Oryza sativa PULP AS A TEMPLATE IN α-ALUMINA NANOCRYSTALLINE SYNTHESIS BY PRECURSOR CALCINING PROCESS

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PULP Oryza sativa SEBAGAI TEMPLAT SINTESA NANOKRISTALIN α-ALUMINA MELALUI PROSES KALSINASI PREKURSOR

ABSTRAK

Sintesis dan karakterisasi *nanopowder* α-alumina dengan menggunakan pulp merang sebagai *template* melalui proses kalsinasi prekursor telah berhasil dilakukan. Penelitian ini bertujuan untuk mempelajari potensi pulp merang sebagai *template* dari *precursor calcination process* yang merupakan metoda relatif lebih murah dibandingkan metode sol gel dalam mensintesis α-alumina. Perbandingan berat antara prekursor dan pulp adalah 1:2. Pengaruh temperatur kalsinasi terhadap pembentukan α-alumina ditetapkan dengan variasi temperatur kalsinasi pada 900°C, 1000°C, dan 1100°C. Analisis diffraksi Sinar-X (XRD) digunakan untuk mengetahui perubahan fasa kristal, struktur, dan ukuran kristal yang terbentuk pada suhu kalsinasi tersebut. Karakterisasi SEM dilaksanakan untuk mengetahui morfologi dari serbuk α-Al_2O_3. Berdasarkan karakterisasi XRD, sampel alumina yang disintesis membentuk fasa α-Al_2O_3 dan γ-Al_2O_3. Ukuran kristal yang terbentuk berskala nanometer, yaitu untuk α-Al_2O_3 ukuran kristal terbesar adalah 46,6 nm. Hasil karakterisasi SEM, terlihat bahwa α-Al_2O_3 membentuk struktur trigonal atau bentuk batang dan planar, ukuran partikel akan semakin membesar dengan meningkatnya temperatur kalsinasi.

Kata kunci : *nano powder*, α-alumina, proses kalsinasi prekursor, pulp merang.

ABSTRACT

Synthesis and characterization of α-alumina nano powder with Oryza sativa pulp as template by precursor calcining process have been successfully conducted. The aim of this experiment is to study the potential of Oryza sativa pulp as a template of precursor calcining process method that is relatively cheaper than that of sol gel method in α-alumina synthesis. Weight ratio between precursor and Oryza sativa pulp was 1 : 2. The effect of calcination temperature on α-alumina synthesis in this research is set by variation of calcination temperature at 900°C, 1000°C, and 1100°C. In this research, X-Ray Diffraction (XRD) analysis is used to investigate the transformation of crystal phase, structure and size of the crystal formed by the calcinations temperature. Scanning Electron Microscope (SEM) characterization is used to identify morphology of α-Al_2O_3 powder. Based on XRD characterization result, synthesized alumina sample forms α-Al_2O_3 and γ-Al_2O_3 crystal phases. The formed crystallite size is in nanometer dimension for α-Al_2O_3 which biggest crystallite size is 46.6 nm. According to SEM characterization result, it is shown that α-Al_2O_3 formed rhombohedral or bar shape and planar. The particle size will increase along with the elevation of calcination temperature.

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Key words : nano powder, α-alumina, precursor calcining process, oryza sativa pulp

INTRODUCTION

Research on nanoparticles, including synthesis, characterization of the structural, chemical and physical properties, and application in various fields of technology, represents a fundamental cornerstone of nanoscience and nanotechnology. Many different synthesis techniques gave access to nanomaterials with a wide range of compositions, well-defined and uniform crystallite sizes, extraordinary and unprecedented crystallite shapes, and complex assembly properties. Although gas-phase processes are successfully employed for the low-cost production of large quantities of nanopowders, it seems that liquid-phase synthesis are more flexible with regard to the controlled variation of structural, compositional, and morphological features of the final nanomaterials. Liquid phase routes include coprecipitation, hydrolytic as well as nonhydrolytic sol gel processes, hydrothermal or solvothermal methods, templated derived nanoparticle synthesis and biomimetic approaches. However, often the synthesis protocol for a targeted material involves not just one, but a combination of several of these methods M. (Niederberger and Pinna, 2009).

