

Synthesis of aluminium hydrates by a precipitation method and their use in coatings for ceramic membranes

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Abstract

Aluminum hydrates were synthesized using $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ as the starting material by the precipitation method. The phases of the obtained powder were amorphous, boehmite, bayerite and nordstrandite depending on the pH of the solutions. The weight loss of the powders by dehydration was increased with the lowering pH condition of solution. Aluminum hydrates transformed to $\alpha\text{-Al}_2\text{O}_3$ via $\gamma\text{-Al}_2\text{O}_3$, $\delta\text{-Al}_2\text{O}_3$ and $\theta\text{-Al}_2\text{O}_3$, and particle sizes were grown by increment of the heating temperature. The crystallite size and specific surface area were rapidly changed over 1100°C which is the formation temperature of the $\alpha\text{-Al}_2\text{O}_3$ phase. The $\gamma\text{-Al}_2\text{O}_3$ powder was coated on an intermediate layer of ceramic membrane by the slip casting method, and an unsupported membrane was also prepared for comparison. The supported microfiltration layer showed a porous structure with small grains, but the unsupported layer revealed interconnected larger grains. Grain growth was more dominant in the unsupported layer than in the supported one due to interaction between the support and the supported layer. An ultrafiltration membrane with homogeneous microstructure was formed using boehmite particulate sol, and abnormal grain growth in unsupported membrane was also observed similar to microfiltration layer. © 2001 Published by Elsevier Science Ltd. All rights reserved.

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1. Introduction

A membrane can be defined as a semi-permeable selective barrier between two phases. A ceramic membrane has been focused upon for its unique characteristics in the separation process of industrial waste streams, food process, biomedical process and chemical process.¹

The use of a ceramic membrane instead of a polymeric one gives some advantages such as high thermal and chemical stability, pressure resistance, longer lifetime, good defouling properties and catalytic properties.² Because a homogeneous microstructure without crack, defect and uniform pore size distribution are necessary for the use of a membrane, the use of uniform size particles gives better control over the pore size

distribution of a ceramic membrane.^{3,4} The advantages of the solution technique, which is one of the powder preparation techniques, are high purity, chemical homogeneity, small and uniform particle size, and controlled particle shape. Solution techniques have continued to be dominant in the preparation of multi component oxide systems.⁵

The precipitation method used in this work is one of the solution techniques and is still a powerful and widely used method.^{5–7} The $\gamma\text{-Al}_2\text{O}_3$ and boehmite powder are used for microfiltration (MF) and ultrafiltration (UF) membranes.^{8–10} An ultrafiltration membrane of alumina is commonly made with the sol-gel method using aluminum alkoxide.^{1,2,11–14} In earlier works using alkoxide, Leenaars et al.^{13–14} investigated the microstructural evolution of supported and unsupported alumina membranes. Similar results about titania membrane were reported by Kumar et al.,^{15,16} but alkoxide raw materials are relatively expensive, so

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particulate sol via a chemical synthetic route was adopted in this study. Aluminum hydrates were synthesized by the precipitation method, and alumina powder was obtained by subsequent heat treatment. The obtained powders were applied to ceramic MF and/or UF membrane as coating materials. The powder properties and its coating characteristics will be discussed.

2. Experimental

Aluminum chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, Showa Chemical Co., Japan) was used as starting material. $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in distilled water, and the pH of resulting solution was 3.0. NH_4OH as precipitation agent was added into the solution, the pH of the solution was controlled to 7, 8, 9 and 10, and the solution stirred with a magnetic stirrer. The shape of the precipitated powder was observed by transmission electron microscope (TEM; Philips Co., The Netherlands).

Filtering of the solution and washing of the powder with distilled water were performed until Cl^- ions were not detected by 1M of AgNO_3 solution and, then, ethanol was used to wash the powder for three times. The filtered powder was dried in oven at 100°C for 24 h, and dried powders prepared with various pH conditions were heated for 1 h at 600, 800, 1000, 1100, 1200 and 1300°C .

A tubular type ceramic support (Sen Bool Sintering Co., Korea) which is a alumina based porous body with mean pore diameter of $10\ \mu\text{m}$, was made by the extrusion method. An intermediate layer was coated by the slip casting method on the ceramic support to prevent the penetrating of fine powders into the support. The raw powder of the intermediate layer is $\alpha\text{-Al}_2\text{O}_3$ (Almatra Co., Korea) whose mean particle size is $1.8\ \mu\text{m}$.

