Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Hydrogen generation by hydrolysis of MgH_2 and enhanced kinetics performance of ammonium chloride introducing

Minghong Huang [a,b], *Liuzhang Ouyang* [a,b,c,*], *Hui Wang* [a,b], *Jiangwen Liu* [a,b], *Min Zhu* [a,b]

[a] *School of Materials Science and Engineering, Key Laboratory of Advanced Energy Storage Materials of Guangdong Province, South China University of Technology, Guangzhou, 510641, PR China*

[b] *China-Australia Joint Laboratory for Energy & Environmental Materials, South China University of Technology, Guangzhou, 510641, PR China*

[c] *Key Laboratory of Fuel Cell Technology of Guangdong Province, South China University of Technology, Guangzhou, 510641, PR China*

ARTICLE INFO

Article history:
Received 28 November 2014
Received in revised form
27 February 2015
Accepted 12 March 2015
Available online 3 April 2015

Keywords:
Hydrogen generation
Ammonium chloride
Magnesium hydride
Hydrolysis

ABSTRACT

Apparent activation energies of MgH_2 hydrolysis in deionized water were deduced for the first time being 58.06 kJ/mol. This paper also reports the mechanisms of MgH_2 hydrolysis and the effects of NH_4Cl on the kinetics of magnesium hydride hydrolysis. Experimental results show that hydrogen generation via MgH_2 hydrolysis exhibited the highest rates in 4.50 wt% NH_4Cl solution. This is because addition of NH_4Cl could effectively decrease the compactness of magnesium hydroxide. It is also found that addition of NH_4Cl could effectively enhance the hydrolysis kinetics and lead to a reduction of the apparent activation energy of MgH_2 hydrolysis. The apparent activation energies of MgH_2 hydrolysis decreased from 58.06 kJ/mol in deionized water to 50.86 and 30.37 kJ/mol in 0.5 and 4.5 wt% NH_4Cl solutions, respectively. MgH_2-4.5 wt% NH_4Cl system showed the fastest hydrolysis rate, producing 1310 mL g^{-1} hydrogen in 5 min, 1604 mL g^{-1} hydrogen in 10 min, and 1660 mL g^{-1} hydrogen in 30 min at 60 °C. The results reveal that NH_4Cl may be a promising reagent for promoting the hydrolysis of MgH_2 for hydrogen generation systems, which demonstrated a new method to improve the hydrolysis of MgH_2.

Introduction

Because of the high energy density of hydrogen (142 MJ/kg, around three times higher than that of oil [1,2]) and cleanness [3–6], energy from hydrogen holds promise as a form of clean energy. However, for hydrogen to be considered as the energy vector of the future, it must address the concerns raised by the conventional energy sources, namely renewability and environment protection [7,8]. The main problems with this energy

* *Corresponding author*. Key Laboratory of Fuel Cell Technology of Guangdong Province, South China University of Technology, Guangzhou, 510641, PR China. Tel.: +86 20 87114253; fax: +86 20 8711276.
E-mail address: meouyang@scut.edu.cn (L. Ouyang).

http://dx.doi.org/10.1016/j.ijhydene.2015.03.058

include hydrogen storage, availability of infrastructures and the need for high efficiency in hydrogen generation. Concerning hydrogen production, there are various possibilities concerning the feedstocks, the energy used for the production and the processes [9]. Recently, hydrolysis was found to be a convenient technology for hydrogen production. It has attracted increased attention because of its safety and its amenability to mild reaction conditions [10–12]. Various metal hydrides (e.g., LiH [13], $NaBH_4$ [14,15], $LiBH_4$ [16,17] are used in fuel cells because they can release hydrogen via reactions with water at suitable temperatures. For instance, sodium borohydride was once regarded as a promising material for hydrogen storage and was studied for its practical application. The fuel cell minivan by Daimler Chrysler successfully applied the millennium cell using the sodium borohydride ($NaBH_4$) system [18]. However, the US DOE advises against the use of $NaBH_4$ for onboard automotive hydrogen storage [19] because of its low effective gravimetric capacities for hydrogen storage and because of the inefficiency of $NaBO_2$ recycling [10].

