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Hydrogen evolution performance of magnesium alanate prepared by a mechanochemical metathesis reaction method

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Abstract−Solvent-free magnesium alanates were prepared by a mechanochemical metathesis reaction method (ball milling method) with a variation of milling time. For the purpose of comparison, magnesium alanate was also prepared by metathesis reaction method in the presence of diethyl ether. The formation of magnesium alanate ($Mg(AlH_4)_2$) and magnesium alanate-diethyl ether ($Mg(AlH_4)_2 \cdot Et_2O$) adduct was confirmed by XRD measurements. In both magnesium alanates, hydrogen evolution occurred in the first step decomposition. The starting temperature for hydrogen evolution of the solvent-free magnesium alanates decreased with increasing milling time, whereas the amount of hydrogen evolution of the solvent-free magnesium alanates increased with increasing milling time. The maximum amount of hydrogen evolution of the $Mg(AlH_4)_2 \cdot Et_2O$ adduct was slightly larger than that of the solvent-free $Mg(AlH_4)_2$, but the starting temperature for hydrogen evolution of the $Mg(AlH_4)_2 \cdot Et_2O$ adduct was much higher than that of the solvent-free $Mg(AlH_4)_2$. The addition of a small amount of titanium to the solvent-free $Mg(AlH_4)_2$ greatly reduced the hydrogen evolution temperature of titanium-doped $Mg(AlH_4)_2$. However, the maximum amount of hydrogen evolution of the titanium-doped $Mg(AlH_4)_2$ was smaller than that of the solvent-free $Mg(AlH_4)_2$.

Key words: Magnesium Alanate, Mechanochemical Metathesis Reaction, Thermal Decomposition, Hydrogen Storage

INTRODUCTION

Hydrogen has attracted considerable attention as a promising fuel and an alternate energy source due to its clean, renewable, and non-polluting nature [1-10]. However, hydrogen storage and hydrogen transportation systems are very difficult to handle because hydrogen is the lightest material on earth. Therefore, hydrogen storage technologies have been extensively studied for the efficient use of hydrogen energy [11-13]. Although the compression or liquefaction of hydrogen represents a feasible method for hydrogen storage, a number of problems remain to be solved from the standpoint of safety and energy efficiency [14]. Thus, developing an efficient system for hydrogen storage would be a challenging work for the successful realization of a hydrogen economy society.

Among the various materials used for hydrogen storage, alkali and alkali earth metal alanates have attracted considerable attention as promising materials due to their high capacity for hydrogen storage and low decomposition temperature for hydrogen evolution [15-20]. Since the report of Bogdanovi and Schwickardi, showing that the decomposition of sodium alanate can be reversed by the addition of titanium or iron [21], many works in the field of reversible hydrogen storage system using alanate materials have been reported. Although the capacity of alanate materials for hydrogen storage is high and the kinetics of thermal decomposition for hydrogen evolution appears to be promising, the process used for reversible hydrogen storage after hydrogen evolution needs to be improved.

It is known that magnesium alanate retains a higher capacity for hydrogen storage than sodium alanate [22]. It has also been reported that magnesium alanate readily decomposes at temperatures below 200 °C [23]. In these early papers, several preparation reactions for magnesium alanates have been proposed as shown below.

$$4MgH_2+2AlCl_3 \rightarrow Mg(AlH_4)_2+3MgCl_2 \quad (1)$$

$$MgH_2+2AlH_3 \rightarrow Mg(AlH_4)_2 \quad (2)$$

$$2LiAlH_4+MgBr \rightarrow Mg(AlH_4)_2+2LiBr \quad (3)$$

The thermal decomposition behavior of alanate materials for hydrogen evolution has also been investigated [23-25]. However, the kinetics of thermal decomposition of pure magnesium alanate has not been clearly elucidated, because all the samples examined so far have contained an alanate-solvent adduct in the course of preparation. Moreover, there was a significant discrepancy in enthalpy change during the first step decomposition [16]. Therefore, it would be desirable to prepare magnesium alanate without any solvents for the clear understanding of the thermal decomposition behavior of this compound.

