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Hydrothermal synthesis of submicrometer crystals of boehmite

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Abstract

The effect of solvents, mechanically ground gibbsites and amorphous hydrated alumina gels on the formation of well-crystallized and submicrometer-sized crystals of boehmite was studied. Nearly monodispersed boehmite particles of 0.2–0.3 μm with a parallelogram shape were hydrothermally synthesized from ball-milled gibbsite in water at 200°C for 6 h. The 100 nm-sized crystals of boehmite were prepared from amorphous hydrated alumina gels at 255°C for 24 h. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Powders with a controlled particle size and morphology are required for a wide variety of applications such as ceramics and catalysts. In particular, nanometer (1–100 nm) and submicrometer (100 nm–1 μm)-sized particles are needed for high-performance materials. Conventional methods for making these fine particles include solution chemistry, vapor-phase synthesis and mechanical grinding of solid phases.

Hydrothermal synthesis offers a low-temperature, direct route to submicrometer oxide powders with a narrow size distribution avoiding the calcination step required in sol–gel processing.[1] The advantage of hydrothermal synthesis is illustrated by the preparation of $BaFe_{12}O_{19}$[2] and $SrFe_{12}O_{19}$[3] ferrites. Single-phase ferrite particles of ~1 μm were obtained at 200–300°C compared with a temperature between 1150 and 1250°C in the conventional solid-state synthesis by heating a mixture of α-Fe_2O_3 and $BaCO_3$ or $SrCO_3$. In addition, well-crystallized and nearly monosized particles $\geqslant 1$ μm of yttrium aluminum garnet (YAG), which is useful in such applications as CRT phosphor screens, have been successfully obtained by hydrothermal processing.[4] There is potential for extending hydrothermal method to a wide range of composition for both oxide and non-oxide powders.[1]

Hydrated aluminas or aluminum hydroxides are used in a wide range of industries. Important uses requiring large tonnages are as fillers in plastics and polymer products and for the production of aluminum chemicals. A modest amount is used for the production of alumina-based adsorbents and catalysts.[5] Boehmite (α-$Al_2O_3\cdot H_2O$ or α-AlOOH) is a major constituent of the European bauxites. Well-crystallized boehmite is prepared from amorphous or crystalline hydrated aluminas such as gibbsite and bayerite by hydrothermal transformation under water vapor pressure at temperatures above 150°C, and usually consisted of polydispersed particles of 1–10 μm. The hydrothermal synthesis of boehmite has been extensively studied,[6–8] but the method of controlling its particle size and morphology has not yet been established. The purpose of the present study is to find the hydrothermal conditions producing well-crystallized and monodispersed submicrometer-size particles of boehmite.

2. Experimental procedures

Boehmite (α-$Al_2O_3\cdot H_2O$) was hydrothermally synthesized from gibbsite or amorphous hydrated alumina gels packed into Ag tube (internal volume of 52 ml) or Teflon one (internal volume of 15 ml) in an autoclave (internal volume of 125 ml) at 200–300°C for 0–48 h in different solvents such as H_2O, and 0.5 N solutions of NaOH, KOH, NH_4OH and KI. Gibbsite (α-$Al_2O_3\cdot 3H_2O$) was supplied from Nippon Light Metal

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Co. (BHP39 high-purity aluminum hydroxide) and contained 99.94% $Al(OH)_3$ and 0.06% Na_2O according to the analytical certificate. The amorphous hydrated alumina gel was prepared as follows. Aluminum isopropoxide (AIP 0.025 mol) was dissolved into ethanol (50 ml), and then this solution was hydrolyzed by addition of a distilled water and 0.5 N HNO_3 (AIP:HNO_3 = 1:0.16 in mol) at 0°C or room temperature and aged for 24 h. The gel obtained thus was amorphous to X-ray. Hydrothermal synthesis of boehmite from the gels was carried out at 255°C for 24 h under the water vapor pressures of 7–91 MPa. After the reaction, the product in Ag tube was washed with a distilled water and then dried at 50°C, and the solution in Teflon tube was subjected to pH and ^{27}Al NMR measurements.

