

Hydrothermal Synthesis of Boehmite Plate Crystals

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Large plate crystals of boehmite up to 4 μm were prepared from $\text{Al}(\text{NO}_3)_3$ solutions with the addition of NaOH under hydrothermal conditions at 250°C for 6 h. The conditions to obtain monodispersed boehmite large plate crystals were determined to be in the range of OH/Al molar ratio from 3.5 to 3.8 and Al concentration from 1.3 to 2.0 mol/kg. Bayerite formed by mixing the starting materials changed to gibbsite at 200°C, and at the same time boehmite started to crystallize from gibbsite. Even after complete phase change from gibbsite, small boehmite crystals grew larger by dissolution and precipitation mechanism. The key to obtain boehmite large plate crystals is the preparation of homogenous fine boehmite crystals by quickly heating fine gibbsite crystals to the boehmite stable region, as well as the selection of OH/Al molar ratio and Al concentration.

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1. Introduction

Plastic materials are now widely used in various fields. Ceramic fillers can improve the properties of plastics such as mechanical strength, electric conductivity, heat conductivity, fire retardancy and so on. It is pointed out that ceramic fillers to improve thermal conductivity of plastics should have intrinsic thermal conductivity, and the morphology of filler particles including size, shape, and particle size distribution, plays important roles in determining the conductivity of the polymer-ceramic composite.¹⁾ Thus, preparation of ceramic powders consisting of particles with controlled morphology is demanded for ceramic fillers.

Boehmite, one of polymorphs of aluminum oxyhydroxides, is the main precursor for γ -alumina which is widely used as a catalyst. Controlling particle morphology of boehmite is of the greatest interest to improve the potentialities of alumina in catalysis, because alumina obtained by calcination of boehmite inherits the morphology from the original boehmite. Many studies^{2)–6)} have been carried out to get γ -alumina for catalysts with high porosity and large surface area from boehmite, but few studies to get large plate boehmite crystals.

Fluoride processes¹⁾ have been used to prepare platelet-shaped alumina powders, because the presence of fluorine significantly promotes crystal growth during the conversion of low-temperature alumina phases to crystalline α -alumina by calcination.⁷⁾ Hill and Danzer¹⁾ prepared hexagonal-shaped α -alumina platelets with average diameters ranging from 7 to 33 μm at 1000°C by calcination of dried powders obtained from aqueous solutions of boehmite and hydrofluoric acid. Though large plates of alumina were obtained by this technique, fluorine is released in air because crystal growth is promoted by a reaction of continuous evaporation-condensation of aluminum fluoride. However, eduction of fluorine is strictly regulated by the emission standard.

Hydrothermal method is a useful method to prepare ceramic powders consisting of particles with controlled morphology.⁸⁾ Boehmite, aluminum oxyhydroxide, has a stable region under hydrothermal conditions. In this study, boehmite plate crystals were hydrothermally prepared from aluminum nitrate solutions with addition of sodium hydroxide. The addition of sodium hydroxide is one of the keys to prepare plate crystals of boehmite, because boehmite with the orthorhombic structure (JCPDS 21-1307) crystallizes to fibrous forms under acidic hydrothermal conditions.^{2),9)} The preparation conditions to get large plate crystals were determined, and the

formation mechanism was discussed in this paper.

2. Experimental

Hydrothermal treatments were carried out at 250°C for 6 h in a Hastelloy C lined autoclave with the inner volume of 20 cm^3 . The autoclave was heated with a heating rate of about 2.5°C/min. in an oven and rotated to agitate the content. The starting materials were commercially available chemicals (Wako Pure Chem. Ind., Ltd.) of $\text{Al}(\text{OH})_3$ (gibbsite as shown in Fig. 6A-a), $\text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and NaOH. One of the Al sources and NaOH were placed in the autoclave with deionized water to control Al concentration and OH/Al molar ratio. The fill ratio was about 60%. After hydrothermal treatments, the products were washed with water and dried at 50°C. They were identified by powder X-ray diffraction (XRD, Rotaflex, Rigaku Co.) and observed by a scanning electron microscope (SEM, S-350, Hitachi Ltd.).

