Rapid Hydrogen Generation from Aluminum-Water System Using Synthesized Aluminum Hydroxide Catalyst

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Abstract—Catalytic effect of Al(OH)₃ on the hydrogen generation from Al/water system is evaluated. The Al(OH)₃ powders are synthesized from various molar ratios of Al(NO₃)₃ : NaOH = 1:3 ~ 1:5. It was found that the Al(OH)₃ catalyst derived from the ratio Al(NO₃)₃ : NaOH = 1:3.5~1:4 in an ice bath exhibits the best catalytic effect and exerts the highest hydrogen generation rate. Over 95% yield of hydrogen from a 3 g Al/50 ml water system (with 15 g Al(OH)₃ and pH=12) can be generated within 100 s. That is, using specially synthesized Al(OH)₃ catalyst at a Al:Al(OH)₃:H₂O=3:15:50 weight ratio, very rapid hydrogen generation rate (~667 ml/g-Al min) without using any alloying elements or extreme corrosive condition, can be realized.

Index Terms—Aluminum hydroxide, aluminum nitrate, hydrogen generation.

I. INTRODUCTION

Hydrogen generated from the reaction of aluminum (Al) and water has been regarded as an unwanted byproduct in the corrosion of Al metals. However, since the increasing demand of clean energy and mobile hydrogen storage system, the hydrogen produced from the reaction of Al and water becomes feasible and is an attractive study topic recently [1]. However, the generation of hydrogen from Al/water system is slow due to the thin layer of aluminum oxide on the surface of Al. The generation of hydrogen can be achieved by using highly corrosive basic solution such as aluminum hydroxide (pH>13) [2]. Additives such as aluminum hydroxide [3], sodium stannate in sodium hydroxide solution [4], [5], hot water [6], CaO [7] were reported to be effective for enhanced generation of hydrogen, where serious corrosive conditions can be avoided. Alloying method such as Al-Ga alloys [8], [9], Bi doping [10], or milling additives such as SnCl₃ [10] or KCl/NaClI [11], and activated treatment on Al powders [12]-[14] are also employed to enhance the generation of hydrogen. However, these methods, accompanying with potential pollution, high cost and additional energy supply, are not very attractive. Z.Y. Deng et al. [15]-[18] reported that γ-Al₂O₃ is an excellent modifier for aluminum power for hydrogen generation. In their study, a powder mixture of Al and Al(OH)₃ was used to sinter and form porous Al/γ-Al₂O₃ composite. From his systematical studies [19], [20], it is known that smaller size of starting metal Al powder, higher temperature and coating with Al(OH)₃ will greatly assist the hydrogen generation of Al/water system. He proposed [20] that hydroxide and oxides could dissociate water molecules and promote the hydration of the passive oxide film on Al particle surfaces.

In our previous studies [21]-[23], Al(OH)₃ was proved to be very effective to promote hydrogen generation from Al/water system when it is in small size and low crystallinity. In the present study, in order to further enhance the effectiveness of Al(OH)₃ powders on the reaction of Al and water, specially synthesized Al(OH)₃ were evaluated. That is, to produce effective Al(OH)₃ catalyst, molar ratio of precursors Al(NO₃)₃/NaOH has been studied. By using effective Al(OH)₃ powders and a proper Al/Al(OH)₃/water ratio, we are able to produce ~100% yield of hydrogen within 120 s starting at room temperature.

II. EXPERIMENTAL PROCEDURE

Aluminum nitrate nonahydrate (Al(NO₃)₃·9H₂O, ≥98.0%, SHOWA), and sodium hydroxide (NaOH, ≥97%, Sigma-Aldrich) were purchased and used for the preparation of aluminum hydroxide. Mole ratios of Al(NO₃)₃ to NaOH such as 1:3, 1:3.5, 1:4, 1:4.5, and 1:5 to produce effective Al(OH)₃ powders were carried out at room temperature as well as in an ice bath. These aluminum hydroxides were evaluated their effects on the reaction of Al/H₂O system. Deionized (D.I.) water (pH=7.0, resistivity > 18M Ω-cm), and metallic Al powders (325 mesh, purity ≥99.5%, APS 7-15μm, CAS # 7429-90-5, Alfa Aesar) were used for all experiments of hydrogen generation in this study.

