Hydrogen generation by hydrolysis reaction of magnesium hydride

Y. KOJIMA, K.-I. SUZUKI, Y. KAWAI
Toyota Central R&D Labs., Inc., Nagakute-cho, Aichi-gun, Aichi 480-1192, Japan
E-mail: kojima@mosk.tytlabs.co.jp

Fuel cells which are actuated with hydrogen (H_2) and oxygen (O_2) have been under development in order to overcome problems of energy and environment in future. The energy obtained upon a reaction of H_2 and O_2 is directly converted into electric energy. Since a fuel cell has efficiency much higher than that of conventional combustion engines, FCV (fuel cell vehicle) is expected to be a car having high efficiency [1, 2]. One of the most widely envisioned sources of fuel for FCV is H_2. Therefore, it is necessary to have a storage tank of H_2 to start the system quickly.

Hydrogen can be stored in tanks of compressed [2, 3] or liquefied H_2 [3], or by adsorption on activated carbon [4], carbon nanotubes [3, 5, 6] and graphite nanofiber [7, 8] or in a hydrogen-absorbing alloy [9] or in a chemical hydride such as NaH [10], LiH [11], $NaAlH_4$ [12] or $NaBH_4$ [13–21].

Among these methods, attention has recently been given to a hydrolysis of chemical hydride (ionic hydride) such as NaH [10], LiH [11] and $NaBH_4$ [13–21]. PowerBall Technologies and Thermo Technologies proposed NaH and LiH, respectively [10, 11]. NaH and LiH vigorously react with water. Therefore, NaH is coated with a resin film, and the film is cut to generate hydrogen in the presence of water on demand [10]. LiH is prepared as slurry with light mineral oil and the dispersion has been found to be stable for a long period of time at normal temperature and pressure [11]. $NaBH_4$ is stable compared with other chemical hydride and is easy to handle [13–21]. At room temperatures, only a small percentage of the theoretical amount of H_2 is liberated by hydrolysis reaction of $NaBH_4$ and H_2O [22], but the hydrolysis is accelerated by the use of catalysts [13–21].

The hydrolysis of magnesium hydride (MgH_2) is of interest for the generation of H_2 because the byproduct [$Mg(OH)_2$] by the hydrolysis reaction of MgH_2 is recycled back to MgH_2 using general reactions (electrolytic refining and the reaction of hydrogen on magnesium) [23–25]. However, the hydrolysis reaction of MgH_2 is very slow due to the formation of $Mg(OH)_2$ layer [26]. When MgH_2 is to be used for the generation of H_2, a rapid reaction is desired. The hydrolysis of MgH_2 has been known to be accelerated by using nanocrystalline MgH_2 [26], or by adding acids [26, 27].

In this paper, we present an investigation of the hydrolysis of MgH_2 using an acid and a catalyst.

MgH_2 (Aldrich, molecular weight: 26.34, density: 1.45 g/cm^3) was used for the reaction with water. MgH_2 is a light gray crystalline powder, and evolves H_2 at high temperatures above 320 °C under normal pressure [28].

On contact with water, it decomposes slowly to form H_2 and $Mg(OH)_2$. It is hard to dissolve $Mg(OH)_2$ into water, i.e., the concentration of the saturated solution is only 1.9 mg/L (291 K).

In the previous paper, we found that Pt-$LiCoO_2$ was an excellent catalyst for releasing hydrogen by hydrolysis of $NaBH_4$ solution [22]. In this experiment, Pt-$LiCoO_2$ was selected because of its high activity. Pt-$LiCoO_2$ catalyst was synthesized using a conventional impregnation techniques [22]. Dinitrodiammine platinum (II) nitric acid solution [$Pt(NO_2)_2(NH_3)_2$, 33 ml, Pt content of 50 g/L, Tanaka Kikinzoku Kogyo K. K., Japan] and lithium cobaltate powder ($LiCoO_2$, Nippon Chemical Industries Co., Ltd., product name Cellseed 5) were mixed. The mixture was held at 523 K for 5 h. The dried powder was calcined for 2 h in air at 723 K, thereby coating Pt on the metal oxide. Thus, the Pt-metal-oxide catalysts contained a Pt content of 1.5 wt%.

The H_2 generation amount was determined as follows. The catalyst [conventional impregnation method (Pt-$LiCoO_2$): 10–50 mg] and 50 mg of MgH_2 were packed into an Erlenmeyer flask having a volume of 100 ml, and subsequently 5 g of water or a acetic acid aqueous solution (acetic acid: 2 wt%) were added at room temperature (23 °C) by use of a syringe. Then, H_2 generation amounts were determined from the change in level of the volumetric burette in a gas analyzer made by Sibata Scientific Technology, Ltd., Japan. The gas generated was identified as H_2 by a gas chromatograph.

Crystalline structure of the byproduct by the hydrolysis reaction of MgH_2 using acetic acid was investigated by wide angle X-ray diffraction. The X-ray diffraction pattern was recorded at room temperature using a Rigaku Denki Rad-B over a range of diffraction angle (2θ) from 3 to 80 ° with Cu K_α radiation (30 kV, 30 mA) filtered by a monochrometer.