3. Results and discussion

3.1 Preparation from gibbsite

The chemical gibbsite was used as an Al source. When a large amount of NaOH was added over 4.2 of OH/Al molar ratio, no solid products were obtained. White products were obtained after hydrothermal treatments with OH/Al molar ratio less than 4.0. The XRD results showed that all products obtained by the hydrothermal treatments were pure boehmite. **Figure 1** shows SEM photographs of the products obtained with a fixed Al concentration (2.0 mol/kg) by varying OH/Al molar ratios. Even when gibbsite was treated in pure water (OH/Al molar ratio = 3.0), small plate-like crystals of boehmite were formed (Fig. 1(a)). The size of the boehmite crystals increased with the increase in the amount of added NaOH.

3.2 Preparation from $\text{Al}(\text{NO}_3)_3$

Even when soluble $\text{Al}(\text{NO}_3)_3$ was used as a starting material, the similar results with those obtained from the solid gibbsite were given. By the addition of a large amount of NaOH, no solid products were formed. In the region with OH/Al molar ratio less than 4.0, pure boehmite was obtained, but the morphology and size of boehmite crystals were different depending on OH/Al molar ratio and Al concentration. When the Al concentration was fixed to 2.0 mol/kg, very fine crystals were formed under neutral conditions (**Fig. 2(a)**), and the size of boehmite crystals was increased with the increase in OH/Al molar ratio (Fig. 2). The high OH/Al

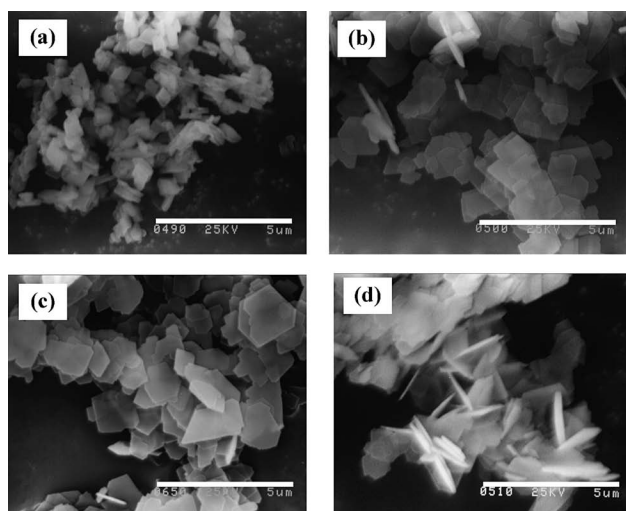


Fig. 1. Boehmite crystals obtained from gibbsite with conditions of Al 2.0 mol/kg and OH/Al molar ratio (a) 3.0, (b) 3.5, (c) 3.8, and (d) 4.0, respectively. (bar = 5 μm)

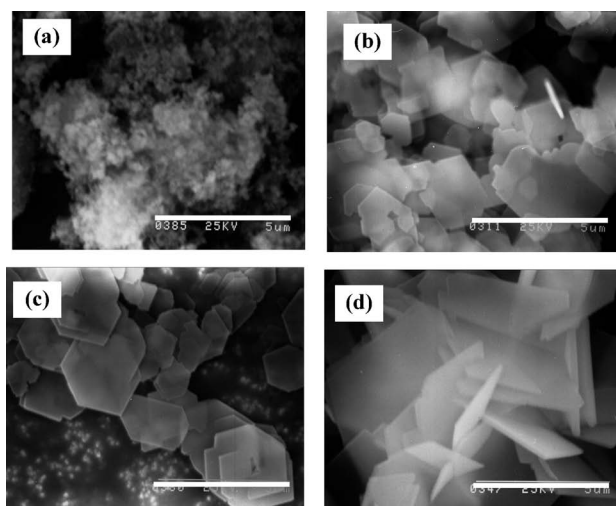


Fig. 2. Boehmite crystals obtained from $\text{Al}(\text{NO}_3)_3$ under conditions of Al 2.0 mol/kg and OH/Al molar ratio (a) 3.0, (b) 3.5, (c) 3.8, and (d) 4.0, respectively. (bar = 5 μm)

molar ratio resulted in interconnection of large plate crystals (Fig. 2(d)). In the region with OH/Al molar ratio from 3.5 to 3.8, the size of crystals increased with the decrease of Al concentration, as shown by the comparison of Figs. 3(c)–(d) and (e)–(f), respectively. However, further decrease of the Al concentration resulted in decrease of size of boehmite crystals (Figs. 3(a), (b)). Thus, the conditions under which mono-dispersed large boehmite crystals with hexagonal plate morphology up to 4.0 μm were determined to be in the rhomb in Fig. 4.