Aluminum hydroxide is obtained by following well-known chemical reaction:

\[
\text{Al(NO}_3\text{)}_3 + 3\text{NaOH} \rightarrow 3\text{Na(NO}_3\text{)}_2 + \text{Al(OH)}_3
\]  

That is, 0.1 M Al(NO₃)₃ and 0.3~0.5 M NaOH were firstly produced in D.I. water. The Al(NO₃)₃ aqueous solution was gradually dripped into a NaOH solution by stirring for 24 h at room temperature (R.T.) or in an ice bath (<5°C). The white precipitates Al(OH)₃ was separated from the liquid by centrifugation. After wash twice using 0.01M HCl aqueous solution and three times of D.I. water, the precipitates were freeze-drying for use.

Firstly, in order to search the best Al(OH)₃ catalyst for hydrogen generation, experiments controlled at room temperature are carried out. One gram of various Al(OH)₃ catalysts 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°C ± 1°C). The hydrogen generated...
was measured by a precision gas flow meter (Alicat Scientific, Inc.) connected after passing a condensing cold trap. Secondly, for the rapid hydrogen generation experiments, the best Al(OH)<sub>3</sub> catalyst from the first study was used for the system Al:Al(OH)<sub>3</sub>:H<sub>2</sub>O in the weight ratio 3:15:50 [23] without temperature control. The generation of hydrogen will be enhanced due to the in-situ exothermic reaction [23]. The water displacement method using two 2000-ml cylinder meters (reading data error ± 20 ml) was employed to measure the hydrogen generation because of the sharp speed of the generation rate.

To further understand the influence of synthesized Al(OH)<sub>3</sub> powders on hydrogen generation, the activation energy for the reaction of Al/water system with/without catalyst were calculated. The powders were added to 200 ml of deionized water and sealed in a conical flask. All of the experiments were carried out at 25±1°C, 35±1°C, 45±1°C, 55±1°C using circulating water bath. No magnetic stirring was employed within the reaction flask. The hydrogen generated was measured using a silicone tube passing through a water bath at room temperature to the precision gas flow meter that automatically recorded the output data in a notebook computer every second until the reaction reached 100% yield of hydrogen (=1360 ml per g of Al). The cooling water bath is used to minimize the water vapor.

The synthesized Al(OH)<sub>3</sub> product powders were characterized with an analytical PW3040/60 X’Pert Pro X-ray diffractometer using Cu Kα radiation equipped a Ni filter over the angular range of 10°–80° (2θ) at a scanning rate of 4° min<sup>−1</sup> and a step size of 0.01°. Field-emission scanning electron microscopy (FESEM, JEOL JSM 7600F) was employed to characterize the morphology of the powders.

III. RESULTS AND DISCUSSION

A. Hydrogen Generation

Fig. 1 shows the hydrogen generation from 1 g Al in 200 ml D.I. water with 1 g various Al(OH)<sub>3</sub> catalysts, i.e. the reaction using weight ratio of Al:Al(OH)<sub>3</sub>:H<sub>2</sub>O=1:1:200 at room temperature. pH value of the solution is ~9.5. It shows that the Al(OH)<sub>3</sub> from synthesized conditions such as 1:3, 1:4.5, and 1:5 are not good. The Al(OH)<sub>3</sub> obtained at 1:3.5 and 1:4 are helpful to hydrogen generation. In particularly, synthesis ratio of 1:3.5 and 1:4 in ice bath enhances the catalytic effect. The synthesized ratio without caption is referred to those synthesized at room temperature condition.

In the rapid generation experiments without temperature control, i.e., Al:Al(OH)<sub>3</sub>:H<sub>2</sub>O in the weight ratio 3:15:50, we firstly demonstrate the hydrogen generation without using Al(OH)<sub>3</sub> catalyst at 50 ml D.I. water at pH=12.6 using 3 g Al, as shown in Fig. 2. It is clear that, in this condition, the reaction takes more than 20 h to generate hydrogen significantly. We also conducted experiments at pH value lower than 12. As expected, without using Al(OH)<sub>3</sub> catalyst at a solution with pH ≤ 12, it is hardly observe any significant hydrogen generation from 3 g Al/50 ml D.I. water system in a reasonable duration (> 30 h). However, when Al(OH)<sub>3</sub> is used, the situation is dramatically different. Fig. 3 shows the effect of Al(OH)<sub>3</sub> derived from 1:4 ratio on the hydrogen generation. It is clear that Al(OH)<sub>3</sub> in ice bath assists ~100% yield of hydrogen from Al/water reaction within 120 s.