In this work, magnesium alanates were prepared by a mechanochemical metathesis reaction method using magnesium chloride and sodium alanate in the absence of any solvents. A magnesium alanate sample was also prepared by a metathesis reaction method in the presence of diethyl ether to investigate the effect of solvent on the hydrogen evolution performance of magnesium alanate. The crystal structures and hydrogen evolution performance of the prepared magnesium alanates were then examined. Titanium-doped magnesium alanate was also prepared with an aim of investigating

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the effect of titanium addition on the hydrogen evolution performance of magnesium alanate.

EXPERIMENTAL

1. Preparation of Magnesium Alanate

Magnesium alanates were prepared by a mechanochemical metathesis reaction method in the absence of any solvents, according to a similar method reported in the literature [17]. In short, magnesium chloride (Sigma-Aldrich, 99.9%) and sodium alanate (Sigma-Aldrich, 90%) powders with a molar ratio of 1 : 2 were mixed in a glove box, where the water vapor and oxygen levels were maintained at below 5 ppm. The solid mixture and four Cr-steel balls (diameter=7.2 mm) were placed in a ball miller (SPEX-8000). The milling was carried out for 9, 15, and 30 min for the preparation of three solvent-free magnesium alanate samples.

A magnesium alanate was also prepared by a metathesis reaction method in the presence of a solvent to investigate the effect of solvent on the hydrogen evolution performance of magnesium alanate. Magnesium chloride (4.76 g, 0.05 mol, Sigma-Aldrich, 99.9%) and sodium alanate (5.4 g, 0.1 mol, Sigma-Aldrich, 90%) were separately dissolved in 200 ml diethyl ether (Sigma-Aldrich, 99.9%) that had been distilled over sodium metal. These two solutions were then mixed at room temperature. The resulting white suspension was stirred for 8 h with reflux and then allowed to stand overnight. After the suspension was filtered, the solid product was dried under a vacuum at room temperature. To minimize the effect of residual solvent (diethyl ether) in the prepared magnesium alanate, the dried magnesium alanate sample was further evacuated under a vacuum at 90 °C.

Titanium-doped magnesium alanate was prepared by a mechanochemical metathesis reaction method in the absence of any solvents, with an attempt to examine the effect of titanium addition on the hydrogen evolution performance of magnesium alanate. For this purpose, magnesium chloride (Sigma-Aldrich, 99.9%) and sodium alanate (Sigma-Aldrich, 90%) powders with a molar ratio of 1 : 2 were mixed in a glove box, and titanium trichloride (2 mol% on titanium basis, Sigma-Aldrich, 99.9%) was then added to the mixture. The resulting mixture and four Cr-steel balls (diameter=7.2 mm) were placed in a ball miller (SPEX-8000). The milling was carried out for 60 min to obtain a titanium-doped magnesium alanate.

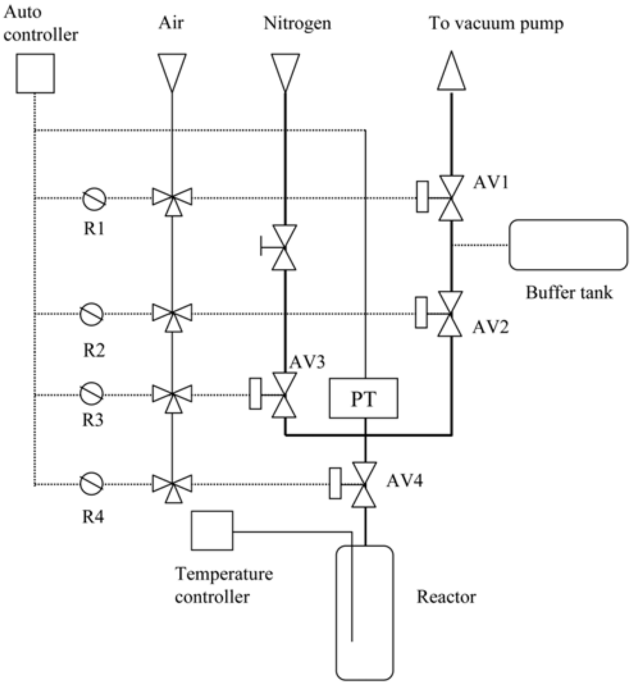

Fig. 1. Schematic diagram of the apparatus for pressure-composition isotherm (P-C isotherm) measurements.