4. Discussion

4.1 Effects of NaNO_3

The comparison of boehmite crystals obtained from different starting materials (Figs. 1 and 2) clearly shows that the crystals obtained from $\text{Al}(\text{NO}_3)_3$ were larger than those from the chemical gibbsite even under the same preparation conditions. The formation of boehmite from different starting

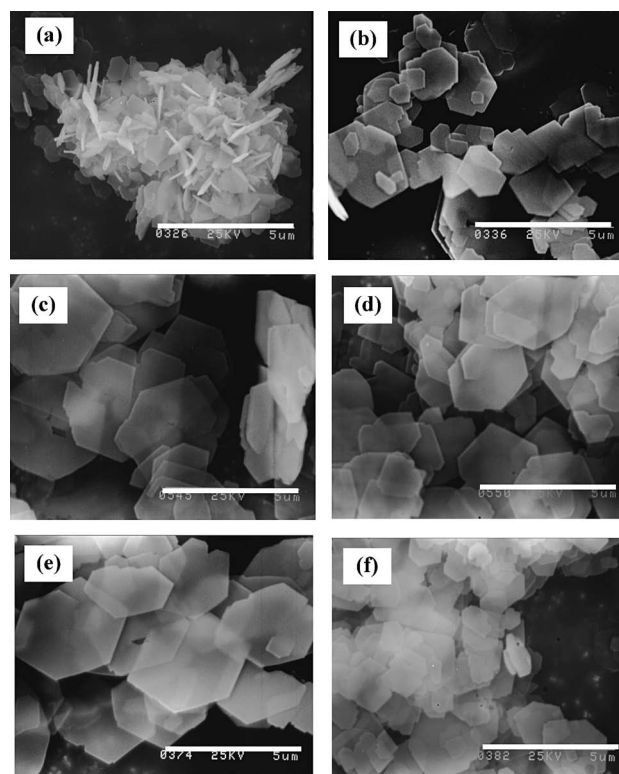


Fig. 3. Boehmite crystals obtained from $\text{Al}(\text{NO}_3)_3$ with conditions of OH/Al molar ratio 3.5, Al 1.2 (a), 1.45 (b), 1.67 (c), 2.5 mol/kg (d), OH/Al molar ratio 3.8, Al 1.3 (d) and 2.5 mol/kg (f). (bar = 5 μm)

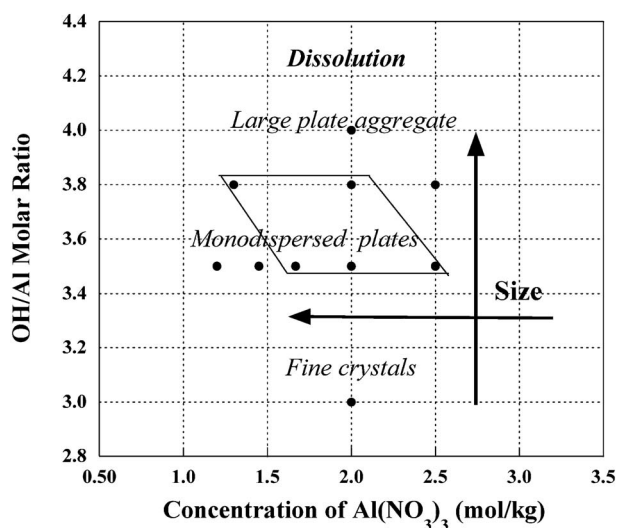
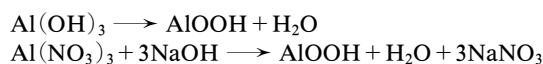


Fig. 4. Diagram for experimental conditions. Black circle shows the preparation conditions of boehmite crystals of which SEM photographs are shown in figures.

materials with OH/Al molar ratio of 3.0 is described by the following chemical equations, respectively.