In recent years, many researchers have turned their attention to MgH_2 hydrolysis. Magnesium hydride is a compound with a large hydrogen storage capacity (7.6 wt%). If MgH_2 hydrolysis uses water produced by a fuel cell, then the density of hydrogen increases to 15.2 wt%. Hydrogen can be released through the following reaction:

$$MgH_2 + 2H_2O \rightarrow Mg(OH)_2 + 2H_2\uparrow \quad \Delta H = -277 \text{ kJ/mol} \qquad (1)$$

Evidently, hydrolysis can occur spontaneously at room temperature without any special conditions for reaction. However, the byproduct of magnesium hydroxide hydrolysis is poorly soluble in water (1.9 mg/L at 291 K) [20]. Therefore, hydrolysis immediately terminates when a passive magnesium hydroxide layer forms on the unreacted MgH_2 surface. Previous study shows that the maximum conversion of MgH_2 does not exceed 30% in 1 h in direct hydrolysis, which is inadequate for practical application [21,22]. To solve this problem, several methods have attempted to improve the hydrolysis properties of MgH_2. These methods mainly include nanostructuring [23–25], changing the aqueous solution [25–30], and ball-milling of MgH_2 powder mixed with metal hydride [31–33] or chloride [34]. These approaches effectively improve the hydrogen yield and improve the kinetics of hydrogen generation. However, several key problems remain. These include the lack of control of the rate of hydrogen production. Such problems lead to failure in meeting the requirements for it commercial application. Therefore, studies aimed to find a new method to improve the hydrolytic properties of MgH_2.

Ammonium salts have been applied in hydrogen generation. Makhaev et al. [30] enhanced the hydrolytic properties of MgH_2, but they did not elucidate the kinetic properties and activation energy of MgH_2 hydrolysis in pure water or in aqueous solutions of ammonium salts. The hydrolytic properties of MgH_2 in ammonium chloride solution at various temperatures and the kinetics of spontaneous hydrolysis of MgH_2 in water and in NH_4Cl solution at 20–95 °C were investigated in the present study. Specifically, the activation energies of MgH_2 hydrolysis in the presence and absence of NH_4Cl solution were calculated.

Experiment

MgH_2 (Sigma Aldrich, 95%) was used as starting material. Pure water and NH_4Cl solution were used as media to study the effect of NH_4Cl on hydrolysis. Equipment used in this experiment is shown in Fig. 1. The apparatus consisted of a section for hydrolysis and another for collecting and measuring hydrogen. The latter section consisted of a 150 mL flask with three openings: one for introducing water or solution, one for releasing hydrogen exhaust, and another for holding a thermometer. Here, MgH_2 powder reacted with deionized water or NH_4Cl solution. A syringe was used to control the amount of water or aqueous solution. A thermostatic water bath (Yuhua Instrument Co.) was used to control the temperature of the flask to observe the effect of temperature on hydrogen generation. The temperature of the water bath was set within 20°C–95 °C in the hydrogen generation experiments. Considering that the hydrolysis properties of MgH_2 in deionized water was quite poor at low temperature, so we chose relatively higher temperature in order to obtain the basic hydrolysis data, which are different with the hydrolysis in NH_4Cl solutions.

The MgH_2 powder size is about 50 μm MgH_2 powder (100 mg) in a flask was allowed to react with 20 mL of deionized water or 4.5 wt% NH_4Cl solution. Besides, 10 mL of 0.5 wt% NH_4Cl solution was also used to react with 100 mg powder to study the effect of NH_4Cl when the amount of NH_4Cl is not excessive. The amount of hydrogen was quantified by water displacement in an inverted graduated cylinder over a water-filled tank. The reactor and cylinder were connected by a Teflon tube.

The hydrolysis products were passed through a drying cabinet at 100 °C and then analyzed by a Mini Flex 600 X-ray diffractometer using Cu K_α radiation. Patterns were recorded in the 2θ range of 10°–90° at a scanning rate of 0.05° s^{-1}.

Results and discussion

Kinetics of hydrogen generation

Fig. 2 shows the kinetics of hydrogen generation by the reaction of MgH_2 with deionized water, with 0.5 wt% NH_4Cl solution, and with 4.5 wt% NH_4Cl solution at various temperatures. For deionized water, as shown in Fig. 2(a (the red curve)), as expected, the rate of hydrogen generation increased with increasing temperature. Basically, the reaction of MgH_2 in deionized water was observed the poor hydrolysis performance. The hydrolysis yield was relatively low and the sample only generated 114 mL g^{-1} hydrogen in 5 min, 174 mL g^{-1} hydrogen in 10 min, 209 mL g^{-1} hydrogen in 30 min and 819 mL g^{-1} hydrogen in 2 h at 60 °C. This is due to that $Mg(OH)_2$ formed on the surface of MgH_2, hydrolysis entered an induction period after initial rapid reaction during the first few minutes. On the other side, some of the MgH_2 powder floated on the water surface because of its poor wettability. The