Some gibbsite samples were ground in air for 2 and 6 h, respectively, in a p-7 planetary ball mill (Fritsch, Idar-Oberstein, Germany). A 12 ml alumina jar and four alumina balls of 12 mm in diameter were used. The grinding was interrupted every 15 min, and the sample was scraped from the balls and the sides of the jar and then reloaded to continue grinding. The ground samples were also subjected to hydrothermal processing under the same conditions as described above. The reagents used were purchased from Kanto Chemical Co., Inc.

Powder X-ray diffraction (XRD) patterns were obtained with a RINT-2000 (Rigaku Denki) using Ni-filtered CuK_α radiation (40 kV, 25 mA). Scanning electron microscopy (SEM) was carried out with a field-emission FE-SEM microscope (JEOL, JSM-6300F) at

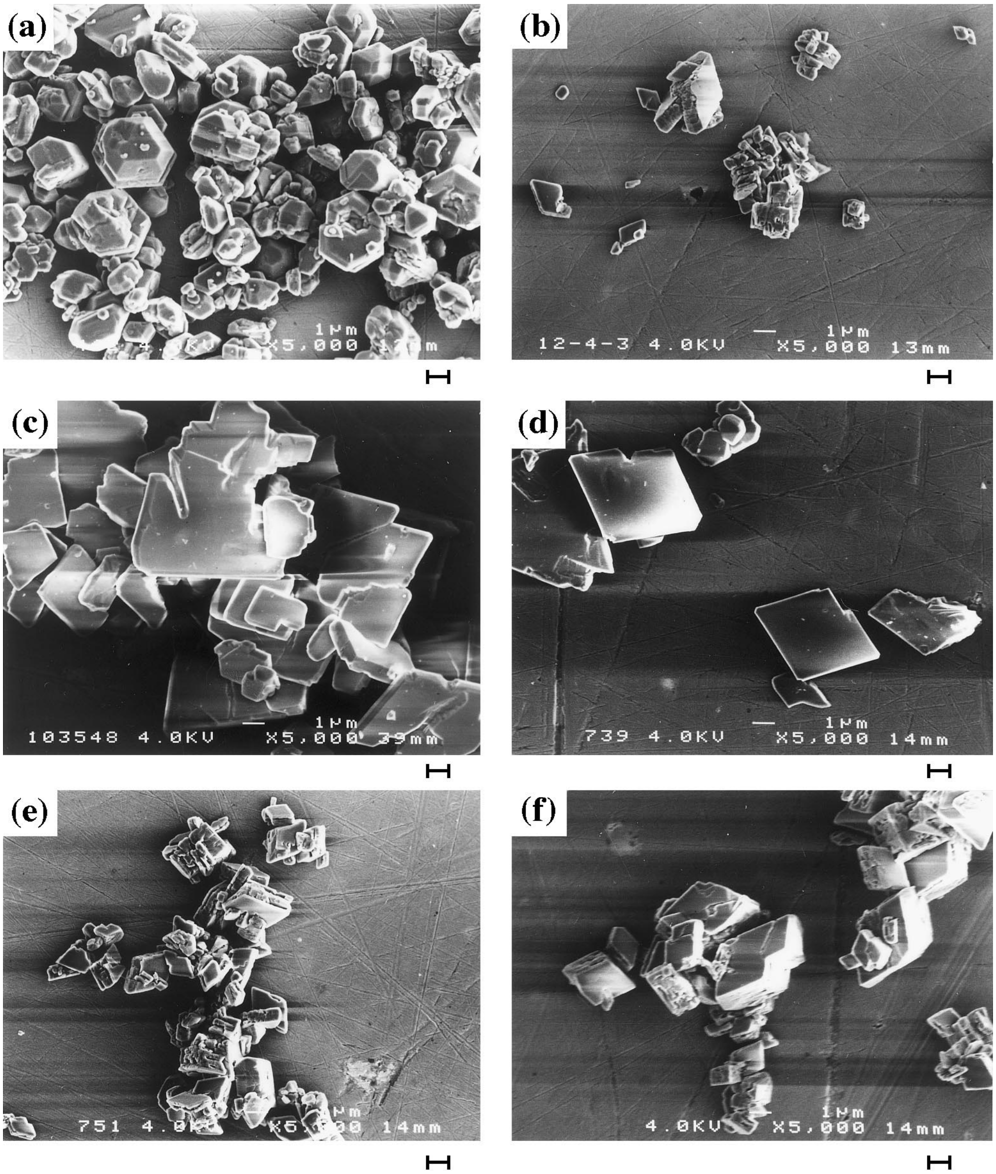

Fig. 1. SEM microphotographs of (a) gibbsite and (b–f) boehmites synthesized hydrothermally from gibbsites under the following conditions. (b) 283°C, 26.5 MPa, 48 h in water; (c) 297°C, 28.4 MPa, 48 h in 0.5 N NaOH solution; (d) 280°C, 24.5 MPa, 48 h in 0.5 N KOH solution; (e) 260°C, 30.4 MPa, 48 h in 0.5 N NH_4OH solution; (f) 275°C, 32.3 MPa, 48 h in 0.5 N KI solution. The scale bar shown is 1 μm.

an accelerating voltage of 4 kV and an emission current of 8 μA. The powder sample dispersed in ethanol by ultrasonication was placed as a drop on a brass stub, dried and then coated with a sputtering-deposited gold film. ^{27}Al NMR spectra were recorded on a Bruker MSL-400 high-resolution NMR spectrometer at a resonance frequency of 104.262 MHZ and a magnetic field strength of 9.4 T. Chemical shifts were recorded with respect to an aqueous solution of $Al(H_2O)_6Cl_3$ used as an external standard. Particle size distribution (Stokes diameter) was measured by gravity sedimentation in a centrifugal automatic particle analyzer CAPA-300 (Horiba Co.). This technique permits the plotting of the cumulative area percent of particles against the equivalent surface and volume diameter. The addition of 0.2 wt% sodium hexametaphosphate solution as a dispersant and the use of ultrasonication were adopted to insure complete dispersion of the particles before measurement.

