

Preparation of nano mullite from activated kaolin and gibbsite at a low temperature

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Nanomullite powders were successfully prepared from activated kaolin and gibbsite. Kaolin activation was performed by the thermal treatment at 800 °C and sulfuric acid treatment. The activation process has changed kaolin structure to produce alumina, silica, and aluminosilicate phases, as given by XRD result. The XRD result was corroborated and was proved by the result of electron diffraction TEM analysis, the activated kaolin consisted of α - Al_2O_3 , quartz, and mullite phases. Nanomullite was prepared from the activated kaolin, gibbsite, and sulfuric acid and was calcined at 400 °, 600 °, 800 °, and 1200 °C. Crystallization of the as-prepared mullite in the temperature range of 400 °–1200 °C produced mullite, α - Al_2O_3 , and spinel phases at 400 °C. A further phase transformation of the mullite sample maintained mullite and α - Al_2O_3 phases at 1200 °C. The grain sizes of mullite powders are found to be less than 100 nm at a calcination temperature of 1200 °C. The electron diffraction (ED) patterns of the calcined mullite are indexed to the mullite phase with the crystal plane orientations of (310), (030), (101), (001), (201), (040) and (121). These results are in agreement with the XRD result for the calcined mullite at 1200 °C.

Key words: nanomullite, kaolin, gibbsite, H_2SO_4 , activation process, calcination.

Introduction

Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) is one of the secondary mineral of aluminosilicates, the only stable phase in the Al_2O_3 - SiO_2 binary system and a promising material for both conventional and advanced ceramic applications because of its excellent thermal, electrical, and mechanical properties including low density ($3.17 \text{ g} \cdot \text{cm}^{-3}$), low thermal conductivity ($k = 2.0 \text{ Wm}^{-1} \text{ K}^{-1}$), low thermal expansion coefficient ($20/200 \text{ }^\circ\text{C} = 4 \times 10^{-6} \text{ K}^{-1}$), low dielectric constant ($\epsilon = 6.5$ at 1 MHz) [1, 2, 3, 4, 5, 6, 7].

The type of precursors used for the synthesis and preparation of mullite are important on the shape-forming characteristics, sinterability, and the final properties of the product [8]. Various attempts have been made to prepare mullite powder in submicrometer and nano meter, such as hydrothermal processing, spray pyrolysis, chemical vapour deposition (CVD), and the alkoxide hydrolysis method [9, 10], a precipitation method [11], and sol gel processing [12]. Most of these methods involve very high cost starting materials and processing techniques that made them not suitable for large scale commercial production. However, less expensive alternative ways of preparing mullite using raw materials like clay, kaolinite, alumina, gibbsite and boehmite have been become a focus of research [7, 13, 14].

Kaolin, one of the aluminosilicates, has been used as a combined source of SiO_2 and Al_2O_3 . Kaolinite, the

main constituent of kaolin, has chemical structure of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (39.8% alumina, 46.3% silica, 13.9% water) which represents two-layer crystal (silicon-oxygen tetrahedral layer joined to alumina octahedral layer exist alternately) [15, 16]. The stoichiometric 3:2 mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) is a thermodynamically stable phase in the SiO_2 - Al_2O_3 system. The mullite is thus formed after firing kaolinite at elevated temperature [13]. Nevertheless, the amount of SiO_2 in kaolinite is much higher than that in mullite and forms cristobalite to accompany the formation of mullite at a temperature higher than 1000 °C; hence, alumina sources such as gibbsite, bauxite, aluminum salts, etc. are added to the kaolin in an appropriate amount to meet or to achieve the stoichiometric mullite. The added Al_2O_3 reacts with the excess SiO_2 to form mullite, reducing the glassy phase or cristobalite. Kaolin can be suitable material for production of nano mullite because of having considerable content of alumina and silica in kaolin structure.

In this study, preparation of nanopowder mullite from activated local kaolin (Indonesian kaolin Belitung) and gibbsite is reported using a simple and commercial method. The materials used in this methods, were technical and local compounds and were found in industrially scale. The purposes of this study are to investigate the phase transformation of activated kaolin by calcination process at 800 °C and wet milling with H_2SO_4 solution for 48 hours; and to prepare nanomullite from the activated kaolin and gibbsite. The as-synthesized mullite was calcined at elevated temperatures of 400 °, 600 °, 800 °, and 1200 °C for identification the mullite phase transformation. The final products were identified using XRD, SEM, and TEM.

