

CATALYSIS OF OXIDES IN HYDROGEN GENERATION BY THE REACTION OF AL WITH WATER

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ABSTRACT

Hydrogen generation by the reaction of pure Al powder in water with the addition of Al(OH)_3 , $\gamma\text{-Al}_2\text{O}_3$, $\alpha\text{-Al}_2\text{O}_3$, or TiO_2 at mild temperatures was investigated. It was found that the reaction of Al with water is promoted and the reaction induction time decreases greatly by the above hydroxide and oxides. X-ray diffraction analyses revealed that the hydroxide and oxide phases have no any change during the Al-water reaction, indicating that they are just as catalysts to assist the reaction of Al with water. A possible mechanism was proposed, which shows that hydroxide and oxides could dissociate water molecules and promote the hydration of the passive oxide film on Al particle surfaces.

1. INTRODUCTION

The increasingly serious energy crisis and environment concerns have driven the need for new and environment-friendly energy technologies. Hydrogen is a clean and renewable energy carrier, ideal as a fuel to produce electrical energy in a fuel cell with a high efficiency. However, one of the problems that must be addressed before the widespread use of hydrogen energy, is finding a safe and cost-effective method to store and transport hydrogen, especially for portable and mobile applications [1]. Recently, some in-situ hydrogen-generation materials have attracted considerable attention [2].

Metal Al is an ideal in-situ hydrogen-generation material due to its high electron density and relative low cost [2]. However, a compact and strongly adhesive passive film is developed on Al surfaces upon exposure to atmosphere or aqueous solution, inhibiting the direct reaction of Al with water. Different methods, based on the disruption of the passive oxide film on Al particles, have been proposed for hydrogen generation using Al with water. A traditional approach is to use an alkaline solution, e.g. NaOH as a catalyst to assist the reaction of Al with water [3,4]. Alloying Al by doping Ga, In, Bi, Sn, etc. [5,6] or mechanically milling metal Al with special oxide, graphite or salt powder [7,8] are the new routes to activate Al, which make Al rapidly react with water under ambient condition. At the same time, ceramic oxide modification is an effective method; the modified Al powder could directly react with water and generate hydrogen at room temperature [9-12]. The mechanism analyses for Al-water reaction are also in progress [7,10,13-15], but the exact transport species and their roles in the Al surface passive film during Al-water reaction are required to be clarified further.

Although the above activated Al methods could make Al rapidly react with water, they need an activation procedure to disrupt the passive oxide film on Al particle surfaces, which increases the cost in commercial application. In this work, the fine Al(OH)_3 , $\gamma\text{-Al}_2\text{O}_3$, $\alpha\text{-Al}_2\text{O}_3$, or TiO_2 powder was directly added into water, and then Al powder was put into the water with above hydroxide or oxides. Hydrogen generation by the reaction of Al with water was investigated systematically, indicating that hydroxide or oxides promoted the reaction of Al with water. A possible reaction mechanism was proposed based on the experimental observations.

2. EXPERIMENTAL PROCEDURE

Al powder with the average size of 7.29 μm (99.9% purity, High Purity Chemical Co., Tokyo, Japan), Al(OH)_3 (99.99% purity, 2.5 μm , High Purity Chemical Co.), $\gamma\text{-Al}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$ (99.99% purity, Taimei Chemical Co., Nagano, Japan), and TiO_2 (99.9% purity, High Purity Chemical Co.) powders

were used in the present experiment. The BET surface area of as-received γ -Al₂O₃, α -Al₂O₃ and TiO₂ powders is 190.0, 14.46 and 27.93 m² g⁻¹, respectively [11].

The hydrogen-generation experiment of pure Al powder with water was carried out at mild temperatures in a closed glass reactor with a volume of ~1300 ml, which is airtight and could keep a constant gas pressure of <3 bar for more than 1 week. The detailed set-up of the present equipment can be found in a previous work [16]. When the test began, 250 ml of deionized water was put into the closed glass reactor, then hydroxide or oxide was added into water, and finally pure Al powder was added into the water. A magnetic agitation bar with a speed of ~500 rpm was used to stir the mixture of water and powders, 1 g of Al powder + hydroxide or oxide was used in each test. As the reaction of Al with water only produces hydrogen gas [2], the hydrogen evolution could be determined by the gas pressure in the reactor, which was measured by a manometer with an accuracy of 0.2 kPa (Type: LEO 2, Keller Co., Switzerland). The measurement uncertainty of the system is < 0.5%.