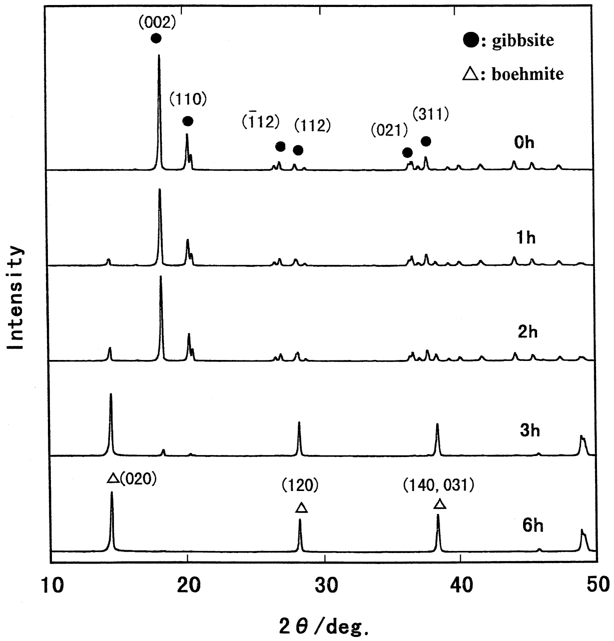

Fig. 2. XRD patterns of gibbsites treated hydrothermally in water at 200°C for 0–6 h.

3. Results and discussion

3.1. Effect of solvents

Fig. 1 shows the effect of solvents used (H_2O, and 0.5 N solutions of NaOH, KOH, NH_4OH and KI) on the particle size and the morphology of boehmite synthesized hydrothermally from gibbsite at 260–300°C for 48 h. The hexagonal plate-like crystals of gibbsite in Fig.1(a) had the area-basis median size, d_{50}, of 4 μm, though with a size distribution of $\leqslant$1–14 μm. They changed to boehmite with a parallelogram shape, though different in size, under the hydrothermal conditions. In particular, as shown in Fig. 1(c) and (d), lamellar microcrystals of boehmite were obtained by using NaOH and KOH solutions as a solvent, respectively. The morphology of these particles was reflected in XRD patterns, showing an extraordinary growth of the (020) diffraction line. This might be attributable to a predominant adsorption of Na^+ or K^+ ions on the ac planes of boehmite and resultant inhibition of crystal growth along the b-direction. It is usually known that the hydrothermal synthesis occurs through a dissolution-recrystallization process. Actually, however, its reaction mechanism is not always well-defined. Recently, Eckert Jr et al. have studied kinetics and mechanism of hydrothermal synthesis of $BaTiO_3$ and estimated a competing reaction of the dissolution-precipitation and in-situ transformation.[9] In order to get more information about hydrothermal transformation of gibbsite to boehmite, the progress of reaction by XRD, and pH and ^{27}Al NMR spectra of the reaction solutions were investigated.

