Research Article

Preparation of Nanosized α-Al$_2$O$_3$ Particles Using a Microwave Pretreatment at Mild Temperature

Hyun Soo Kim,[1] No-Kuk Park,[2] Tae Jin Lee,[2] Myeong-Heon Um,[3] and Misook Kang[1]

[1] *Department of Chemistry, College of Sciences, Yeungnam University, Gyeongbuk, Gyeongsan 712-749, Republic of Korea*
[2] *School of Chemical Engineering, Yeungnam University, Gyeongbuk, Gyeongsan 712-749, Republic of Korea*
[3] *Division of Chemical Engineering, College of Engineering, Kongju National University, Cheonan 330-717, Republic of Korea*

Correspondence should be addressed to Misook Kang, mskang@ynu.ac.kr

This study investigated the effect of microwave pretreatment to reduce the growth temperature of α-Al$_2$O$_3$. The microwave pre-treating of the synthesized powders at 1,000°C produced rhombohedral structured α-Al$_2$O$_3$ 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-Al$_2$O$_3$ 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-Al$_2$O$_3$ 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-Al$_2$O$_3$ 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-Al$_2$O$_3$ 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-Al$_2$O$_3$. Such studies are continuing, but without evident success as yet. In this study, we tried to synthesize a special α-Al$_2$O$_3$ 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-Al$_2$O$_3$ was the main phase for powder samples heated for 4 and 6 min. When heating was extended to 8 min, weak peaks of α-Al$_2$O$_3$ also appeared. For heating times longer than 10 min, α-Al$_2$O$_3$ 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. Ammonia water was added to the mixed solution until pH = 9 for rapid hydrolysis. 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
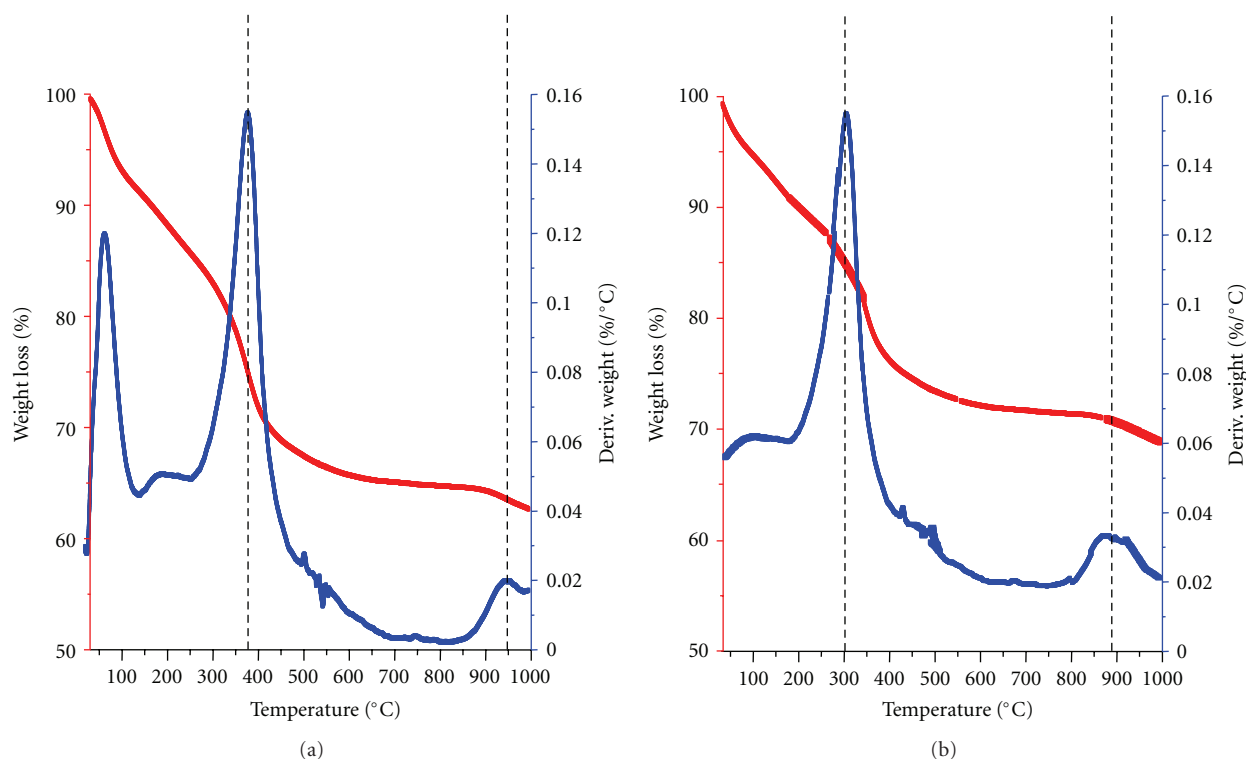
(a)