The difference is the existence of NaNO_3 when $\text{Al}(\text{NO}_3)_3$ is used as a starting material. NaNO_3 may act as a mineralizer

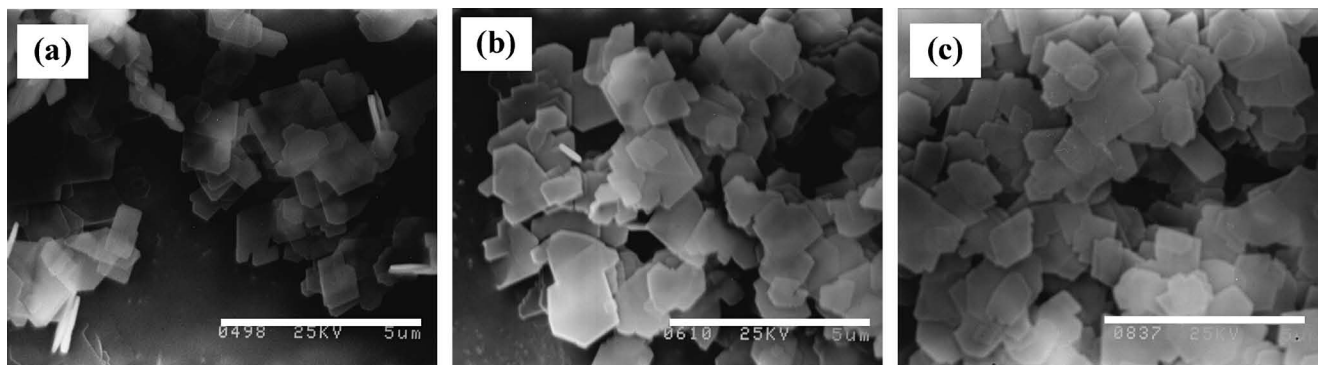


Fig. 5. Boehmite crystals obtained from $\text{Al}(\text{OH})_3$ under conditions of OH/Al molar ratio 3.5 and Al 1.53 mol/kg with addition of NaNO_3 of 0 mol/kg (a), 4.59 mol/kg (b) and under conditions of OH/Al molar ratio 3.0 and Al 1.68 mol/kg with addition of NaNO_3 5.04 mol/kg (c). (bar = 5 μm)

for boehmite crystal growth. In order to remove this difference, NaNO_3 was added to the reaction system of the chemical gibbsite.

Figures 5(a) and (b) show boehmite crystals obtained from the chemical gibbsite under conditions of OH/Al molar ratio 3.5 and Al 1.53 mol/kg with and without addition of NaNO_3 , respectively. Without addition of NaNO_3 , small plate crystals of boehmite were formed (Fig. 5(a)). Even by addition of NaNO_3 (Fig. 5(b)), the size of boehmite crystals was almost same with those obtained without addition of NaNO_3 . Boehmite crystals obtained under conditions of OH/Al molar ratio 3.0 and Al 1.68 mol/kg with addition of NaNO_3 5.04 mol/kg (Fig. 5(c)) are smaller than those obtained from $\text{Al}(\text{NO}_3)_3$ under the same conditions (Fig. 3(a)). The addition of NaNO_3 changed the morphology of boehmite crystals to polygonal shape, but the existence of NaNO_3 cannot explain the reason why larger boehmite crystals were obtained from $\text{Al}(\text{NO}_3)_3$.

4.2 Formation mechanism of boehmite

Boehmite is one of aluminum oxyhydroxides (AlOOH) that are stable at high temperatures in comparison with hydroxides ($\text{Al}(\text{OH})_3$). Thus, the starting $\text{Al}(\text{OH})_3$ changed to boehmite by hydrothermal treatments. When $\text{Al}(\text{NO}_3)_3$ was mixed with NaOH at room temperature, an aluminum hydroxide must precipitate and change to boehmite by hydrothermal treatments. The difference in the starting solid materials may have some effects on final boehmite crystal morphology. In order to observe the course of the reaction, the autoclave was quickly cooled in cold water from a selected temperature during the heating procedure to 250°C under the conditions of OH/Al molar ratio 3.5 and Al 1.67 mol/kg. Figure 6 shows XRD patterns of the products.

The starting chemical of $\text{Al}(\text{OH})_3$ was gibbsite (Fig. 6A-a) and consisted of particles with the size from 1.0 to 2.5 μm (Fig. 7(a)). When it was heated to 200°C, a small diffraction of boehmite was observed in the XRD patterns (Fig. 6A-c). Gibbsite completely changed to boehmite at 230°C (Fig. 6A-e). It took only 12 min to heat the autoclave from 200°C to 230°C. This result suggests the transformation of gibbsite to boehmite is very fast under the hydrothermal conditions used in this study.