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Experimental Procedure

Materials and instruments

Materials used in this research were Indonesian local kaolin (kaolin Belitung), gibbsite, and technical grades of H_2SO_4 solution, sugar, ammonia solution, and alcohol that obtained from local market; whereas instruments used were a mortar, a pot mill, a Heraeus electrical furnace, a Nabertherm electrical furnace, a Phillips PANalytical X-ray diffractometer, a JEOL JSM-35C scanning electron microscope (SEM), and A JEOL-120 keV transmission electron microscope (TEM).

Preparation of activated kaolin Belitung

Kaolin Belitung, a combined source of SiO_2 and Al_2O_3 , was initially activated by a thermal treatment at 800°C . About 251.85 gram of kaolin Belitung was dispersed in 315.78 gram of 95-97% H_2SO_4 solution. The mixture of kaolin and the acid was milled in an alumina pot mill for 48 hours. Then, the leaching kaolin or activated kaolin was prepared for XRD analysis and TEM characterization.

Preparation of nano mullite from the activated kaolin and gibbsite

The mullite precursors were prepared from a mixture of 173 grams kaolin, 224 grams gibbsite ($\text{Al}(\text{OH})_3$), and 20% sulfuric of the total weight. The mixture was milled in the sulfuric acid medium at the condition of pH 2-3 for 24 hours. At the milling time of 23 hours, 100 grams sugar were added into the mixture. The mixture was then neutralized with the addition of ammonia solution until the pH ranging of about 5-6. The mixture was heated in an oven at temperatures of 150°C - 200°C to produce black charcoal-like precursors. The precursors were successfully calcined at 400°C , 600°C , 800°C , 600°C and 1000°C for 5 hours in an electric furnace, resulting white solids. The solids were then milled in the alcohol solvent and were dried in an oven at 100°C , thus producing very fine powders of nano mullite.

Characterization of the nano mullite powder

All calcined powders were characterized by a PAN analytical X-ray instrument, a JEOL JSM-35C SEM, and a JEOL-120 kV TEM. The crystalline phase of nano mullite powder was identified by powder X-ray diffraction (XRD) instrument (XRD, PW 3710 MPD control, Philips, PAN analytical) at 40 Kv and 35 mA with $\text{Cu}/\text{K}\alpha$ ($\lambda = 1.54060 \text{ \AA}$) radiation source. The diffraction patterns were scanned with angular step of 0.020. Quantitative analyses of the diffractogram patterns, including the composition and crystallite sizes of any phases formed at 1200°C , were performed using XRD software. Crystallite sizes of the nano mullite powder calcined at 1200°C were estimated from XRD peak widths using the Scherrer equation [1].

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where D is the crystallite size, K is a shape factor with a value of 0.9-1.4, λ is the wavelength of the X-rays ($1.54056 \text{ \AA}$), θ is Bragg's angle and β is the value of the full width at half maximum (FWHM). XRD patterns were identified using the PDF2 CD-ROM (JCPDS-International Centre for Diffraction Data).

Meanwhile, a transmission electron microscopy (TEM) study was also performed to ensure the crystal phase and grain sizes of the nano mullite powder using a JEM-1400 120 kV TEM and a scanning electron microscope (SEM, JEOL JSM-35C SEM) was used to observe the morphology of nano mullite particles after thermal treatments at 800°C and 1200°C .

Results and Discussion

Mineralogy characteristics of kaolin Belitung before and after activated by calcination and the acid treatment and the mullite phase at the elevated temperatures

The effect of calcination and sulfuric acid in the activation process of kaolin Belitung could be observed in the XRD result, which is presented in Figure 1.

