Thermal stability improvement of porous alumina prepared from anisotropic boehmite particles

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Porous alumina with uniform microstructure was prepared using needle-like boehmite particles. A procedure for improving its thermal stability was examined. Uniform, needle-like boehmite particles were synthesized using a hydrothermal procedure. Porous boehmite was prepared using vacuum filtration of boehmite aqueous suspension. Porous alumina was prepared by heat treatment of the porous boehmite. During heat treatment at 1200°C for 2 h, the specific surface area of the porous boehmite decreased to about one-twentieth (8 m²/g) of the as-prepared porous boehmite. To improve the thermal stability of the porous alumina, La addition to the porous boehmite surface was conducted merely by filtrating La aqueous solution using the porous boehmite itself. The porous alumina with 1.1 mol % of La showed specific surface area of 46 m²/g, even after heat treatment at 1200°C for 2 h.

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1. Introduction

Processing techniques of porous alumina are widely investigated because the alumina is useful in wide applications as filters, filter supports, catalyst supports, adsorbents, and heat insulating materials. A simple method for preparing porous ceramics is merely aggregating the starting particles and using the particles’ interstitial spaces.1–5) Boehmite (γ-AlO(OH)) is suitable as a starting material for production of porous alumina.6–10) Heat treatment at 300–1000°C transforms boehmite particles easily to transition alumina—γ-Al₂O₃, δ-Al₂O₃, and θ-Al₂O₃—with high specific surface area.11) However, a problem persists: the specific surface area of transition alumina decreases steeply at temperatures higher than around 1000°C because of further phase transformation to α-Al₂O₃ and sintering of the particles.12–14) To prevent decreased porosity and specific surface area at high temperature ranges, additives of many kinds have been investigated.15–31) Results show that addition of lanthanum to transition alumina is effective for suppression of their transformation to α-Al₂O₃ and of their accompanying micro-structural change.18, 21–30) An additional approach for the same purpose is decreasing the number of contact points between the particles composing the porous alumina because the contact points between particles are considered to be the nucleation sites of α-Al₂O₃.32) To decrease the particle contact points, morphological control of boehmite particles to anisotropic shapes such as columnar and fibrous shapes has been reported.33–35) In addition, shape anisotropic particles are apparently suitable for constructing a three-dimensional network structure with high porosity.35, 36) Consequently, if morphologically uniform anisotropic boehmite particles are prepared and arrayed in an ideal form, then porous alumina with a uniform microstructure and high porosity can be obtained.37, 38)

The authors have reported a simple fabrication procedure of porous alumina using needle-like particles.39) As starting particles for porous alumina fabrication, anisotropic boehmite particles were prepared using the “gel–sol” method.39) In this method, particles are synthesized through hydrothermal treatment of a highly condensed metal-hydroxide gel. The hydroxide gel functions as a protective colloid as well as a reservoir of the metal ions and/or hydroxide ions to be used for the growth of the product particles. Therefore, this method is suitable for preparing monodispersed particles.40, 41) The obtained boehmite particles were dispersed to NaOH aqueous solution, the particle concentration and the pH value of which was precisely adjusted respectively at 0.05 M and 9 to prepare a stable suspension. The boehmite particles were stacked using vacuum filtration of the boehmite suspension to obtain a porous bulk (in this paper, we designate the prepared porous bulk as “porous boehmite”) with a uniform microstructure. Porous aluminas of different types were also prepared using heat treatment of the porous boehmite. However, results of a previous study showed that thermal stability of the porous boehmite was not so high and the sample that had been heat-treated at higher than 1100°C was unable to sustain the microstructure of the porous boehmite. This study investigated the thermal stability of the porous boehmite in more detail. Moreover, La addition on the porous boehmite surface was conducted to improve the thermal stability of the porous alumina. Generally, La addition to alumina powder was performed using an impregnation method.18, 22, 24, 31) In this method, alumina particles are dispersed to a La-containing solution. Then the solution is dried to impregnate La into the particle surface. However, using an impregnation method for La addition to porous boehmite, which is prepared merely by stacking particles, is difficult. As described above, the porous boehmite was prepared through vacuum filtration using a boehmite suspension with precisely controlled particle concentration and pH. Furthermore, the ionic strength of the suspension should be controlled as low as possible.38) Therefore, we were
Boehmite particle suspension (dispersed in pure water)

- pH control (addition of NaOH aq.)

Boehmite particle suspension

(Particle concentration: 0.05M, pH 9, 20 mL)

- Vacuum filtration
- \( \text{La(NO}_3\text{)}_3\) aq. (0.05 M or 0.5 M, 1 mL)
- Vacuum filtration and drying

Porous boehmite

- Heat treatment

Porous alumina

Fig. 1. Experimental procedure used to prepare porous alumina.

