

HIGH PURITY MESOPOROUS γ - Al_2O_3 FROM KANO KAOLIN IN THE PRESENCE OF POLYETHYLENE GLYCOL 6000 (PEG-6000) SURFACTANT

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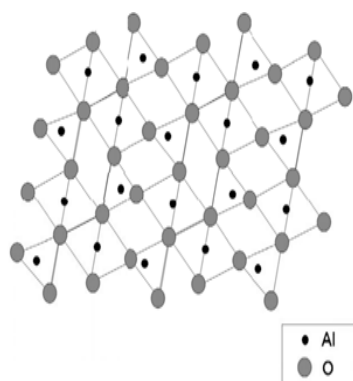
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Graphical abstract



Abstract

Mesoporous γ - Al_2O_3 with large surface area and narrow pore size was synthesized from acid-leachates of calcined kaolin in the presence of polyethylene glycol 6000 (PEG-6000) surfactant at room temperature. The synthesized alumina was characterized by X-ray diffraction (XRD), Nitrogen adsorption-desorption, Fourier transform infra-red spectroscopy (FTIR), field emission scanning electron microscopy (FESEM) with energy-dispersive X-ray analysis (EDX), and thermogravimetric-Derivative thermal analysis (TG-DTA). High-purity mesoporous γ - Al_2O_3 with large surface area of 365.1 m^2/g , narrow pore size distribution centred at 5.3 nm and pore volume of 0.46 cm^3/g was obtained at 500 $^\circ\text{C}$. When the calcination temperature has increased to 700 $^\circ\text{C}$, the surface area decreased to 272.9 m^2/g . Crystallite size calculated using Scherer's equation revealed the average size of 4.33 and 4.12 nm for alumina calcined at 500 and 700 $^\circ\text{C}$, respectively. The excellent pore structural properties (high surface area and large pore volume) of the synthesized mesoporous γ -alumina in the present study will allow for higher loading of active catalytic phases, as such it can be used as catalyst support.

Keywords: Alumina, Kano, kaolin, mesoporous, purity

Abstrak

Mesoporous γ - Al_2O_3 dengan kawasan permukaan yang taburan saiz liang sempit disintesis daripada asid-air larut resap kaolin calcined di hadapan polyethylene glycol 6000 (PEG-6000) surfaktan pada suhu bilik. The alumina disintesis dicirikan oleh sinar-X serbuk (XRD), Nitrogen penjerapan-penyahjerapan, spektroskopi inframerah transformasi Fourier (FTIR), mikroskopi pengimbasan elektron pemancaran medan (FESEM) dengan tenaga-serakan X-ray analisis (EDX), dan analisis terma pembezaan-termogravimetri (TG-DTA). Ketulenan tinggi mesoporous γ - Al_2O_3 dengan kawasan yang besar permukaan 365,1 m^2/g , taburan saiz liang sempit 5.3 nm dan isipadu liang 0.46 cm^3/g telah diperoleh pada 500 $^\circ\text{C}$, apabila suhu pengkalsinan telah meningkat kepada 700 $^\circ\text{C}$, yang kawasan permukaan berkurangan kepada 272,9 m^2/g . Saiz crystallite dikira menggunakan persamaan Scherer mendedahkan saiz purata 4.33 dan 4.12 nm untuk alumina calcined pada 500 dan 700 $^\circ\text{C}$, masing-masing. Sifat-sifat struktur liang yang sangat baik (kawasan permukaan yang tinggi dan isi padu liang besar) mesoporous γ -alumina disintesis dalam kajian ini akan membolehkan untuk memuatkan lebih tinggi fasa pemangkin aktif, oleh itu ia boleh digunakan sebagai sokongan pemangkin.

Kata kunci: Alumina, Kano, kaolin, mesoporous, kesucian

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1.0 INTRODUCTION

A family of ordered mesoporous materials, M41S, was first synthesized by Mobil researchers in 1992. Since then attention was focused on the area of inorganic porous materials for applications in catalysis, separation and ion exchange. However, it became necessary to modify the synthesis procedure used for M41S family in synthesizing organized mesoporous alumina due to different chemical behaviors of alumina source [1, 2]. Organized mesoporous alumina was first synthesized by Vaudry *et al.* [3] in the presence of long-chain carboxylic acids.