(b)

FIGURE 1: The DT-TG curves sample powders prepared (a) without and (b) with microwave pretreatment.

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 generalization 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 electrophoretic mobility using an electrophoresis measurement apparatus (ELS 8000, Otsuka Electronics, Japan) with a plate sample cell. ELS determinations were performed in the reference 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 deionized 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 ($\sim$50°C) to 1,000°C with a heating rate of 5°C min^{-1} while the chamber was continuously purged with O_2 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 O_2 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 $\sim$ 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 Al_2O_3 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-Al_2O_3 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. Al_2O_3 has a structurally complex oxide comprised of several different metastable phases, gamma- and theta-Al_2O_3 which eventually convert to stable α-Al_2O_3 at 1,200°C. The synthesized α-Al_2O_3 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_{024}), (d_{116}), (d_{018}), (d_{214}), (d_{300}), and (d_{1010}) 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 2 occurred at a lower temperature than that in sample 1. With microwave pretreatment in synthesis steps, the XRD peaks that were assigned to α-Al_2O_3 were clearer and sharper in spite of the heat treatment temperature of only 1,000°C (sample 2). However, no α-Al_2O_3 was produced at this temperature without microwave pretreatment, and finally α-Al_2O_3 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 fast hydrolysis and polycondensation. This indicates that at pH 9 with AIP, the rate of hydrolysis is governed by the hydroxide ion in alkali solutions, so that the amount of water is small due to rapid formation of OH^-. The initial growth leads to a linear chain and the high concentration of OH ions leads to crystallization because the probability of intermolecular reaction is higher than the intramolecular reaction, then the most probable metal-oxygen polymeric network formed by microwave treatment. Conversely the line widths of the peaks were broad, which generally indicates a smaller crystalline domain size. The full width at half maximum (FWHM) height of the peak at 2 theta = 35.14° (104) was measured, and the Scherrer equation [11], $t = 0.9\lambda/\beta\cos\theta$, where λ the wavelength of the incident X-rays, β the FWHM in radians, and θ the diffraction angle, was used to determine the crystalline domain size. The calculated crystalline domain sizes at 1,200°C were 49.5 and 45.7 nm at a special peak of 35.14° (d_{104}) for the α-Al_2O_3 samples, referred to as samples 1 and 2, respectively. This result is proof of the effect of microwave pretreatment in determining the growth.