Unable to add La species to the suspension before the particle stacking. Moreover, we were also unable to soak the porous boehmite itself in a La-containing solution because it readily disintegrates. To avoid these problems, La addition was performed by filtering a La-containing aqueous solution using the porous boehmite itself as a filter. Merely by passing a La-containing solution through the porous structure, adsorption of La can be performed without spoiling the microstructure created by vacuum filtration.

2. Experimental procedure

2.1 Preparation of porous alumina

Reagents used for the preparation of porous alumina were aluminum chloride, sodium hydroxide, and lanthanum nitrate (Wako Pure Chemical Industries Ltd., Japan). Pure water used for the particle synthesis and preparation of boehmite aqueous suspension was prepared using reverse osmosis and deionization (Ellix System; Millipore Corp., USA). To prepare needle-like boehmite particles, 5.1 M NaOH aqueous solution was added slowly to the same volume of 2.0 M AlCl₃ aqueous solution under magnetic stirring at room temperature. The stirring was continued for 10 min after adding AlCl₃ for gelation of the mixed solution. The obtained precursor gel was treated hydrothermally at 140°C for 1 week. After hydrothermal treatment, the obtained particles were washed by centrifugation three times with water and were subsequently freeze-dried. Porous boehmite was prepared using the needle-like boehmite particles (Fig. 1). First, a 0.05 M boehmite suspension of pH 9 was prepared using NaOH aqueous solution. Then, the 20 mL of the suspension was vacuum-filtered to form a porous boehmite by stacking the boehmite particles using a cellulose acetate membrane filter (0.10 µm pore size, 2.1 cm² filtration area). The La addition on the surface of porous boehmite was conducted using filtration. 1 mL of 0.05 M or 0.5 M La(NO₃)₃ aqueous solution was vacuum-filtered through the porous boehmite stacked on the membrane filter. After filtration, the obtained porous bulk samples were dried using a vacuum filtration apparatus. The dried samples were heat-treated at various conditions to obtain porous alumina. The heating and cooling rates of the heat-treatment were 10°C/min.

2.2 Characterization

Crystalline phases of the samples were identified using X-ray diffractometry (XRD; M18X-HF-SRA; Mac Science Ltd., Japan) with monochromated CuKα radiation. The samples’ respective morphologies were observed using scanning electron microscopy (SEM; JSM-6330F; JEOL, Japan). The specific surface area of the samples was measured using single-point BET measurements (Flowsorb II 2300; Micromeritics Instrument Corp., USA). The amount of the lanthanum remaining on the porous boehmite was measured using inductively coupled plasma–atomic emission spectrometry (ICP–AES; SPS 1700HVR; Seiko Instruments Inc., Japan). Lanthanum standard solution (Wako Pure Chemical Industries Ltd., Japan), hydrochloric acid, and nitric acid of grade for atomic adsorption spectrometry (Kanto Chemical Co. Inc., Japan) were used for measurements. The water used for ICP–AES was purified via passage through a Milli-Q® ultrapure water purification system (Millipore Corp., USA). To dissolve the porous boehmite for ICP–AES measurement, samples were soaked in hydrochloric acid (35–37 wt% HCl) and were treated hydrothermally at 200°C for 24 h. The obtained solution was diluted by 1 M nitric acid and the amount of La in the solution was measured using ICP–AES.

3. Results and discussion

Uniform, needle-like boehmite particles were prepared by hydrothermal treatment of a precursor gel. Figure 2 depicts the appearance and an SEM image of the porous boehmite prepared via stacking of the boehmite particles. By vacuum filtration of 0.05 M boehmite aqueous suspension of pH 9, porous boehmite was obtained with no cracks or distortion (Fig. 2(a)). Each boehmite particle was stacked randomly and a uniform pore structure was constructed in porous boehmite (Fig. 2(b)). To obtain porous alumina and to strengthen the porous structure by partial sintering, heat treatment of the porous boehmite was conducted. Figure 3 shows XRD patterns of heat-treated porous boehmite at various temperatures for 2 h. When the porous boehmite was heat-treated at 1000–1100°C, the boehmite particles were transformed to transition alumina phase (mixture of \( \delta-\text{Al}_2\text{O}_3 \) and small amount of \( \delta-\text{Al}_2\text{O}_3 \)). The starting boehmite phase transformed completely to stable \( \alpha-\text{Al}_2\text{O}_3 \) phase by heat treatment at 1200°C for 2 h. Figure 4 shows SEM images of porous boehmite that had been heat-treated at various temperatures for 2 h. When the heat treatment temperature was 1000°C, no microstructural change of the needle-like particles and pore structure from the starting porous boehmite was observed. At 1100°C, although sintering at the contact points between particles apparently progressed slightly, particles retained their needle-like shape. At 1200°C, the needle-like particle morphology changed to a vermicular structure. This structure is a typical \( \alpha-\text{Al}_2\text{O}_3 \) texture formed from boehmite or transition alumina.

