

Microstructural Transformation with Heat-Treatment of Aluminum Hydroxide with Gibbsite Structure

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Aluminum hydroxide with gibbsite structure was prepared, and the microstructural transformation of the sample heat-treated at various temperatures was investigated. The sample was characterized by field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), thermogravimetry and differential thermal analysis (TG-DTA), and BET surface area. The shape of the grains in the prepared sample was hexagonal prism-like morphology. The prepared sample kept a metastable state of alumina phase at higher temperatures than the commercially available gibbsite powders. The prepared gibbsite grains underwent characteristic structural change depending on the calcination temperature. The transformation of the surface morphology was initiated at 400 °C, leading to the formation of cracks with the direction parallel to the basal plane. After calcination at 1200 °C, a large number of grooves were formed on the surface of the lateral planes. The specific structural change of gibbsite induced by the heat treatment was strongly related to the topotactic dehydration from gibbsite and subsequent phase transition to aluminum oxides.

Aluminum hydroxide crystallizes in various structures, such as gibbsite, boehmite, bayerite, and diasporite.^{1,2} Among these crystalline phases, gibbsite-type aluminum hydroxide is the main component in bauxite. Although gibbsite has been mass-produced via the crystallization of supersaturated sodium aluminate solution, this Bayer process has been known as a time-consuming preparation.^{1,3,4}

Aluminum hydroxide is an important intermediate for the production of aluminum oxide, which is readily formed via dehydration with heat treatment. The dehydration process strongly depends on the crystal structure of aluminum hydroxide.^{5–11} In the case of gibbsite, the dehydration proceeds via formation of a variety of metastable transition alumina phases, such as χ -Al₂O₃, γ -Al₂O₃, and θ -Al₂O₃, finally leading to stable α -Al₂O₃ above 1200 °C.¹¹ These metastable aluminas have been widely employed as support oxides for the deposition of precious metal catalysts because of their large surface area and porous microstructure. On the other hand, aluminum hydroxide with diasporite structure is directly transformed into α -Al₂O₃ at 600 °C.¹⁰ This phase transition greatly affects the active metals on the support surface when alumina is used as a catalyst support. Agglomeration and sintering of alumina supports generally gives rise to sintering of metal particles at high temperatures, leading to the deterioration of the catalytic activity.^{12–14} Accordingly, α -Al₂O₃ with low surface area is unsuitable as a catalyst support. We have recently reported that aluminum hydroxide with gibbsite structure undergoes the phase transition to α -Al₂O₃ leaving laminated intra-grain gaps after calcination above 1200 °C.¹⁵ This α -Al₂O₃ material with a unique texture was useful as a catalyst support despite its low surface area, since the sintering

of Pt particles confined in the pores was effectively suppressed at high temperatures. Although the phase transition from gibbsite to α -Al₂O₃ has been intensively investigated, the change of the surface morphology in this process is still unclear.

In this study, the microstructural change of gibbsite grains induced by heat treatment was investigated. The gibbsite grains with hexagonal prism morphology were prepared from sodium aluminate solution by ordinary procedures and then were heat-treated at various temperatures in air. Microstructural transformation of the prepared sample was compared to that of commercially available material, and the effect of the heat treatment on the morphology and particle size of gibbsite was investigated.

Experimental

Sample Preparation. The gibbsite powder was prepared from sodium aluminate solution. Aluminum metal powder (purity 99.99%, Kishida Chemical Co., Ltd., Japan) was dissolved in an aqueous 2 M NaOH solution at 70–90 °C in a Teflon vessel. The solution was stirred at 70 °C for 4 h. The obtained white precipitate was washed with distilled water three times and was dried at room temperature for 2 days and then at 140 °C for 6 h. Subsequently, the resulting powder was calcined at various temperatures for 5 h in air so as to investigate the microstructural change of gibbsite. For comparison, commercially available aluminum hydroxide powders with gibbsite structure (C12S or C301, Sumitomo Chemical Co., Ltd., Japan) were investigated.