2. Characterization and Pressure-Composition Isotherm

The crystal structures of the magnesium alanate samples were examined by X-ray diffraction measurements (Rigaku, D-MAX 2000). The amounts of hydrogen evolution were determined by pressure-composition isotherm measurements. Fig. 1 shows a schematic diagram of the apparatus for pressure-composition isotherm (P-C isotherm) measurements. For the P-C isotherm measurement, each magnesium alanate sample was heated from room temperature to 270 °C at a rate of 5 °C/min. The pressure in the measurement system increased with increasing temperature due to the evolution of hydrogen by the thermal decomposition of magnesium alanate. Pressure changes were automatically converted into the weight of hydrogen evolution by using the van der Waals equation.

RESULTS AND DISCUSSION

1. Effect of Preparation Method

Fig. 2 shows the XRD patterns of magnesium alanates prepared by a mechanochemical metathesis reaction method with the variation of milling time. The intensity of the XRD peak corresponding to sodium alanate phase ($NaAlH_4$, $2\theta=29^o$) continuously decreased with increasing milling time, and the sodium alanate phase almost disappeared after a 30 min-milling. On the other hand, the intensities of the XRD peaks corresponding to magnesium alanate ($Mg(AlH_4)_2$, $2\theta=25^o$) and sodium chloride (NaCl, $2\theta=32^o$ and 46^o) appeared to grow with increased milling time. These results indicate that the mechanochemical metathesis reaction method employed in this work

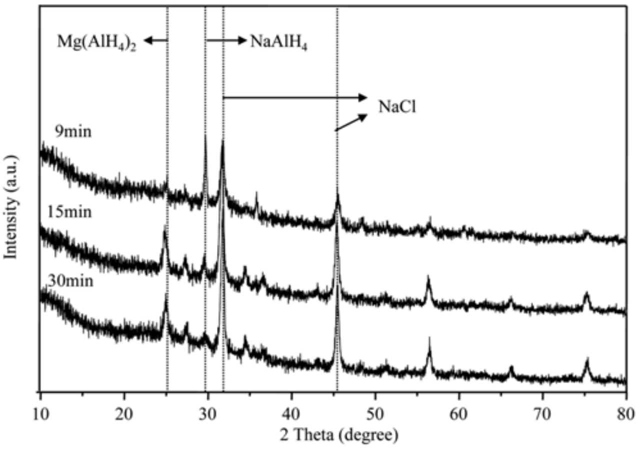

Fig. 2. XRD patterns of magnesium alanates prepared by a mechanochemical metathesis reaction method with a variation of milling time.

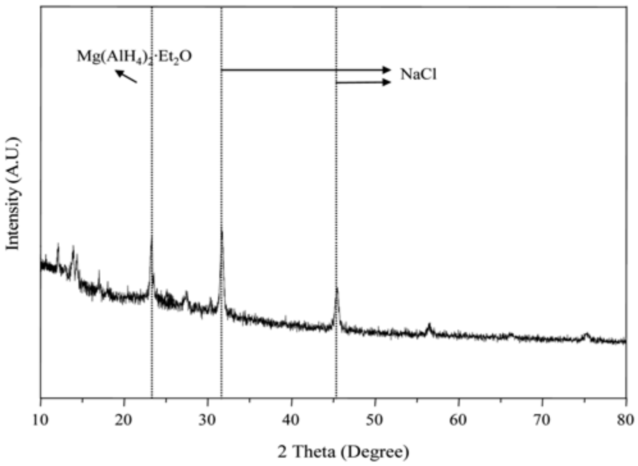

Fig. 3. XRD pattern of magnesium alanate prepared by a metathesis reaction method in the presence of a solvent (diethyl ether).

was very efficient for the preparation of solvent-free magnesium alanates.

