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Influence of Annealing Temperature on the Phase Transformation of Al_2O_3

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Abstract. In the present study, Al_2O_3 powders were prepared via a self-propagating combustion method using citric acid as a combustion agent. Effects of annealing temperature on the phase transformation of the prepared powders were studied on samples annealed at 800 °C and 1000 °C. The Al_2O_3 samples were characterized using X-Ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and N_2 adsorption-desorption measurements. The XRD results showed that pure η -phase and pure α -phase of Al_2O_3 were obtained at 800 °C and 1000 °C, respectively. Their crystallite sizes are totally different as can be seen clearly from the FESEM micrographs. The η - Al_2O_3 sample annealed at low temperature has crystallite size smaller than 10 nm compared to the α - Al_2O_3 sample annealed at higher temperature which has crystallites from few microns to hundreds microns in size. From the BET (Brunauer-Emmett-Teller) method, the specific surface area for both samples are $59.4 \text{ m}^2\text{g}^{-1}$ and $3.1 \text{ m}^2\text{g}^{-1}$, respectively. It is proposed that the annealing temperature less pronounced for the morphology, but, it is significant for the phase transitions as well as the size and the specific surface area of the Al_2O_3 samples.

INTRODUCTION

Alumina (Al_2O_3) has been known to be one of the most widely used ceramic materials. It has been used in many applications such as coatings [1], catalyst [2], electrical insulator [2,4], etc. These various applications were attributable to different phases of Al_2O_3 . Al_2O_3 can be existed in several transition phases of γ , η , θ and α that depend strongly on the preparation methods and experimental conditions. In literatures, the α - Al_2O_3 reported to be the most stable phase of alumina that usually obtained at higher annealing temperatures. The temperature is mainly responsible for the phase transitions. At temperature range of 500 °C and 700 °C, the γ - Al_2O_3 material was formed [5,6], the annealing at 750 °C exhibited the η - Al_2O_3 [7], and the θ - Al_2O_3 were formed between 900 °C and 1000 °C [6,8]. The stable α - Al_2O_3 can be formed at 1100 °C and above [1,5,9].

There are various methods have been reported to produce Al_2O_3 powders such as sol-gel [10,11], hydrothermal [12], co-precipitation [13] mechanical milling [1] and combustion [14,15]. The combustion method is a promising technique to synthesize pure Al_2O_3 materials due to its simplicity, fast and environmental benign. It implies a reduction-oxidation (redox) reaction to give the desired products [16]. The stable phases of Al_2O_3 were formed when using various combustion agents such as urea [17,18], glycine [19], triethanolamine [7] etc. However, the aforementioned combustion agents are known to give a more violent combustion. Citric acid is another option that can be used to safely combust the starting material of aluminium in aqueous medium to form the Al_2O_3 materials. Jiang [14] reported the formation of the most stable α - Al_2O_3 at 1050 °C using citric acid as a combustion agent. The controlled synthesis of the Al_2O_3 with specific phase is a challenging aspect to be studied because it is a highly sensitive to thermal treatment. The stable Al_2O_3 with nano dimensions and large specific surface area are key issues

in nanomaterials research. The promising of combustion method has motivated us to synthesize the stable alumina at mild temperature using less violent combustion agent.

In the present study, we were attracted to synthesize Al_2O_3 powders via a self-propagating combustion method by using citric acid due to its simplicity and non-violent reaction. This study discusses the effect of annealing temperature on the phase transformation of the synthesized Al_2O_3 powders. A study on the morphology of the powders were also done as well as the specific surface area of the powders.

EXPERIMENTAL

Al_2O_3 powders were prepared using a self-propagating combustion method. Stoichiometric amounts of aluminium nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99.9%)) was completely dissolved in ultra-pure deionised water (from TKA Labtower (EDI: 15–10 M Ω cm). Citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ (99%)) was slowly introduced into the aqueous solution of aluminium nitrate under vigorous stirring. The amount of combustion agent was determined by calculating the oxidant to combustion agent molar ratios of 1:1. The mixture was heated at 350 °C until combustion occur. The precursor materials were grounded using an agate mortar until fine powders were obtained. Powders were annealed at 800 °C and 1000 °C for 48 hours to give pure Al_2O_3 samples.

Phase analysis of the samples were performed using the PANalytical X'Pert Pro MPD diffractometer with Cu- K_α radiation as the beam source. The Bragg-Brentano optical configuration in ambient conditions was used during the data collection. The morphology and crystallite size of the samples were examined by a field emission scanning electron microscope (FESEM: JEOL JSM-7600F). The N_2 adsorption-desorption isotherms of the prepared Al_2O_3 were measured at -196 °C using a BELSORP-mini II instrument from BEL Japan Inc. The obtained isotherms were further analysed using a BET (Brunauer-Emmett-Teller) method for determining the specific surface area of the samples.