SEM images of the α-Al_2O_3 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-Al_2O_3 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/P_0). The mean pore diameter, D_p, was calculated from $D_p = 4VT/S$, where VT is the total volume of pores, and S the BET surface area. The adsorption-desorption isotherms of N_2 at 77 K for the α-Al_2O_3 powders, samples 1 and 2, were calculated as shown in Figure 4, and the values are also summarized in the table. Both α-Al_2O_3 powders in this study showed isotherms belong to III type in the IUPAC classification [13]. The synthesized α-Al_2O_3 samples in this study did not have any pores and however the BET surface area was more increased with microwave pretreatment to19.30 $m^2 g^{-1}$ 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-Al_2O_3 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-Al_2O_3 particles of sample 2 were positively charged to a maximum of 78.85 mV at pH 3, which indicated that the α-Al_2O_3 colloidal existed stably while having a small aggregation. Above this pH, the positive charges of the α-Al_2O_3 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-Al_2O_3 particles of sample 1 were also positively charged to a maximum of 71.51 mV.
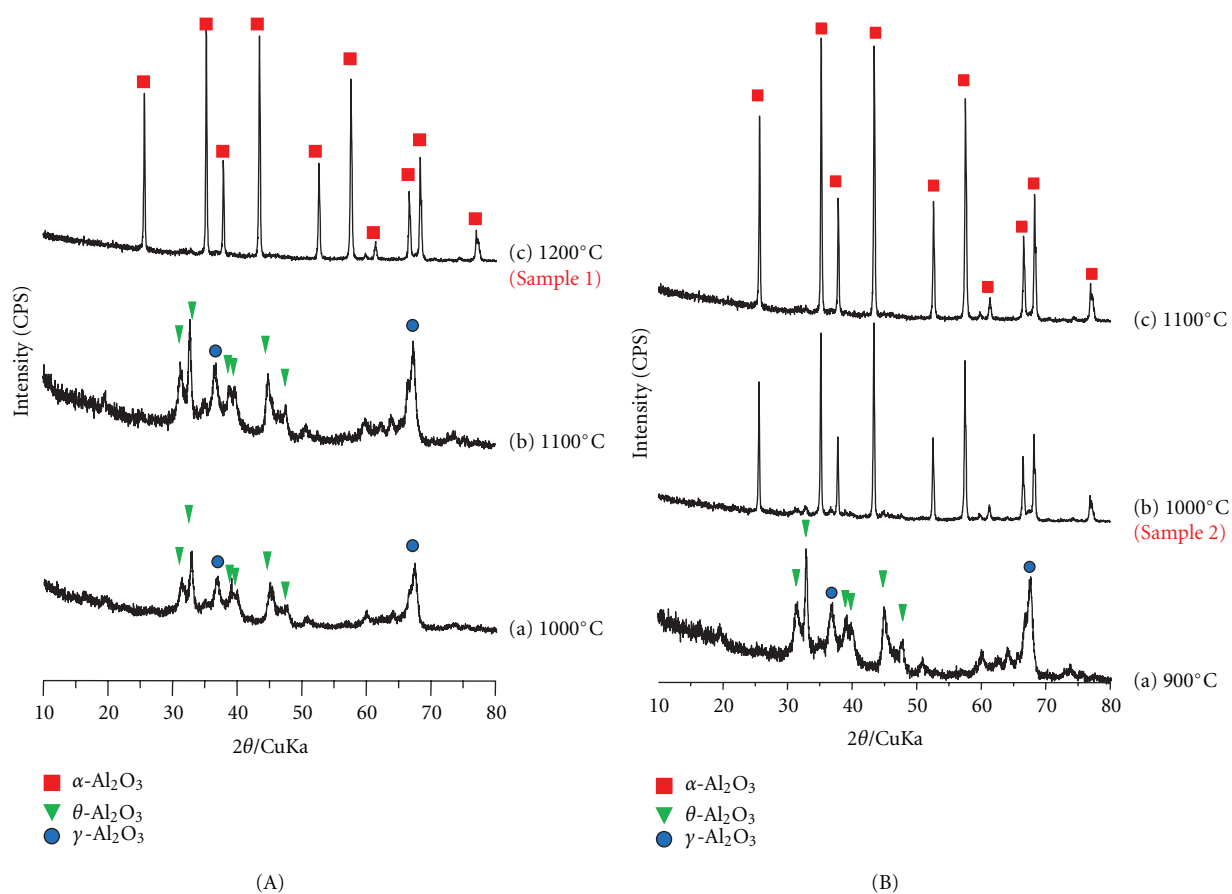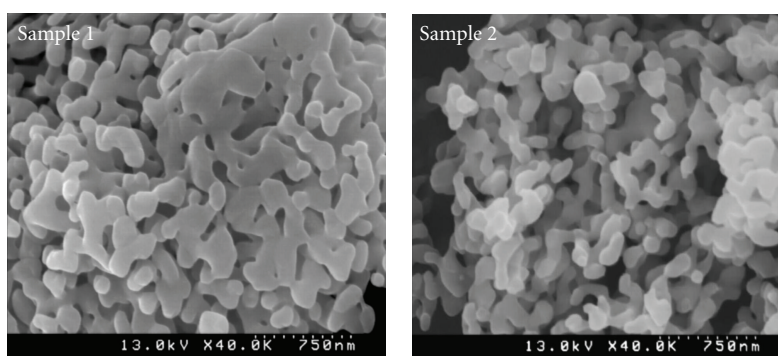
FIGURE 2: The XRD patterns of the alumina phases prepared with and without microwave pretreatment according to calcinations temperatures. (A) without microwave pretreatment and (B) with microwave pretreatment.