Fig. 2 shows the XRD patterns of gibbsites treated hydrothermally in water at 200°C for 0–6 h. Use of water as a solvent is profitable to eliminate alkali species. The corresponding SEM microphotographs are shown in Fig. 3. Reaction time of 0 h was given when the temperature of autoclave reached to a desired reaction temperature. In Fig. 2, the strongest peak 020 of boehmite began to appear after 1 h, increased abruptly after 3 h and only the phase of boehmite was observed after 6 h. The plot of intensity ratio of [boehmite(020)/{gibbsite(002) + boehmite(020)}] against reaction time showed a S-type curve, obeying a nucleation-growth controlled Avrami-Erofeev equation $-\ln(1-\alpha)^{1/3} = kt$. The difference in the morphology of hexagonal plate-like microcrytals for gibbsite in Fig. 3(a) and parallelogram ones for boehmites in Fig. 3(e) and (f) suggests that the hydrothermal transformation of gibbsite to boehmite is controlled by a dissolution-recrystallization process. In Fig. 3(c) and (d), a few of tiny parallelogram microcrystals of boehmite can be seen on the gibbsite crystals. The stepwise patterns appeared on the gibbsite crystals may indicate the traces of the dissolution reaction of these particles.

Fig. 4 shows ^{27}Al NMR spectra of the reaction solutions after the hydrothermal reactions were carried out at 200°C for 0, 2 and 6 h, respectively. The pH values were also given in the figure. No peak was observed after the reaction of 0 h, whereas only one peak of ^{27}Al NMR spectrum was observed at 79.9 ppm after the reaction of 2 h and increased remarkably after 6 h. This peak corresponds to $Al(OH)_4^-$ ion species,[10,11] different from the Al_{13} tridecamer species, $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}{}^{7+}$, which is formed in an acidic solutions of Al.[10,12] In fact, the pH values of the solutions measured after the reactions of 0, 2 and 6 h were 6.3, 7.6 and 10.4, respectively. This increase in pH value is attributable to