Alumina is prepared from hydroxide $[\text{Al}(\text{OH})_3]$ and oxyhydroxide $[\text{AlO}(\text{OH})]$ by dehydration at elevated temperatures. Depending on the precursor and condition of heat treatment, different crystal phases of alumina exist which are collectively known as γ -alumina, and in various studies were named using the Greek alphabet: χ , δ , ϵ , γ , η , κ , θ , and ρ . The most stable crystal form of alumina is α -alumina, which is obtained by heating the precursors above 1200 °C. These phases represent various degrees of ordering of aluminium atoms in an essentially cubic closest packing of oxygen atoms, described as a defect spinel structure, since there are only 21 and 1/3 metal atoms arranged at random in the 16 octahedral and 8 tetrahedral positions of that structure. Among these transition aluminas, γ - and η -aluminas are important as catalysts and catalyst support, primarily due to their high surface area [4].

Clays are molecularly engineered aluminium/magnesium silicates having 1:1 or 1:2 layer structures [5]. They are thermally inert, environmentally friendly and inexpensive mineral which make it more economical and safer than the expensive and toxic aluminium alkoxides or inorganic salts as a source of aluminium for synthesis of mesoporous γ - Al_2O_3 . Despite these advantages possessed by kaolin as precursor for alumina, few works were reported on the synthesis of mesoporous alumina from kaolin [1, 6-9].

The uses of kaolin depend on several factors including but not limited to the geological conditions under which the kaolin is formed, the total mineralogical compositions of the kaolin deposits, and its physical and chemical properties. Although there are reports on the synthesis of mesoporous alumina from different kaolin, there is none using Kano kaolin. Impact detailed study, characterization and analysis of this kaolin are still limited, hence, the need to assess its potentiality for the synthesis of alumina.

Polyethylene glycol $[\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}]$ (PEG-6000) was selected in the present synthesis procedure because it is considered environmentally benign due to its nontoxicity and biodegradability, coupled with the high number of oxygen atoms that can form bond with the aluminium ions to control crystal growth of the mesoporous alumina [10]. Additionally, the interaction between PEG and precursor will be

done through hydrogen-bonding that will result in easy removal of the template during calcination thereby preventing sintering.

The present research reports environmentally benign synthesis of high-purity mesoporous alumina with large surface area and narrow pore using kaolin as precursor in the presence of polyethylene glycol 6000 (PEG-6000) as surfactant.

2.0 METHODOLOGY

The kaolin was mined from Getso town, Kano state, Nigeria. Hydrochloric acid and sodium hydroxide were purchased from QR $\text{\textcircled{R}}$ CTM, and polyethylene glycol 6000 (PEG-6000) from Fisher. All chemicals are of analytical grade and used without further purification.

2.1 Synthesis Of Mesoporous Alumina

The kaolin was calcined into metakaolin and the metakaolin leached with 6 M hydrochloric acid. The suspension was filtered and 5 M solution of NaOH added in excess to the filtrate to precipitate impurities. After filtration 6 M HCl was added to the filtrate with stirring to adjust the pH to 7, the precipitate formed was filtered and washed with deionized water. The precipitate obtained was mixed vigorously with a solution of PEG-6000 containing 10 g in 100 mL of water for 2 hours. The suspension was then aged for 48 hours at room temperature; filtered, washed with deionized water; dried at 120 °C, followed by calcination at 500 °C and 700 °C for 4 hours, to obtain Al_2O_3 -500 and Al_2O_3 -700, respectively.

2.2 Characterization

The kaolin sample was calcined at 600 °C for 3 hours to obtain the loss on ignition. The chemical composition was determined using energy dispersive X-ray fluorescence spectrometer NEXCG (USA). Structural phase analysis was carried out on a Bruker D8 having Siemens Diffractometer D5000 with Cu-K α radiation (40 kV, 40 mA, $\lambda = 1.5406\text{\AA}$) (USA). The morphology was determined by field emission electron microscopy (FESEM) (SupraTM 35 VP operating at 10kV) (Germany). The TG-DTG analysis was carried out using Perkin Elmer Simultaneous Thermal Analyzer (STA 8000) (USA) in the temperature range of 50 °C to 1200 °C and heating rate of 10 °C/min. Nitrogen adsorption-desorption was used to determine the surface area, pore size distribution and pore volume at -196 °C using Fisher Thermo Scientific SURFER (USA), prior to analysis all samples were dehydrated and degassed by evacuation at 300 °C for 3 h. Perkin Elmer 1650 Infra-Red Spectrometer (USA) was used for FTIR analysis of samples in the range of 4000 cm^{-1} to 400 cm^{-1} .