Sample Characterization. The samples were characterized by using the following equipment. X-ray diffraction (XRD) patterns were recorded by using Cu K α radiation on a RIGAKU Ultima IV diffractometer for phase identification in the samples. Thermo-

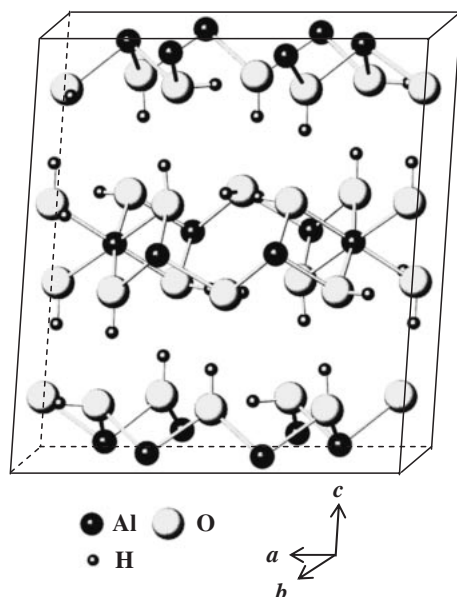


Figure 1. Crystal structure of aluminum hydroxide with gibbsite structure.

gravimetry (TG) and differential thermal analysis (DTA) were conducted under air flow with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ (SII Nanotechnology Inc., EXTRA6000 TG/DTA 6300). Microstructural observation was carried out using a JEOL JSM-6705F field emission scanning electron microscope (FE-SEM). BET surface area was determined by N_2 adsorption at liquid nitrogen temperature using a BEL Japan Belsorp-mini II analyzer. Prior to the measurement, the samples were pretreated under vacuum at $300\text{ }^{\circ}\text{C}$ for 30 min.

Results and Discussion

Crystal Structure of Gibbsite. The gibbsite crystal is classified to a monoclinic space group ($P2_1/n$). The perspective view of the crystal structure of gibbsite is illustrated in Figure 1. The reported lattice parameters are $a = 8.684\text{ }\text{\AA}$, $b = 5.078\text{ }\text{\AA}$, $c = 9.736\text{ }\text{\AA}$, and $\beta = 94.54^{\circ}$.^{16,17} The pseudohexagonal structure of gibbsite consisted of stacked layers along the c axis. Each layer is composed of edge-shared AlO_6 octahedra. Two-thirds of the octahedral sites are occupied by aluminum cations in each bi-layer of the close-packed oxygen atoms of hydroxy groups. Half of the hydroxy groups contribute to intralayer hydrogen bonds, and the other half to interlayer hydrogen bonds along the c direction. This layered crystal structure affected the morphology of aluminum oxide formed by dehydration from gibbsite as well as that of aluminum hydroxide.

Characterization of Gibbsite. The XRD pattern of the prepared white powder is shown in Figure 2. The pattern agreed with that of gibbsite (JSPDS File Card No. 33-0018). An anomalously strong peak ascribable to the diffraction from (002) planes was observed at $2\theta = 18.3^{\circ}$. This indicates that the gibbsite grains in this white particle possess anisotropic crystal habit with a well-grown stacking along the c direction.

Figure 3 shows an FE-SEM image of the powder sample. The shape of the grains in the sample was hexagonal prism-like morphology. Hereafter, the hexagonal faces of each grain are

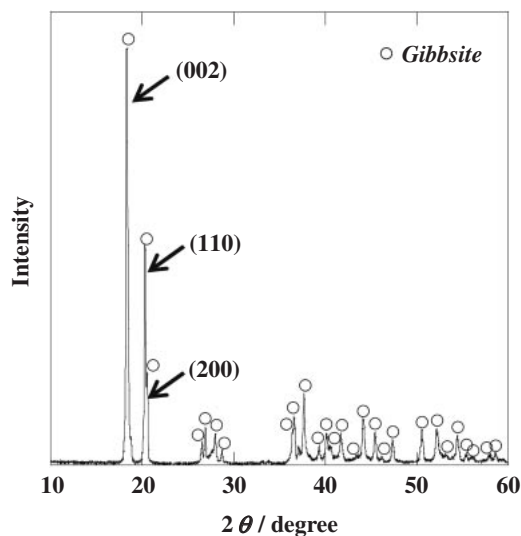


Figure 2. XRD pattern of the prepared gibbsite powder.