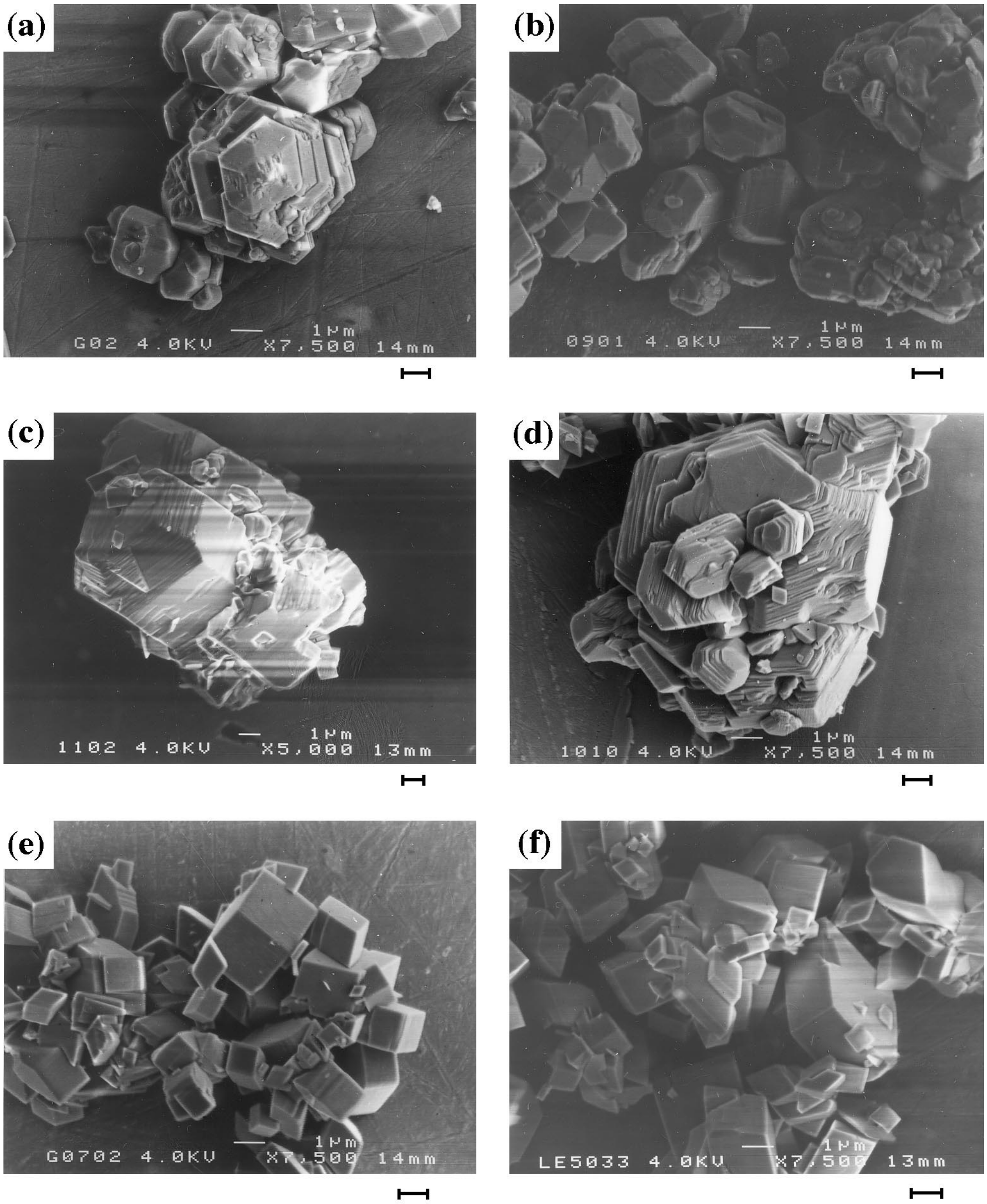

Fig. 3. SEM microphotographs of gibbsites treated hydrothermally in water at 200°C for 0–6 h. (a) gibbsite; (b) 0 h; (c) 1 h; (d) 2 h; (e) 3 h; (f) 6 h. The scale bar is 1 μm.

an increase in the dissolved amount of sodium (0.06 wt% Na_2O) remained in gibbsite crystals. It is required in future to identify the Al-polycations formed by a polymerization-condensation of $Al(OH)_4^-$ ions in alkali solutions.

3.2. *Effect of grinding of gibbsite*

As can be seen from Figs. 1 and 3, the particle size of boehmite synthesized hydrothermally was not monodispersed, but polydispersed, which probably resulted from a wide size distribution of gibbsite used as a starting material. The gibbsite divided finely by a mechanical grinding must lead to the formation of fine, monodispersed boehmite. Therefore, the effect of grinding of gibbsite on the formation of monodispersed boehmite was investigated.

Fig. 5 shows the SEM microphotographs of gibbsites ground for 2 and 6 h, and boehmites synthesized hydrothermally from them in water at 200°C for 6 h. The XRD patterns of gibbsite ground for 2 and 6 h showed the broadening and the decrease in intensity of the (002) and (110) diffraction lines of gibbsite. It can be seen from the figure that both the ground gibbsites were composed of particles of 1 μm or below and boehmites obtained from them were also composed of nearly monodispersed particles of 0.2–0.3 μm with a parallelogram shape. The area-basis median size, d_{50}, measured

