Research Article

Preparation of Nanosized α-Al₂O₃ Particles Using a Microwave Pretreatment at Mild Temperature

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This study investigated the effect of microwave pretreatment to reduce the growth temperature of α-Al₂O₃. The microwave pretreating of the synthesized powders at 1,000°C produced rhombohedral structured α-Al₂O₃ with high specific surface area and dispersion; however the structure accumulated among the particles was seen above 1,200°C when the microwave did not pretreated.

1. Introduction

Alumina is an advanced ceramic with wide applications in electrical insulating, microelectronics, polishing, and various material matrixes, depending on the structural diversity. Particularly, the α-Al₂O₃ powder has considerable potential for a wide range of applications like sapphire crystal growth, electronics, semiconductors, and catalysts, because of having excellent thermal conductivity and resistance, and larger strength and hardness. In general, aluminum hydroxide at 500°C to form γ-alumina which then transforms to δ-alumina and θ-alumina before becoming α-Al₂O₃ in the range of 1,200–1,400°C, depending on the procedure [1–3]. However, little research is presently being conducted on the synthesis of α-Al₂O₃ because the high formation temperature makes it more difficult to create a structure at a lower temperature. Recently several studies on the preparation of α-Al₂O₃ have tried to lower the formation temperature by using additives [4, 5]. It has been suggested that the metal-organic-derived alumina could lower the transformation temperature of α-Al₂O₃. Such studies are continuing, but without evident success as yet. In this study, we tried to synthesize a special α-Al₂O₃ powder at lower temperature than the ordinary temperatures in previous papers [1–3].

As an idea, the microwave pretreatment is introduced in this study. Xie et al. [6] reported the densification and grain growth of alumina by microwave processing; microwave heating showed enhanced densification processing and short sintering time as compared to conventional heating. Ebadzadeh and Asadian [7] also represented that nanosized alumina powder was obtained through microwave heating (2.45 GHz and 900 W) for different times. The γ-Al₂O₃ was the main phase for powder samples heated for 4 and 6 min. When heating was extended to 8 min, weak peaks of α-Al₂O₃ also appeared. For heating times longer than 10 min, α-Al₂O₃ was the only crystalline phase present. Microwave instrument used in this paper has high efficiency that the input energy is converted to heat more than 90%. Thus, the reaction mixture as a whole is heated evenly, which eventually results in shortening of reaction time [8].

2. Experimental

Aluminum isoporoxide (AIP; Wako Pure Chem. Ltd.) was used as an aluminum precursor. Ammonia water was used for pH control. First, the AIP and iso-propanol solvent were well mixed until an evenly white colloidal solution was obtained. Here obtained colloidal solution was divided to two solutions. One of the two solutions was evaporated at 60°C for 6 h and the other
solution was treated by microwave with 800 W for 15 min.
Each of them was named as sample 1 and sample 2. The
samples were heated in flowing air at a rate of 10 °C/min
in the range of 900–1,200 °C at intervals of 100 °C, and then
maintained isothermally at this temperature for 3 h.

The prepared materials were identified using powder
XRD (model MPD from PANalytical) with nickel-filtered
CuKα radiation (30 kV, 30 mA) at 2-theta angles of 10–80°.
The scan speed was 10°/min, and the time constant was
1 s. The sizes and shapes of the materials were measured
by field emission SEM/energy-dispersive X-ray spectroscopy
(FESEM/EDS; S-4100, Hitachi, Yeungnam University Instrumental
Analysis Center, Korea). The specific surface area
was calculated according to the BET theory that gives the
isotherm equation for multilayer adsorption by generaliza-
tion of Langmuir’s treatment of the unimolecular layer. The
BET surface areas were measured using a Micrometrics ASAP
2000 instrument. The materials were degassed under vacuum
at 120 °C for 1 h before the BET surface measurements. Then
the samples were thermally treated at 300 °C for 30 min. The
BET surface areas of the materials were measured through
nitrogen gas adsorption using a continuous flow method
with a mixture of nitrogen and helium as the carrier gas.
The zeta potentials of the materials were determined by elec-
trophoretic mobility using an electrophoresis measurement
apparatus (ELS 8000, Otsuka Electronics, Japan) with a plate
sample cell. ELS determinations were performed in the refer-
ence beam mode at a laser light source wavelength of 670 nm,
modular frequency of 250 Hz, and scattering angle of 15°. The
standard error of the zeta potentials, converted from
the experimentally determined electrophoretic mobility was
typically <1.5% and the percent error <5%. To measure the
zeta potentials, 0.1 wt% of each sample was dispersed in de-
ionized water and the pH of the solution was adjusted to 7.
Relative molecular diameter size distributions of the various
solutions were also measured by using this equipment. The
zeta potential distributions were obtained by averaging
2 or 3 runs. Thermal gravimetric analysis measurements
were collected using a PerkinElmer thermal gravimetric
analysis (TGA) equipped with a platinum crucible. Samples
were heated from room temperature (~50 °C) to 1,000 °C
with a heating rate of 5 °C min⁻¹ while the chamber was
continuously purged with O₂ gases at a rate of 25 mL/min.