The $\gamma\text{-Al}_2\text{O}_3$ powder precipitated at pH 8 and heated at 600°C for 1 h was coated on the intermediate layer by the slip casting method. The coated $\gamma\text{-Al}_2\text{O}_3$ layers were dried in an oven at 50°C for 24 h, and heated for 1 h at 1300°C . An unsupported membrane was also prepared by drying of the water solvent. A small amount of $\gamma\text{-Al}_2\text{O}_3$ slurry was poured in a polyvinyl chloride petri dish and dried at 50°C .

The heating condition of the unsupported membrane was same as that of the supported layer.

A UF membrane was formed on a MF layer using boehmite sol, which was prepared by dispersing the boehmite powder in distilled water and controlling the pH of the solution with HNO_3 . The other experimental conditions were the same as that of the MF layer.

The change of crystalline phases and crystalline size of the obtained aluminum hydrates was analyzed with X-ray diffraction (XRD; M18XHF-SRA, Mac. Science Co.) using $\text{CuK}\alpha$ radiation. Crystalline size was calculated by

Scherrer's equation using the FWHM of XRD peaks.¹² The specific surface area of the obtained powder was measured by BET (Brunauer-Emmett-Teller, Quantachrome Autosorb-1) method. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed in air at a heating rate of $10^\circ\text{C}/\text{min}$ in order to determine the thermal properties of the powders.

The surface and cross-section of intermediate, support and unsupported MF layer, and UF layer were observed by scanning electron microscope (SEM; Hitachi Co., Japan).

3. Results and discussion

$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was completely dissolved in distilled water. After dropping of NH_4OH , the solution changed from transparent to opaque. Fig. 1 shows the morphology of as-precipitated powder under pH 8 and dried powder at 100°C for 24 h observed by TEM. Nano-meter sized particles were formed, and agglomeration of the nano-particles was also observed by SEM.

Fig. 2 is the XRD peaks of dried powders prepared under different pH. As the pH value increased from 7 to 10, phases of obtained aluminum hydrates were changed from amorphous to boehmite (AlOOH), bayerite ($\text{Al}(\text{OH})_3$), and nordstrandite ($\text{Al}(\text{OH})_3$). It can be attributed to an increased amount of OH^- ions from added NH_4OH .

The TG and DTA curves for powders dried at 100°C for 24 h are shown in Fig. 3. As the pH of the solution was increased, the weight loss of the powders was reduced during heating. A rapid change in weight occurred resulting from the dehydration of $\text{Al}(\text{OH})_3$ between 250 and 300°C in powder prepared under pH 10. The absorbed water was evaporated at 80°C shown in DTA curves. A large endothermic peak appeared in

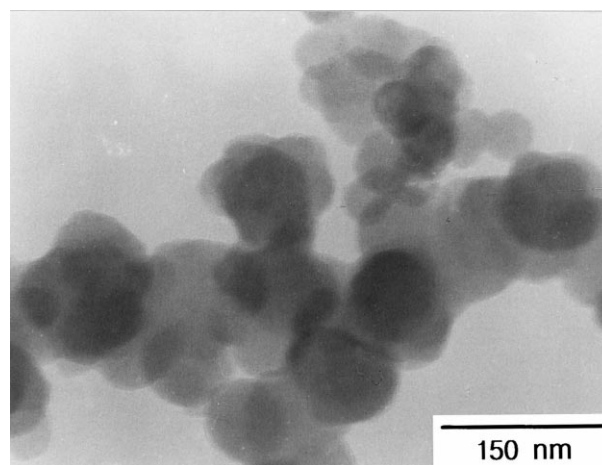


Fig. 1. TEM micrograph of as-precipitated powder under pH 8 and dried powder at 100°C for 24 h.

the powder (pH = 10) near 280°C, and it is similar to TG analysis. Exothermic peak near 340°C might be due to the transformation of aluminum hydrates to transient Al_2O_3 phase, as will be described in the XRD result.