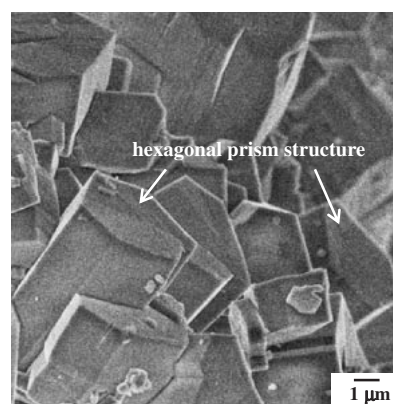
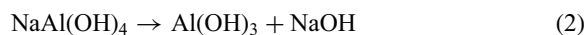
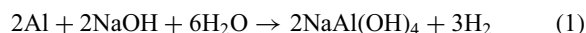


Figure 3. FE-SEM image of the prepared gibbsite powder.

expressed as basal planes. Generally, the morphology of the gibbsite grains has been reported to be pseudohexagonal with (001) basal plane, and (100) and (110) lateral planes.^{18–21} Therefore, the crystalline grains have grown along the c direction. The hexagonal crystallographic planes were piled up to form hexagonal prismatic grain. The formation process in this experiment can be represented by the following reactions 1 and 2.



Phase Transition of Gibbsite. The TG-DTA profiles of the prepared powder sample are shown in Figure 4. A sharp endothermic peak at ca. $290\text{ }^{\circ}\text{C}$ was observed. A weight loss in this temperature range was in good agreement with the calculated value (23.1%) by assuming the dehydration of aluminum hydroxide, i.e., $\text{Al}(\text{OH})_3 \rightarrow \text{AlOOH} + \text{H}_2\text{O}$. In addition, a shoulder endothermic peak appeared at ca. $220\text{ }^{\circ}\text{C}$. This additional peak corresponds to dehydration from the surface of gibbsite particles.^{8,11,22} A broad endothermic peak appeared at ca. $500\text{ }^{\circ}\text{C}$. The total weight loss up to $600\text{ }^{\circ}\text{C}$ was 34.0% in each sample, which agreed with the expected value (34.6%) for the complete dehydration to alumina:

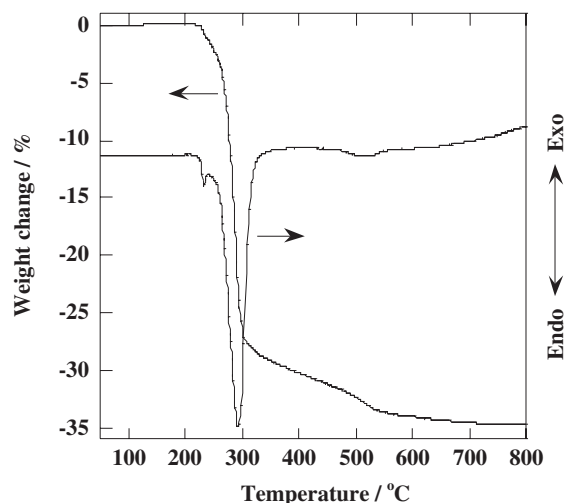


Figure 4. TG-DTA profiles of the prepared gibbsite powder.

$2\text{Al}(\text{OH})_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$. Thus, the endothermic peak at ca. 500 °C is ascribable to the dehydration reaction from boehmite to Al_2O_3 . It was therefore clarified that the dehydration of gibbsite to form alumina via boehmite was completed below 600 °C.

