ORIGINAL RESEARCH

Rapid hydrogen generation from aluminum–water system by adjusting water ratio to various aluminum/aluminum hydroxide

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Abstract The effect of Al(OH)₃ on the hydrogen generation from Al/water system is evaluated. Four synthesized and one commercial Al(OH)₃ powders are employed to investigate their assistance to the hydrogen generation from Al/water system at room temperature. It was found that the Al(OH)₃ product derived from Al(NO)₃ precursor exhibits the best catalytic effect and exerts the highest hydrogen generation rate. 100 % yield of hydrogen (1,360 ml/g Al at 25 °C) can be achieved within 6 min at a proper Al:Al(OH)₃:H₂O weight ratio (3:15:50). That is, by adjusting Al:Al(OH)₃:H₂O ratio, the highest hydrogen generation rate ever reported so far, without using any alloying elements or corrosive additives, can be achieved.

Keywords Water · Aluminum hydroxide · Hydrogen generation

Introduction

Hydrogen is an ideal energy source due to its harmless effect to environment [1]. However, the storage and transportation of hydrogen gas is still challenging nowadays. One solution to this issue is to development a use-ondemand hydrogen source. Aluminum, abundant in earth, has low density, high capacity and excellent activity to water and is a superior material for hydrogen generation

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using effective Al(OH)₃ powders and taking advantages of exothermic heat from the Al-water reaction.

Experimental procedures

Chemicals

Aluminum nitrate nonahydrate (Al(NO₃)₃·9H₂O, \geq 98.0 %, SHOWA), aluminum chloride nonahydrate (AlCl₃·6H₂O, >97.0 %. SHOWA), sodium aluminate (NaAlO₂, >99.0 %, SHOWA), and sodium hydroxide (NaOH, \geq 97 %, Sigma–Aldrich) were purchased and used for the preparation of aluminum hydroxide. Commercial Al(OH)₃ $(0.5 \ \mu m, \ge 98 \ \%, \ NanoAmor)$ was also purchased and used directly. Reaction product Al(OH)₃ from the reaction of Al and water counts the fifth source of aluminum hydroxide. These five aluminum hydroxides were evaluated for their effects on the reaction of Al/H₂O system. Deionized (D.I.) water (pH = \sim 7.0, resistivity >18 M Ω cm), and metallic Al powders (325 mesh, purity ≥99.5 %, APS 7–15 µm, CAS # 7429-90-5, Alfa Aesar) were used for all experiments of hydrogen generation in this study.

Preparation of aluminum hydroxide

Aluminum hydroxide derived from $AlCl_3$, $Al(NO_3)_3$ and $NaAlO_2$ are obtained by following procedures according the well-known chemical reactions as follows:

 $\begin{aligned} \text{AlCl}_3 + 3\text{NaOH} &\rightarrow 3\text{NaCl} + \text{Al(OH)}_3 \tag{1} \\ \text{Al(NO}_3)_3 + 3\text{NaOH} &\rightarrow 3\text{Na(NO}_3)_3 + \text{Al(OH)}_3 \tag{2} \\ \text{AlCl}_3 + 3\text{NaAlO}_2 + 6\text{H}_2\text{O} &\rightarrow 3\text{NaCl} + 4\text{Al(OH)}_3 \end{aligned} \tag{2}$

That is, 0.1 M AlCl₃, Al(NO₃)₃, and 0.4 M NaOH, NaAlO₂ were first produced in D.I. water. The NaAlO₂ aqueous solution was obtained by dissolving NaAlO₂ in D.I. water at 50 °C. The AlCl₃ aqueous solution was gradually dripped into a NaOH solution by stirring for 24 h. The white precipitates Al(OH)₃ were separated from liquid by centrifugation. After washing twice using 0.01 M HCl aqueous solution and three times using D.I. water, the precipitates were freeze-dried for use. This Al(OH)3 powder obtained was referred as Al(OH)₃-AlCl₃. The Al(OH)₃ powders derived from Al(NO₃)₃ and NaOH solutions follow the same procedure described above. This Al(OH)₃ powder obtained was referred to as Al(OH)₃-Al(NO₃)₃. The third Al(OH)₃ powder was obtained from the reaction of AlCl₃ and NaAlO₂ solution, whose fabrication process was the same as that for Al(OH)₃-AlCl₃ except the aqueous solution was obtained at 50 °C. The fourth Al(OH)₃ powder was obtained by the reaction of metallic Al powder in D.I. water at 35 °C [reaction (4)], which took more than 18 h to complete. This $Al(OH)_3$ powder obtained was referred as $Al(OH)_3$ -Al reacted.

$$2AI + 6H_2O \rightarrow 2AI(OH)_3 + H_2 \tag{4}$$

The fifth Al(OH)₃ powder (0.5 μ m, \geq 98 %, NanoAmor) is commercially purchased and used as-received.