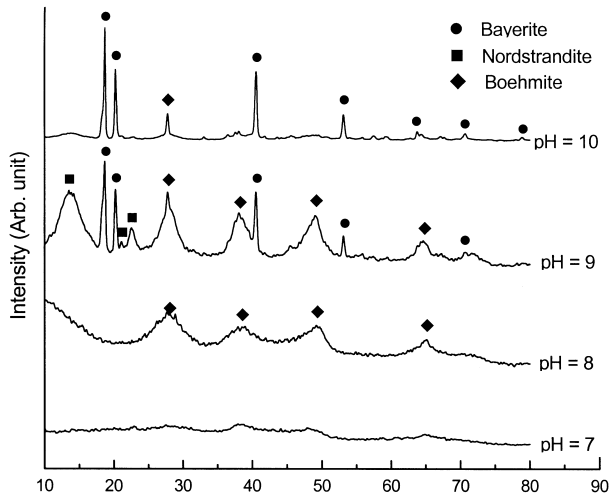


Fig. 2. XRD peaks of dried powders synthesized under different pH.

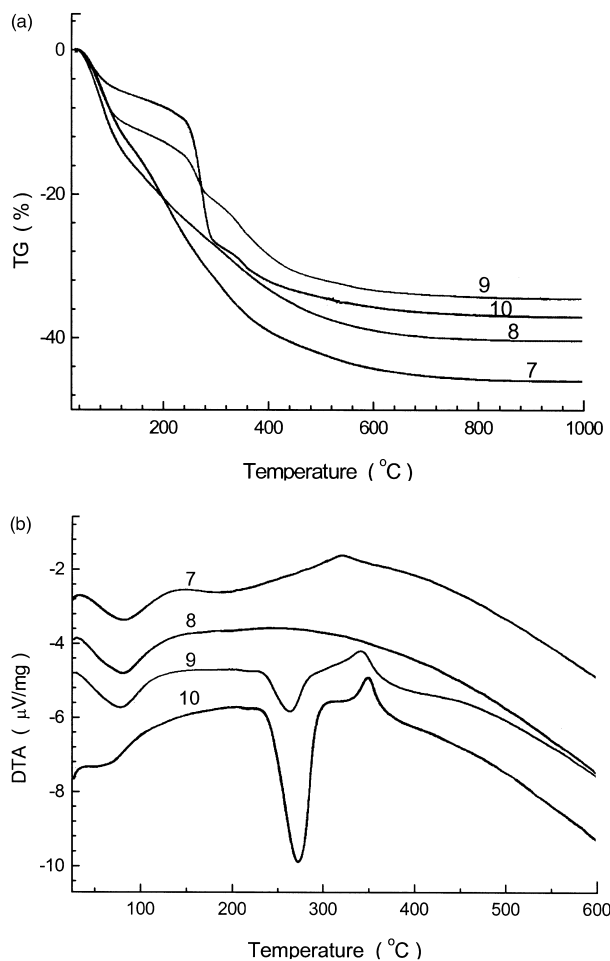


Fig. 3. (a) TG and (b) DTA curves of dried powders synthesized under different pH, digit means pH value.

Fig. 4 shows XRD peaks of dried and calcined powders precipitated under pH of 8 and 10, respectively. Dehydration of the boehmite phase in dried powder occurred during heating, and $\gamma\text{-Al}_2\text{O}_3$ phase was detected in calcined powder heated at 600°C. As the calcined temperature increased, $\gamma\text{-Al}_2\text{O}_3$ transformed to $\delta\text{-Al}_2\text{O}_3$, $\theta\text{-Al}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$ which is the most stable phase of the Al_2O_3 phase.^{13,17} These transformations have been characterized in terms of pore development.^{6,18} Aluminum hydrate was transformed to $\alpha\text{-Al}_2\text{O}_3$ at a lower temperature in powders precipitated under low pH value, because the powders dehydrated at a lower temperature, as shown in TG analysis. The crystalline size of powders was calculated by Scherrer's equation using XRD peaks.¹² Table 1 shows the variation of crystalline size and specific surface area in powders with different annealing temperature and pH of solution. The crystalline size decreased at 600°C, and it might be attributed to dehydration of skeleton structure powder around 280°C.^{13,18} The $\gamma\text{-Al}_2\text{O}_3$ crystallites are formed within the boehmite crystal, thereby creating new pores. The

