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Formation characteristics of an aluminum hydroxide fiber by a hydrolysis of aluminum nano powder

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Formation of aluminum hydroxide by a hydrolytic reaction of nano aluminum powder synthesized by a pulsed wire evaporation (PWE) method has been studied. The type and morphology of the hydroxides were investigated with various initial pH and temperatures. The nano fibrous boehmite (AlOOH) was formed predominantly over 40°C of the hydrolytic temperature, while the bayerite ($Al(OH)_3$) was formed predominantly below 30°C with a faceted crystalline structure. As a result, the boehmite showed a much larger specific surface area (SSA) than that of bayerite. The highest SSA of the boehmite was found about 409 m^2/g.

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1. Introduction

Alumina fibers are widely used as an adsorbent, catalysis, and medical filters due to their high specific surface area. The alumina is normally obtained by calcinating the aluminum hydroxides and the physical characteristics of alumina such as size and morphology depend mainly on the physical properties of the aluminum hydroxides [1]. Fibrous aluminum hydroxides have a large specific surface area, and various methods including melt spinning [2], extrusion [3], and sol-gel [4–8] have been used to synthesize the nano fibrous aluminum hydroxides. So far the sol-gel method is very common and well known to synthesize an aluminum hydroxide fiber using the aluminum alkoxides of inorganic sol precursors, because this method has a good homogeneity, high purity, and low sintering temperature, but has a long processing time and a difficulty in burning out the organics. In this paper, a new and relatively simple and fast synthesis procedure, by hydrolyzing nano size aluminum metal powder in the water, was used by us to produce an aluminum hydroxide fiber with a high specific surface area [9–11]. The formation characteristics of the nano hydroxide fiber were examined by varying the hydrolysis conditions such as temperature, pH, and reaction time in the water.

2. Experimental

In order to prepare the nano aluminum powder for the starting materials, the pulse wire evaporation (PWE) method [12] was applied. The PWE technique involved an explosion of the metal wire by a high density current pulse (between 10^4 and 10^6 A/mm^2) normally produced by discharging a capacitor bank. Details on the processing conditions of Al particles were summarized in Table I. The resulted nano aluminum particles were spheres with the sizes of about 80–100 nm in diameter including the thin passivation layer of 2–3 nm. One gram of the nano aluminum powders were dipped into distilled water of 200 ml and then ultrasonically dispersed and stirred at the different pH and temperature for hydrolysis.

The hydrolysis products were sampled at the different time interval depending on the experimental conditions to examine the morphology and physical properties by drying in an oven at 60°C for 12 h after passing through a 0.2 μm-sized filter. The completion times of the hydrolysis reaction were set in most cases based on the fibrous hydroxide formation, which were known to have the largest specific surface area. The temperatures were varied from 30 to 80°C and the pH from 3 (by 0.1 M HNO_3), 6 (by distilled water), and 9 (by 0.5 M KOH).

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TABLE I. The processing condition of PWE for producing Al particles

Diameter of Al wire	0.45 mm
Length of exploded Al wire	88 mm
Applied voltage	26 kV
Atmosphere	Ar gas
Pressure of chamber	4 bar

Transmission electron microscope (TEM, JEOL 200CX, Japan) was used for the observation of the morphology and size. X-ray diffraction (XRD, Rigaku D/MaxIII, Japan) was applied for a phase analysis. The BET (Belsorp-mini, Japan) was used for a measurement of the specific surface area by a nitrogen adsorption technique. Paperless recorder (DXA200,Yokogawa) was used for a measurement of the temperature changes during a hydrolysis.

3. Results and discussion

Fig. 1 showed the typical examples of the hydrolysis reaction behaviors at the different reaction time intervals carried out at the experimental condition of pH 6 and 50°C. The hydroxide types at the early reaction time of 15 min, aluminum metals were dominant but subsequently changed to boehmite at 50th minutes and then bayerite was dominant at 158 min. The boehmite at the reaction time of 50th minutes, in the Fig. 3, was fibrous shape with the largest specific surface area. These results of the phase transition from amorphous aluminum hydroxide, boehmite and then finally stable bayerite during the hydrolysis were well confirmed with the results of Hart [13], Bye [14], Mista [15], and Thiruchitrambalam [16]. One of the important difference from Hart was the hundred times faster reaction time of phase transition with complete hydrolysis of the aluminum metal due to the special characteristics of nano powder in this study, comparing with 20 days and about 100 nm in hydrolysis depth of the aluminum metal sheet in case of Hart.