The XRD patterns of the sample calcined at various temperatures for 5 h are shown in Figure 5. The boehmite phase appeared at 200 °C in addition to sharp and dominant diffraction from the gibbsite phase. At the calcination temperature of 400 °C, the boehmite and $\chi\text{-Al}_2\text{O}_3$ phases became dominant accompanied with a disappearance of the gibbsite phase, and the phase transition to aluminum oxide was completed at 600 °C. In the range of 600–1000 °C, the sample underwent complicated transition between a variety of aluminas, such as $\chi\text{-Al}_2\text{O}_3$, $\gamma\text{-Al}_2\text{O}_3$, $\kappa\text{-Al}_2\text{O}_3$, and $\theta\text{-Al}_2\text{O}_3$, leading to the formation of $\alpha\text{-Al}_2\text{O}_3$ above 1200 °C. Generally, gibbsite is dehydrated and converted via two pathways below 1200 °C: (i) the transition to metastable aluminas via boehmite; (ii) the direct formation to $\chi\text{-Al}_2\text{O}_3$.^{7,9} Thus, the transition process of the prepared sample appears to involve both pathways. Figure 6 shows BET surface area of the prepared sample calcined at various temperatures. The surface area decreased with an increase in the calcination temperature.

Microstructural Change with Heat Treatment. Figure 7 shows FE-SEM images of the gibbsite samples calcined at various temperatures. The texture was significantly changed depending on the calcination temperature. In the sample calcined at 200 °C, the morphology of each grain was hexagonal prismatic which was almost the same as the untreated one in Figure 3. After calcination at 400 °C, however, a number of cracks were observed on the lateral surfaces. The cracks have grown in parallel direction to the basal plane of the hexagonal grain and deepened with an increase in calcination temperature. The original hexagonal shape of the grains was retained even after heating to 1000 °C. It is suggested that the formation of the cracks on the surface resulted from the phase transition from boehmite to $\gamma\text{-Al}_2\text{O}_3$. Aluminum hydroxide with boehmite structure was formed by the heat treatment of gibbsite below 400 °C. It is expected from the crystal structure

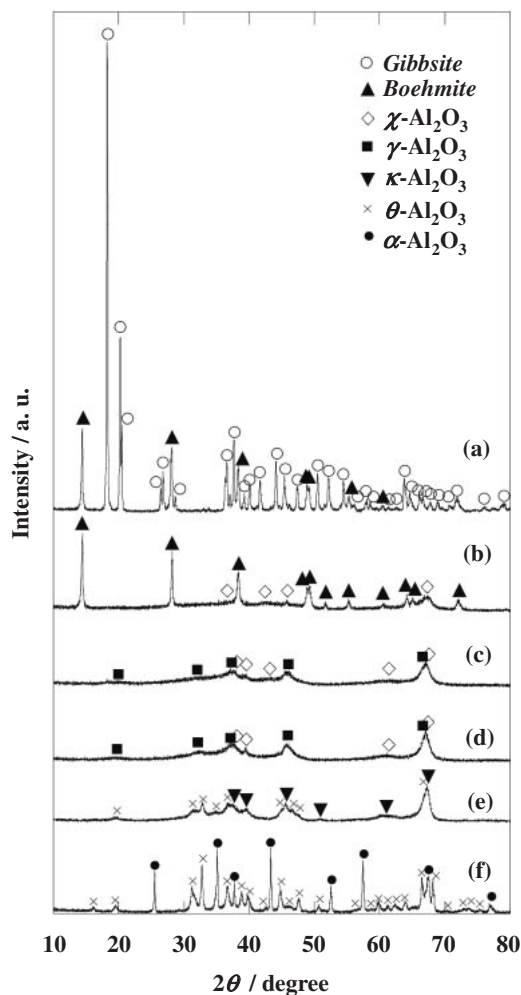


Figure 5. XRD patterns of the prepared sample calcined at various temperatures for 5 h: (a) 200, (b) 400, (c) 600, (d) 800, (e) 1000, and (f) 1200 °C.

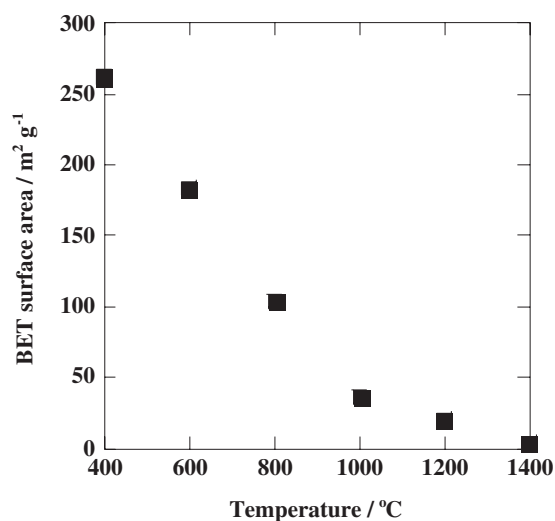


Figure 6. BET surface area of the prepared sample as a function of calcination temperature.