Hence, this system will be used for traffic and emergency management. Several environments that will study traffic flow and emergency condition are shown in Figure 4.

3.0 RESULTS AND DISCUSSION

3.1 Chemical Composition

The XRF analysis was conducted to estimate the chemical composition of the kaolin and chemical changes that took place after alumina synthesis, it is presented in Table 1. The loss on ignition of 11.62% may be as a result of organic matter lost and/or some non-metals like sulphur which could have been removed from the clay in the form of SO₂ [11]. After synthesis, the composition of Al₂O₃ was found to be 90.8% in the AlOOH precursor and 96.6 and 98% in Al₂O₃-500 and Al₂O₃-700 respectively. The 90.8% observed for the AlOOH precursor may be due to the presence of water that cannot be detected by the XRF analysis. After calcination the percentage of Al₂O₃ increased up to 98%, indicating very high purity of the synthesized mesoporous alumina and proving the benefit of using the procedure for synthesizing pure alumina from local kaolin.

Table 1 Percentage composition by mass in Kaolin, AlOOH precursor and alumina

Elemental Composition (%)	Kaolin	AlOOH	Al ₂ O ₃ -500	Al ₂ O ₃ -700
Si	51.51	1.06	0.459	0.408
Fe	1.27	0.0516	0.0303	0.0297
K	0.74	0.0268	0.0236	0.0871
Mn	0.060	0.0031	ND	0.0025
Ti	0.052	0.0041	0.0029	0.0025
Ca	0.046	0.0627	0.0327	0.0449
Al ₂ O ₃	34.69	90.8	96.6	98.0

3.2 TG-DTG Analysis

TG-DTG curve of the precursor presented in Figure 1, indicates three major weight losses. The first weight loss, amounting to 12.75%, between 50 to 190 °C corresponds to an endothermic peak at 83.97 °C on the DTG curve is assigned to the release of physically adsorbed water, second one appeared in the region of 210 to 310 °C equalled to 8.85% matches the second endothermic peak on the DTG curve at 273.77 °C which may be assigned to the removal of template through Hofmann degradation reaction below 250 °C and the decomposition and/or combustion reaction above 250 °C [12]. The fact that the boiling point of PEG is less than 300 °C, support the proposition that the second mass loss is due to the removal of template [13]. The third weight loss of about 10.52% occurred between 320 to 590 °C conforming with the third endothermic peak at 327.67 °C on the DTG curve which may be attributed

to the removal of chemically adsorbed water molecules and conversion of precursor to alumina. Above 600 °C the weight loss process stabilized, it indicates the beginning of various alumina phase transformation and it also implies the thermal stability of the synthesized mesoporous alumina [14]. From the dehydroxylation reaction of boehmite shown below;



The theoretical weight loss is about 16%, which is comparable with the observed weight loss from the TG curve, this suggests the precursor to be aluminium oxyhydroxide not aluminium hydroxide.

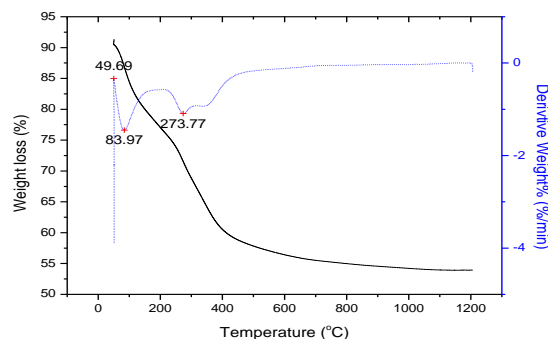


Figure 1 TG-DTG curve of the precursor

The differential scanning calorimetry DSC of the alumina precursor presented in Figure 2 agrees with the TG-DTG result, three endothermic peaks can be observed at 86.40, 351.99 and 627.97 °C. The first peak may be attributed to desorption of physically adsorbed water molecules, the second due to the release of chemically desorbed water molecules and decomposition and/or combustion of the surfactant template and the last may be associated with the phase transition process of the alumina [15, 16].