3. Results and Discussion

Figure 1 shows the DT-TG curves after the two aluminum
hydroxide powders prepared with and without microwave
pretreatment, which were heated from room temperature
to 1,000 °C with a heating rate of 5 °C min⁻¹ while the
chamber was continuously purged with O₂ gases at a rate
of 25 mL/min. There are three weight loss points with
exothermic reaction, destruction of isopropyl alcohol solvent
at 100 °C, oxidation of hydrocarbons at around 300 ~ 380 °C,
and combustion of cokes at near 900 °C. The hydrocarbons
over alumina powders were more easily oxidized in sample
2 prepared with microwave pretreatment (300 °C) than
in sample 1 prepared without microwave pretreatment
(380 °C). Otherwise the Al(OH)₃ obtained in the water
solvent was converted to the Al₂O₃ by the condensation
reaction near 200°C, and with increasing temperature the expulsion of water molecules from the skeletal structure leads to sample weight loss. Another paper [9] has reported the appearance of boehmite, γ-alumina, θ-alumina, and a mixture of θ- and γ-Al2O3 at 300, 500, 700, and 900°C, respectively. In general, the phase transition occurs without the weight loss and therefore the phase transforms in this study are expected at 450 to 850°C. Notable result is that the phase temperatures were shifted to the lower with microwave pretreatment.

Figure 2 compares the XRD patterns of the alumina phases prepared with and without microwave pretreatment in synthesis steps at 900, 1,000, 1,100, and 1,200°C calcinations temperatures. Al2O3 has a structurally complex oxide comprised of several different metastable phases, gamma- and theta-Al2O3 which eventually convert to stable α-Al2O3 at 1,200°C. The synthesized α-Al2O3 particles in most samples exhibited peaks at 2 theta angles of 25.57, 35.14, 37.76, 43.33, 46.16, 52.53, 57.47, 61.27, 66.49, 68.18, and 76.84, corresponding to the (d(012)), (d(104)), (d(110)), (d(113)), (d(202)), (d(204)), (d(116)), (d(108)), (d(214)), (d(300)), and (d(000)) spaces, respectively [10]. They were ascribed to the rhombohedral structure and assigned to JCPDS file no. 88-0826. The XRD patterns have been presented for both the samples at 900°C. However, the intensities for each peaks were more increased in sample 2 compared to sample 1. As most significant result, the α-crystallization in sample 1 occurred at a lower temperature than that in sample 1. With microwave pretreatment in synthesis steps, the XRD peaks that were assigned to α-Al2O3 were clearer and sharper in spite of the heat treatment temperature of only 1,000°C (sample 2). However, no α-Al2O3 was produced at this temperature without microwave pretreatment, and finally α-Al2O3 structure was seen at 1,200°C (sample 1). These results revealed the significant effect of the microwave pretreatment on the crystallinity, because microwave treatment processing is a superior method in several chemical processes to induce crystallinity, because microwave treatment processing leads to sample weight loss. Another paper [9] reported the expulsion of water molecules from the skeletal structure of α-Al2O3 at 1,200°C.

SEM images of the α-Al2O3 particles prepared samples 1 and 2 are shown in Figure 3. This figure revealed to the rice-shapes in sample 2 with the range of 180~200 nm, however, the interaction of a spherical crystal transformed to the particle aggregated in sample 1. The atomic compositions on the surface of the synthesized α-Al2O3 powders were analyzed by EDS and the results are summarized under the table, which revealed the presence of Al and O as the only elementary components of two samples with an Al:O atomic ratio of about 6:4. With microwave pretreatment, the measured Al:O ratio revealed a little higher aluminum content than that without, and a denser form. Our previous experience has demonstrated that a lower oxygen concentration and higher density result in fewer defects, and a more regular and stable structure.

The BET surface areas of the catalysts were measured by nitrogen gas adsorption using a continuous flow method with a mixture of nitrogen and helium as the carrier gas. The pore size distribution is an important characteristic for porous materials. Among these methods, Barrett-Joyner-Halenda (BJH) plots are a suitable method for the range of nanopores [12]. The relative pressure at which pore filling takes place by capillary condensation can be calculated from Kelvin’s equation. By using Kelvin’s equation, the pore radius in which the capillary condensation occurs actively can be determined as a function of the relative pressure (P/P0). The mean pore diameter, Dp, was calculated from Dp = 4VT/S, where VT is the total volume of pores, and S the BET surface area. The adsorption-desorption isotherms of N2 at 77 K for the α-Al2O3 powders, samples 1 and 2, were calculated as shown in Figure 4, and the values are also summarized in the table. Both α-Al2O3 powders in this study showed isotherms belong to III type in the IUPAC classification [13]. The synthesized α-Al2O3 samples in this study did not have any pores and however the BET surface area was more increased with microwave pretreatment to 19.30 m2 g−1 compared to 13.18 without microwave pretreatment.