According to the ideal-gas equation, hydrogen yield α can be written

$$\alpha = \frac{(P - P_{initial})(V_{reactor} - V_{H_2O} - V_{Al})}{n_0 RT}, \quad (1)$$

where P is the total gas pressure in the reactor; $P_{initial}$ is the initial gas pressure in the reactor, which was measured before the hydrogen-generation test; $V_{reactor}$, V_{H_2O} and V_{Al} are the volumes of the reactor, water and Al powder, respectively; n_0 is the theoretical hydrogen moles by reacting all of metal Al; R is the gas constant and T is the reaction temperature. Moreover, at least two same tests were carried out to check the reproducibility of each hydrogen-generation curve.

An X-ray diffractometry was used to analyze the phases in the Al-water reaction byproducts. Scanning electron microscopy (SEM) was used to observe the morphologies of as-received pure Al, hydroxide and oxide powders.

3. RESULTS AND DISCUSSION

3.1. Hydrogen-Generation Tests

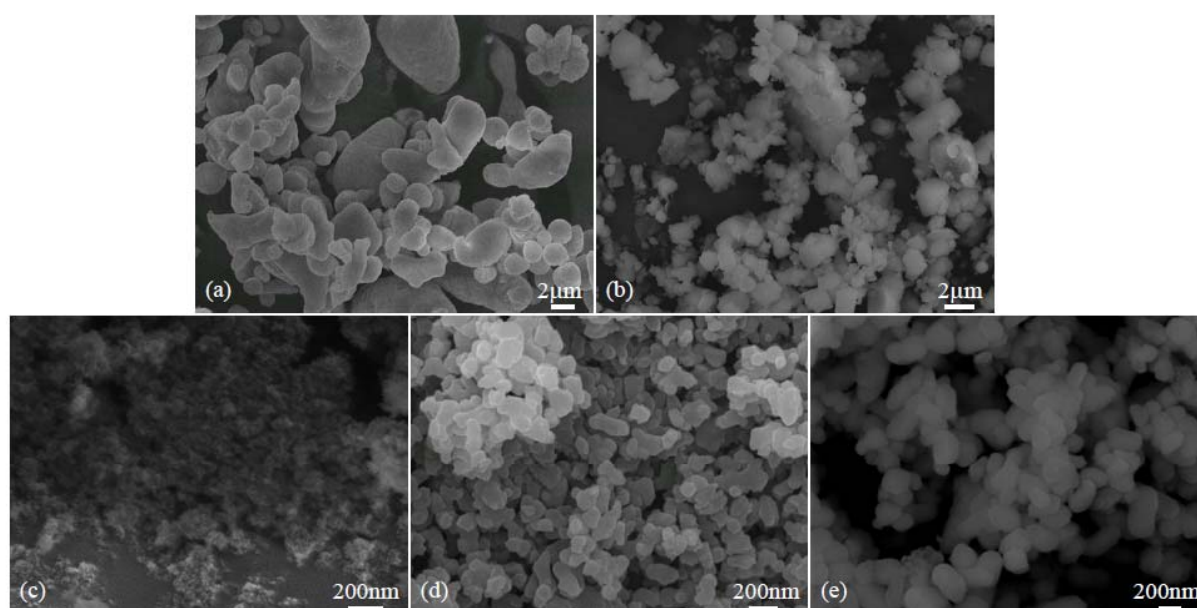


Figure 1. SEM micrographs of (a) pure Al, (b) Al(OH)₃, (c) γ -Al₂O₃, (d) α -Al₂O₃, and (e) TiO₂ powders

Fig. 1 shows the SEM morphologies of as-received Al powder, $\text{Al}(\text{OH})_3$ powder and different oxides. It can be seen that Al particle surfaces are dense and smooth, Al particles are not exactly spherical and some of them are elongated. There are some agglomerates in oxides and hydroxide, especially for $\gamma\text{-Al}_2\text{O}_3$ powder, which has a very fine grain size of several nanometers [9].