Experimental

One gram of various $Al(OH)_3$ was put into a flask and 200 ml D.I. water was added and shaken for a uniform mixture. One gram of Al powder was then added into this mixture for reaction. The temperature is kept constant by putting the flask in a circulated water bath $(25 \pm 1 \text{ °C})$. The hydrogen generated was measured by a precision gas flow meter connected after passing a condensing cold trap. In order to search an optimum combination of Al, $Al(OH)_3$ and water for hydrogen generation, the amount of D.I. water was modified to be 200, 100, and 50 ml for the commercial 0.5 µm $Al(OH)_3$ powder. The quantity of $Al(OH)_3$ in 200 ml D.I. water was also changed to 3, 5, 8, and 15 g. Finally, the metal Al powder was ranged from 1, 2, and 3 g in 50 ml D.I. water and 15 g of $Al(OH)_3$.

Characterizations

All of the experiments were carried out at room temperature (25 ± 1 °C) using circulating water bath. The water displacement method was used to measure hydrogen generation using two 2,000-ml cylinder meters (reading data error ± 20 ml) because of the rapid speed of the hydrogen generation. After the reaction was completed, the product powders were characterized with an analytical PW3040/60



Fig. 1 XRD data for the four synthesized Al(OH)₃ powders

ID	Al(OH) ₃ -Al(NO ₃) ₃	Al(OH) ₃ -AlCl ₃	Al(OH)3-NaAlO2	Commercial as-received 0.5 µm	By-product after Al/water reaction
Crystalline phase	Gibbsite + Bayerite	Gibbsite + Bayerite	Bayerite	Gibbsite	Bayerite
Assigned name	α , β -Al(OH) ₃	α , β -Al(OH) ₃	β -Al(OH) ₃	α -Al(OH) ₃	β -Al(OH) ₃
Particle size (µm)	0.2–0.5	0.2–0.5	0.5–2	0.5–2	1–3

Table 1 Summary of various Al(OH)3 powders used in this study

Fig. 2 FESEM of Al(OH)₃ from a Al(NO₃)₃, b AlCl₃, c NaAlO₂, d commercial 0.5 µm, e Al—reacted



X'Pert Pro X-ray diffractometer using Cu K α radiation and an Ni filter over the angular range of 10°–80°(2 θ) at a scanning rate of 4° min⁻¹ and a step size of 0.01°. Fieldemission scanning electron microscopy (FESEM, JEOL JSM 7600F) was employed to characterize the morphology of the powders.

Results and discussion

Crystal phases and morphologies

Figure 1 shows the XRD results for the four synthesized aluminum hydroxide powders. The two-theta values for



gibbsite (α) and bayerite (β) are 18.392° and 18.785°, respectively. The Al(OH)₃ synthesized from Al(NO)₃ and AlCl₃ exhibits two mixed phases, i.e. α (gibbsite) and β (bayerite), while those obtained from NaAlO₂ and Al/water reaction are only of β phase. Gibbsite (α) and bayerite (β) differ in the way that the double layers of coordinated OH⁻ and Al⁺³ are stacked to form the three-dimensional crystal units [18]. The commercial Al(OH)₃ is purely gibbsite (not shown). Table 1 summarizes the characteristic data of all Al(OH)₃ used in this study. Figure 2 shows the FESEM images of all Al(OH)₃ powders. Powders obtained from Al(NO₃)₃ exhibit smaller crystal sizes with hexagonal thin plates randomly stacking together, while those from AlCl₃, NaAlO₂ and Al/water reaction are more bar or barrel-like morphology.

Hydrogen generation

Figure 3 shows the hydrogen generation from 1 g Al in 200 ml D.I. water with 1 g various catalysts, i.e. five different Al(OH)₃ and one γ -Al₂O₃. The yield "100 %" means the theoretical value of 1,360 ml hydrogen generated per gram Al metal in water. The performance of Al(OH)₃ obtained from Al(NO)₃ precursor stands out among all aluminum hydroxides. The reason for this difference will be discussed later. Figure 4 shows the effect of various amounts of commercial 0.5 µm Al(OH)₃ on the hydrogen generation in 1 g Al/50 ml D.I. water system. It is clear that higher amount of Al(OH)₃ promotes the reaction of Al and water. We noticed that the exothermic reaction of Al/water reaction may also assist the hydrogen generation. Previous report [13] also indicated that higher temperature assisted hydrogen generation significantly. In the experiment in Fig. 4, temperature of the reacting flask



Fig. 3 Hydrogen generation from 1 g Al in 200 ml D.I. water with various 1 g Al(OH)₃. Known effective additive, γ -Al₂O₃, was also evaluated

increases due to the smaller amount of water, as shown in Fig. 5, i.e. the exothermic reaction of Al/water heats up the system. When the weight ratio of Al:Al(OH)₃:water is 1:15:50, the system temperature could go up to 49 °C. In the meantime, the hydrogen generation yield was also enhanced due to the raised temperature, as shown in Fig. 6. Figure 6 shows the effect of various quantities of commercial 0.5 µm Al(OH)₃ in 50, 100, and 200 ml D.I. water on the hydrogen generation of 1 g Al/water system in 2 h. When water is only 50 ml, the exothermic reaction promotes hydrogen yield significantly within 2-h reaction period.