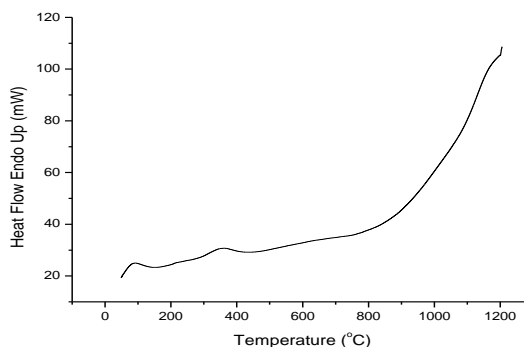


Figure 2 DSC curve of the precursor

3.3 XRD Analysis

The wide-angle X-ray diffraction pattern presented in Figure 3, depicts the spectra obtained for the precursor and the γ -alumina. The characteristic diffraction peaks of the precursor are those of Aluminium oxide hydroxide (AlOOH) (JCPDS Card no. 21-1307) that indicates the orthorhombic structure of the precursor, the five diffraction peaks are observed at $2\theta = 12^\circ, 28^\circ, 38^\circ, 49^\circ$ and 65° corresponding to [0 2 0], [1 2 0], [0 3 1], [2 0 0] and [0 0 2] crystal planes respectively. The XRD pattern of the precursor showed a good crystallinity, which can be connected to the small amount of impurities present [9].

The calcined samples showed characteristic peaks at $2\theta = 32^\circ, 38^\circ, 46^\circ$, and 67° that correspond respectively to [2 2 0], [3 1 1], [4 0 0] and [4 4 0] crystal planes (JCPDS Card no 10-0425) which is that of a face-centered cubic lattice belonging to γ -Al₂O₃. The absent of peak at 65° consistent with [0 0 2] crystal plane, characteristic of boehmite indicates the formation of γ -alumina. The XRD result corroborates the observation in the XRF analysis indicating high purity of the synthesized mesoporous alumina. It also confirmed the assertion from the TG analysis that the precursor is boehmite.

The crystallite size of the alumina was calculated using Scherer's formula from the three most intense peaks; $38^\circ, 46^\circ$ and 67° and the results obtained are 5.40, 3.61 and 3.98 nm with an average of 4.33 nm for Al₂O₃-PEG-500 and 4.96, 3.93 and 3.46 nm with an average of 4.12 nm for Al₂O₃-PEG-700. The result indicates that increasing the calcination temperature has little effect on the crystallite size. For the precursor the average crystallite size was found to be 3.21 nm.

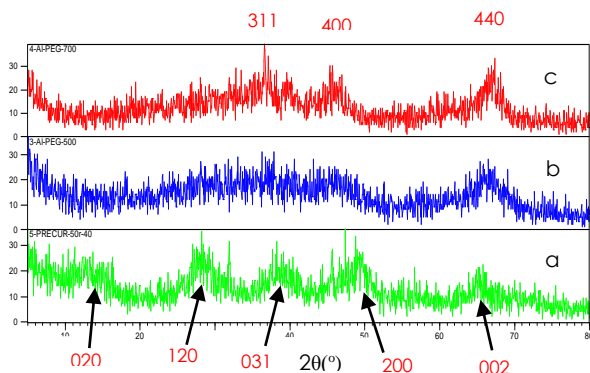


Figure 3 XRD pattern of; a. precursor b. Al₂O₃-500 and c. Al₂O₃-700

3.4 FTIR Analysis

The FTIR spectra of the precursor as well as that of Al₂O₃-500, Al₂O₃-700 and commercial alumina are presented on Figure 4. All samples showed broad bands around 3480 cm^{-1} assigned to the stretching

vibration of structural OH attached to Al₂O₃ indicating the presence of molecular water and around 1635 cm^{-1} due to δ OH bending vibration mode of adsorbed water. Both bands around 3480 cm^{-1} and 1635 cm^{-1} decreased with increasing calcination temperature [17]. The band around 1075 cm^{-1} is attributed to symmetrical Al-OH bending modes and it confirmed the formation of boehmite [9, 18]. This further supports the observation from the TGA and XRD results that the precursor is aluminium oxide hydroxide.

Bands around $949.7, 470.3, 453.0, 428.3$ and 414.1 cm^{-1} can be assigned to C-O-C and CH₂- vibration that originate from the surfactant, and their absence after calcination implies that the alumina is free from surfactant. The band around 785 cm^{-1} is attributed to the stretching mode of AlO₄ and that around 590 cm^{-1} is associated to stretching vibration mode of AlO₆. The formation of alumina is confirmed by the absorption band around 1404 cm^{-1} and absence of band around 1075 cm^{-1} [7, 9]. All the peaks present in the commercial alumina are also present in the synthesized alumina, further confirming the formation of alumina.