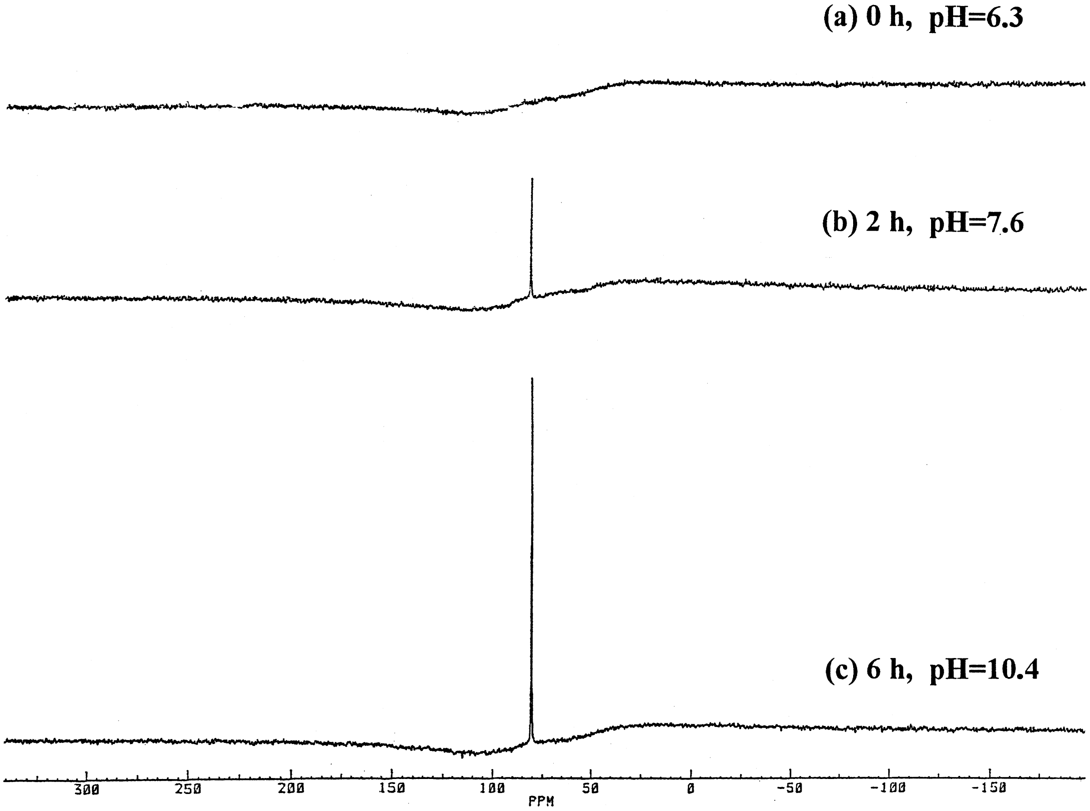

Fig. 4. ^{27}Al NMR spectra of the reaction solutions after the hydrothermal reactions were carried out at 200°C for (a) 0, (b) 2 and (c) 6 h, respectively.