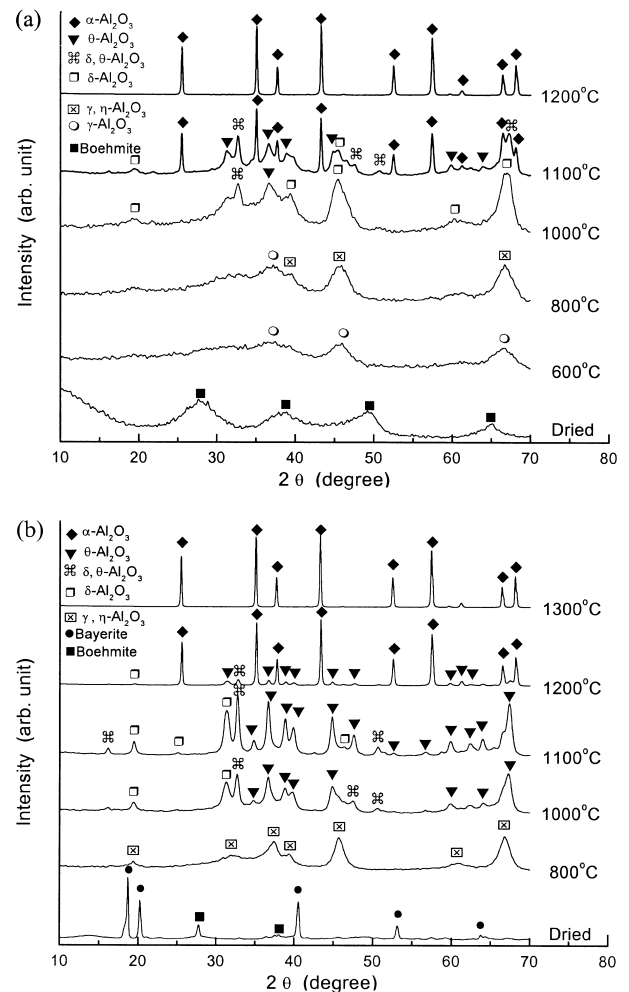


Fig. 4. XRD peaks of dried and calcined powders: (a) pH = 8 and (b) pH = 10.

hydration of boehmite is topotactic and occurs to form γ - Al_2O_3 having well-defined pore structure.¹⁸ The crystalline size increased with increasing annealing temperature, and increased abruptly over 1100°C. The specific surface area of powder decreased with increasing annealing temperature. When the α - Al_2O_3 began to appear over 1100°C, the specific surface area also showed rapid change.¹³

Fig. 5 shows SEM micrographs for surface and cross-section of supported and unsupported MF ceramic membrane. Fig. 5(a) shows the multi-layer ceramic membrane consisted of support, intermediate layer and MF layer of alumina from right to left. The thickness of

the intermediate and MF layers are 25 and 35 μm , respectively. The interface between intermediate and MF layer is shown in Fig. 5(b). The MF layer consisted of smaller particles compared to the intermediate layer, and cracking or peeling of the layer did not occur. The microstructures for the surface of the supported and unsupported top layer are shown in Fig. 5(c) and (d). The supported layer showed porous structure constituted the grains with narrow size distribution between 200 and 300 nm. In contrast, the unsupported layer revealed interconnected grains, which is a typical microstructure of an α - Al_2O_3 membrane,¹⁹ and had larger grains compared to the supported layer. It is known that

Table 1
Crystalline size and specific surface area of dried and calcined powders with heating temperature

		Dried	600°C	700°C	800°C	1000°C	1100°C	1200°C
Crystalline size (\AA)	pH=7	–	–	–	–	–	115	363
	pH=8	–	–	–	–	58	367	425
	pH=9	207	53	54	58	70	174	428
	pH=10	286	–	60	68	82	179	422
	Specific surface area (m^2/g)	418	287	260	235	162	82	9
	pH=9	367	183	267	217	129	82	10
	pH=10	321	236	274	206	97	64	17