On the other hand, the precipitate obtained by mixing $\text{Al}(\text{NO}_3)_3$ and NaOH at room temperature was bayerite (Fig. 6A-a), a polymorph of $\text{Al}(\text{OH})_3$, which consisted of aggregates of very fine crystals (Fig. 7(b)). When bayerite was heated to 150°C, gibbsite started to crystallize (Fig. 6B-

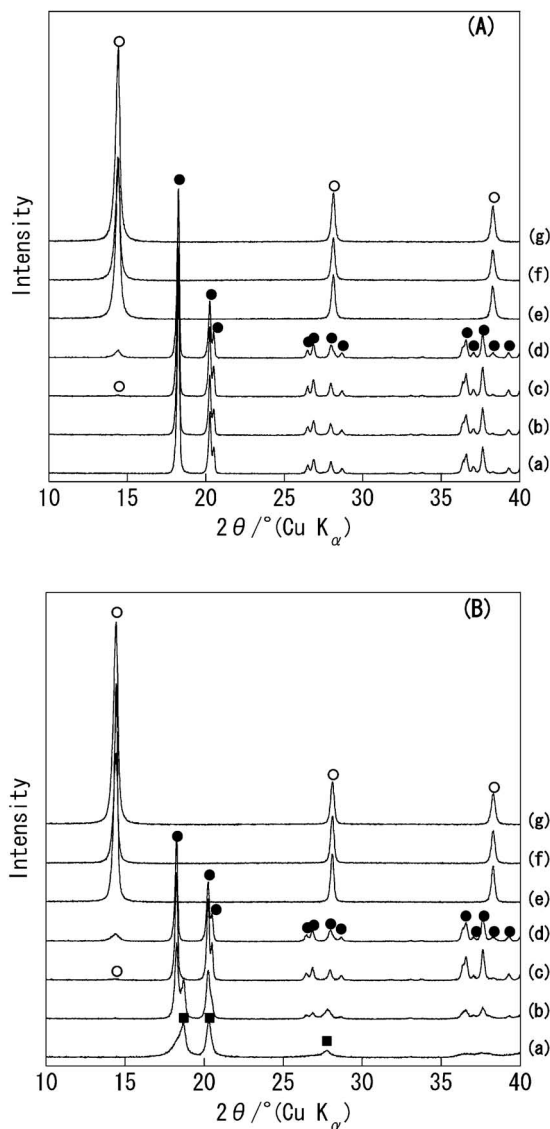


Fig. 6. XRD patterns of the products obtained from (A) gibbsite and (B) $\text{Al}(\text{NO}_3)_3$ at (a) room temperature, and by quenching from (b) 150°C, (c) 200°C, (d) 210°C, (e) 230°C, (f) 240°C, and (g) 250°C with conditions of OH/Al molar 3.5 ratio and Al 1.67 mol/kg. ■: Bayerite, ●: gibbsite, ○: boehmite

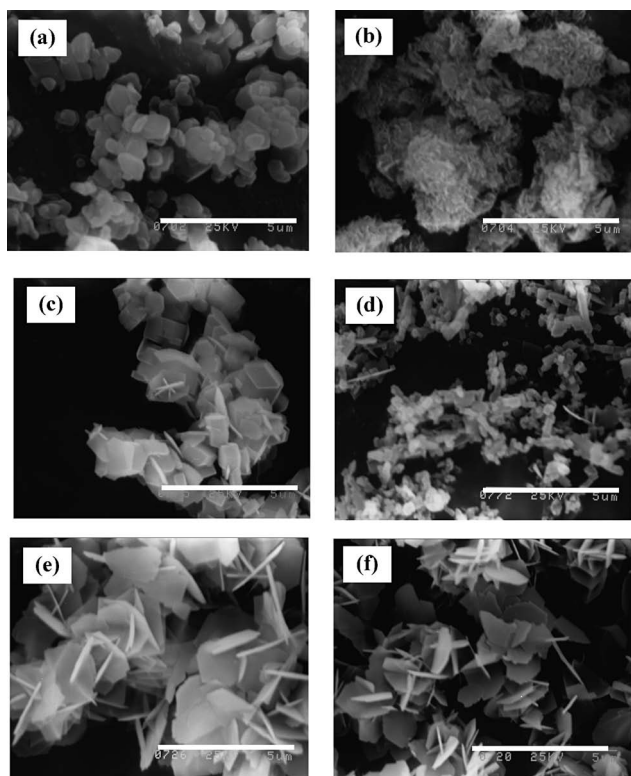


Fig. 7. SEM photographs of gibbsite (a), bayerite obtained from $\text{Al}(\text{NO}_3)_3$ at room temperature (b), and products obtained by quenching from 210°C (c, d) and 250°C (e, f). The products were prepared from gibbsite (c, e) and $\text{Al}(\text{NO}_3)_3$ (b, d, f) with conditions of OH/Al molar ratio 3.5 and Al 1.67 mol/kg. (bar = 5 μm)

b). By further heating to 200°C, bayerite completely changed to gibbsite. At the same time, a small amount of boehmite started to crystallize at 200°C (Fig. 6B–c), and gibbsite completely changed to boehmite at 230°C (Fig. 6A–e).