RESULTS AND DISCUSSION

The combustion synthesis using citric acid is observed to be a less violent redox reaction compared to, for example, glycine. The combustion phenomena starts with the bubbling of solution. The solution was seen to be light yellowish in colour. When the solution starts to thicken, smouldering occurs giving out thick yellow fumes. The precursors are found to be white-yellowish powders. After annealing at 800 °C and 1000 °C for 48 hours, the final products are obtained, the samples are observed to be white in colour.

Figure 1 shows the XRD patterns of the samples. The sample annealed at 800 °C (Figure 1 (a)) has XRD peaks with low intensities which are relatively broad. It is indexed to $\eta\text{-Al}_2\text{O}_3$ phase (ICDD reference number 01-077-0396). $\eta\text{-Al}_2\text{O}_3$ phase belong to the cubic crystal system with Fd-3m space group. It can be observed that the stable phase for Al_2O_3 which is $\alpha\text{-Al}_2\text{O}_3$ phase can be obtained after annealing at 1000 °C as shown in Figure 1 (b). The diffraction peaks are indexed according to the ICDD reference number 01-088-0826. The indexed pattern indicates that this sample is pure and belongs to the rhombohedral crystal system with R-3c space group. It can be seen clearly the sample annealed at 800 °C has broad peaks that suggested very small crystals of $\eta\text{-Al}_2\text{O}_3$ were formed. At higher annealing temperature of 1000 °C, the Al_2O_3 is not only increased in crystallite size conferring to the sharp peaks, but also the phase was changed to α phase as the most stable form. This significant different in size agrees very well to the value of full width at half maximum (FWHM) of the $\eta\text{-Al}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$ peaks, which demonstrate the XRD peaks broadening. This will be further confirmed using the FESEM micrographs. It is worth to mention that the highly crystalline of $\alpha\text{-Al}_2\text{O}_3$ can be formed at 1000 °C, it is lower than the reported temperatures using similar combustion agent of citric acid [1,14,18].