Fig. 2(a) shows the hydrogen evolution from deionized water using pure Al powder at 25°C under different initial pressures. It can be seen that pure Al powder could react with water and generate hydrogen at room temperature in an initial vacuum of 0.04 bar, though there is a long induction time (79.2 h) for the beginning of the reaction. About 92% of metal Al was consumed after reaction for 119.3 h. However, when the initial pressure is the atmospheric pressure (1 bar), there was no observable hydrogen generation even after the reaction of pure Al powder with water for 151 h, which is consistent with our feeling in daily life that metal Al does not react with water under ambient condition. Fig. 2(b) shows the hydrogen evolution from deionized water using Al powder with the addition of 30 vol% oxide or hydroxide (the fraction in Al powder + oxide or hydroxide) at 25°C in an initial vacuum of 0.04 bar. It can be seen that the hydrogen-generation performance was promoted significantly when hydroxide or oxide was directly added into water. Hydroxide and oxide greatly decreased the induction time for the beginning of the reaction. $\text{Al}(\text{OH})_3$, $\gamma\text{-Al}_2\text{O}_3$, $\alpha\text{-Al}_2\text{O}_3$, and TiO_2 decreased the induction time of Al with water from 79.2 h to 5.5 h, 2.4 h, 12.1 h and 11.2 h, respectively, indicating that different oxides and hydroxide have different effects on the reaction dynamics of Al with water. Here a vacuum reaction environment was chosen, because in the practical application the evacuation would be done in a vessel at the beginning in order to get a pure hydrogen gas.

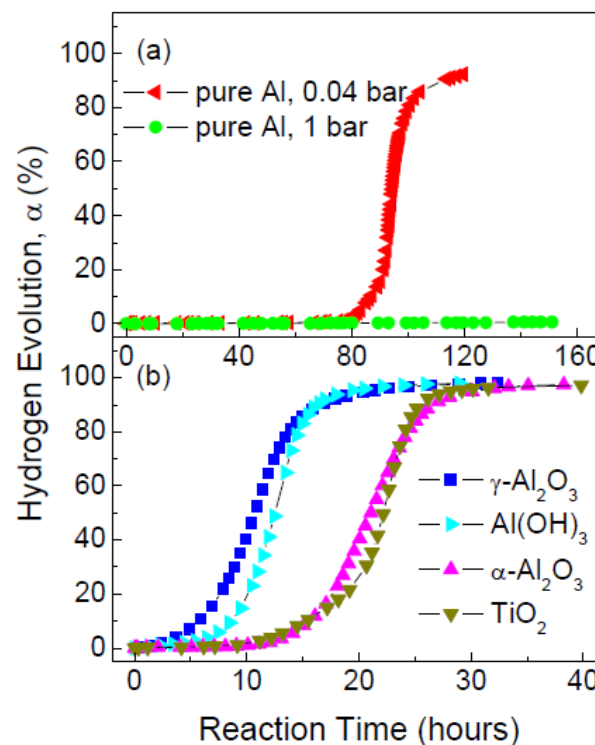


Figure 2. H_2 evolution from deionized water using (a) pure Al powder under different initial pressures and (b) Al powder with the addition of 30 vol% oxide or hydroxide under an initial pressure of 0.04 bar, where the reaction temperature is 25°C

The hydrogen-generation rate of Al with water at room temperature in Fig. 2(b) is relatively slow, however, the reaction of Al with water is exothermic and its reaction heat reaches as high as 426.5 kJ/mol [2]; so the reaction of Al with water is self-heating, especially for the Al to H_2O weight ratio

being 1:5 to 1:10 in the practical application, and the water temperature would increase rapidly with the reaction progress, in this case the hydrogen-generation rate of Al with water would be promoted considerably. In fact, the experiment of Jung et al. [4] indicated that the temperature of Al with water could increase from room temperature to > 80°C in a model device. Fig. 3(a) shows the hydrogen evolution from deionized water using Al powder with the addition of 30 vol% γ -Al₂O₃ at different temperatures. It can be seen that the reaction of Al with water is speeded up with the temperature increase. At 50°C, the reaction of Al with water was almost finished within just 2 h. Fig. 3(b) shows the repeatability of the present experiment.