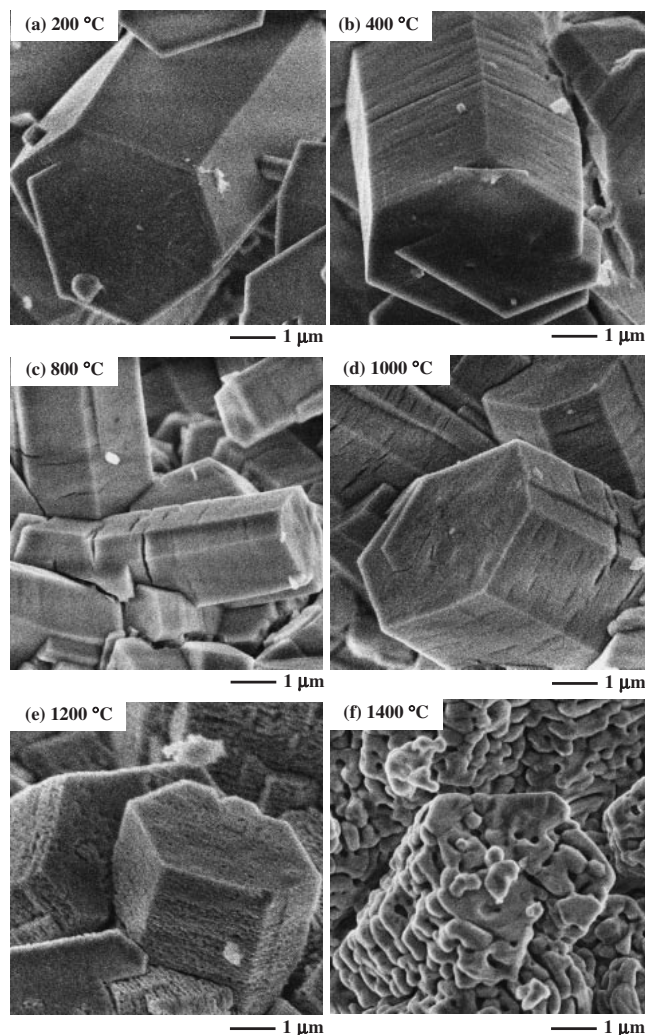


Figure 7. FE-SEM images of the prepared sample calcined at various temperatures for 5 h: (a) 200, (b) 400, (c) 800, (d) 1000, (e) 1200, and (f) 1400 °C.

of gibbsite that the dehydration proceeds via topotactic phase transition. From the layered structure of gibbsite in Figure 1, the elimination of water molecules from the crystal gave rise to compaction of the layers along the *c* direction, leaving the pseudohexagonal packing of oxygen ions. Boehmite belongs to a layered crystal structure, and the complete transition to γ - Al_2O_3 with a defective spinel structure proceeded at ca. 500 °C.²³ The transformation of boehmite has been studied in detail.^{24,25} The collapse of the layered structure of boehmite proceeds by elimination of water and the displacement of aluminum atoms, leading to the formation of cracks. A similar change of surface morphology is confirmed in iron(III) hydroxide, cobalt(II) hydroxide, magnesium hydroxide, and cadmium hydroxide, resulting in the formation of a porous microstructure at high temperatures.^{26–29} Therefore, the structural change of gibbsite at low temperatures is expected to be initiated by the elimination of water from the interlayer gap by retaining the high packing density of aluminum and oxygen in the layers. As shown in Figure 5 on the other hand, a part of gibbsite underwent the phase transition to χ - Al_2O_3 at ca. 600 °C in the other dehydration pathway. χ -Alumina phase is

composed of stacked layers, which are largely disordered along the *c* direction.^{2,30,31} Thus, the layered structure is maintained up to 1000 °C, until the transition to κ -phase proceeded as shown in Figure 5. The layered crystal structure collapsed above 1000 °C accompanied by the conversion into κ -phase. Thus, it is concluded that the formation of the cracks at low temperatures is mainly ascribable to the phase transition via boehmite.