Al(OH)<sub>3</sub> synthesized at 1:4 at room temperature takes about 180 s to yield over 95% H<sub>2</sub> production. The hydrogen generation peak rate is as high as 2000 ml per 3 g Al-min<sup>−1</sup> (~667 g·Al-min<sup>−1</sup>) when 1:4 ice bath Al(OH)<sub>3</sub> is used in the 3:15:50 reacting system. With Al(OH)<sub>3</sub> catalyst, solution with pH < 12 such as 11 and 10 will take a little more time, as shown in Fig. 3. In these low pH conditions, without using Al(OH)<sub>3</sub> catalyst, we cannot observe such rapid generation of hydrogen. Since the solution is not acidic enough, Al(OH)<sub>3</sub> cannot be synthesized at room temperature condition. The Al(OH)<sub>3</sub> synthesized at ratio 1:3.5 and 1:4 in ice bath are very effective catalysts to promote hydrogen generation from Al/water system. Their effectiveness are shown in Fig. 4 and Fig. 5, respectively. In Fig. 4, we demonstrate the over...
95% yield of hydrogen from 3 g Al/50 ml H\textsubscript{2}O system within 100 s. Furthermore, the consecutive addition of the second batch of 3 g Al in the exact same solution, where the temperature is raised to more than 70°C due to the first 3 g Al reaction, produces hydrogen at even faster rate. When the temperature is slightly dropped to 50°C, we then add the third batch 3 g Al powder into the solution. The over 95% yield of hydrogen is still very rapid (~40 s), as shown in Fig. 4. The reason for faster generation rate from the consecutive batches can be explained by the help of high temperature. The catalytic effect of Al(OH)\textsubscript{3} obtained at 1:4 in ice bath is quite similar to that of 1:3.5 in ice bath, as shown in Fig. 5. From the results of Fig. 1, Fig. 4 and Fig. 5, we could conclude that the different effectiveness of Al(OH)\textsubscript{3} synthesized at 1:3.5 and 1:4 in ice bath can only be appreciated at slow reaction system using 200 ml water, and are both quite effective at rapid reaction system.

**B. Characteristics of Al(OH)\textsubscript{3} and Mechanism of Enhancement**

Fig. 6 shows the XRD results for the synthesized Al(OH)\textsubscript{3} powders. All synthesized Al(OH)\textsubscript{3} powders are crystalline. The dots denotes the gibbsite phase (α phase). Only the 1:3 is relatively weak. For the ratios 1:4.5, and 1:5, there are mixed phases of gibbsite and bayerite (β phase). For the ratios 1:4, 1:3.5, and 1:3, the crystalline phase are mainly bayerite. Those crystalline phases obtained in ice bath can only be appreciated at slow reaction system using 200 ml water, and are both quite effective at rapid reaction system.

Fig. 4. Al(OH)\textsubscript{3} (1:3.5) in ice bath assists the hydrogen generation over 95% yield of 3 g Al/50 ml H\textsubscript{2}O system in 100 s. The consecutive batches, the 2\textsuperscript{nd} and 3\textsuperscript{rd}, are even faster than the first one, which yield 95% hydrogen in 30 s and 40 s, respectively.

Fig. 5. Al(OH)\textsubscript{3} (1:4) in ice bath also exhibits similar catalytic effect to those of 1:3.5 in Fig. 4. Hydrogen production is over 95% yield in 100 s. The consecutive batches, the 2\textsuperscript{nd} and 3\textsuperscript{rd}, yield 95% hydrogen around 60 s.

Fig. 6. XRD of Al(OH)\textsubscript{3} synthesized using various molar ratios at room temperature.

Fig. 7. Compare the intensity of Al(OH)\textsubscript{3} obtained at room temperature and those in ice bath. Those synthesized in ice bath is slightly in lower intensity.