The hydrolysis reaction of MgH_2 is as follow [26, 27].

$$MgH_2 + 2H_2O \rightarrow Mg(OH)_2 + 2H_2 \qquad (1)$$
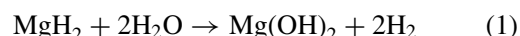
The H_2 generation amount of this reaction is 6.5 wt% when the weight of water is taken into account. In fuel cell application, if the water produced by the fuel cell is redirected to MgH_2, then the H_2 generation amount increases to 15.4 wt%. In our experiment, the H_2 yield was determined by the following equation.

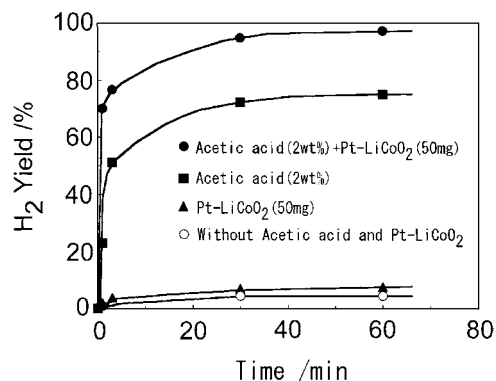$$H_2 \text{ Yield} = W_h/(0.154 \cdot W_s) \qquad (2)$$

Figure 1 Hydrogen production profiles for reaction of MgH$_2$ with water using acetic acid and Pt-LiCoO$_2$ at 296 K.

where W_h is the H$_2$ generated (g), W_s is the amount of MgH$_2$(g). The value of 0.154 is the theoretical H$_2$ generation amount per unit weight of MgH$_2$. The reaction profile of MgH$_2$ for reaction with water carried out at 296 K is shown in Fig. 1. Without using an acid and a catalyst, the amount of H$_2$ increases with time and approaches to a constant conversion value of 4%. The H$_2$ generation is accelerated slightly by using the Pt-LiCoO$_2$ catalyst as shown in Fig. 1 (H$_2$ yield at 60 min: 7%).

Fig. 1, however, shows that the H$_2$ generation dramatically increases when an aqueous solution (2 wt%) of acetic acid was injected into the vessel [MgH$_2$ (50 mg) mixed with Pt-LiCoO$_2$ catalyst (50 mg)] at 296 K. After 60 min, the H$_2$ yield reaches a value of 97%. When the content of the catalyst was decreased from 50 to 10 mg, the H$_2$ yield decreased in the early stages (1 min: 70–63%, 3 min: 77–70%), but the values at the equilibrium state (60 min) were equal (97%). Furthermore, when the aqueous solution of acetic acid was injected into the vessel containing MgH$_2$ (50 mg) alone, the H$_2$ yield was 75% at 60 min. These results indicate that the H$_2$ generation is greatly improved by using both the acetic acid and Pt-LiCoO$_2$ catalyst.

To determine the remaining species existing after the H$_2$ generation reaction of MgH$_2$ with aqueous solution of acetic acid, vacuum drying of the reaction residue was carried out at room temperature. X-ray diffraction was used to determine the structure of the remaining material. Fig. 2 illustrates the X-ray diffraction intensity curve of the reaction residue together with the data of Mg(OH)$_2$ [29], Mg(CH$_3$COO)$_2$ [29] and MgH$_2$ [29].
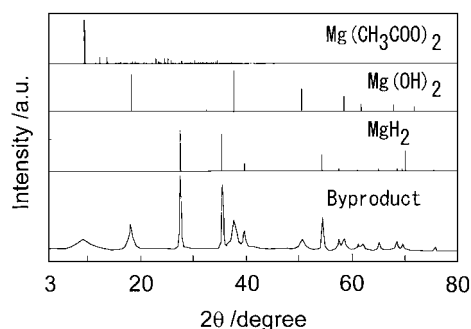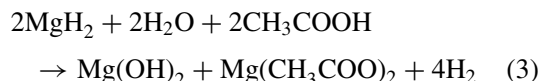
We have found that the remaining material is a mixture of Mg(OH)$_2$, Mg(CH$_3$COO)$_2$ and MgH$_2$.

Thus, the hydrolysis reaction of MgH$_2$ using acetic acid is explained by the following reaction.

$$2MgH_2 + 2H_2O + 2CH_3COOH$$
$$\rightarrow Mg(OH)_2 + Mg(CH_3COO)_2 + 4H_2 \quad (3)$$

The rate of this reaction was found to be greatly enhanced by using Pt-LiCoO$_2$ as a catalyst. An explanation of this catalysis function is that electrons are discharged through the Pt-LiCoO$_2$ catalyst from H$^-$ ion from MgH$_2$. H$^-$ ion is then oxidized to give molecular H$_2$. On the other hand, this electron can reduce the H$^+$ in water and H$_2$ gas is generated. It is considered that the activity of the catalyst is increased by the acetic acid because the acid dissolves the Mg(OH)$_2$ layer on the MgH$_2$ particles.

In conclusion, it was indicated that the H$_2$ yield by the hydrolysis reaction of MgH$_2$ using both acetic acid and Pt-LiCoO$_2$ was high compared with that using acetic acid alone.

Acknowledgments

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Figure 2 X-ray diffraction intensity curve of byproduct, together with the data of Mg(CH$_3$COO)$_2$, Mg(OH)$_2$, and MgH$_2$.

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