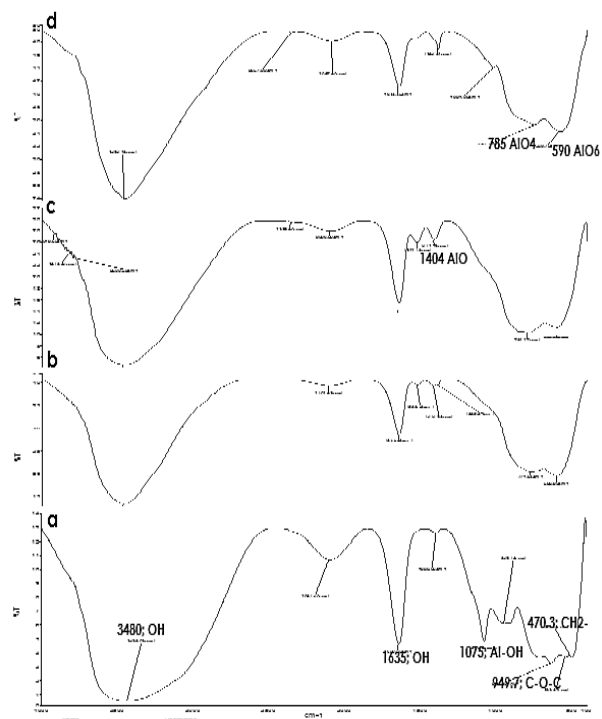


Figure 4 FTIR spectra of a. precursor, b. Al₂O₃-500, c. Al₂O₃-700 and d. commercial alumina

3.5 Porosity Measurement

The N₂ adsorption-desorption isotherm and pore size distribution curves are presented in Figures 5 and 6. The existence of type IV isotherm with H2 hysteresis loops indicates the formation of mesoporous materials. The adsorption and desorption branches of the hysteresis loop closed at high relative pressure

indicated that the pores are formed by the interstices between plate-like aggregates [19].

The pore size distribution for Al_2O_3 -500 shows narrow distribution centred at 5.3 nm, the narrow pore size distribution can be attributed to the steeper curve in the capillary condensation while the limiting pore volumes of $0.46 \text{ cm}^3/\text{g}$ resulted from saturation of the isotherms at higher P/P_0 values [20].

High surface area of 365.1 and $272.9 \text{ m}^2/\text{g}$ were obtained for Al_2O_3 -500 and Al_2O_3 -700, respectively. Addition of surfactant plays an important role in obtaining mesoporous alumina with high surface area, well define porosity and distribution centred at higher relative pressure [18, 21]. Alumina with large surface area, narrow pore-size and excellent thermal stability would have excellent catalytic activity [16].