One of alternative synthesis methods to prepare nano material is by using a natural polymer as a template precursor process. Several nano materials synthesized using this method are Au/TiO_2, SnO_2, ZrO_2, Ag dan ITO (Bozell, 2011). Many types of pulp can be obtained from nature, for example Oryza sativa pulp. Oryza sativa pulp can be used as a template and a ligand on nanomaterial preparation, because the pulp contains celluloses and hemicelluloses.

Cellulose is a polysaccharide, consisting of a linear chain of several hundred to over ten thousand β(1→4) linked D-glucose units (Fig. 1), whereas hemicellulose contains many different sugar monomers. Hemicelluloses contain most of the D-pentose sugars. A pentose is a monosaccharide with five carbon atoms. Pentoses are organized in two groups, namely aldopentoses, having aldehyde fuctional group at position 1; and ketopentoses, having keton functional group in position 2 or 3 (Fig.2). Either cellulose or hemicellulose can be considered as polyalcohol, because each monomer units has hydroxyl groups, which can react to form alcohol derivatives (Nelson and Cox, 2004).

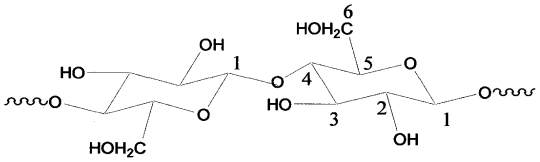

Figure 1: (β1-4) Link D-Glucose Monomer Units of Cellulose Polymer

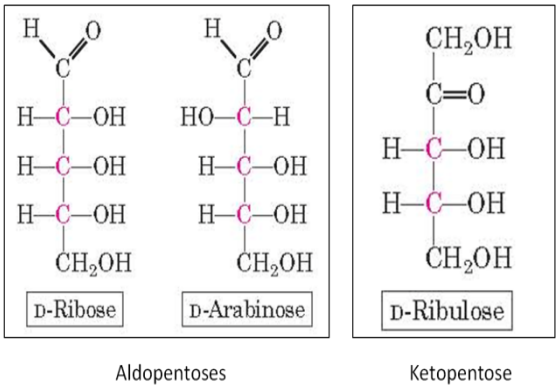

Figure 2: D-Pentose Sugars: Aldopentoses and Ketopentose

Therefore, The presence of pulp, during the preparation of nano material, significantly can reduce the tendency to agglomeration in the as-synthesized material particles. The cellulose coating on the material particle surfaces results in reduced particles aggregation due to the steric hindrance provided by the polymer, producing small crystallite particles of material (Shukla, S., *et al.*, 2002).

Alumina (Al_2O_3) is an oxide material showing outstanding physical and chemical properties, such as the highest strength among oxides, excellent abrasion resistance, heat resistance, high dielectric strength at high voltage, and high resistance to chemical attack. Therefore, those characteristics enable Al_2O_3 to have been used widely as a part of IC-board, as an optical material, as support for catalysts, as a medium for pulverization and polishing (Young Lee, *et al.*, 2004). However, such applications demand a particular nanosize powder. It seems that nanosize alumina powders will be indispensable for the processing needs of various electronic materials and devices in the future (Yu-Chen Lee, *et al.*, 2007). The synthesis and control of

materials in nanometer dimensions can produce new material properties and device characteristics in unprecedented ways. Controlled structures, large interfaces, density power and other unique characteristics are the sample of nano-materials properties superiority so that it can access new and improves their properties and functionalities. Besides that nanopowder will have characteristic as follows:

- Particle size is ranging of about 10-100 nm;
- Grain size distributtion is narrower;
- There is no macroscope aglomerations;
- More homogenous in chemical and physical;
- Chemical composition and purity of nano material can be controlled;
- Material morphology also can be controlled (Roco, M.C. and Bainbridge, W.S., 2001; Siegel, R.W. *et al.*, 1998; Anonymous, 2004; Guozhong Cao, 2004).