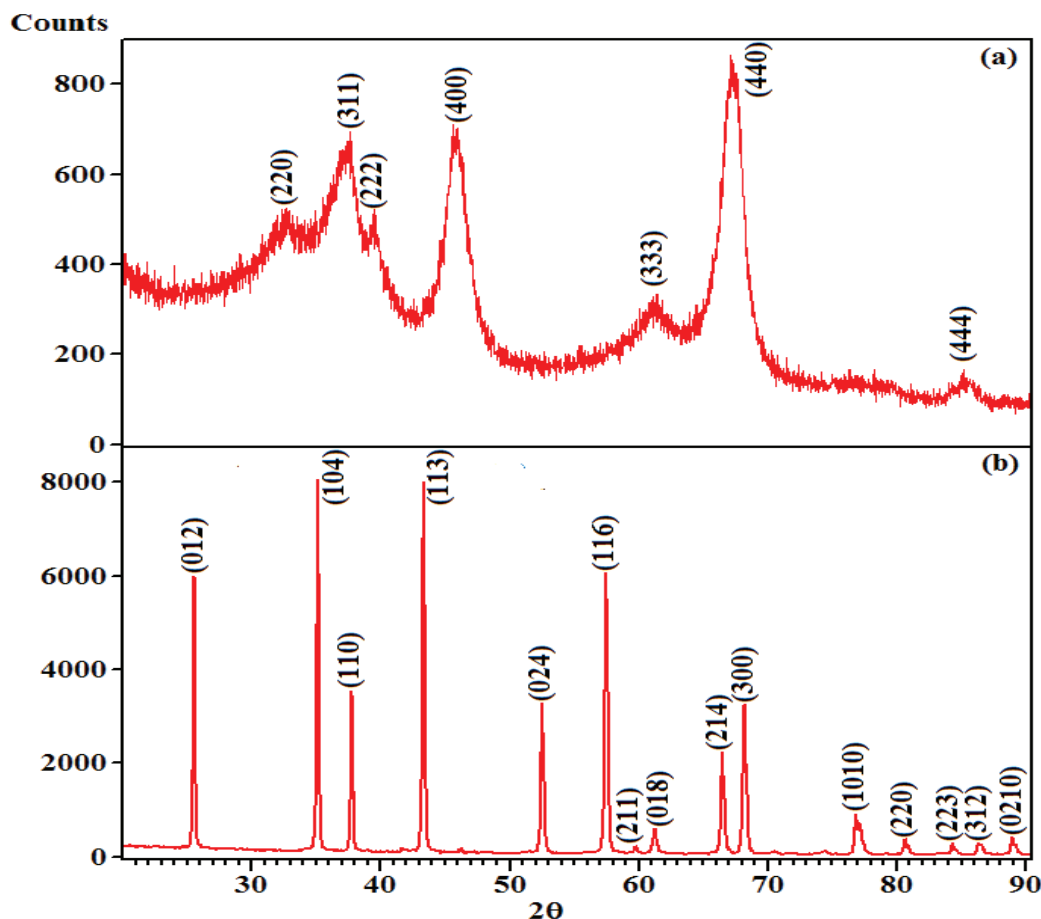


FIGURE 1. The XRD patterns of (a) η - Al_2O_3 and (b) α - Al_2O_3

The FESEM micrographs of the synthesized Al_2O_3 are given in Figure 2. The annealing temperature seems to influence the crystallite sizes of the samples. As expected, the sample annealed at lower temperature (800 °C) exhibited relatively much smaller crystallite size than the sample annealed at high temperature (1000 °C). Herein, the η - Al_2O_3 sample obtained at 800 °C, shown in Figure 2 (a), has crystallite size smaller than 10 nm that comparable to the XRD analysis. Meanwhile, as shown in Figure 2 (b), the highly stable α - Al_2O_3 give larger crystallites from a few microns to hundred microns in size attributed to high annealing temperature of 1000 °C. The FESEM micrographs supports the XRD analysis whereby the crystallite size of the 800 °C sample is less than 10 nm and this explains why the XRD peaks show considerable broadening compared to the 1000 °C sample.

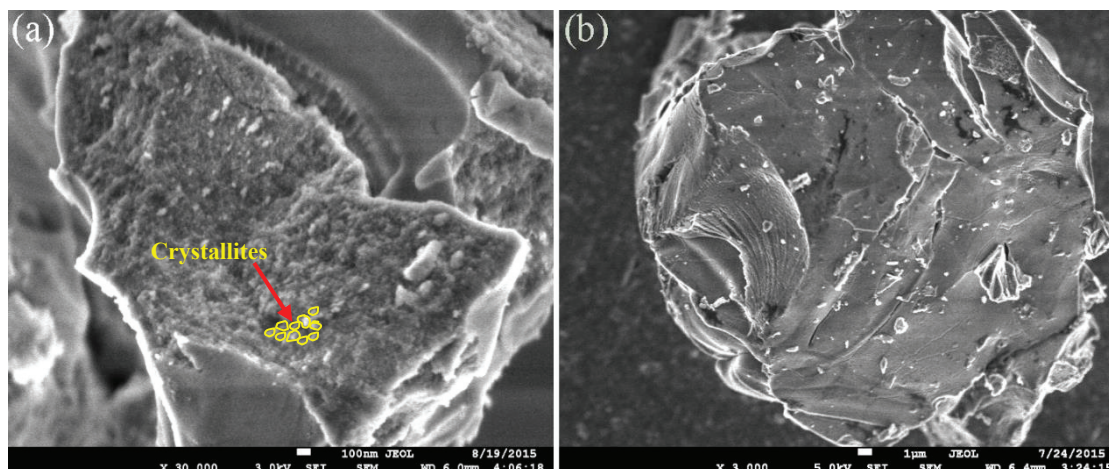


FIGURE 2. The FESEM images of Al_2O_3 samples anneal at (a) 800 °C and (b) 1000 °C

The annealing temperature also affecting the specific surface area of the Al_2O_3 samples. The specific surface area of $\eta\text{-Al}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$ were calculated from the obtained N_2 adsorption-desorption isotherms using Brunauer-Emmett-Teller (BET) method. It is determined to be $59.4 \text{ m}^2\text{g}^{-1}$ for $\eta\text{-Al}_2\text{O}_3$ and $3.1 \text{ m}^2\text{g}^{-1}$ for $\alpha\text{-Al}_2\text{O}_3$. It has found that the nano $\eta\text{-Al}_2\text{O}_3$ has a higher surface area to volume ratio than the micron $\alpha\text{-Al}_2\text{O}_3$ that obtained at a higher temperature.

CONCLUSION

In this work, η - and α -phases of Al_2O_3 are obtained via a self-propagating combustion method annealed at 800 °C and 1000 °C for 48 hours. It suggests that the η -phase transforms into the α -phase as increasing the annealing temperature from 800 °C to 1000 °C. All the XRD, FESEM and BET results have shown good agreement with each other, demonstrating that the 800 °C sample contains very fine crystallites than the 1000 °C sample. Therefore, this combustion synthesis route can be optimized for obtaining the required phases of Al_2O_3 .

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