Figure 1 shows typical XRD patterns of pure kaolin Belitung before and after activation by thermal and acid treatments, respectively. The XRD analysis of pure kaolin Belitung in Figure 1, shows that the kaolin consisting of kaolinite, the main component with the strong peaks of kaolinite main crystals planes at diffraction angles of 12.385° [001] and 25.016° [002]; and quartz as the minor component. When the kaolin was activated by thermal and acid treatments, the XRD result showed the sample significantly having different mineral compositions and XRD pattern with pure kaolin, as shown in Figure 1. The mineral phases identified in the activated kaolin were aluminosilicates, cristoballite, and $\alpha\text{-Al}_2\text{O}_3$, the most stable alumina phase with the strong

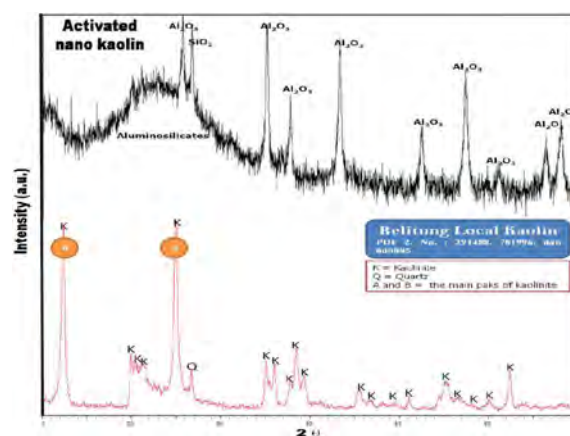


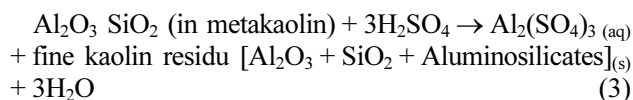
Fig. 1. The typical XRD pattern of pure kaolin and activated kaolin by thermal and acid treatments

peaks of α - Al_2O_3 main crystals planes at diffraction angles of 25.676° [012], 35.1493° [104], 43.315° [113], and 57.465° [116].

During kaolin activation process by the calcination treatment at 800°C , the dehydroxylation of kaolin occurred in which the structure of kaolin degraded and two molecule waters were released. The first present of dehydroxylation was identified by changes of mechanical, electrical properties and also by weight loss. The results of isothermal firing show that the dehydroxylation begins at $\sim 420^\circ\text{C}$ [16, 17]. The chemical equation describing this process is:



The result of dehydroxylation is a new phase called a meta kaolinite, which is an amorphous phase. After activation kaolin by thermal treatment at 800°C , the activation was followed by acid treatment in which the calcined kaolin was dispersed in H_2SO_4 solution. During the acid treatment, some alumina compounds in kaolin were extracted and dissolves in H_2SO_4 leading to formation of aluminum sulfate (according the XRD result).



According to the reaction (3), since kaolin was activated by thermal and acid treatments, fine kaolin residu or activated kaolin lacks of alumina compound. Therefore, alumina gibbsite was mixed with kaolin to produce mullite. The addition of sulfuric acid into the mixture was to convert gibbsite molecules to boehmite molecules, which was the more reactive transition aluminas [18].

Figure 2 shows the XRD pattern of the nano mullite from activated kaolin Belitung and activated gibbsite after thermal treatment at elevated temperatures. The figure shows the powder XRD patterns of the mullite sample calcined at 400°C , 600°C , 800°C , and 1200°C . The profiles of phase changes of mullite with temperature are mostly same to those indicated by Figure 2. After calcination for 5 hours at 400°C , 600°C , and 800°C , mullite, α - Al_2O_3 and spinel phases were identified as the existing phases in the sample. The peak intensities of those phases increased and began to appear stronger as the calcination temperature elevated. The peak patterns of those phases were clearly observed after the sample calcined at 800°C . However, by increasing temperature from 800°C to 1200°C , the spinel peaks disappeared, whereas the mullite and α - Al_2O_3 peaks increased significantly and strongly at 1200°C . The main desired phase, mullite was shown by two main with broadening and overlapping sharp peaks of mullite and α - Al_2O_3 at diffraction angles 2θ

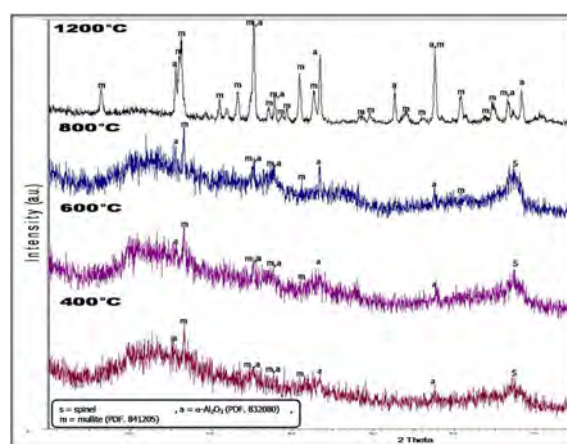


Fig. 2. The typical XRD patterns of nano mullite from activated kaolin and activated gibbsite at the calcining temperatures of 400°C , 600°C , 800°C , and 1200°C .

