250 ºC under 1 MPa for the catalyzed Mg. Particularly, it is of interest that the H-absorption reaction proceeds even at RT and the amount of H-absorption reaches up to about 4.5 mass% within 15 sec. Furthermore, it is noteworthy that the product quickly absorbs hydrogen gas at RT even under lower hydrogen pressures than 0.1 MPa. Actually, it was confirmed that the total gas pressure became lower than 10 kPa within 10 min after the product was exposed to hydrogen gas pressure of 0.1 MPa in the closed system. Therefore, this suggests that the catalyzed Mg is available for the collection of boil-off hydrogen from liquid hydrogen tank or leaked hydrogen from high pressure tank even at any places without any heat sources. Further, at any places where extra heat sources can be provided, these products are useful as one of the reversible stationary H-storage systems.

At 150 and 250 °C, more than 5.0 mass% of hydrogen is absorbed under 1 MPa within 30 sec. Finally, the total amount of the H-absorption reaches up to 5.0, 5.7 and 5.7 mass%, respectively, at RT, 150 and 250 ºC after 8h hydrogenating treatment.

In addition, we notice that the speed of H-absorption at the initial reaction stage in the short reaction time scale within 10 sec decreases with increasing temperature. On the contrary, in the long reaction time scale, the absorption speed increases with increasing temperature as is evident from the inset of Fig. 1. Generally, the kinetics of H-absorption has been considered to be controlled by a thermally activated process like the Arrenius-type one. Then, the H-absorption behavior in the long reaction time scale could be understood, which might correspond to the diffusion process of hydrogen atom in the inner part of Mg metal itself. However, the H-absorption process in the initial short time region can not be understood in a straight way. Similar results have been reported by Barkhordarian et al. at high temperatures of 250 and 300 ºC [11-12]. Further work is undertaken to understand this unusual phenomenon.

Figure 2(a) shows the behavior of the H-desorption reaction of the catalyzed MgH_2 after the rehydrogenation. The product desorbs 5.3 mass% hydrogen within 100 min even at ~163 ºC under purified helium flow atmosphere with zero hydrogen partial pressure. Since the desorption curve looks to be of exponential type, the logarithm of a normalized hydrogen concentration, $F(t) = \ln y(t)$, is plotted as a function of time in Fig. 2(b), where $y(t)$ indicates the hydrogen concentration in the product normalized by the hydrogen content at $t = 0$. The good linearity in Fig. 2(b) indicates that the H-desorption reaction is of first order. Barkhordarian et al. have reported that H-desorption reaction for MgH_2 catalyzed with 1 mol% Nb_2O_5 at 250 ºC followed the interface controlled model, $(1\text{-}y^{1/2}) = kt$ [11]. Our result is not consistent with Barkhordarian's result. However, we have claimed that the behavior of first order reaction is a universal phenomenon in the ballmilled MgH_2 with some suitable catalysts [12].

The activation energy of H-desorption for the catalyzed MgH_2 can be determined by using the Kissinger plot, which is deduced from the first order reaction [12]. Figure 3(a) shows the TDMS profiles at several heating rates from 1 to 20 ºC/min as a function of temperature for the product. From the Kissinger plot shown in Fig. 3(b), the activation energy E_{des} for H-desorption is estimated to be 71±3 kJ/mol H_2. The value E_{des} ~71 kJ/mol is comparable to enthalpy change ΔH ~74 kJ/mol of H-desorption reaction from MgH_2. Therefore, this indicates that the activation energy of hydrogen desorption is sufficiently decreased by the catalytic effect of Nb_2O_5.

4. Conclusion

The kinetics of hydrogen absorption and desorption reactions were investigated for the MgH_2 composite doped with 1 mol% Nb_2O_5 by ballmilling for 20h. The composite after dehydrogenation at 200 °C absorbs gaseous hydrogen of ~4.5 mass% even at room temperature under 1 MPa within 15 sec and finally its capacity reaches up to more than 5 mass%. Furthermore, the product quickly absorbs hydrogen gas at room temperature even under a hydrogen pressure lower than 0.1 MPa. At 150 and 250 °C, hydrogen gas of more than 5.0 mass% is absorbed within 30 sec and finally its capacity reached up to 5.7 mass%.

On the other hand, the catalyzed MgH_2 after rehydrogenation desorbs ~6 mass% hydrogen at 160 ºC within 100 min under a helium flow with zero hydrogen partial pressure. The H-desorption is followed by the first order reaction. From the Kissinger plot, the activation energy for the H-desorption was estimated to be E_{des} ~71 kJ/mol H_2. The value is comparable to enthalpy change ΔH ~74 kJ/mol of H-desorption reaction from MgH_2. Therefore, this result indicates that the activation energy of hydrogen desorption is sufficiently decreased by the catalytic effect of Nb_2O_5.