Many methods have been conducted to synthesize alumina either in submicron or nano metres, namely: 1) Sarikaya and colleagues (Sarikaya and Akinc, 1988), prepared alumina microshells by calcining the precursor with the emulsion evaporation technique; on the other hand, Lin *et al.* (2002), used the chemical precipitation method to prepare an alumina precursor via an emulsified boehmite gel with oleic acid, subsequently calcined to 1300°C for 20 min under a controlled atmosphere, the final product being α-Al_2O_3 nano-sized powder. Yu-Chen Lee, *et al.* (2007), prepared nanoalumina powder by calcining an emulsion precursor derived from aqueous $Al(NO_3)_3$ solution that mixed with oleic acid, then calcined to 1000°C for 2 hour, and obtained final product of nano α-Al_2O_3 with average size of crystallite particles was 50-100 nm. Bastomi *et al.* (2009), synthesized submicron α-Al_2O_3 by using precursor process method.

The aim of this work is to evaluate phase transformation of alumina using a pulp template. XRD analysis was conducted to identify crystalline phase and crystal size of calcined alumina powders at the temperatures of 900°C, 1000°C, and 1100°C using X-Ray Phillips Pan Analytical instrument. Meanwhile Scanning Electron Microscope SEM JEOL JSM-35C was performed to observe particles morphology.

Experimental Procedure

The procedure of this research consisted of three steps, namely :

1) The preparation of alumina precursor;
2) The calcinations process; and
3) Characterization.

Synthesis of α-Al_2O_3

About 11.25 grams of $Al(NO_3)_3.9H_2O$ as a precursor was dissolved in 600 ml aqua bidest and stirred at magnetic stirrer for 15 minutes. Then, about 22.5 grams of *Oryza sativa* pulp was put into the solution slowly along with stirring for 15 minutes. A weight ratio of precursor to pulp is 1:2. Here in after, 25% ammonia solution was added slowly into the mixture until a hydrolysis was occurred by checking pH of the solution was equal to 7. Then an aging process was conducted for 48 hours. After aging process, the solution was filtered until an aluminum hydroxide gel mixed with pulp was obtained. A sample from filtration was divided to three, but previously, carbon content of sample must be removed by firing it at the temperature of 400°C for 3 hours at oxidative furnace.

Precursor Calcination Process

After sample was divided into three parts, then sample was calcined at the temperatures of 900°C, 1000°C, and 1100°C for 90 minutes, the samples were labeled based on temperature calcination, namely: Al_2O_3-900°C, Al_2O_3-1000°C, and Al_2O_3-1100°C.

Characterization

All synthesized sample, namely Al_2O_3-900°C, Al_2O_3-1000°C, and Al_2O_3-1100°C were characterized by XRD and SEM. The crystalline phase of calcined powder and average crystallite size were determined by X-rays powder diffraction using Pan Analytical X-ray. Meanwhile, a scanning electron microscope (SEM) JEOL JSM-35C was used to observe the morphology and the sizes of crystallite.

RESULT AND DISCUSSION

Alumina Precursor Phase Transformation

Figure 3 shows XRD patterns of the Al_2O_3 sample calcined at the temperatures of 900°C, 1000°C, and 1100°C. According to the three XRD patterns, it is shown that three phases of Al_2O_3 has been formed, such as α-Al_2O_3, γ-Al_2O_3 and θ-Al_2O_3 phases. The phases of α-Al_2O_3 and θ-Al_2O_3 are formed on the sample calcined at the temperatures of 1000°C and 1100°C, Nevertheless, the crystallinity of θ-Al_2O_3 phase at those temperatures is very small. It is sign by low intensity of XRD pattern for those phase peaks. The peaks for θ-Al_2O_3 phase are at angles of 2θ: 31.29°, 36.94°, 38.66°, and 44.84°. The main phase of sample calcined at the temperatures of 1000°C and 1100°C is α-Al_2O_3, it is signed by three main peaks with high intensity at 2θ angles of 35.17°, 43.37°, and 57.53° whose each of them presents their crystal plane orientations at (104), (113), and (116) respectively.