Fig. 8 shows FESEM morphologies of various synthesized Al(OH)\textsubscript{3} powders. It is clear that 1:4.5 and 1:5 at room temperature have large rod-like crystals, while the 1:3.5 and 1:4 are plate-like. The 1:3 R.T. image shows small and round shaped particles. The ratio 1:3.5 and 1:4 in ice bath exhibits much smaller plate-like crystals than their counterparts obtained at room temperature, as shown in Fig. 8.

The plate-like crystals of 1:3.5 and 1:4, obtained either at room temperature or ice bath, may play an important role on the assistance to the hydrogen generation from Al/water system. It is then considered that edges and corners of the hexagonal plate-like crystal structure are the active sites for the dissociation of water molecules into OH\textsuperscript{-} and H\textsuperscript{+}. The mechanism scheme can be depicted in Fig. 9.
Fig. 8. FESEM for the synthesized Al(OH)₃ powders. The synthesized condition is denoted in white texts at the lower left corner.

Fig. 9. Mechanism of enhanced hydrogen generation via the easy hydration process of the passive oxide film on Al particle surface under the assistance of bayerite in aqueous solution.

The higher surface area of Al(OH)₃ obtained at 1:3.5 and 1:4 in ice bath may further enhance these activities of plate-like crystals in the hydrogen generation of Al/water system. The surface area of Al(OH)₃ powders derived from 1:3.5 and 1:4 is shown in Table I. Ratio 1:3.5 results in higher surface area than that of 1:4. The ice both condition increases the activity of these plate-like crystals by reducing their sizes. To further elucidate the influences of these plate-like crystals, activation energies of the hydrogen generation using various Al(OH)₃ were calculated.

The activation energy can be derived from Arrhenius
equation: \( k = \text{Aexp}(-E_a/RT) \), slope = \(-E_a/R\), where \( E_a \) is the activation energy. \( k \) is the rate constant at 25, 35, 45, and 55°C, using 200 ml D.I. water and temperature controlled system. Take 1 g pure Al in 200 ml D.I. water as an example, as shown in Fig. 10 (a) and (b), respectively. We have obtained an activation energy of 158 kJ/mole for pristine Al in water, i.e. without using Al(OH)_3 catalyst. In this way, we are able to calculate the activation energy of hydrogen generation when Al(OH)_3 is used in 200 ml water system. It is concluded that 1:3.5 and 1:4 in ice bath have the lowest activation energy for hydrogen generation, as shown in Table I.

It is considered that the small size and sharp edge of the randomly stacking hexagonal plate-like crystals of Al(OH)_3 render the crystal edges and corners very active on the dissociation of water molecules into OH\(^-\) and H\(^+\). The special morphology of Al(OH)_3 is considered to be very effective to react with dense Al_2O_3 protecting layer on the metal Al particles that in turn assists the following reaction we proposed [22]:

\[
\text{Al}_2\text{O}_3 + \text{Al(OH)}_3 \rightarrow 3\text{AlO(OH)} 
\]

(2)

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

\[
2\text{Al} + 6\text{AlO(OH)} \rightarrow 4\text{Al}_2\text{O}_3 + 3\text{H}_2 
\]

(3)

By utilizing special synthesized catalyst Al(OH)_3 and the in-situ exothermic reaction of Al/water system, we are able to produce over 95% yield of hydrogen within 100 s at a solution with pH=12.

Fig. 10. (a) hydrogen generation vs. duration for pristine 1g Al in 200 ml D.I. water, (b) rate constant at different temperatures.

IV. CONCLUSIONS

We have demonstrated the novel catalytic effect of Al(OH)_3 powders on the hydrogen generation from Al/H_2O system. When Al(OH)_3 powders were obtained from a ratio Al(NO_3)_3 : NaOH = 1:3.5-1:4, the small size and sharp edge of the hexagonal plate-like crystals promotes the hydrogen generation from Al/water system significantly. This special morphology of Al(OH)_3 is considered to be very effective to react with dense Al_2O_3 layer on Al particles. In addition, when an optimum combination of Al/Al(OH)_3/water (3:15:50) for hydrogen generation is employed, the self-heating exothermic reaction from a large quantity of initial Al powder in a minimum water is able to produce high temperature more than 90°C and consequently succeed in rapid hydrogen generation (≥95% yield within 100 s), making this system an ideal candidate for a hydrogen source in a use-on-demand system.

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