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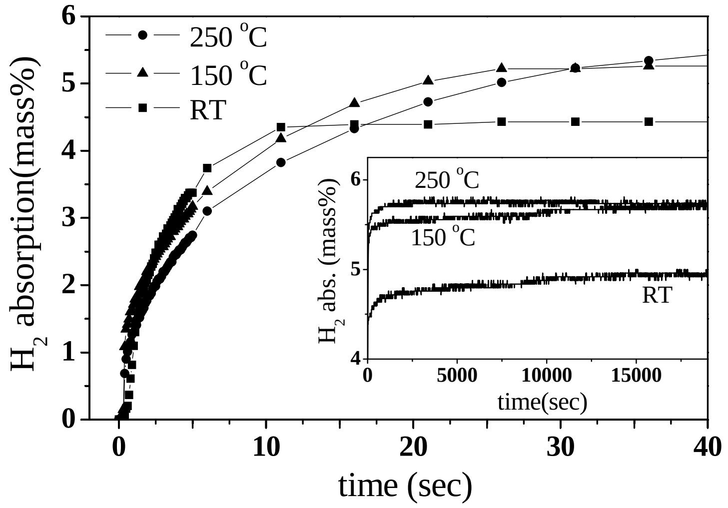

Figure 1. The amount of hydrogen absorption as a function of reaction time for the catalyzed Mg at room temperature RT (~20 ºC), 150 °C and 250 °C under 1 MPa hydrogen.

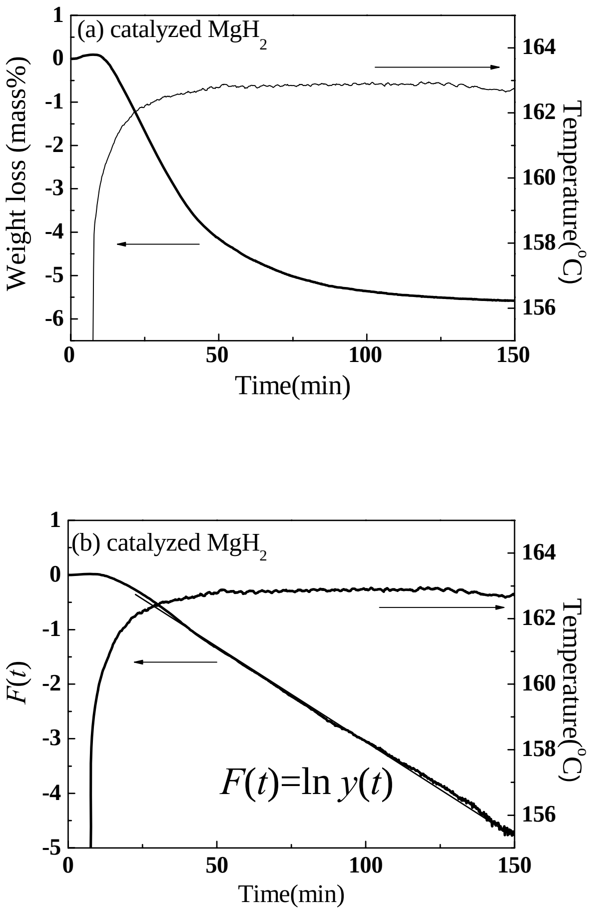

Figure 2. (a) Weight loss due to H-desorption and the aspect of temperature fluctuation around fixed temperatures as a function of H-desorption reaction time and (b) normalized hydrogen concentration function $F(t)$, and the aspect of temperature fluctuation around fixed temperatures as a function of H-desorption reaction time for the catalyzed MgH_2.

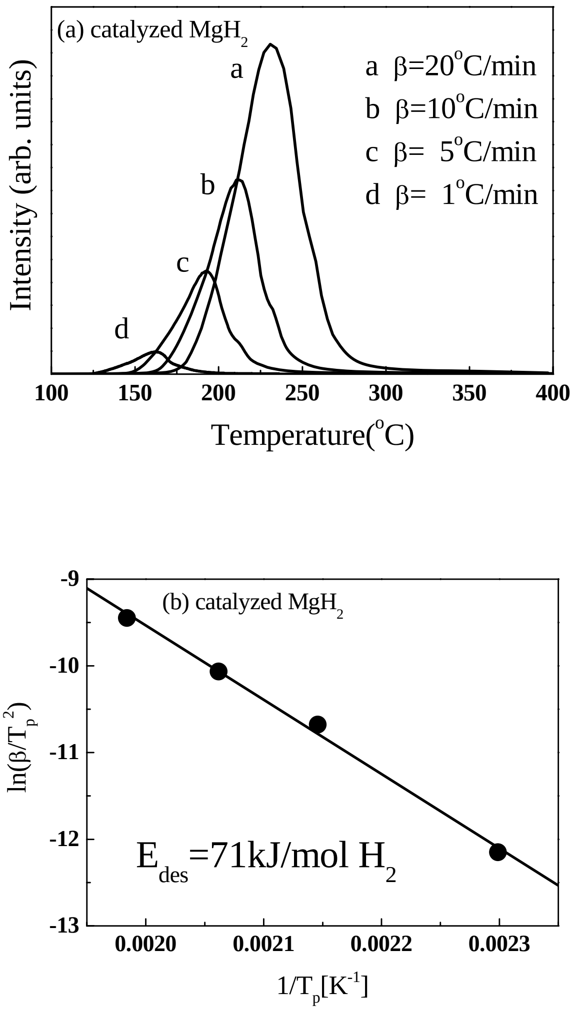

Figure 3. (a) TDMS of hydrogen under various heating rates (*β*=1,5,10,20 ºC/min) from the catalyzed MgH_2 The intensities of longitudinal axis indicates the amount of hydrogen desorption per unit time. (b) Kissinger plots for the hydrogen desorption reaction for the catalyzed MgH_2. Notations: T_p indicates the peak temperatures in thermal desorption spectra.