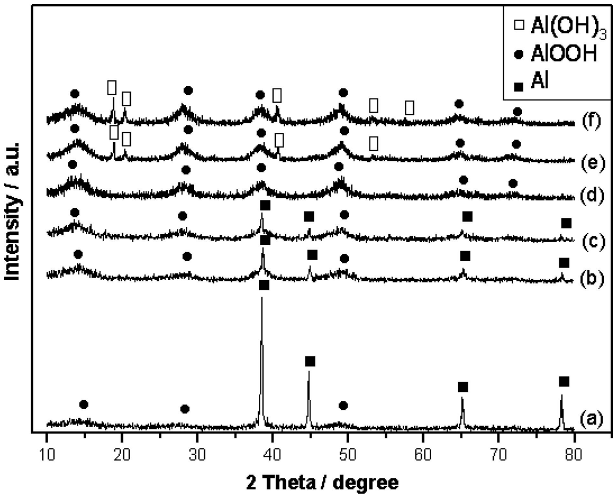

Figure 1 XRD patterns of the boehmite and bayerite phases during a hydrolysis at pH 3, 6, and 12.

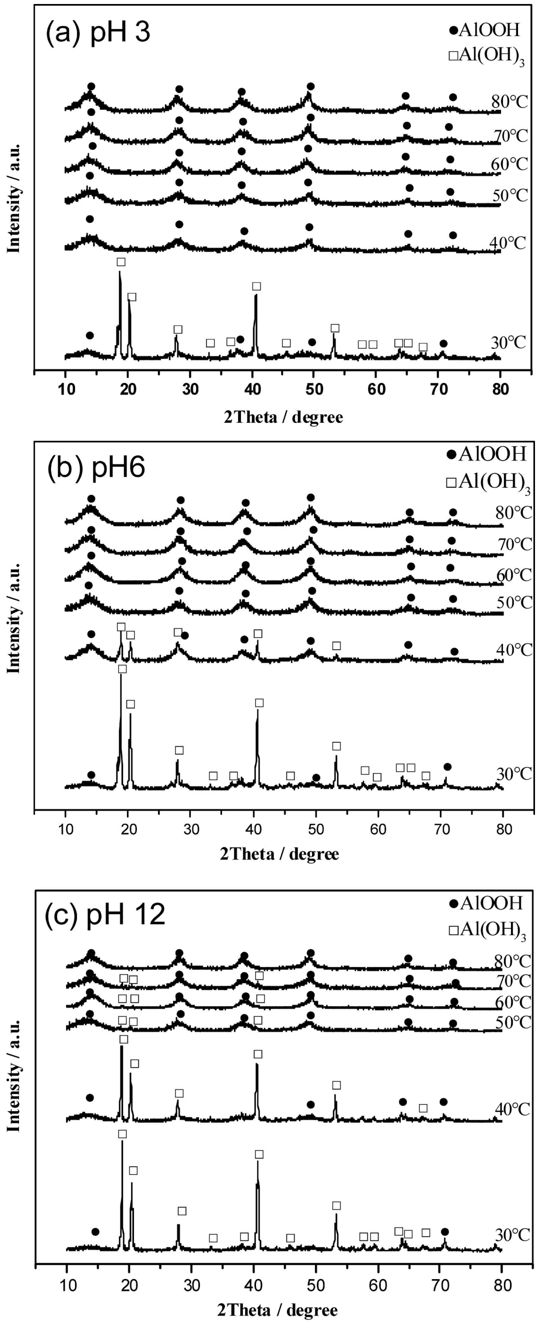

Figure 2 TEM photographs of the boehmite and bayerite phases during a hydrolysis at pH = 3, 6, and 12.