To suppress the morphological change and decrease in specific surface area, La addition on the porous boehmite was conducted. La addition was performed merely by vacuum filtration of...
La(NO$_3$)$_3$ aqueous solution through the as-prepared porous boehmite. At the filtration stage, no particle was re-dispersed into the aqueous solution and no difference was observed in appearance between that without La addition and La-added samples. For ICP–AES measurements, the La added porous boehmites were dissolved by hydrothermal treatment using hydrochloric acid. The samples were dissolved completely after hydrothermal treatment. The amounts of La that remained on the porous boehmite were 1.1 and 6.1 mol% per Al in boehmite, respectively for samples prepared using 0.05 M and 0.5 M La(NO$_3$)$_3$ aqueous solution. Although most of the La passed through the porous boehmite, the La(NO$_3$)$_3$ aqueous solution was clear even after filtration. For that reason, the filtrated La(NO$_3$)$_3$ aqueous solution might be reused easily for this process. The La-added specimens were heat-treated to evaluate the thermal stability of the porous structure. All of the samples kept the similar appearance to that of porous boehmite and no cracks or distortions were observed even after the heat treatment at 1200°C for 1 h or 2 h. Figure 5 shows XRD patterns of the La-added samples that had been heat-treated at 1200°C for 1 h or 2 h. The effect of heating time was not observed clearly on the XRD patterns. After heat treatment, the sample prepared using 0.05 M La aqueous solution (abbreviated as 0.05 M-La) became transition alumina: a mixture of δ-Al$_2$O$_3$ and small amount of θ-Al$_2$O$_3$ (Figs. 5(c) and 5(d)). Small amount of La on the boehmite particle surface efficiently suppressed the transformation from transition alumina to α-Al$_2$O$_3$. Diffraction peaks assigned to La related compounds were not detected in the XRD patterns of 0.05 M-La sample. Therefore, it was assumed that La species modified the surface of alumina phase and it inhibited the nucleation of α-Al$_2$O$_3$ and sintering of transition alumina particles. The XRD patterns of the sample prepared using 0.5 M La aqueous solution (abbreviate to 0.5 M-La) showed formation of LaAlO$_3$ (Figs. 5(e) and 5(f)). The relation between the La/Al ratio and the formed crystalline phases was almost coincident with the reported La added alumina samples prepared using the impregnation method.$^{24,26,29}$ Figure 6 shows SEM images of without La addition and La added samples heat-treated at 1200°C. When the heat treatment time was set for 1 h, the 0.05 M-La sample (Fig. 6(c)) retained a microstructure resembling that of the as-prepared porous boehmite (Fig. 2(b)), although the morphology of the sample without La addition was apparently changed (Fig. 6(a)). The particles of the heat-treated 0.5 M-La sample also exhibited a needle-like shape. However, they had smoother surfaces than those of the 0.05 M-La sample. In addition, neckings were observed at the contact points between needle-like particles (Fig. 6(e)), which might have been caused by the formation of LaAlO$_3$ phases on the surface and contact points. Although no time dependence was observed in XRD patterns (Fig. 5), the morphology of the