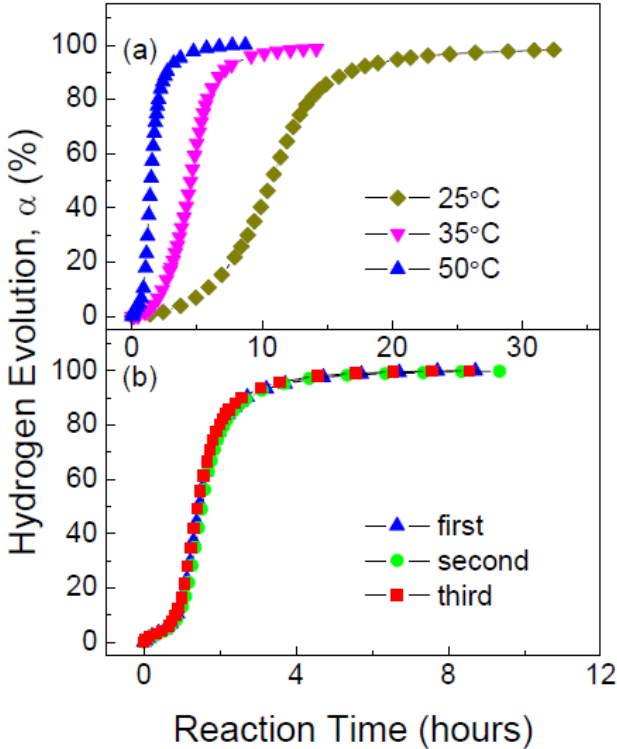


Figure 3. H₂ evolution from deionized water using Al powder with the addition of 30 vol% γ -Al₂O₃ (a) at different temperatures, and (b) three same tests at 50°C, showing the repeatability of the experiment, where the initial pressure is 0.04 bar

3.2. Phases in Reaction Byproducts

Fig. 4 shows the X-ray diffraction patterns of reaction byproducts of Al powder after reaction in water without and with the addition of 30 vol% oxide or hydroxide. After pure Al powder was put into water at 25°C under atmospheric pressure for 151 h, there is no detectable phase change in its phase composition (Fig. 4a), indicating that micrometer Al powder is difficult to react with water under ambient condition. However, after pure Al powder was put into water at 25°C in an initial vacuum of 0.04 bar for 119.3 h, the diffraction peaks of metal Al disappeared and a new bayerite phase was detected (Fig. 4b), indicating that pure Al powder completely reacted with water and generated hydrogen, which is consistent with the results in Fig. 2(a). Fig. 4 also shows that when pure Al powder was put into the water with hydroxide or oxide for a suitable period at 25°C in an initial vacuum of 0.04 bar, all of the Al diffraction peaks disappeared and there was a new bayerite phase, indicating that metal Al was consumed after the reaction. However, the diffraction peaks of Al(OH)₃, γ -Al₂O₃, α -Al₂O₃, and TiO₂ have no change, implying that these hydroxide and oxides have no any phase change during the reaction and they are just as catalysts to assist the reaction of Al with water. The reaction equation of Al with water can be written