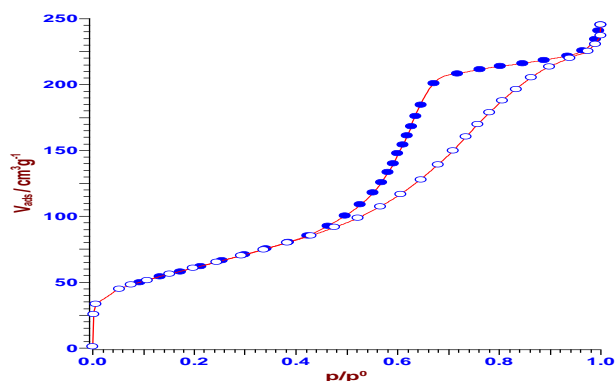


Figure 5 N_2 -Adsorption-desorption isotherm of Al_2O_3 -500

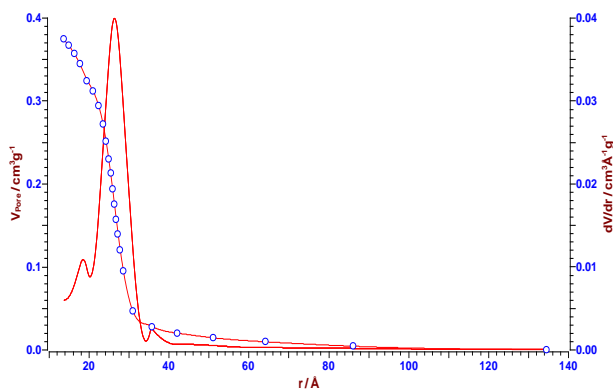


Figure 6 Pore distribution (B.J.H.) of Al_2O_3 -500

3.6 FESEM-EDX Analysis

The FESEM images of the precursor and alumina are depicted in Figure 7, the morphology of the boehmite precursor portray a wormhole-like structure. Al_2O_3 -500 and Al_2O_3 -700 retained the morphology of the boehmite indicating that addition of surfactant caused little change in the morphology of the precursor. However, there is agglomeration of the particles and they became aggregated, and the wormhole-like structure appeared more distinct. The fact that the γ -alumina retained the morphology of the precursor can be attributed to the weak interaction between boehmite and surfactant, which

is considered not strong enough to destroy the hydrogen bonding interaction between the boehmite layers [18]. Furthermore, the transformation of boehmite to γ -alumina is known to be topotactic, hence γ -alumina is likely to maintain the original morphology of the boehmite precursor [22].

From the EDX analysis, only peaks of aluminium and oxygen can be observed for both the precursor and alumina, indicating the suitability of the synthesis procedure for the preparation of high purity alumina. This result agrees well with the XRD and XRF results that also betoken high purity of the synthesized γ -alumina.

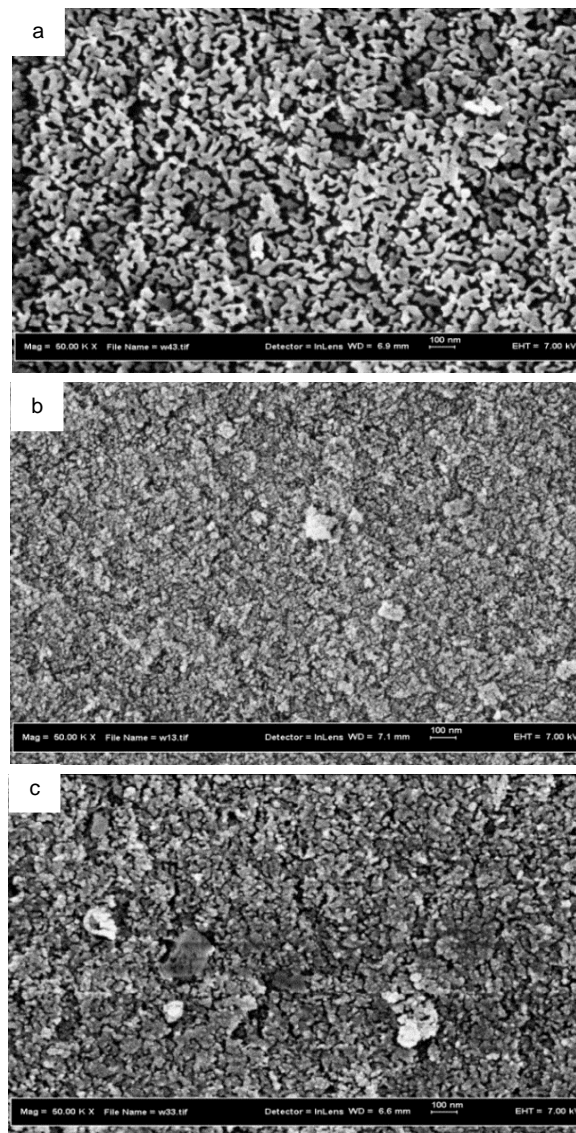


Figure 7 FESEM images of (a) precursor, (b) Al_2O_3 -500 and (c) Al_2O_3 -700

4.0 CONCLUSION

High purity mesoporous γ -alumina was successfully synthesized from Kano kaolin in the presence of PEG-6000, as revealed by the XRF result that indicated high percentage composition of up to 98% Al_2O_3 . The alumina displayed large surface area of $365.1 \text{ m}^2/\text{g}$, narrow pore size distribution centred at 5.3 nm and pore volume of $0.46 \text{ cm}^3/\text{g}$, with good thermal stability. Crystallite size calculated using Scherer's equation revealed an average size of 4.33 nm which agree with the pore size distribution. Mesoporous alumina with large surface area, high thermal stability and narrow pore-size distribution is a potential material in adsorptive and catalytic applications.

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