Fig. 3 shows the XRD pattern of magnesium alanate prepared by a metathesis reaction method in the presence of a solvent (diethyl ether). Compared to the solvent-free magnesium alanate ($Mg(AlH_4)_2$) prepared by a mechanochemical metathesis reaction method (Fig. 2), the XRD peak corresponding to magnesium alanate phase shifted from $2\theta=25^{\circ}$ to $2\theta=23^{\circ}$ due to the formation of a magnesium alanate-diethyl ether ($Mg(AlH_4)_2\cdot Et_2O$) adduct [15,26-28]. It is known that the ether in the $Mg(AlH_4)_2\cdot Et_2O$ adduct decreases the kinetics of thermal decomposition, and thus, increases the hydrogen evolution temperature [29]. This indicates that diethyl ether should be removed from the $Mg(AlH_4)_2\cdot Et_2O$ adduct for efficient hydrogen evolution. In this work, therefore, the $Mg(AlH_4)_2\cdot Et_2O$ adduct was evacuated under a vacuum at 90 °C to minimize the effect of residual diethyl ether in the $Mg(AlH_4)_2\cdot Et_2O$ adduct. However, it was very difficult to remove the diethyl ether completely from the $Mg(AlH_4)_2\cdot Et_2O$ adduct, because alanate materials have a good affinity for organic solvents.

2. Hydrogen Evolution by Thermal Decomposition of Magnesium Alanate

Hydrogen evolution by the thermal decomposition of magnesium alanate occurs according to the following two steps [16]. The first step decomposition starts at around 120 °C, while the second step decomposition starts at around 280 °C [16,26,30].

$$Mg(AlH_4)_2 \rightarrow MgH_2+2Al+3H_2 \qquad \text{(first step)}$$
$$MgH_2+2Al \rightarrow 1/2Al_3Mg_2+1/2\ Al+H_2 \qquad \text{(second step)}$$

Fig. 4 shows the hydrogen evolution profiles of magnesium alanates prepared by a mechanochemical metathesis reaction method with a variation of milling time. It is noteworthy that hydrogen evolution by the thermal decomposition of magnesium alanates occurred in the first step decomposition. The starting temperature for hydrogen evolution decreased with increasing milling time. Furthermore, the amount of hydrogen evolution increased with increasing milling time up to 30 min. At longer milling time than 30 min, however, the amount of hydrogen evolution was not changed significantly. The starting temperature for hydrogen evolution and the amount of hydrogen evolution showed the same trend as that of the XRD peak intensities of the magnesium alanates (Fig. 2). The maximum amount of hydrogen evolution observed for the 30 min-milled magnesium alanate was 3.2 wt%, in good agreement with the theoretical value of 3.9 wt% (because the sample prepared by a mechanochemical metathesis reaction method contains 2 mol of sodium chloride for 1 mol of magnesium alanate, the theoretical hydrogen content of the sample is 3.9 wt%).

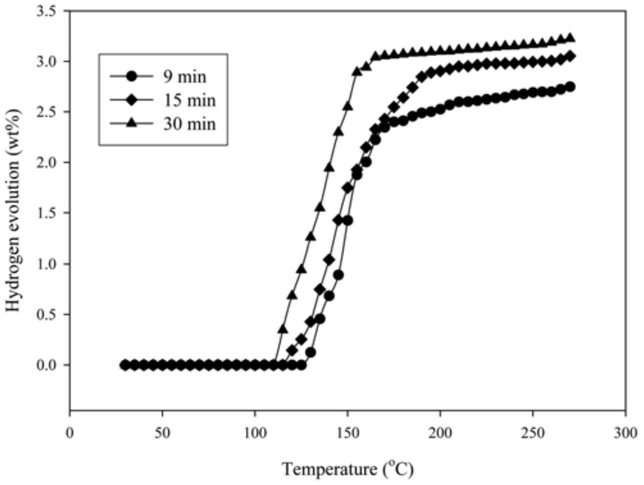

Fig. 4. Hydrogen evolution profiles of magnesium alanates prepared by a mechanochemical metathesis reaction method with a variation of milling time.