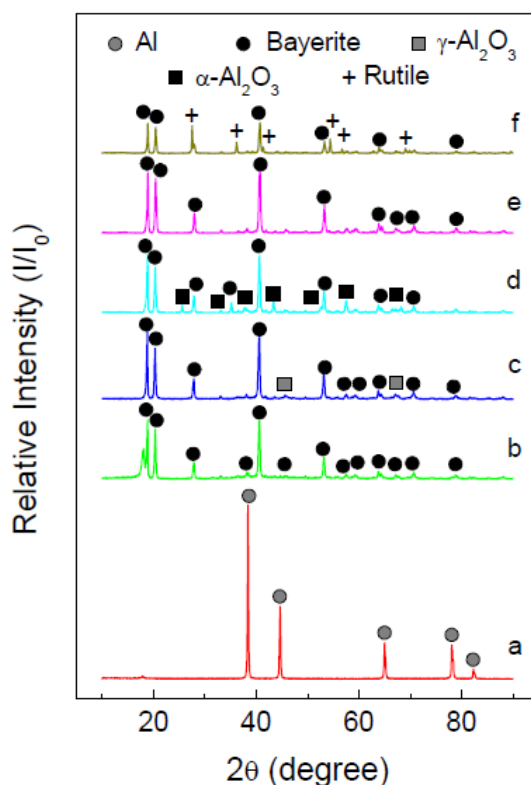


Figure 4. X-ray patterns for (a) pure Al powder after reaction for 151 h, (b) pure Al powder after reaction for 119.3 h, (c) Al powder with the addition of 30 vol% $\gamma\text{-Al}_2\text{O}_3$ after reaction for 32.4 h, (d) Al powder with the addition of 30 vol% $\alpha\text{-Al}_2\text{O}_3$ after reaction for 38.3 h, (e) Al powder with the addition of 30 vol% $\text{Al}(\text{OH})_3$ after reaction for 29 h, and (f) Al powder with the addition of 30 vol% TiO_2 after reaction for 39.8 h, where the reaction temperature is 25°C , the initial pressure in (a) is 1 bar and the others are 0.04 bar

3.3. Mechanism Analyses

It is well known that the passive oxide film on Al surface is compact and thermodynamically stable under ambient condition, which provides a well corrosion resistance. As a result, the passive oxide film on Al surface must break before the reaction of inner Al. Deng et al [10] proposed a physicochemical mechanism for the continuous reaction of Al with water and gave a critical condition under which the reaction occurs. In their analyses, there is a hydration reaction in the passive oxide film on Al surfaces when the Al particles are put into water. This hydration process involves the disruption of Al-O-Al bonds via hydrolysis to form Al-OH species, one Al-O-Al linkage is broken to form two Al-OH for each water molecule consumed. Extensive hydration eventually produces oxyhydroxide or hydroxide phases such as AlOOH and $\text{Al}(\text{OH})_3$ that are thermodynamically more stable than Al_2O_3 at room temperature [17,18]



When the hydrated front meets the inner Al surface, condensation reactions can occur in which two hydroxide ions recombine to generate an oxide linkage and a water molecule (the reverse of hydrolysis), because aluminum hydroxide phases are known to be thermodynamically unstable in contact with metal Al [17]. In this case, the inner Al would react with water molecule and release H_2 . Because of the limited H soluble capacity in Al particles and the low permeability of the hydrated

oxide film toward H_2 , H_2 molecules accumulate and form small H_2 gas bubbles at the Al: Al_2O_3 interface (see Fig. 1 in [10]). When the reaction equilibrium pressure in H_2 bubbles exceeds a critical gas pressure that the hydrated oxide film can sustain, the film on Al particle surfaces breaks and the reaction of Al with water continues.

According to the analyses by Deng et al [10], there is an induction time for the beginning of the reaction of Al with water, which is responsible for the hydration process in the passive oxide film, i.e. the H diffusion saturation in bulk Al and the accumulation of H_2 molecules in H_2 bubbles to reach the critical gas pressure. The existence of this induction time has been confirmed by the previous experiments [10,11] and also by this work. Because the decrease in environmental gas pressure decreases the critical gas pressure in H_2 bubbles at the Al: Al_2O_3 interface (see Eq. (13) in [10]) and shortens the hydration process, the induction time for the beginning of the reaction in vacuum is shorter than that under atmospheric pressure, as shown in Fig. 2(a).

In this research, $Al(OH)_3$, $\gamma-Al_2O_3$, $\alpha-Al_2O_3$, and TiO_2 powders were directly added into water and Al powder was added subsequently, which is very different from the situation of ceramic surface modification [10]. However, the induction time for the beginning of the reaction decreased as well (Fig. 2). In fact, $Al(OH)_3$, $\gamma-Al_2O_3$, $\alpha-Al_2O_3$, and TiO_2 powders are chemically neutral and stable under ambient condition, and X-ray diffraction patterns indicated that their phases have no any change after the reaction of Al with water. These means that $Al(OH)_3$, $\gamma-Al_2O_3$, $\alpha-Al_2O_3$, and TiO_2 powders in aqueous solutions are just as the catalysts to assist the reaction of Al with water. The above phenomena probably are closely related to the surface chemistry of oxides and hydroxide.