Samples	Atomic composition (%)	
	Al	O
Sample 1	59.62	40.37
Sample 2	60.39	39.61

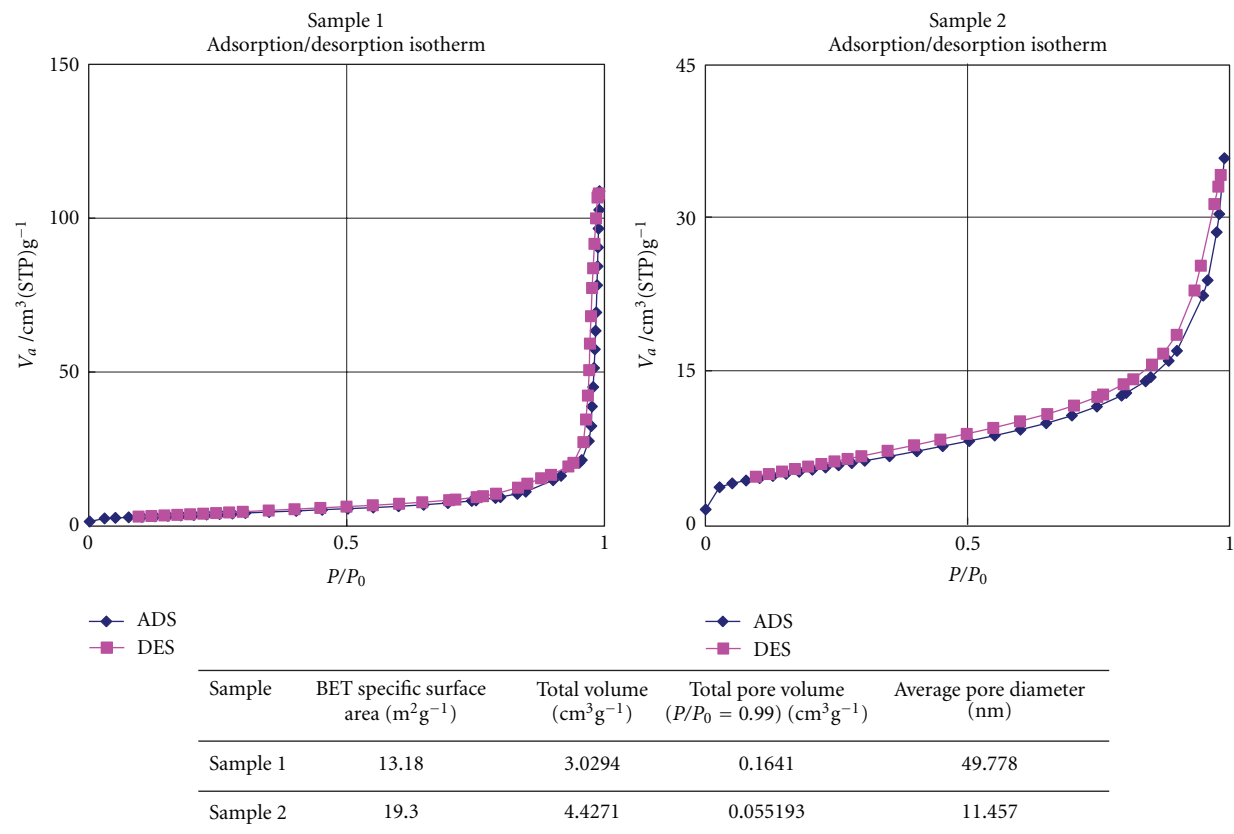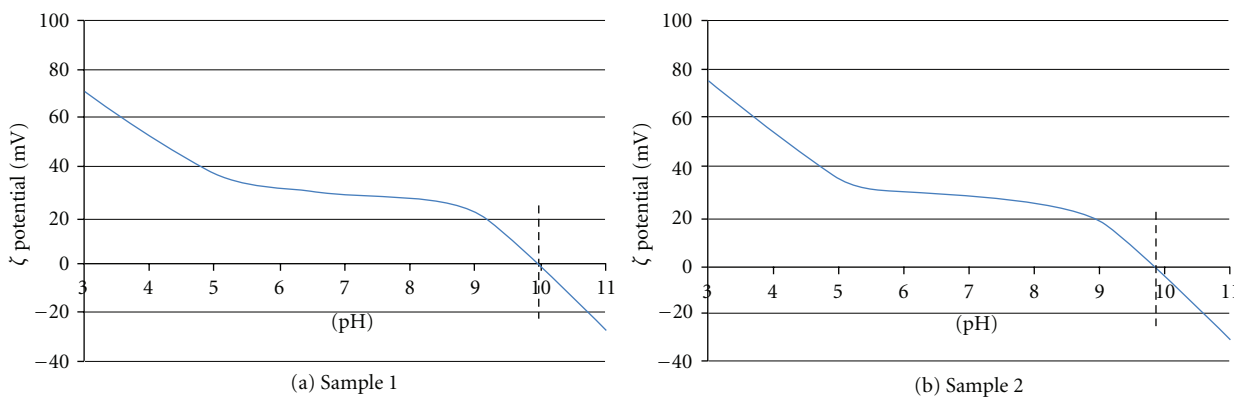FIGURE 3: The SEM images and the atomic compositions analyzed by energy-dispersive X-ray spectroscopy (EDS) study.