For other synthesized Al(OH)₃ powders, the enhancement of hydrogen generation is even more effective, as shown in Fig. 7. Figure 7 demonstrates that the hydrogen yield when the weight ratio of Al:Al(OH)₃:H₂O is fixed at



Fig. 4 Effect of commercial 0.5 µm Al(OH)₃ quantity in 50 ml D.I. water to hydrogen generation of Al/water system



Fig. 5 Temperature rises differently when various amount of water are used for reaction with 1 g Al powder





Fig. 6 Effect of quantity of commercial 0.5 μ m Al(OH)₃ in various amount of D.I. water on the hydrogen generation of 1 g Al/water system in 2 h



Fig. 7 Effect of various Al(OH)_3 in the ratio of 1:15:50 for Al:Al(OH)_3:H_2O

1:15:50 for various Al(OH)₃. Al(OH)₃-Al reacted is not presented here due to its slow generation rate, as we have already learned from Fig. 3. It is clear that Al(OH)₃ obtained from Al(NO₃)₃ assists 100 % yield of hydrogen from Al/water reaction in only 15 min. By taking advantage of exothermic reaction of Al/water system, we can promote 100 % hydrogen yield even faster using higher quantity of metal Al powders. Figure 8 shows that this expectation is correct. When 3 g Al powder is used for reaction in 50 ml water, the exothermic heat is significant and the reaction of hydrogen generation is enhanced. 100 % yield of hydrogen can be released in 6 min! The temperature is raised up to 95 °C in this particular condition, as shown in Fig. 9. The hydrogen generation rate (ml/ min) is also depicted in Fig. 9. The hydrogen generation



Fig. 8 Effect of increasing amount of Al on the hydrogen yield from 15:50 for Al(OH)₃:H₂O system. Al(OH)₃ is obtained from Al(NO₃)₃



Fig. 9 Temperature profile and hydrogen generation rate per min at the ratio of 3:15:50 for Al:Al(OH)₃:H₂O system described in Fig. 8

rate reaches its peak at the fourth minute where the system temperature is also at its peak. The peak rate is as high as 1,920 ml per 3 g Al-min⁻¹. After this peak rate, the material consumed up and the hydrogen generation rate declined rapidly.

The reason why Al(OH)₃ obtained from Al(NO₃)₃ is so effective to enhance the hydrogen generation from the Al/ water system, while those obtained from other precursors are less effective, is still under investigation. The surface area of Al(OH)₃ powders obtained from Al(NO₃)₃ is not particularly high, being only 6 m²/g. One possible reason is its small size and sharp edge of its randomly stacking hexagonal plate-like crystals. The special morphology of Al(OH)₃–Al(NO₃)₃ is considered to be very effective to react with dense Al₂O₃ protecting layer on the metal Al particles that in turn assists the following reaction we proposed [17]:



 $Al_2O_3 + Al(OH)_3 \rightarrow 3AlO(OH)$ (5)

The boehmite AlO(OH) could readily react with fresh metal Al as follows:

$$2AI + 6AIO(OH) \rightarrow 4Al_2O_3 + 3H_2 \tag{6}$$

By utilizing the in situ self-heating due to the exothermic reaction of Al/water system, we are able to produce 100 % yield hydrogen within 6 min without using alkaline solution (pH < 10).

Conclusion

We have demonstrated the novel effect of Al(OH)₃ powders on the Al/H₂O system for generating hydrogen. When Al(OH)₃ powders were obtained from Al(NO₃)₃ precursor, small size and sharp edge of this hexagonal plate-like crystals promote hydrogen generation from Al/water system significantly. This special morphology of Al(OH)₃ is considered to be very effective to react with dense Al₂O₃ layer on Al particles. In addition, an optimum combination of Al/Al(OH)₃/water (3:15:50) for hydrogen generation is revealed. By utilizing the self-heating exothermic reaction from a large quantity of initial Al powder in a minimum water, the reaction is able to produce high temperature up to 95 °C and consequently rapid hydrogen generation (100 % yield within 6 min, i.e. 1,360 ml H_2/g Al), making this system an ideal candidate for a hydrogen source in a use-on-demand system.

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Conflict of interest The authors declare that they have no competing interests

Authors' contributions YK is the main investigator and carried out most of the experiments, HT and TY help the measurements. HW is supervisor. All authors read and approved the final manuscript.

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