The zeta potential is an important parameter in colloidal stability, since it reflects the variation in surface potential for a specific material [14]. These powders were derived from the solution route at low temperature; therefore, zeta potential studies were conducted to understand the surface charge of these powders. Figure 5 shows the zeta-potential data of an aqueous suspension of synthesized α-Al2O3 of samples 1 and 2. No electrolyte was added to control the ionic strength of the solutions. The zeta potentials of samples 1 and 2 suspensions were significantly decreased with increasing pH. The surface charges were transferred from positive in acidic solution to negative in alkali solution. For sample 1, the isoelectric point was at pH 10 with large aggregation, but otherwise at pH = 9.7 in sample 2. The α-Al2O3 particles of sample 2 were positively charged to a maximum of 78.85 mV at pH 3, which indicated that the α-Al2O3 colloidal existed stably while having a small aggregation. Above this pH, the positive charges of the α-Al2O3 particles were decreased with the same trend of mobility, resulting in the fastest mobility with an average aggregated diameter of 506.9 nm. Otherwise, the α-Al2O3 particles of sample 1 were also positively charged to a maximum of 71.51 mV.
Figure 2: The XRD patterns of the alumina phases prepared with and without microwave pretreatment according to calcinations temperatures. (A) without microwave pretreatment and (B) with microwave pretreatment.

Figure 3: The SEM images and the atomic compositions analyzed by energy-dispersive X-ray spectroscopy (EDS) study.
Figure 4: The adsorption-desorption isotherm curves of N\textsubscript{2} at 77 K on the synthesized samples 1 and 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET specific surface area (m\textsuperscript{2}g\textsuperscript{-1})</th>
<th>Total volume (cm\textsuperscript{3}g\textsuperscript{-1})</th>
<th>Total pore volume (P/P\textsubscript{0} = 0.99) (cm\textsuperscript{3}g\textsuperscript{-1})</th>
<th>Average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>13.18</td>
<td>3.0294</td>
<td>0.1641</td>
<td>49.778</td>
</tr>
<tr>
<td>Sample 2</td>
<td>19.3</td>
<td>4.4271</td>
<td>0.055193</td>
<td>11.457</td>
</tr>
</tbody>
</table>

Figure 5: The zeta-potential data of an aqueous suspension of synthesized \(\alpha\)-Al\textsubscript{2}O\textsubscript{3}, samples 1 and 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\zeta) potential (mV)</th>
<th>pH3</th>
<th>pH5</th>
<th>pH7</th>
<th>pH9</th>
<th>pH11</th>
<th>Diameter in colloidal (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>(\zeta) potential (mV)</td>
<td>71.51</td>
<td>37.03</td>
<td>28.3</td>
<td>20.91</td>
<td>–27.38</td>
<td>–27.38</td>
</tr>
<tr>
<td></td>
<td>Mobility (cm\textsuperscript{2}Vs)</td>
<td>(5.52 \times 10^{-4})</td>
<td>(2.89 \times 10^{-4})</td>
<td>(2.21 \times 10^{-4})</td>
<td>(1.63 \times 10^{-4})</td>
<td>(2.14 \times 10^{-4})</td>
<td>735.8</td>
</tr>
<tr>
<td>Sample 2</td>
<td>(\zeta) potential (mV)</td>
<td>78.85</td>
<td>37.4</td>
<td>29.85</td>
<td>18.49</td>
<td>–31.21</td>
<td>–31.21</td>
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<tr>
<td></td>
<td>Mobility (cm\textsuperscript{2}Vs)</td>
<td>(6.15 \times 10^{-4})</td>
<td>(2.92 \times 10^{-4})</td>
<td>(2.33 \times 10^{-4})</td>
<td>(1.44 \times 10^{-4})</td>
<td>(2.44 \times 10^{-4})</td>
<td>506.9</td>
</tr>
</tbody>
</table>
4. Conclusions

This study demonstrated the effect of microwave pretreatment to reduce the growth temperature of $\alpha$-$\text{Al}_2\text{O}_3$ compared to ordinary temperatures. Most significantly, the microwave pretreating of the synthesized powders at 1,000 $^\circ\text{C}$ produced rhombohedrally structured $\alpha$-$\text{Al}_2\text{O}_3$ with the range of 180~200 nm; however, the structure accumulated among the particles was seen above 1,200 $^\circ\text{C}$ when the microwave did not pretreated. The surface areas were larger in $\alpha$-$\text{Al}_2\text{O}_3$ synthesized by microwave pretreatment compared to that without treatment. Electrophoretic light scattering (ELS) measurement in aqueous solution at pH $= 3$ revealed positive surface charges in the $\alpha$-$\text{Al}_2\text{O}_3$ synthesized with microwave pretreating, which indicated that the $\alpha$-$\text{Al}_2\text{O}_3$ colloidal existed stably while having a small aggregation.

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References