FIGURE 4: The adsorption-desorption isotherm curves of N_2 at 77 K on the synthesized samples 1 and 2.

Sample	BET specific surface area (m^2g^{-1})	Total volume (cm^3g^{-1})	Total pore volume ($P/P_0 = 0.99$) (cm^3g^{-1})	Average pore diameter (nm)
Sample 1	13.18	3.0294	0.1641	49.778
Sample 2	19.3	4.4271	0.055193	11.457

(a) Sample 1

(b) Sample 2

		pH3	pH5	pH7	pH9	pH11	Diameter in colloidal (nm)
Sample 1	ζ potential (mV)	71.51	37.03	28.3	20.91	-27.38	
	Mobility (cm^2/Vs)	5.52×10^{-4}	2.89×10^{-4}	2.21×10^{-4}	1.63×10^{-4}	2.14×10^{-4}	735.8
Sample 2	ζ potential (mV)	78.85	37.4	29.85	18.49	-31.21	
	Mobility (cm^2/Vs)	6.15×10^{-4}	2.92×10^{-4}	2.33×10^{-4}	1.44×10^{-4}	2.44×10^{-4}	506.9

FIGURE 5: The zeta-potential data of an aqueous suspension of synthesized α-Al_2O_3, samples 1 and 2.

4. Conclusions

This study demonstrated the effect of microwave pretreatment to reduce the growth temperature of α-Al$_2$O$_3$ compared to ordinary temperatures. Most significantly, the microwave pretreating of the synthesized powders at 1,000°C produced rhombohedrally structured α-Al$_2$O$_3$ with the range of 180~200 nm; however the structure accumulated among the particles was seen above 1,200°C when the microwave did not pretreated. The surface areas were larger in α-Al$_2$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 α-Al$_2$O$_3$ synthesized with microwave pretreating, which indicated that the α-Al$_2$O$_3$ colloidal existed stably while having a small aggregation.