of 25.998° , 26.297° , and 25.629° corresponding to the (120) and (210) crystals planes of the mullite and the (012) crystal plane of the α - Al_2O_3 , respectively. Quantitative analyses of the diffractogram patterns, including the crystallite sizes and phase compositions of α - Al_2O_3 and γ - Al_2O_3 , were performed for calcined alumina powder using XRD software. The quantitative results show that the phases formed in calcined mullite powder consisting of the mullite phase about 58.7% having crystallite sizes about 13-38 nm (PDF 2. 84-1205) and the α - Al_2O_3 phase about 41.3% having crystallite sizes about 32-46 nm (PDF 2. 83-2080). The higher alumina content in the mullite powder was probably caused by the excess addition of gibbsite at the preparation process. The presence of sugar, during the preparation, was to reduce the tendency to agglomeration in the as-synthesized mullite particles. The sugar molecule coating on as-prepared mullite particle surfaces results in reduced particle aggregation due to the steric hindrance provided by the sugars.

Microstructures and analysis of electron diffraction patterns TEM in the activated kaolin and the calcined mullite powders

Figure 3 shows typical TEM bright field images and electron diffraction patterns (ED) of kaolin activated by thermal and acid treatments, using a JEM-1400 120 kV transmission electron microscope. The electron diffraction (ED) patterns of the activated kaolin are indexed to the α - Al_2O_3 phase with the crystal plane orientations of (024), (116), and (110); the quartz phase with the crystal plane orientations of (100), (101), (200) and (202); and the mullite phase with the crystal plane orientations of (030), (101), (110) and (001). This ED result corroborates the XRD result for the activated kaolin sample, showing the formation of the α - Al_2O_3 , silica, and aluminosilicate phases in the sample. The aluminosilicate phases in the activated kaolin probably correspond to the mullite phases, as shown by the ED

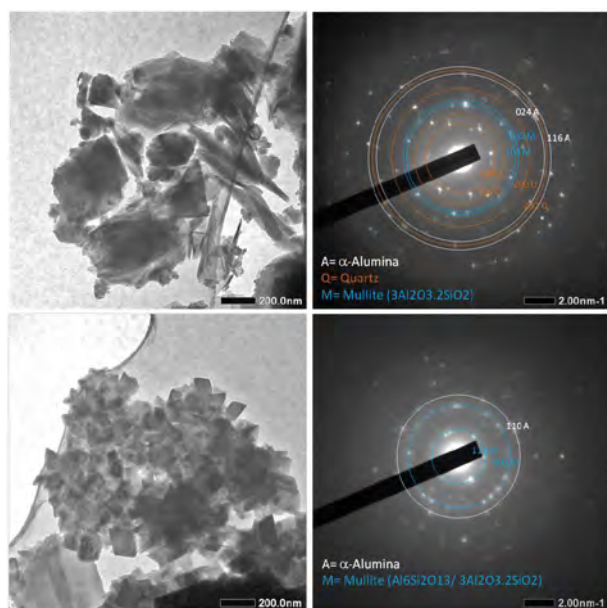


Fig. 3. Typical TEM images of kaolin activated by thermal and acid treatments.

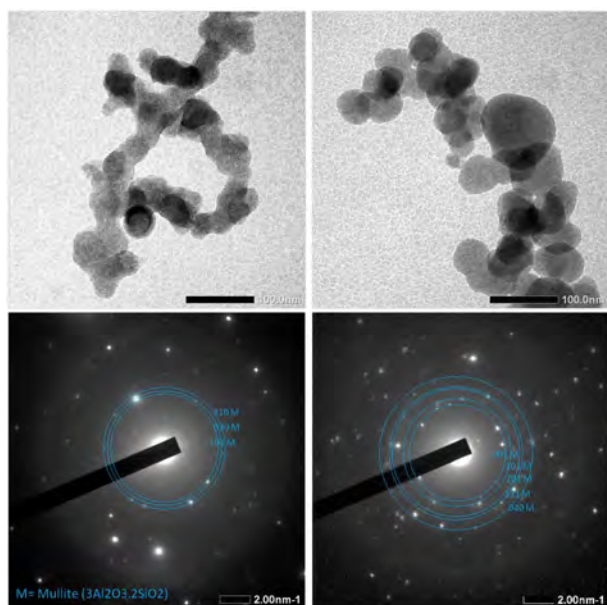


Fig. 4. Typical Bright Field TEM images of mullite powder calcined at 1200 °C.