Figs 2–4 represented the type, morphology, and the specific surface area of the aluminum hydroxides to obtain the fibrous hydroxides by hydrolysis of nano aluminum powder at the temperatures from 30°C to 80°C and pH of the 3, 6, and 12, respectively. When the precipitation of the aluminum hydroxide gels was formed by the hydrolysis of the Al particles, bubbles of H_2 gas were generated as a by-product. Referring to the X-ray diffraction results shown in Fig. 2, it was found that the main phase was either boehmite or bayerite depending on the hydrolysis conditions. Bayerite has a monoclinic structure and lattice constants of $a = 0.868$ nm, $b = 0.507$ nm, $c = 0.972$ nm, $\beta = 94°34'$[7]. On the other hand, boehmite

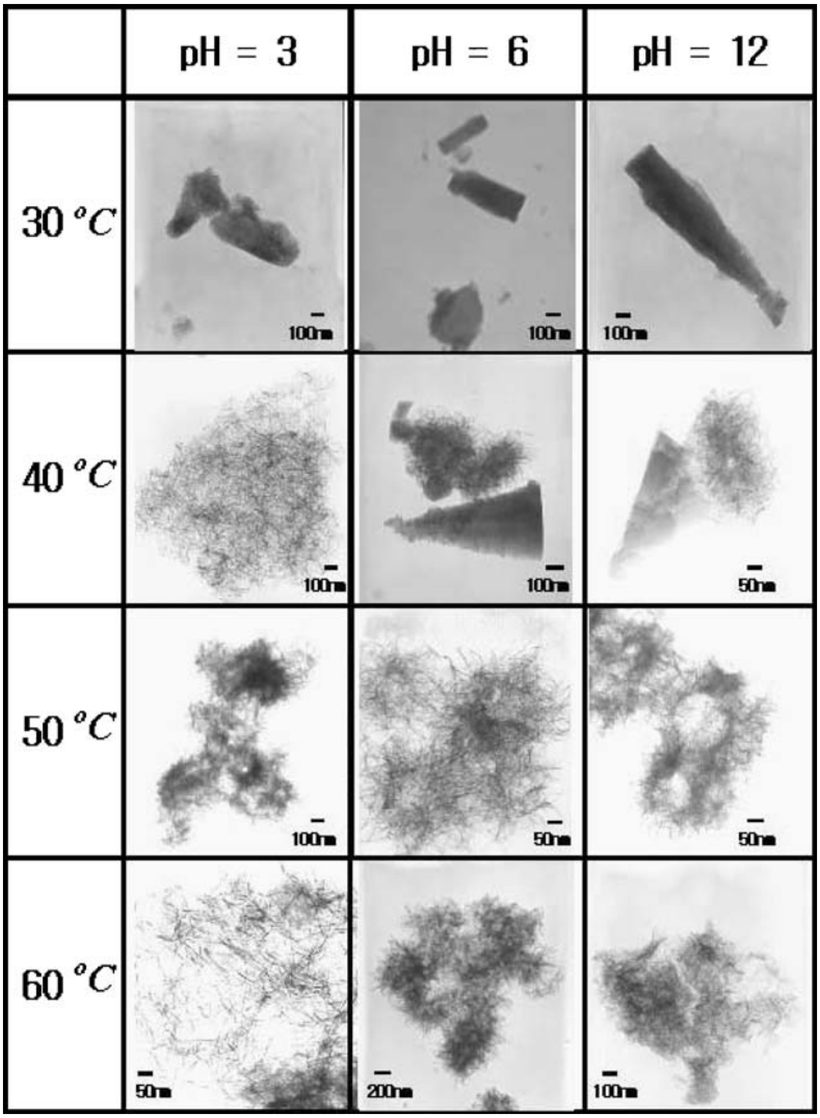

Figure 3 Specific surface area of the hydrated powders from a variation of the pH and temperature.