The texture of the sample was significantly changed by heat treatment above 1200 °C. In the sample calcined at 1200 °C, the difference in the morphology between the basal and the lateral planes was obvious. A large number of grooves were preferentially observed in the lateral plane, which were propagated from the cracks parallel to the basal plane. The hexagonal prismatic external geometry of grains was retained. The laminated microstructure has been developed in the original hexagonal prismatic grains. After calcination at 1400 °C, the sample exhibited an intricate structure. The hexagonal basal plane deformed and was porous. As shown in Figure 5, the phase transition to α - Al_2O_3 proceeded above 1200 °C. Accordingly, the formation of porous structure originated in the transition to α -phase.

As mentioned above, aluminum hydroxide of gibbsite structure is transformed into α - Al_2O_3 with highly oriented grooves by calcination at elevated temperatures. We have reported previously that sintering of Pt particles located inside the groove was often affected by the restriction in the gap between α - Al_2O_3 slabs.¹⁵ Growth of Pt particles confined in the gap of the slabs was effectively suppressed. The present investigation focused on the specific structural change of gibbsite induced by the heat treatment. The cracks formed at low temperatures are developed into the grooves between α - Al_2O_3 slabs after heating at 1200 °C for grains with well-grown hexagonal prismatic morphology. Porous α - Al_2O_3 with laminated microstructure and high thermal resistance is a suitable structure to suppress the agglomeration of supported precious metal particles. Thus, it will be applicable as a catalyst support for the sintering inhibition of precious metal particles.

Effect of the Heat Treatment on the Morphology and Particle Size.

The heat-induced transformation of the prepared sample was compared with those of commercially available ones. The effect of the heat treatment on the morphology and particle size of gibbsite was investigated. X-ray diffraction patterns of C12S and C301 samples are basically the same as that in Figure 2; i.e., these samples are also categorized as gibbsite. The dehydration process of C12S and C301 was analogous to that of the prepared sample. However, the transition temperature to α -phase was different from the prepared sample. The XRD patterns of C12S and C301 calcined at 1200 °C for 5 h are shown in Figure 8. Complete phase transition to α - Al_2O_3 proceeded for each sample, as the patterns consisted of a single phase of α - Al_2O_3 . As shown in Figure 5 on the other hand, the transition to α -phase was incomplete in the prepared sample. Therefore, it can be concluded that the phase transition in the prepared sample was retarded even at 1200 °C. Table 1 summarizes BET surface area of the prepared sample, C12S, and C301 calcined at 1200 or 1400 °C. The surface area of the prepared sample was larger than those of other samples after calcination at 1200 °C, though

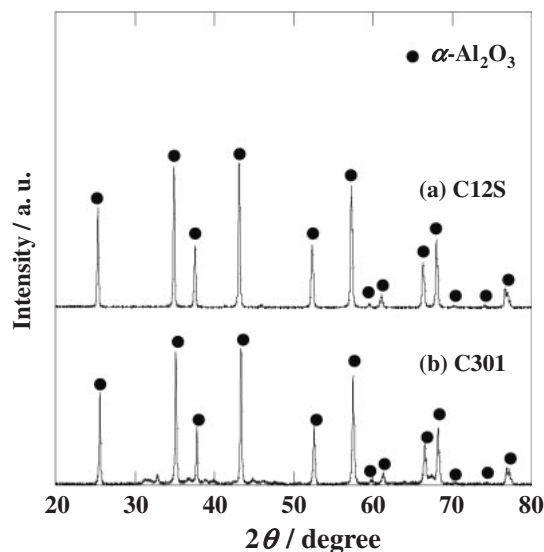


Figure 8. XRD patterns of commercially available gibbsite powders calcined at 1200 °C: (a) C12S and (b) C301.