TEM results. Besides, the ED results emphasize that the thermal and acid treatments has dissolved some alumina compounds from kaolin to be aluminum sulphate (aq) and has inverted kaolin to produce alumina, silica, and aluminosilicates, as given by reaction (3).

Figure 4 shows typical TEM bright field images and electron diffraction patterns (ED) of activated kaolin based mullite where an appreciable formation of agglomerates after thermal treatment at 1200 °C can be seen, using a JEM-1400 120 kV transmission electron microscope. Fine particles such as nanomullite particles, since they have large surface areas, often agglomerate

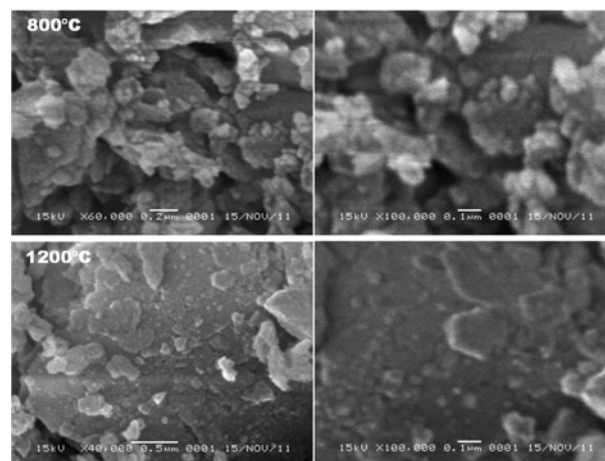


Fig. 5. Typical SEM images of mullite powder calcined at 800 °C

through the adhesion of the particles to each other to form secondary particles to minimize the total surface area or interfacial energy of the system. The nanomullite particles are very freely for adhesion because of the strong *van der Waals* forces of attraction, which is significantly higher in nanoparticles [19]. The grain sizes of mullite powders are found to be less than 100 nm at a calcination temperature of 1200 °C. The electron diffraction (ED) patterns of the mullite sample are indexed to the mullite phase with the crystal plane orientations of (310), (030), (101), (001), (201), (040) and (121). These results corroborate the XRD result for the calcined mullite at 1200 °C, showing the formation of the mullite phase in the sample.

Typical SEM micrographs of the mullite samples calcined at 800 ° and 1200 °C using JEOL JSM-35C SEM, are shown in Figure 5. The formation of agglomerates in the mullite sample grains are clearly observed, as shown in Figure 5. However, the micrographs represent most region of the mullite powder produced from the mixture of activated kaolin and activated gibbsite which calcined at 1200 °C having an average grain size below 100 nm.

Conclusion

Nanomullite powders were successfully prepared from activated kaolin and gibbsite; and then were calcined at 400 °, 600 °, 800 °, and 1200 °C. Kaolin activation was performed by the thermal treatment at 800 °C and sulfuric acid treatment. It is concluded that the activation process of kaolin has changed its mineral structure, resulting alumina, silica, and aluminosilicate phases in the kaolin composition, as given by XRD result. These results were verified by the electron diffraction results of the activated kaolin, showing the formation α -Al₂O₃, quartz, and mullite phases. Crystallization of the as-prepared mullite in the temperature range of 400 °-1200 °C produced mullite, α -Al₂O₃, and spinel phases at 400 °C. A further phase transformation of the mullite

sample maintained mullite and α -Al₂O₃ phases at 1200 °C in which the grain sizes of the mullite powders are found to be less than 100 nm. The electron diffraction (ED) patterns of the calcined mullite are indexed to the mullite phase with the crystal plane orientations of (310), (030), (101), (001), (201), (040) and (121). These results are in agreement with the XRD result of the calcined mullite at 1200 °C.

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