has an orthorhombic structure and lattice constants of = 0.369, $b = 1.221$ nm, $c = 0.872$ nm [17]. It can be seen that the bayerite phase was dominant at 30°C and the boehmite phase became dominant over 40°C in the acid solution at pH3. On the other hand, in the neutral region at pH6, the bayerite phase was also dominant at 30°C. However bayerite and boehmite coexisted at 40°C. Only the boehmite phase existed over 50°C. In the alkali solution at pH12, bayerite existed mainly at 30°C. And both bayerite and boehmite appeared at 40°C like the neutral region. The bayerite phase can even be observed over 50°C. After a hydrolysis, the amount of either the boehmite or bayerite was different, depending on the reaction temperature and pH. Boehmite is dominant at a high temperature and low pH, while the bayerite phase became dominant at a low temperature and high pH. Moreover, the bayerite showed a crystalline structure with a facet interface while the boehmite has a fibrous form with a high specific surface area as shown in Fig. 3. The maximum specific surface area of the fibrous boehmite was 409 m^2/g formed at 60°C in pH 12 as shown in Fig. 4.

A highly exothermic hydrolytic reaction of the Al particles occurred with a slight temperature increase as soon as the particles were immersed in distilled water at various initial temperatures as shown in Fig. 5. In order to investigate the phase evolution during a hydrolysis, the temperature of the water was measured throughout the hydrolytic reaction. Boehmite-producing reaction occurred for a relatively short time and became fast as the temperature increased above 50°C. The main phases at 50°C were Al metals, boehmite, and bayerite as shown in Fig. 1. It can be explained that the sharp temperature increase resulted from the acceleration of the aluminum dissolution and boehmite growth. Generally, Al releases 3 electrons into the water and becomes an Al^{3+} ion according to the oxidation ($Al \rightarrow Al^{3+} + 3e^-$). During this, a reduction by absorbing the 3 electrons should be taken

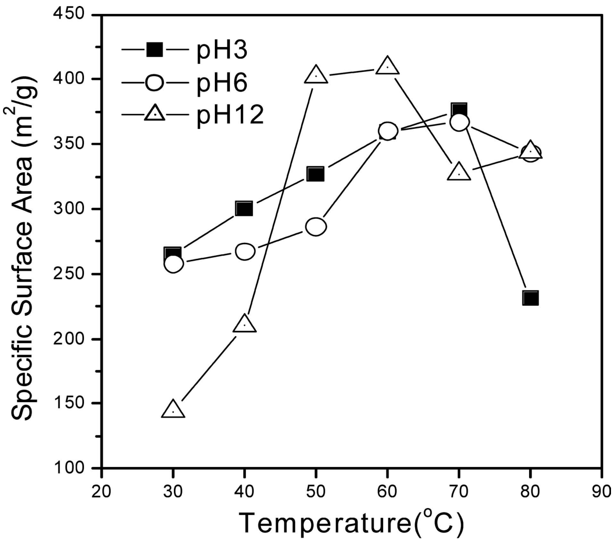

Figure 4 Temperature changes with respect to the reaction time at pH6.

place to be electrically neutralized. In the extremely acid solutions, abundant H^+ ions were reduced to hydrogen gas by joining the electrons ($3H^+ + 3e^- \rightarrow 3/2H_{2(g)}$). However, in the extremely alkali solution, the reduction reaction ($3H_2O + 3e^- \rightarrow 3/2H_2 + 3OH^-$) occurred and produced hydrogen gas and the hydroxide ion (OH^-). Thus Al^{3+} were neutralized by joining the hydroxide ions and then formed amorphous $Al(OH)_3$. In the neutral solution Al also reacted with water and generated hydrogen gas. Finally, it became amorphous aluminum hydroxides of $Al(OH)_3$. In Fig. 1, these aluminum hydroxides were being crystallized to become a more stable boehmite and bayerite phase in water as time passes. G. C. Bye [14] reported that amorphous hydroxide gels became crystalline particles by a polymerization and were condensed to a pseudo-boehmite phase. These were further re-crystallized to a more stable bayerite phase with smaller specific surface areas.