La(NO$_3$)$_3$ aqueous solution through the as-prepared porous boehmite. At the filtration stage, no particle was re-dispersed into the aqueous solution and no difference was observed in appearance between that without La addition and La-added samples. For ICP–AES measurements, the La added porous boehmites were dissolved by hydrothermal treatment using hydrochloric acid. The samples were dissolved completely after hydrothermal treatment. The amounts of La that remained on the porous boehmite were 1.1 and 6.1 mol% per Al in boehmite, respectively for samples prepared using 0.05 M and 0.5 M La(NO$_3$)$_3$ aqueous solution. Although most of the La passed through the porous boehmite, the La(NO$_3$)$_3$ aqueous solution was clear even after filtration. For that reason, the filtrated La(NO$_3$)$_3$ aqueous solution might be reused easily for this process. The La-added specimens were heat-treated to evaluate the thermal stability of the porous structure. All of the samples kept the similar appearance to that of porous boehmite and no cracks or distortions were observed even after the heat treatment at 1200°C for 1 h or 2 h. Figure 5 shows XRD patterns of the La-added samples that had been heat-treated at 1200°C for 1 h or 2 h. The effect of heating time was not observed clearly on the XRD patterns. After heat treatment, the sample prepared using 0.05 M La aqueous solution (abbreviated as 0.05 M-La) became transition alumina: a mixture of δ-Al$_2$O$_3$ and small amount of θ-Al$_2$O$_3$ (Figs. 5(c) and 5(d)). Small amount of La on the boehmite particle surface efficiently suppressed the transformation from transition alumina to α-Al$_2$O$_3$. Diffraction peaks assigned to La related compounds were not detected in the XRD patterns of 0.05 M-La sample. Therefore, it was assumed that La species modified the surface of alumina phase and it inhibited the nucleation of α-Al$_2$O$_3$ and sintering of transition alumina particles. The XRD patterns of the sample prepared using 0.5 M La aqueous solution (abbreviate to 0.5 M-La) showed formation of LaAlO$_3$ (Figs. 5(e) and 5(f)). The relation between the La/Al ratio and the formed crystalline phases was almost coincident with the reported La added alumina samples prepared using the impregnation method.$^{24,26,29}$ Figure 6 shows SEM images of without La addition and La added samples heat-treated at 1200°C. When the heat treatment time was set for 1 h, the 0.05 M-La sample (Fig. 6(c)) retained a microstructure resembling that of the as-prepared porous boehmite (Fig. 2(b)), although the morphology of the sample without La addition was apparently changed (Fig. 6(a)). The particles of the heat-treated 0.5 M-La sample also exhibited a needle-like shape. However, they had smoother surfaces than those of the 0.05 M-La sample. In addition, neckings were observed at the contact points between needle-like particles (Fig. 6(e)), which might have been caused by the formation of LaAlO$_3$ phases on the surface and contact points. Although no time dependence was observed in XRD patterns (Fig. 5), the morphology of the
samples was evidently changed with increased heat treatment time from 1 to 2 h. The grain size of the sample without La addition apparently becomes large with increasing treatment time. The La-added samples show a needle-like shape; however, both ends of the needle-like particles become thicker than those of as-prepared particles. In addition, the growth of neckings was observed at the contact points between particles. Although La modification of the transition alumina and formation of LaAlO₃ efficiently inhibit the formation of α-Al₂O₃, diffusion and sintering were not suppressed completely. Table 1 presents the specific surface area of the as-prepared porous boehmite and heat-treated samples. The as-prepared (without heat-treatment) porous boehmite had high specific surface area of 159 g/m². However, the specific surface area of the sample without La addition decreased drastically during heat treatment at 1200°C. This decrease in specific surface area results from the formation of α-Al₂O₃ phase accompanying drastic microstructure change to a vermicular structure with a smooth surface. Both of the La added samples maintained higher specific surface area than that without La addition samples after heat treatment. The 0.05 M-La sample showed a specific surface area of 46 m²/g even after the heat-treatment at 1200°C for 2 h. The decrease in specific surface area of 0.05 M-La sample with extension of the heat treatment time was less than that of 0.5 M-La sample, which might be attributable to the grain growth of the LaAlO₃ phase. Although the specific surface area of 46 m²/g is not the highest value reported for La-containing alumina powders that have been heat-treated at this temperature range, this specific surface area is sufficiently high for the shaped bulk porous alumina with uniform microstructure.

4. Conclusions

Porous aluminas were prepared by stacking needle-like boehmite particles and applying heat treatment. Although uniform porous boehmite was prepared by merely stacking the needle-like boehmite particles, the microstructure was not maintained and the specific surface area was decreased greatly at the high temperature of 1200°C. The La addition to the surface of porous boehmite was conducted by filtration of La(NO₃)₃ aqueous solution using the porous boehmite itself as a filter without spoiling the particle stacked microstructure. The 1.1 mol % La added sample retained a transition alumina phase even after heat treatment at 1200°C. During heat treatment, LaAlO₃ phase was formed on the 6.1 mol % La added sample. The decrease in specific sample area by heat treatment was also greatly suppressed by addition of small amounts of La. The specific surface area of the 1.1 mol % La added sample was 46 m²/g after heat-treatment at 1200°C for 2 h.

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Table 1. Specific surface area of samples

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<th>Specific surface area (m²/g)</th>
<th>La concentration (mol % per Al in boehmite)</th>
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<tbody>
<tr>
<td>Porous boehmite (without heat treatment)</td>
<td>159</td>
<td>—</td>
</tr>
<tr>
<td>Porous alumina (1200°C, 1 h)</td>
<td>23</td>
<td>—</td>
</tr>
<tr>
<td>Porous alumina (1200°C, 2 h)</td>
<td>8</td>
<td>—</td>
</tr>
<tr>
<td>Porous alumina (0.05 M-La, 1200°C, 1 h)</td>
<td>50</td>
<td>1.1</td>
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<tr>
<td>Porous alumina (0.05 M-La, 1200°C, 2 h)</td>
<td>46</td>
<td>1.1</td>
</tr>
<tr>
<td>Porous alumina (0.5 M-La, 1200°C, 1 h)</td>
<td>40</td>
<td>6.1</td>
</tr>
<tr>
<td>Porous alumina (0.5 M-La, 1200°C, 2 h)</td>
<td>30</td>
<td>6.1</td>
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References
Kojima et al.: Thermal stability improvement of porous alumina prepared from anisotropic boehmite particles