Meanwhile, a sample calcined at the temperature of 900°C produced γ-Al_2O_3 phase with three main peaks at diffraction angles of 37.21°, 45.73°, and 66.89° whose each of them present their crystal plane orientations at (311), (400), and (440). Calcination treatments from the temperature of 900°C to 1000°C or even to higher temperature of 1100°C cause crystal phase transformation from γ-Al_2O_3 to α-Al_2O_3. Unfortunately, in those calcination temperatures, the crystal phase transformation from γ-Al_2O_3 to δ-Al_2O_3 even to θ-Al_2O_3 that predominant is undetected, especially for δ-Al_2O_3 phase, which its existence is undetected at all. The crystal phase transformation for δ-Al_2O_3 and θ-Al_2O_3 is possibly occurred at the temperature from 900°C to 1000°C. This is because at a calcination process, energy given is quite a lot so that causes the temperature change is quite fast (Ebadzadeh, T and Asadian, K., 2009). In this research, temperature change at the time of calcination was about ± 15°C/minute.

Crystal Size

Based on main peaks of XRD pattern analyzed, crystal size coulde be calculated using Scherrer equation (Shukla, S., 2002; Kwon, Y. J., 2002).

$$D = \frac{K\lambda}{\beta \cos\theta}$$

whereas D is crystal size, K is constant with value of 1, λ is wavelength of X-Ray, 1,54056 Å, and β

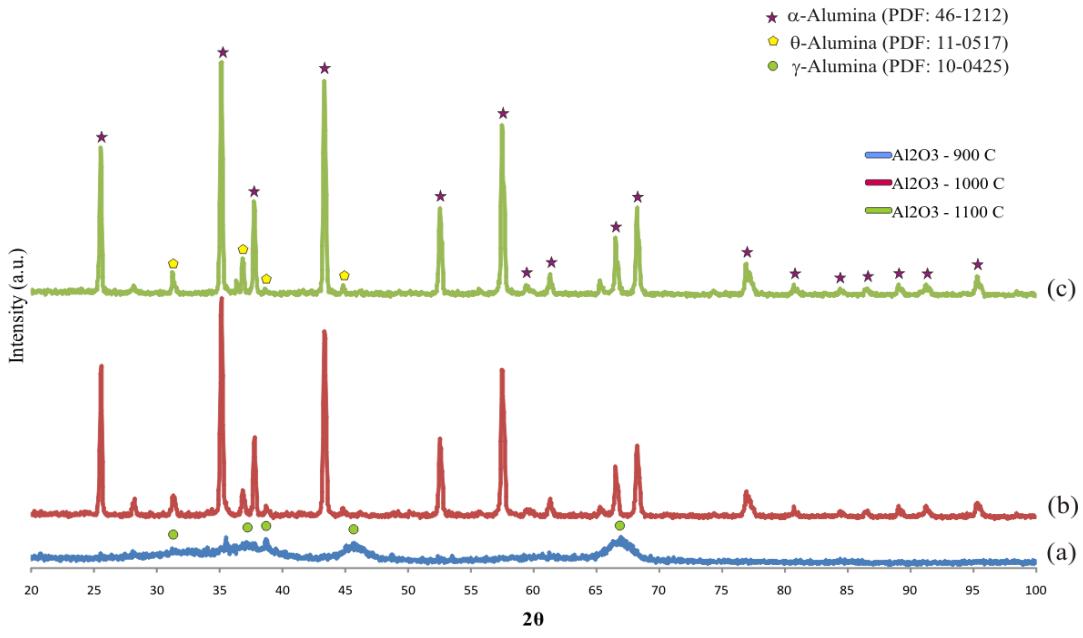

Figure 3. XRD Patterns of The Synthesized Alumina (Al_2O_3), (a) T = 900°C, (b) T = 1000°C, (c) T = 1100°C.

is value of Full Width Half Maximum (FWHM). According to Scherrer equation, hence crystal size of three alumina samples can be calculated and the result is presented at Table 1 and Table 2.