Therefore, the hydrolysis process can be divided into four steps as follows, similar to those proposed for the dehydration of transition alumina [15]. First, as a preliminary period, it required a relatively short time for small amounts of Al powder to contact with water on the surface. Consequently, amorphous aluminum hydroxide (a-$Al(OH)_3$) layers were formed on the surface of the particles. Second, as shown in (a) and (b) of Fig. 1 and Fig. 5, a hydrolysis process occurred on the thin film-like a-$Al(OH)_3$ layer. It can be defined as an induction period. At this stage, the a-$Al(OH)_3$ layer became thicker so that it was difficult to contact with water on the inner core aluminum. It decreased the hydrolysis rate. Third, an acceleratory period appeared that showed a sharp temperature increase due to a dehydration process like a-$Al(OH)_3 \rightarrow$ c-AlOOH(crystalline boehmite) + H_2O as shown in (d) of Figs 1 and 5. In the second stage, a large amount of hydrogen ions might infiltrate into the amorphous aluminum hydroxides. The ions changed to hydrogen gas (H_2). This inner gas pressure lead to surface cracks. Hence, the contact areas between the water and a-$Al(OH)_3$ increased and the reaction rate was accelerated. As a result of the sharply temperature increases, a fibrous boehmite phase appeared as shown in Fig. 5 at 50°C. At a final growth period as shown in (e) and (f) of Figs 1 and 5, the boehmite was further transformed into bayerite as time passes. It depended on the initial temperature of a hydrolysis. In other words, under a high initial temperature, boehmite was transformed to crystallized bayerite after a sharp

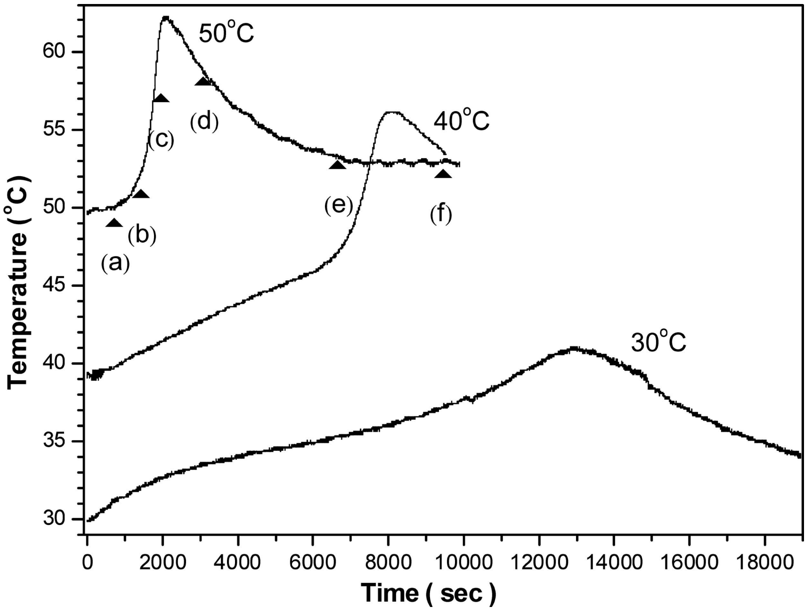

Figure 5 XRD patterns of the Al, boehmite, and bayerite phases during a hydrolysis at 50 and pH6; (a) 15 min, (b) 20 min, (c) 25 min, (d) 50 min, (e) 120 min, and (f) 158 min.

temperature increase, while under a low initial temperature it required a relatively long time to be transformed.

4. Conclusions

The results obtained were summarized as follows;

1. Hydrolysis reaction of the nano aluminum powder formed unstable amorphous aluminum hydroxides. These were crystallized to become a more stable boehmite, and bayerite phase, in sequence.
2. Boehmite produced in the high temperature and acid region, showed a nano fibrous shape with several nm in diameter and several hundreds nm in length having high specific surface areas with a maximum value of 409°m^2/g.
3. In order to obtained nano fibrous boehmite with high surface areas from nano metal powder, the hydrolysis reaction should be done at a high temperature over 50°C, with high acidity, below pH 6, and must be terminated before a transition to the bayerite phase.

Acknowledgments

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