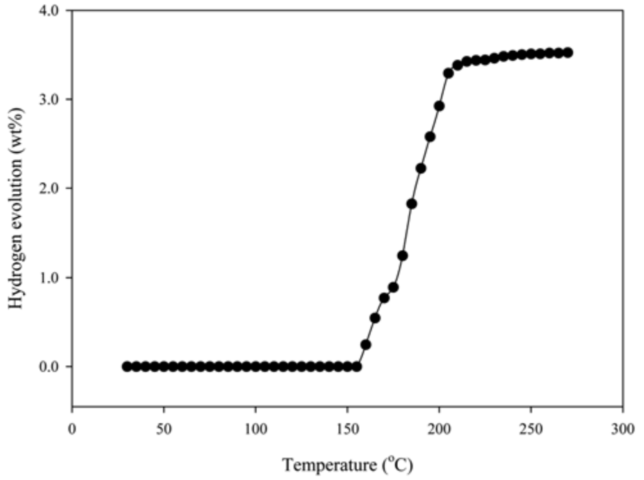

Fig. 5. Hydrogen evolution profile of magnesium alanate prepared by a metathesis reaction method in the presence of a solvent (diethyl ether).

Fig. 5 shows the hydrogen evolution profile of magnesium alanate prepared by a metathesis reaction method in the presence of a solvent (diethyl ether). The maximum amount of hydrogen evolution was 3.5 wt%, and hydrogen evolution began to occur at 160 °C. The starting temperature for hydrogen evolution of the $Mg(AlH_4)_2\cdot Et_2O$ adduct was much higher than that of the solvent-free $Mg(AlH_4)_2$ (Fig. 4). It is believed that the magnesium alanate-diethyl ether ($Mg(AlH_4)_2\cdot Et_2O$) adduct decreased the kinetics of thermal decomposi-

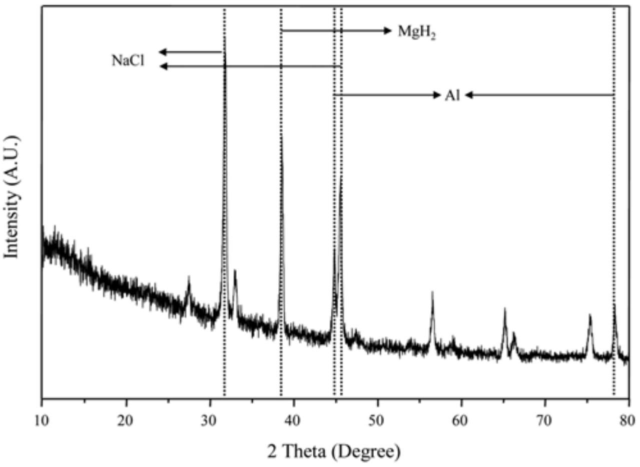

Fig. 6. XRD pattern of solvent-free magnesium alanate obtained after hydrogen evolution at 270 °C for 30 min.

tion by changing the enthalpy during the thermal decomposition step, leading to hydrogen evolution at a high temperature.

Fig. 6 shows the XRD pattern of solvent-free magnesium alanate obtained after hydrogen evolution at 270 °C for 30 min. It is interesting to note that the magnesium alanate phase disappeared after the thermal decomposition. Instead, magnesium hydride ($2\theta=38^{\circ}$) and aluminum ($2\theta=45^{\circ}$ and 77°) phases were clearly observed. This strongly supports the conclusion that hydrogen evolution by the thermal decomposition of magnesium alanates only occurs in the first step decomposition.