Table 1. The Crystal Size of Al_2O_3- 900°C, Al_2O_3-1000°C and Al_2O_3-1100°C.

Orientation	Al_2O_3-900°C	Al_2O_3-1000°C	Al_2O_3-1100°C
(104)	-	44,6 nm	46,6 nm
(113)	-	40,5 nm	43,2 nm
(116)	-	34,6 nm	35,2 nm
(311)	2,4 nm	-	-
(400)	3,6 nm	-	-
(440)	4,1 nm	-	-

According to Table 1, it is shown that crystal size for Al_2O_3-900°C is ranging 2.4 to 4.1 nm. Crystal size for this sample is very small that signed by broadening peak, which size crystal is identical with peak of XRD pattern. When peak of XRD pattern is more broadening, it will indicate crystal size is smaller but its crystallinity formed is not quite well. On the contrary, if peak of XRD pattern is sharpener, crystal size will quite larger and its crystallinity is quite better. Table 2 showed crystals size of Al_2O_3-1000°C and Al_2O_3-1100°C. Crystal size of Al_2O_3-1000°C formed is ranging from 34.6 to 44.6 nm, whether crystal size of Al_2O_3-1100°C, formed is ranging from 35.2 to 46.6 nm. According to Table 1 and Table 2, the higher calcination temperature, the larger crystal size formed. Therefore, sample calcined at the higher temperature (1100°C) has good crystallinity.

Figure 4 shows the result of SEM characterization for Al_2O_3-900°C. Based on Figure 4, it can be seen that microstructure of Al_2O_3-900°C is not homogene because there is particle grain size difference, where there are the large ones and the small ones. This is because crystal growth and phase transformation process that occured at the time of calcination process. Particles size range formed in Al_2O_3-900°C have diameter from 53 to177 nm.

Figure 5 shows the result of SEM characterization for Al_2O_3-1000°C. Based on Figure 4, it can be seen that particles morphology formed have rhombohedral or trigonal structure like a bar. Rhombohedral or trigonal structure is structure of α-Al_2O_3. Particles size range formed in Al_2O_3-1000°C have diameter from 59-94 nm.

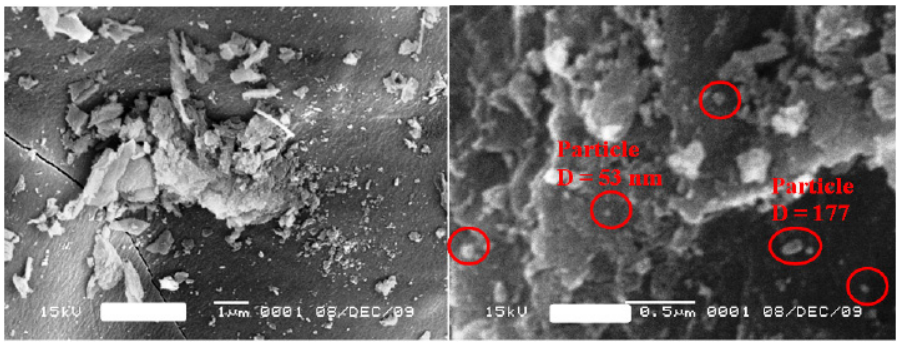

Figure 4. SEM Images of The Alumina (Al_2O_3) at T = 900°C.