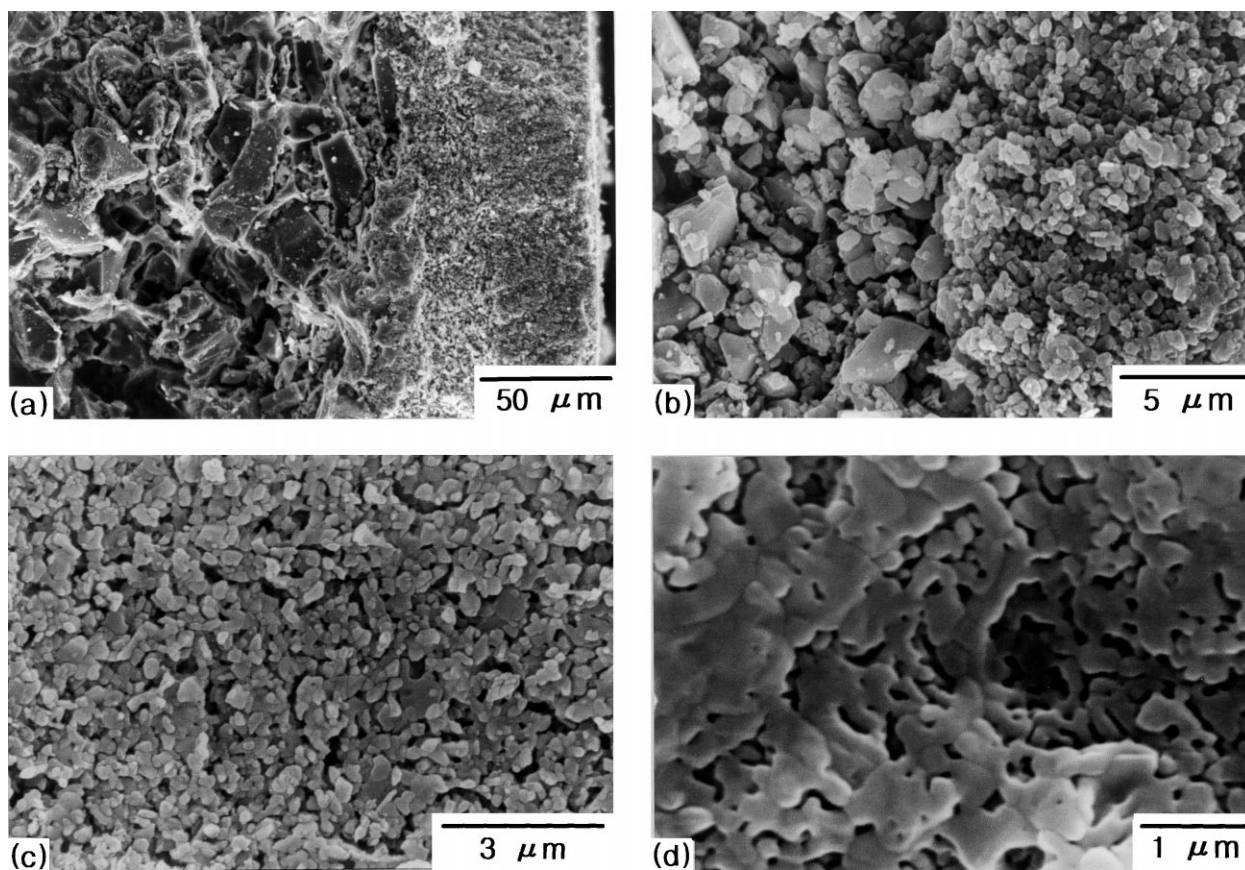


Fig. 5. SEM micrographs for supported and unsupported membrane. (a) cross section of multi-layer; (b) interface between intermediate and MF layer; (c) surface of MF layer (d) surface of unsupported MF layer.

grain growth is more dominant in the unsupported layer than in the supported one. Transformations are accompanied by a volume change. This is a major reason for cracking or peeling of the membrane layer. The volume change of the supported layer can be prevented by the under-layer of intermediate and support. Microstructural difference between the supported and unsupported layers is thought to have resulted from the interaction between top and intermediate layer.^{15,16,20} A