Table 1. BET Surface Area of Prepared Sample, C12S, and C301 Calcined at 1200 or 1400 °C for 5 h in Air

Temperature/°C	BET surface area/m ² g ⁻¹		
	Prepared sample	C12S	C301
1200	20.6	9.2	13.3
1400	3.0	3.2	3.8

the surface area became comparable for all samples after calcination at 1400 °C. This result supports the slow phase transition to α -Al₂O₃ for the prepared sample.

Figure 9 shows FE-SEM images of C12S and C301 before and after calcination at 1200 °C. In the case of C12S, the oriented cracks appeared on the surface after heating at 400 °C. Furthermore, the formation of the grooves in the gaps of the slabs was clearly observed at 1200 °C. Although this structural change was similar to the prepared sample, the characteristic transformation in the texture was observed for C301 with small particles. The particles with porous structure were formed after the heat treatment of 1200 °C. The formation of the pores occurs regardless of the particle size. However, the laminated microstructure was unobservable for the C301 sample after the heat treatment. Thus, it is concluded that well-grown gibbsite grains are essential for the formation of laminated microstructure.

Conclusion

The gibbsite particles with hexagonal prism-like grain morphology were prepared from sodium aluminate solution, and the microstructural change of the samples induced by the heat treatment was investigated. The gibbsite particles precipitated as strong anisotropic crystalline grains with a well-grown direction along the *c* direction. The phase transition from gibbsite to boehmite initiated from 200 °C and that to aluminum oxide via boehmite proceeded above 500 °C. The dehydration process of gibbsite proceeded not only via (i) the transition to metastable aluminas via boehmite, but also via (ii)

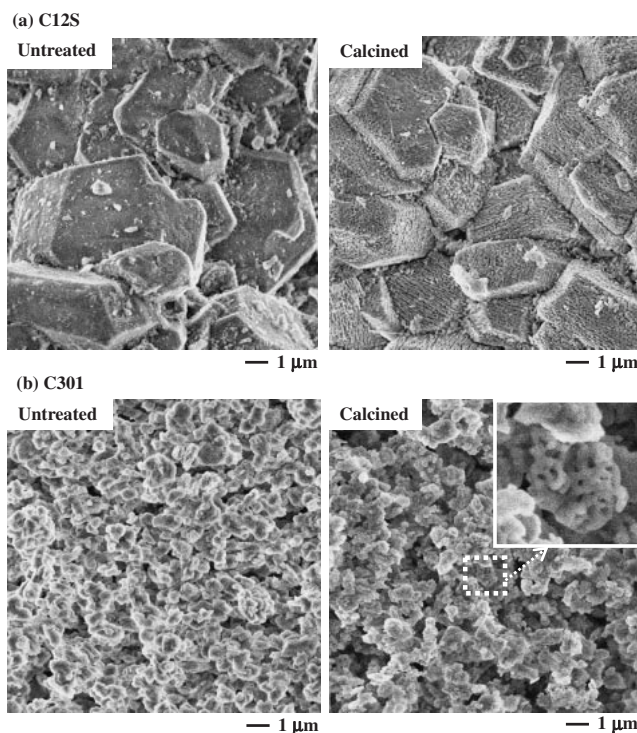


Figure 9. FE-SEM images of commercially available gibbsite powders before and after calcination at 1200 °C: (a) C12S and (b) C301.

the direct transition to χ -Al₂O₃. The texture of the prepared gibbsite grains was drastically changed depending on the calcination temperature. On heating at 400 °C, a number of the cracks developed parallel to the basal plane of the hexagonal prism grains. The structural transformation of gibbsite was initiated by the elimination of water in the interlayer and subsequent phase transition. The formation of the cracks should be ascribable to the phase transition via boehmite. Furthermore, the gibbsite was transformed into laminated morphology by heat treatment above 1200 °C due to the phase transition to α -Al₂O₃. The formation of the pores proceeded regardless of the particle size and the morphology. However, the resultant texture of grains depended strongly on the original shape of the gibbsite crystals. As compared with the commercially available gibbsite samples, the phase transition in the prepared sample proceeds slowly, resulting in high surface area even at 1200 °C.

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