Role of Modification Agent Coverage in Hydrogen Generation by the Reaction of Al with Water

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Previous works indicated that Al particle surfaces could be modified by fine γ -Al₂O₃ grains, which can be used as a hydrogen-generation material, where the fine γ -Al₂O₃ grains were produced by the decomposition of the Al(OH)₃ phase in the mixture. In this work, commercially available γ -Al₂O₃ powder was directly used as the modification agent and mixed with Al powder and heat treated at an elevated temperature. It was found that the modified Al powder produced by directly using γ -Al₂O₃ has an obvious shorter time for complete hydrogen generation than that using Al(OH)₃-produced γ -Al₂O₃. Microstructure analyses revealed that directly using γ -Al₂O₃ powder has a better coverage of fine γ -Al₂O₃ grains on Al particle surfaces than the Al(OH)₃-produced γ -Al₂O₃. This implies that a uniform distribution of modification agents on Al particle surfaces is an important factor for the Al–water reaction dynamics.

I. Introduction

GLOBAL environmental change and temperature rise have spurred scientists to develop new clean and renewable energy technologies. Hydrogen is an ideal fuel, because its oxidation product (water) is environmentally benign. However, storage and transportation of hydrogen remain a problem, due to its low boiling point (-252° C) and very poor compressibility. In the past few years, different methods have been developed to solve this problem, e.g. hydrogen-storage materials and hydrogen-generation materials.^{1–3} However, there is no feasible way for the large-scale use of hydrogen for vehicles, stationary, and mobile applications so far.

Recently, metal Al entered the scope of the research due to its light atomic weight, high electron density, and cheap cost relative to other hydrogen-generation materials, e.g. NaBH₄.⁴ However, the direct reaction of metal Al with pure water is difficult because of a dense passive oxide film that covers the metal Al surface. Several ways were adopted to make metal Al react with aqueous solution or water and generate hydrogen. For example, NaOH solution was used to react with metal Al powder and generate hydrogen. Alloying Al by doping ~20 wt% Ga, In, Bi, Sn, etc. could make metal Al continuously react with pure water and generate hydrogen.^{5–8} However, NaOH is a strong alkali,

which creates environmental pollution concerns in the application. Metals Ga, In, Bi, Sn, etc. are expensive, which increase the cost considerably.

Deng *et al.*^{9,10} found that metal Al particle surfaces could be modified by fine γ -Al₂O₃ grains using a ceramic-processing procedure. The modified Al powder continuously reacted with water and generated hydrogen under an ambient condition. Relative to other ways of activating metal Al, ceramic modification of metal Al powder is simple and cheap. In the above works,^{9,10} the fine γ -Al₂O₃ grains were produced by the decomposition of the Al(OH)₃ phase. In this work, commercially available γ -Al₂O₃ was directly used as the modification agent. The effect of modification agent coverage on Al–water reaction dynamics was investigated.

II. Experimental Procedure

Highly pure Al (99.9% purity, 7.29 µm, High Purity Chemical Co., Tokyo, Japan), Al(OH)₃ (99.99% purity, 2.5 µm, High Purity Chemical Co.), and γ -Al₂O₃ (99.99% purity, surface area 190 m²/g, Taimei Chemical Co., Nagano, Japan) were used in the present experiment. Two kinds of mixtures of Al+Al(OH)₃ and $Al+\gamma - Al_2O_3$ were prepared in a highly pure ethanol solution and ball milled for 24 h using high purity Al₂O₃ balls, then dried and sieved using a 100-mesh nylon sieve. The mixtures were pressed under a unidirectional pressure of 75 MPa to form the green compacts. The compacts were heat treated at a heating rate of 1°C/min and held at a temperature of 600°C in vacuum for 1 h. The heat-treated compacts were mechanically crushed into powder and sieved using a 100-mesh nylon sieve. As the decomposition of Al(OH)3 at elevated temperature produced the γ -Al₂O₃ phase,¹¹ both of the starting mixtures finally became the y-Al₂O₃-modified Al powders, referred to as GMAPs hereafter. The final GMAPs prepared by two different starting mixtures have the same composition of 70 vol% A1+30 vol% γ -Al₂O₃.

The hydrogen-generation experiment of two GMAPs was carried out at a temperature of 22° C. 0.2 g of GMAP was used in each test, which was suspended in 270 mL of distilled water in a Pyrex glass cell. At the beginning of the experiment, the glass cell was evacuated to a low vacuum of 0.03 bar. The gases evolved were determined by the thermal conductivity detector gas chromatograph (Model No. GC-8A, Shimadzu, Kyoto, Japan), which was connected to the glass-made gas-circulating line attached to the Pyrex glass cell. The measurement uncertainties were about 0.05%.¹² The schematic representation of the present hydrogen-generation equipment can be found in Hara *et al.*¹³

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Fig. 1. H₂ evolution from distilled water at 22°C using GMAPs prepared from the starting mixtures of (a) Al+Al(OH)₃ and (b) Al+ γ -Al₂O₃, respectively, where both GMAPs have the same composition of 70 vol% Al+30 vol% γ -Al₂O₃ and 0.2 g of GMAPs was used in each test.

X-ray diffractometry (Model No. RINT2000, Rigaku Co., Tokyo, Japan) was used to analyze the phases in GMAPs and those after reaction with water. Transmission electron microscopy (TEM) was used to observe the morphologies of GMAPs.