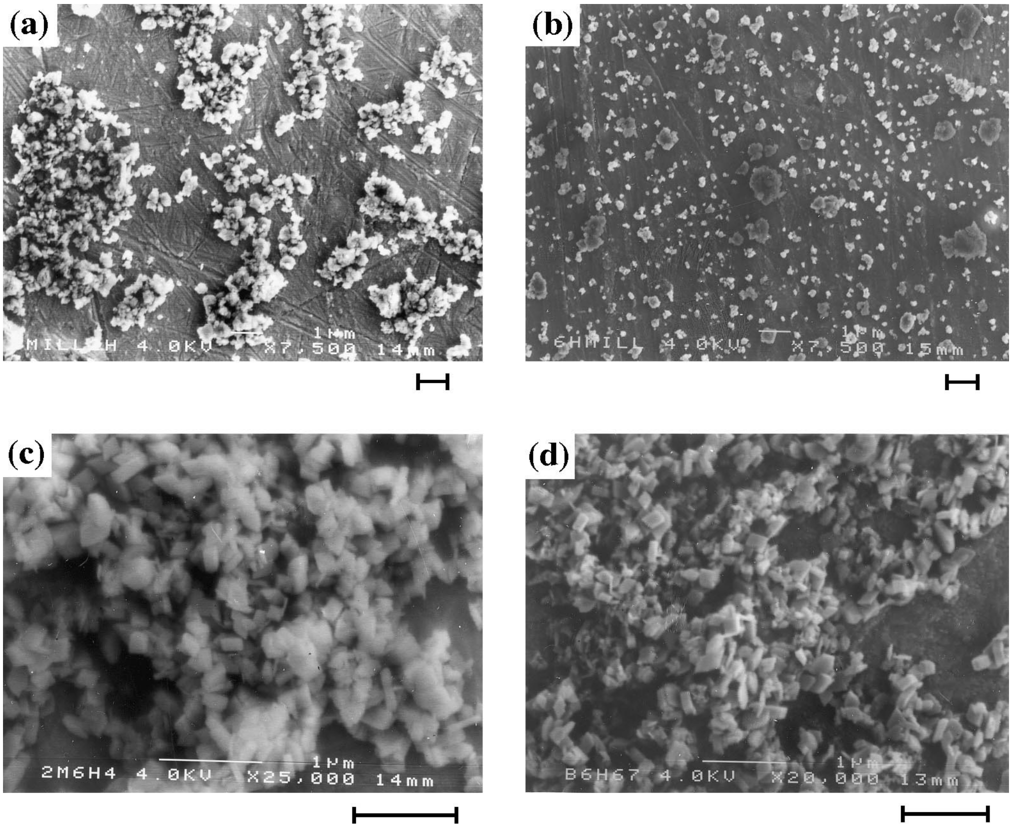

Fig. 5. SEM microphotographs of gibbsites ground for (a) 2 and (b) 6 h, and (c, d) boehmites synthesized hydrothermally from them in water at 200°C for 6 h, respectively. The scale bar is 1 μm.

with a centrifugal automatic particle analyzer, on the other hand, were 1.0 and 0.9 μm for gibbsites ground for 2 and 6 h, and 0.8 and 0.6 μm for boehmites synthesized from them, respectively. The bigger values of particle size of boehmites measured by median size rather than by SEM might be attributable to the state of dispersion or aggregation of samples. Conclusively, it can be emphasized that the submicrometer-sized crystals of boehmite could be hydrothermally synthesized from the mechanically ground gibbsite with a narrow size distribution. In addition, high solubility of fine, active and metastable states of gibbsites obtained by grinding may accelerate the formation of boehmite.

3.3. Formation of 100 nm-sized particles of boehmite

From the above results, it is expected that finer, monodispersed particles of boehmite can be obtained from fine, monodispersed gibbsite. However, it is very difficult to obtain submicrometer-sized particles of gibbsite by mechanical grinding, because of the establishment of a grinding equilibrium in which size diminution and aggregation of particles counteract each other.[13] Then, the hydrothermal synthesis of fine particles of boehmite from amorphous hydrated alumina gel was attempted.

Fig. 6 shows the SEM microphotographs of boehmite synthesized hydrothermally from the gel in water under the conditions of 255°C, 48 MPa and 24 h. It can be seen from the figure that ⩽100 nm-sized and nearly monodispersed microcrystals of boehmite with a parallelogram shape were formed. In the case of amorphous hydrated alumina gels aged at 5°C for 1, 8, 15 or 30 days, almost ⩽100 nm-sized boehmites were synthesized as well. Thus, it was definitely found that the particle size of boehmite synthesized hydrothermally can be basically controlled by the particle size of the starting materials. Its mechanism seems to be explained on the basis of a dissolution-recrystallization process. The particles of gibbsite having the same size may dissolve at the same rate under the same reaction conditions, and subsequent formation of the Al-polycations by a polymerization-condensation of $Al(OH)_4^-$ ions and a homogeneous nucleation of boehmite may lead to the formation of monodispersed particles.

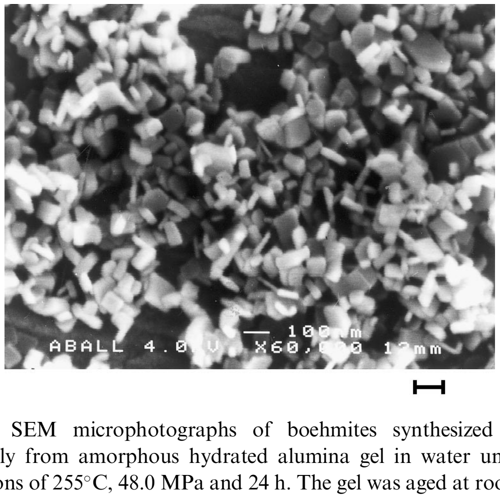

Fig. 6. SEM microphotographs of boehmites synthesized hydrothermally from amorphous hydrated alumina gel in water under the conditions of 255°C, 48.0 MPa and 24 h. The gel was aged at room temperature for 24 h. $AIP/HNO_3 = 1/0.16$ in mol. The scale bar is 100 nm.

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