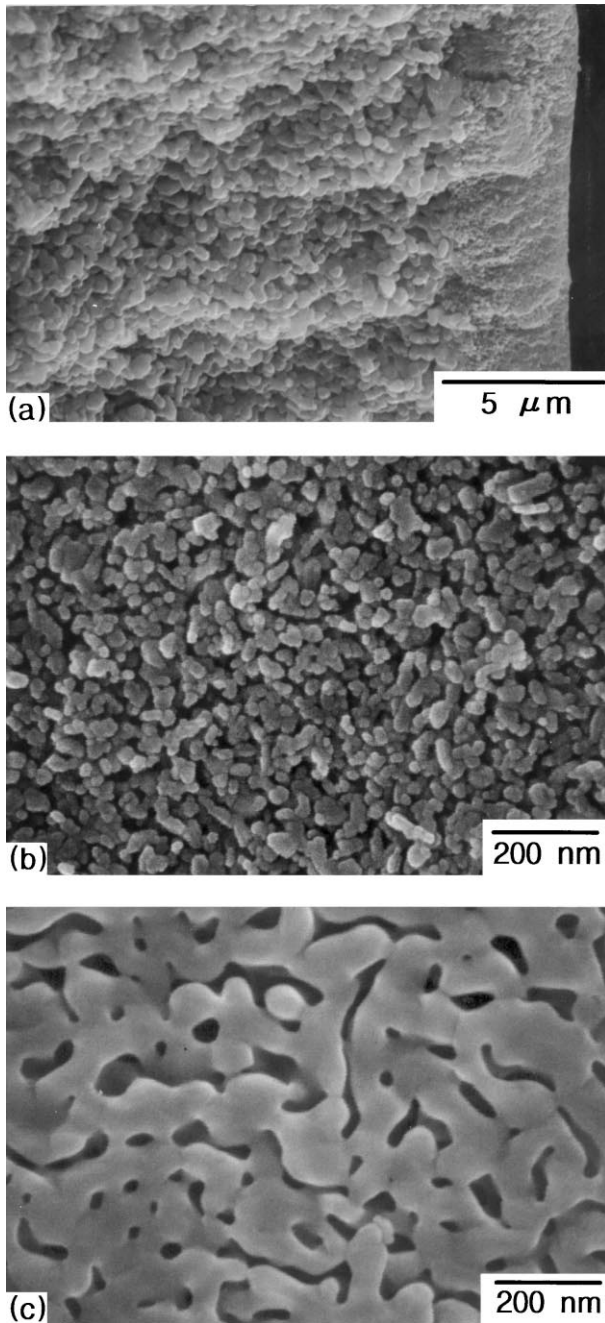


Fig. 6. SEM micrographs for UF membrane heated at 1200°C for 1 h. (a) cross-section; (b) surface of supported top layer; (c) surface of unsupported top layer.

similar phenomenon was observed in a boehmite sol-gel layer.

The cross-section and surface of the UF membrane are shown in Fig. 6. The thickness of the UF layer estimated from the SEM micrograph is about 3 μm, and peeling of the layer was not observed. Alumina membrane using alkoxide with a thickness larger than 5 μm showed some cracks after heat treatment.¹⁴ The top layer has homogeneous microstructure without microcracks or cleavages because the top layer was sufficiently thin. Interaction between the supported and intermediate layers and the top membrane may generate the microstructural difference. This indicates that grain growth occurs faster in the unsupported membrane than in the supported top membrane at the same heating temperature. These results were also obtained in an alumina membrane made with aluminum alkoxide^{13,14} and in titania membrane.^{15,16} Mean pore size is 20 nm measured using N₂ adsorption method. Similar to the unsupported MF layer the unsupported UF layer consisted of interconnecting grains.

Controlling the pore size and microstructure of a UF membrane is being investigated. Second particles such as TiO₂ and ZrO₂ can inhibit the abnormal grain growth of the UF layer. A permeate flux test of MF and/or UF membrane for waste oil separation will be further carried out in a forthcoming study.

4. Conclusions

Aluminum hydrates were synthesized by the precipitation method using AlCl₃·6H₂O as starting material and NH₄OH as precipitation agent. The phases of the obtained powder were amorphous, boehmite, bayerite, and nordstrandite, depending on the pH of the solutions. The absorbed water was evaporated at 80°C, and powders were rapidly dehydrated around 280°C. The weight loss was increased in powders precipitated at lower pH solution. Aluminum hydrates transformed to α-Al₂O₃ via γ-Al₂O₃, δ-Al₂O₃, and θ-Al₂O₃ during heating. As the annealing temperature increased, crystalline size of powders increased and the specific surface area decreased. The crystalline size and specific surface area were rapidly changed over 1100°C when the α-Al₂O₃ phase appeared in the powder. The comparison between a supported and unsupported membrane showed that the supported layer had a porous structure with small grains, but the unsupported layer had interconnected and larger grains. Grain growth is more dominant in the unsupported layer than in the supported one at the same heating temperature, and the microstructural difference between supported and unsupported layer might be attributed to the interaction between the top and intermediate layers. A UF membrane was formed using boehmite particulate sol, and

showed a homogeneous microstructure. Inserting the second phase particles into boehmite sol can give narrow pore size distribution in a ultrafiltration membrane.

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