3. Hydrogen Evolution of Titanium-Doped Magnesium Alanate

When transition metals are doped in alanate materials, the kinetics of thermal decomposition of alanate materials is enhanced [31-34]. To enhance the kinetics of thermal decomposition of magnesium alanate, titanium-doped magnesium alanate containing 2 mol% of titanium was prepared by a mechanochemical metathesis reaction method in the absence of any solvents. In the preparation of the sample, a mixture of magnesium chloride, sodium alanate, and titanium trichloride was milled at high energy for 60 min to reduce the grain size of the compound. Fig. 7 shows the hydrogen evolution profile of 2 mol% titanium-doped magnesium alanate. The titanium-doped magnesium alanate shows a lower starting temperature for hydrogen evolution than the solvent-free magnesium alanate. It is clear that titanium had a significant effect on the kinetics of thermal decomposition. The kinetics of thermal decomposition of magnesium alanate was enhanced by the addition of a small amount of titanium. However, the maximum amount of hydrogen evolution of the titanium-doped magnesium alanate was smaller than that of the magnesium alanate. It was also observed that the hydrogen evolution temperature became a little lowered and the amount of hydrogen evolution was slightly decreased, with increasing titanium content from 2 mol% to 3 mol%. This may be due to the reduction of titanium trichloride by alanate at the expense of hydrogen. It is likely that the powerful ball milling, which provided sufficient energy to evolve a significant amount of stored hydrogen during the milling process, is also partly responsible for the reduced amount of hydrogen evolution of the titanium-doped magnesium alanate [26].

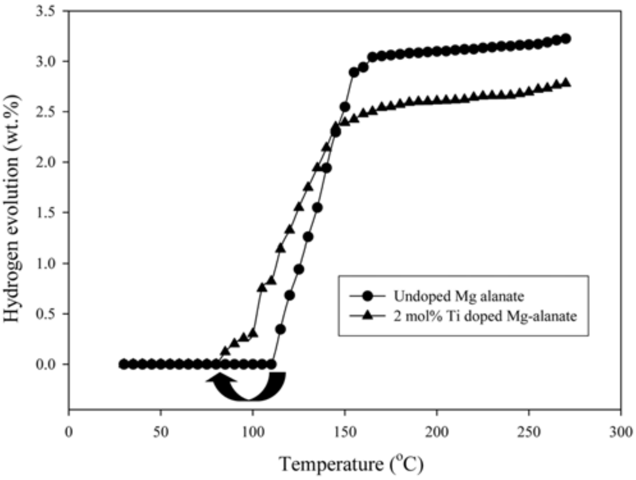

Fig. 7. Hydrogen evolution profile of titanium-doped magnesium alanate (2 mol% of titanium).

CONCLUSIONS

Solvent-free magnesium alanates were prepared by a mechanochemical metathesis reaction method with a variation of milling time. A magnesium alanate was also prepared by a metathesis reaction method in the presence of diethyl ether for the purpose of comparison. The formation of $Mg(AlH_4)_2$ and $Mg(AlH_4)_2 \cdot Et_2O$ adduct was well confirmed by XRD measurements. Hydrogen evolution by the thermal decomposition of magnesium alanates occurred in the first step decomposition. The starting temperature for hydrogen evolution of the solvent-free magnesium alanate decreased with increasing milling time, and the amount of hydrogen evolution of the solvent-free magnesium alanates increased with increasing milling time. The maximum amount of hydrogen evolution observed for the 30 min-milled solvent-free magnesium alanate was 3.2 wt%. The maximum amount of hydrogen evolution of the $Mg(AlH_4)_2 \cdot Et_2O$ adduct was slightly larger than that of the solvent-free $Mg(AlH_4)_2$, but the starting temperature for hydrogen evolution of the $Mg(AlH_4)_2 \cdot Et_2O$ adduct was much higher than that of the solvent-free $Mg(AlH_4)_2$. The addition of a small amount of titanium had a significant effect on the hydrogen evolution performance of the solvent-free $Mg(AlH_4)_2$. The titanium-doped $Mg(AlH_4)_2$ showed a lower starting temperature for hydrogen evolution than the solvent-free $Mg(AlH_4)_2$, but the maximum amount of hydrogen evolution of the titanium-doped $Mg(AlH_4)_2$ was smaller than that of the solvent-free $Mg(AlH_4)_2$.

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