Acknowledgments

References

[1] M. M. Martín-Ruiz, L. A. Pérez-Maqueda, T. Cordero et al., "High surface area α-alumina preparation by using urban waste," *Ceramics International*, vol. 35, no. 6, pp. 2111–2117, 2009.

[2] Y. S. Yoo, K. Y. Park, K. Y. Jung, and S. B. Cho, "Preparation of α-alumina nanoparticles via vapor-phase hydrolysis of AlCl$_3$," *Materials Letters*, vol. 63, no. 21, pp. 1844–1846, 2009.

[3] F. Mirjalili, M. Hasmaliza, and L. C. Abdullah, "Size-controlled synthesis of nano α-alumina particles through the sol-gel method," *Ceramics International*, vol. 36, no. 4, pp. 1253–1257, 2010.

[4] J. G. Li and X. Sun, "Synthesis and sintering behavior of a nanocrystalline α-alumina powder," *Acta Materialia*, vol. 48, no. 12, pp. 3103–3112, 2000.

[5] X. Su, J. Li, and J. Mater, "Low temperature synthesis of single-crystal alpha alumina platelets by calcining bayerite and potassium sulfate," *Journal of Materials Science & Technology*, vol. 27, no. 11, pp. 1011–1015, 2011.

[6] Z. Xie, J. Yang, and Y. Huang, "Densification and grain growth of alumina by microwave processing," *Materials Letters*, vol. 37, no. 4-5, pp. 215–220, 1998.

[7] T. Ebadzadeh and K. Asadian, "Microwave-assisted synthesis of nanosized α-Al$_2$O$_3$," *Powder Technology*, vol. 192, no. 2, pp. 242–244, 2009.

[8] M. Addamo, M. Bellardita, D. Carriazo et al., "Inorganic gels as precursors of TiO$_2$ photocatalysts prepared by low temperature microwave or thermal treatment," *Applied Catalysis B*, vol. 84, no. 3-4, pp. 742–748, 2008.

[9] S. M. Kim, Y. J. Lee, K. W. Jun, J. Y. Park, and H. S. Potdar, "Synthesis of thermo-stable high surface area alumina powder from sol-gel derived boehmite," *Materials Chemistry and Physics*, vol. 104, no. 1, pp. 56–61, 2007.

[10] H. Liu, G. Ning, Z. Gan, and Y. Lin, "Emulsion-based synthesis of unaggregated, spherical alpha alumina," *Materials Letters*, vol. 62, no. 10-11, pp. 1685–1688, 2008.

[11] W. B. Allen, O. Kenneth, R. Thomas, and Y. C. Ignatius, "On the estimation of average crystallite size of zeolites from the Scherrer equation: a critical evaluation of its application to zeolites with one-dimensional pore systems," *Microporous and Mesoporous Materials*, vol. 117, no. 1-2, pp. 75–90, 2009.

[12] Q. Zhao, X. Zhou, M. Ji, D. Wu, T. Jiang, and H. Yin, "Synthesis of ordered cubic mesoporous ZrMCM-48 molecular sieve with aid of fluoride ions," *Colloids and Surfaces A*, vol. 384, no. 1–3, pp. 513–518, 2011.

[13] M. D. Donohue and G. L. Aranovich, "Classification of Gibbs adsorption isotherms," *Advances in Colloid and Interface Science*, vol. 76-77, pp. 137–152, 1998.

[14] V. Gallardo, M. E. Morales, M. A. Ruiz, and A. V. Delgado, "An experimental investigation of the stability of ethylcellulose latex: correlation between zeta potential and sedimentation," *European Journal of Pharmaceutical Sciences*, vol. 26, no. 2, pp. 170–175, 2005.