For example, $\gamma-Al_2O_3$ has a defect spinel structure in which the oxygen lattice is built up by a cubic close-packed stacking of oxygen layers and aluminum atoms occupy octahedral and tetrahedral sites. In $\gamma-Al_2O_3$, some cation sites are vacant, so $\gamma-Al_2O_3$ likes a “reactive sponge” which can store and release water in a reactive way [18], and H_2O molecules are easy to be broken and dissociated into ions when they meet $\gamma-Al_2O_3$ [19]. Therefore, in aqueous solution when $\gamma-Al_2O_3$ particles contact with Al particles, the ions dissociated from H_2O molecules on $\gamma-Al_2O_3$ surfaces are easy to hydrate with the passive oxide film on Al particle surfaces and promote the hydration process, as schematically shown in Fig. 5.

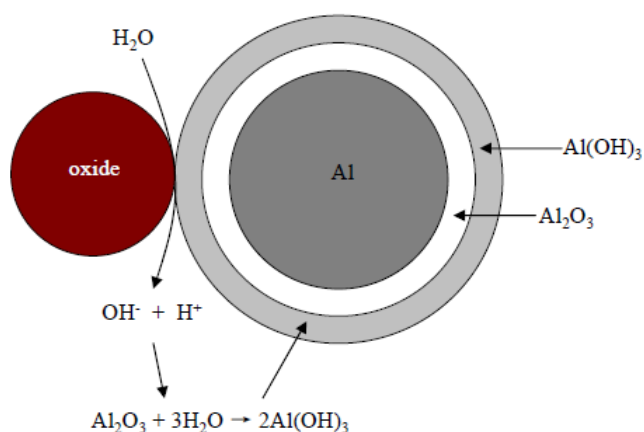


Figure 5. Schematic representation of the hydration process of the passive oxide film on Al particle surface under the assistance of other oxides in aqueous solution

In fact, the similar surface activity to $\gamma-Al_2O_3$ was also found in $\alpha-Al_2O_3$ and TiO_2 , e.g. water molecules could be dissociated on $\alpha-Al_2O_3$ (0001) surface [20,21]. Oxygen vacancies in the rutile TiO_2 surface layer are shown to dissociate water through the transfer of one proton to a nearby oxygen atom, forming two hydroxyl groups for every vacancy [22,23]. The catalytic effect of $Al(OH)_3$ on the

reaction of Al with water was also found in alkaline and other aqueous solutions [3,14]. In Fig. 2, γ - Al_2O_3 is the best to decrease the induction time for the reaction of Al with water among $\text{Al}(\text{OH})_3$, γ - Al_2O_3 , α - Al_2O_3 , and TiO_2 , probably the surface activity of γ - Al_2O_3 is the best among them. This is not strange because γ - Al_2O_3 is a very popular catalyst support in chemical industry.

4. CONCLUSIONS

In this work, $\text{Al}(\text{OH})_3$, γ - Al_2O_3 , α - Al_2O_3 , or TiO_2 powder was directly added into deionized water, and the hydrogen-generation behavior of Al powder with water in the aqueous solutions was investigated systematically. The results showed that hydroxide or oxides could greatly decrease the induction time for the beginning of the reaction and promote the reaction dynamics of Al with water. X-ray diffraction analyses revealed that the hydroxide and oxide phases have no any change during the Al-water reaction, implying that they are just as catalysts to assist the reaction of Al with water. Mechanism analyses showed that the above oxides or hydroxide have a high surface activity and could dissociate H_2O at their surfaces. When Al particles contact these oxide or hydroxide particles in aqueous solution, the ions dissociated from H_2O molecules on oxide and hydroxide surfaces are easy to hydrate with the passive oxide film on Al particle surfaces and promote the hydration process.

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