III. Results and Discussion

Figure 1 shows the gas evolution from the distilled water at 22° C containing the GMAPs with the composition of 70 vol% A1+30 vol% γ -Al₂O₃ prepared from two different starting mixtures. In addition to hydrogen, no other gases were detected during the reaction. It is clear that both of the GMAPs from two different

starting mixtures could completely react with water and generate hydrogen. However, the complete reaction time of the GMAP prepared from the Al+ γ -Al₂O₃ mixture (referred to as G-GMAP hereafter) is obviously shorter than that from the Al+Al(OH)₃ mixture (referred to as A-GMAP hereafter). It took ~34.1 and 69.8 h for G-GMAP and A-GMAP to completely react with water, respectively. The main difference in the reaction dynamics between G-GMAP and A-GMAP is at the beginning of the reaction. The induction time for the beginning of the reaction for A-GMAP is ~35 h, but the corresponding induction time for G-GMAP is just ~3 h. After the beginning of the reaction, the hydrogen-generation rate of A-GMAP and G-GMAP is almost the same.

Figure 2 shows TEM micrographs of original Al powder, asreceived A-GMAP, and G-GMAP, respectively. It can be seen that pure Al particle surfaces are smooth and dense. After modification, the Al particle surfaces were covered by fine γ -Al₂O₃ grains and not as smooth as pure Al particles, as clearly shown in Fig. 2(c). TEM photos in Fig. 2 indicated that there is a more uniform coverage of γ -Al₂O₃ on the Al particle surfaces of G-GMAP than that of A-GMAP. In fact, just part of the Al particle surfaces of A-GMAP was covered by fine γ -Al₂O₃ grains, e.g. the part indicated by arrow in Fig. 2(b). The nonuniform coverage of γ -Al₂O₃ in A-GMAP originates from the large sizes of Al(OH)₃ particles, because the Al(OH)₃ particles retained their original morphology after decomposition at an elevated temperature.¹⁴ In this case, the rigid contact between Al(OH)₃ particles and Al particles in the starting mixture confines the coverage of the Al(OH)₃-produced γ -Al₂O₃ grains on Al particle surfaces.

Figure 3 shows the X-ray patterns of as-received A-GMAP and G-GMAP and those after reaction with water. It can be seen that all the Al(OH)₃ phase have decomposed into the γ -Al₂O₃ phase after heat treatment. The γ -Al₂O₃ phase produced by Al(OH)₃ has a surface area of 187 m²/g measured by the BET method, which is almost the same as that of commercial γ -Al₂O₃ powder used in this work. Figure 3 indicates that bayerite



Fig. 2. Transmission electron micrographs of (a) the original Al powder and as-received GMAPs prepared from the starting mixtures of (b) Al+Al(OH)₃ and (c) Al+ γ -Al₂O₃, respectively.



Fig. 3. X-ray patterns for (a) the as-received GMAP prepared from the starting mixture of Al+Al(OH)₃, (b) that in (a) after reaction with water at 22°C for 69.8 h, (c) as-received GMAP prepared from the starting mixture of Al+ γ -Al₂O₃, and (d) that in (c) after reaction with water at 22°C for 34.1 h.

 $(Al(OH)_3)$ is the reaction byproduct of GMAPs with water at 22°C. The reaction equation can be written as

$$2\text{Al} + 6\text{H}_2\text{O} \rightarrow 2\text{Al}(\text{OH})_3 + 3\text{H}_2\uparrow$$
 (1)

This reaction produces 3.7 wt% hydrogen (weight ratio of generated H₂ to Al and H₂O).

The reaction dynamics analyses¹⁰ indicated that there is an induction time for the beginning of the reaction, because it takes some time for the gas pressure in the H_2 bubbles at the Al:Al₂O₃ interface on Al particles to reach a critical gas pressure. Exceeding this critical gas pressure would lead to the breakage of Al surface oxide films and the continuous hydrogen generation. Al surface modification is related to the phase transformation and weakening of Al surface oxide films.^{9,10} The phase transformation of Al surface oxide films depends on the existence of modification agents, i.e. γ -Al₂O₃ grains, because there is a lower nucleation energy barrier on γ -Al₂O₃ grains than that of free nucleation. The better coverage of γ -Al₂O₃ grains on Al particle surfaces would result in more part of the Al surface oxide film transforming into the γ -Al₂O₃ phase so that the surface oxide films become weaker and easier to be broken; this means that the critical gas pressure in the H_2 bubbles at Al:Al₂O₃ interface becomes lower.¹⁰ As it takes a shorter time to accumulate H_2 to reach a lower critical gas pressure, and good coverage of γ -Al₂O₃ grains on Al particle surfaces in G-GMAP leads to a short induction time for the beginning of the reaction. This is why G-GMAP has a shorter complete hydrogen-generation time than A-GMAP. In this way, if the coverage of modification agents is improved further, the complete hydrogen-generation time would become even shorter.

IV. Conclusions

In this work, commercially available γ -Al₂O₃ powder was directly used to modify Al particle surfaces. The modified Al powder produced by directly using γ -Al₂O₃ has an obvious shorter time for complete hydrogen generation than that using Al(OH)₃-produced γ -Al₂O₃ in the previous work. Microstructure analyses indicated that directly using γ -Al₂O₃ powder has a better coverage of fine γ -Al₂O₃ grains on Al particle surfaces than the Al(OH)₃-produced γ -Al₂O₃, leading to a shorter induction time for the beginning of the reaction. This implies that a uniform distribution of modification agents on Al particle surfaces is important for the fast Al–water reaction.

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