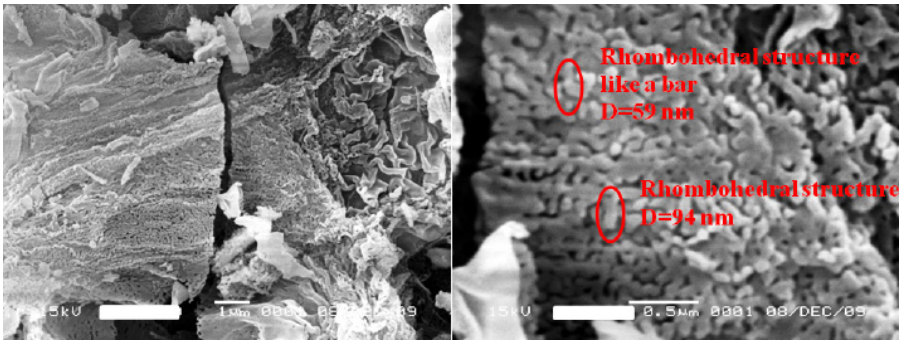

Figure 5. SEM Images of The Alumina (Al_2O_3) at T = 1000°C.

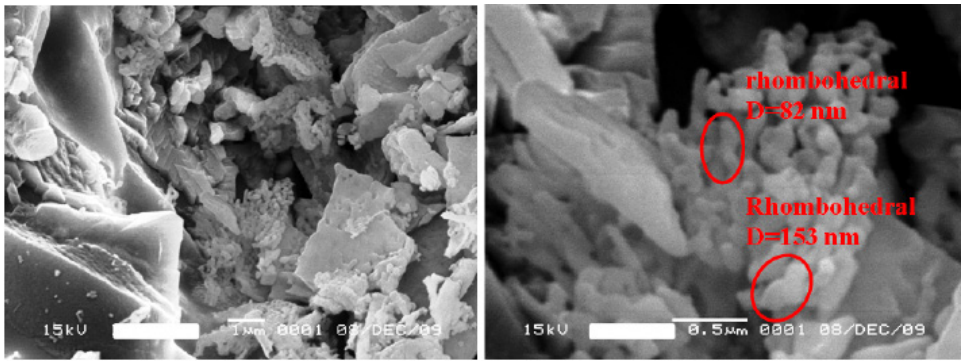

Figure 6 SEM Images of The Alumina (Al_2O_3) at T = 1100°C.

Figure 6 shows the result of SEM characterization for Al_2O_3-1100°C. Because crystal phase formed in this sample is dominantly α-Al_2O_3, with the crystal structure is rhomobohedral. Diameter range of rhombohedral structures in this sample are from 82 to 153 nm.

Temperature variabel at calcination process had great effect particle morphology. In sample calcined at the temperature of 900°C, morphology formed has granular cubic structure. This is because the sample has γ-Al_2O_3 phase, which is meta stable phase (Sarikaya and Akinc, 1988). While samples calcined at the temperatures of 1000°C and 1100°C have rhombohedral structure because the phase has been changed to α-Al_2O_3. Phase of α-Al_2O_3 is the stable phase of alumina.

CONCLUSION

1. Synthesis of α-alumina nano powder has been conducted by using *Oryza sativa* pulp as template in precursor calcination process, with crystals size for α-Alumina are 34.6-46.6 nm.
2. α-alumina is formed at calcination temperatures of 1000 °C and 1100 °C, while γ-alumina is formed at calcination temperature of 900°C.
3. SEM characterization result showed α-alumina morphology had rhombohedral structure looked like a bar, while γ-alumina formed granular cubic structure.
4. Particle size that measured based on SEM characterization result is in nanometer dimension, namely 53-177 nm for alumina at Tkal = 900 °C, meanwhile for α-alumina, particle diameter is measured from rhombohedral structure, namely 59-94 nm for Tkal = 1000°C and 82-153 nm for Tkal = 1100°C. (Tkal = calcination temperature).

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