Figures 7(c) and (d) show the products obtained by quenching from 210°C. According to X-ray diffractions of the products obtained by quenching from 210°C (Fig. 6 A–d, B–d), the products consisted of gibbsite with a small amount of boehmite. Some plate crystals of boehmite were observed on the larger gibbsite crystals when the chemical gibbsite was used as a starting material (Fig. 7(c)). Gibbsite crystals grew larger by heating to 210°C. On the other hand, fine gibbsite crystals were observed when $\text{Al}(\text{NO}_3)_3$ was used as a starting material (Fig. 7(d)). In the both cases, boehmite plate crystals were clearly observed though the amount of boehmite was very small at 210°C. This result suggests that boehmite crystals grew fast after the nucleation. The nucleation of boehmite must be the rate controlling reaction in the transformation of gibbsite to boehmite under the conditions used in this study. Though the XRD patterns did not show the clear evidence, it is reasonable to estimate that the transformation from gibbsite obtained from $\text{Al}(\text{NO}_3)_3$ to boehmite is faster than that from the chemical gibbsite because gibbsite crystals obtained from $\text{Al}(\text{NO}_3)_3$ were very small in comparison with those from the chemical gibbsite. In other words, a larger number of boehmite nuclei were formed in the $\text{Al}(\text{NO}_3)_3$ system, which resulted in formation of smaller boehmite crystals. In fact, boehmite crystals obtained from $\text{Al}(\text{NO}_3)_3$ by quenching from 250°C (Fig. 7(f)) were smaller than those

from the chemical gibbsite (Fig. 7(e)).

The card house structure was seldom observed in the products obtained after hydrothermal treatment at 250°C for 6 h. This structure may be caused by quenching. The boehmite crystals (Fig. 3(c)) obtained from $\text{Al}(\text{NO}_3)_3$ by the hydrothermal treatment at 250°C for 6 h with conditions of OH/Al molar ratio 3.5 and Al 1.67 m were much larger than those (Fig. 7(f)) obtained by quenching from 250°C under the same conditions. This result suggests that the crystals grew by Ostwald ripening mechanism while the temperature was kept at 250°C. On the other hand, the boehmite crystals obtained from the chemical gibbsite did not grow large by keeping the temperature at 250°C and the final product prepared by the hydrothermal treatment at 250°C for 6 h consisted of small boehmite crystals with the size similar to that shown in Fig. 1 (b). This result suggests that smaller boehmite crystals grow larger by dissolution and precipitation mechanism and this stage of the reaction is important to get large plate boehmite crystals.

5. Conclusion

Boehmite was prepared from the chemical gibbsite and $\text{Al}(\text{NO}_3)_3$ by hydrothermal treatment at 250°C for 6 h. The amount of added NaOH and Al concentration had large effects on the morphology of boehmite crystals, but the addition of NaNO_3 had no effects. The conditions to obtain mono-dispersed boehmite large plate crystals from $\text{Al}(\text{NO}_3)_3$ were determined to be in the range of OH/Al molar ratio from 3.5 to 3.8 and Al concentration from 1.3 to 2.5 mol/kg.

Larger plate crystals of boehmite were obtained from $\text{Al}(\text{NO}_3)_3$ than the chemical gibbsite. When $\text{Al}(\text{NO}_3)_3$ was used as a starting material, fine bayerite crystals were formed by mixing with NaOH at room temperature. Bayerite changed to gibbsite and boehmite started to crystallize at 200°C. Gibbsite quickly changed to boehmite during heating to 230°C. The nucleation of boehmite is the rate controlling reaction in the transformation of gibbsite to boehmite under the conditions used in this study. Even after complete phase change from gibbsite, small boehmite crystals grew larger by keeping the temperature at 250°C for 6 h. The key to obtain boehmite large plate crystals is the preparation of homogenous fine boehmite crystals by quickly heating fine gibbsite crystals to the boehmite stable region, as well as the selection of OH/Al molar ratio and Al concentration.

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