

Synthesis of Gamma-Alumina from Kankara Kaolin as Potential Zeolite Active Matrix

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ABSTRACT

Commercial fluid catalytic cracking catalysts are manufactured using zeolites dispersed on an amorphous matrix, which is mostly alumina. Alumina is widely used as catalyst support in many heterogeneous catalytic processes owing to its high surface area, superior chemical activity and low cost. In compounded zeolite catalyst it serves as the active matrix which aids the conversion of the bulkiest molecules in the feed owing to its larger pore size than zeolite. Large specific surface area gamma-alumina ($\gamma\text{-Al}_2\text{O}_3$) was synthesized by hydrothermal method using Kankara kaolin as starting material. Thermal treatment of ammonium alum prepared from the filtrate of the dealuminated metakaolin was employed to obtain the alumina. Crystalline aluminum sulfate with 39 wt% Al_2O_3 was obtained at calcination temperature of 800°C with 3 h soaking. Gamma-alumina was produced at 850°C with 3 h soaking time, having specific surface area of $166\text{ m}^2/\text{g}$. The weight percent of Al_2O_3 content in the synthesized and commercial gamma-alumina were 85% and 89% respectively as obtained from the XRF analysis. Good comparison was also observed in the diffractogram of the synthesized and commercial gamma-alumina from the XRD analysis. The Scanning Electron Microscopy (SEM) image showed the platy hexagonal shape of the gamma-alumina.

Keywords: Gamma-alumina, zeolite, kaolin

INTRODUCTION

The current fluid catalytic cracking (FCC) catalysts consist of a complicated combination of different materials, which have different functions (Corma, 1992). The pore size of the zeolite limits the activity to the molecules that access the active sites. Commercial FCC catalysts are manufactured using 1-2 μm zeolite dispersed on an amorphous matrix forming 60 μm particles (Scherzer, 1993). Zeolites are microporous aluminosilicate minerals used for numerous commercial and domestic applications. The content of zeolite in zeolite catalyst is not greater than 3-15% (Salahudeen *et al.*, 2014). Zeolite Y is used commercially as catalyst in petroleum refinery because of its high concentration of active acid sites, its high thermal stability, high size selectivity and its crystal size is in the approximate range of 0.2 – 0.5 μm and pore diameter of 7.4Å (Htay, 2008). The matrix comprises 60-80 % commercial FCC catalyst and usually contains synthetic and natural components (Wang, 2006; Htay, 2008). Clay is

the natural component and amorphous silica or silica-alumina is the synthetic portion (Htay, 2008). Matrix composition can influence catalyst performance but to a lesser extent than the zeolite component (Scherzer, 1994). An active matrix contains acid sites associated with aluminum atom, e.g. alumina (Hosseini, 2011). The active matrix is characterized by high surface area and they usually enhance bottom conversion and gasoline octane number (Scherzer, 1993). Among the different alumina available, gamma-alumina is the most important one that is used in catalyst formulation (Scherzer, 1993; Wang, 2006; Hosseini, 2011), due to its high surface area, thermal stability, outstanding mechanical properties and nature of interaction with zeolite active phases (Salahudeen, 2012). Alumina heated at temperature below 1100°C is considered as amorphous materials in spite of the fact that they have important adsorptive and catalytic properties (Santos, 2000; Hosseini, 2011). Above 1100°C it changes into crystalline alpha-alumina phase (Santos, 2000). The most

common method of producing alumina is by the hydrothermal technique and the reaction takes place in water medium. Solvothermal process involves the use of organic solvent (Santos, 2000). The absence of commercial deposits of bauxite, being the primary source of alumina, in Nigeria, as well as the rapid depletion of bauxite deposits globally call for urgent development of alternative sources of alumina production (Aderemi, 2009). The production of alumina from Kankara kaolin in Katsina State, Nigeria has been reported in literature (Aderemi, 2009) but the target applications were not as catalyst support. On the other hand most of the works on the development of alumina support have been from conventional raw materials; bauxite and corundum (Kloprogge, 2002; Meor-Yusoff, 2007). This study was aimed at the preparation of high surface gamma-alumina from Kankara kaolin, with large pore size and to compare it with the commercially available gamma-alumina.

MATERIALS and METHODS

White grade raw kaolin was sourced from Kankara town in Katsina State, Nigeria, by selective mining and wet beneficiation process carried out in accordance with reported procedures (Ahmed, 1987; Edomwonyi-Otu, 2009). The beneficiated kaolin was calcined to 750°C for 2 h, to obtain the reactive phase of kaolin known as metakaolin. For batch, 50 g of metakaolin was mixed in 185ml distilled water and properly stirred. 169 ml 96 wt.% sulfuric acid was added to the mixture in a fume cupboard. After about 30 min 286 ml water was added to quench the reaction. The product was filtered using high vacuum pump (ES-100, Edward, England) filtration set-up using sinta glass as filtering medium. Thirty-three (33) g of ammonium sulfate (Analar grade BDH, Poole, U.K) was completely dissolved in the filtrate and cooled in a refrigerator (Thermocool, C1202, England, U.K.) at 0°C for 6 h. The ammonium

alum crystals formed were filtered using the filtration set-up, then dried at 250°C for 4 h in an electric oven (TM OV-420, 0-260°C, Gallenkamp, England, U.K.). The dried alum was calcined at various temperatures ranging from 700°C to 900 °C, and the soaking time was varied from 1 to 4 h in an exposed element furnace (TIKIR 11/12, Heraeus, Holland). The elemental composition (in oxide form) of the products obtained were determined using the Energy Dispersive X-Ray Florescence (ED-XRF) machine (Mini Pal 4, PANalytical, Holland), and the X-ray diffraction (XRD) patterns were obtained using diffractometer (Empyrean, PANalytical, Holland) employing Cu K α radiation ($\lambda=0.154$ nm). The textural properties (surface area, pore size and pore volume), of the products were determined from Brunauer-Emmett-Teller (BET) technique by N₂ adsorption at -196°C using Tristar 3000 Micrometrics equipment. The morphology was determined using Emission Scanning Electron Microscope (Zciss) at 20000 magnification.

RESULTS and DISCUSSION

Figure 1, shows the trend of specific surface area of ammonium alum calcined at 800°C for different soaking time. Decrease in surface area was observed between soaking time of 1 h and 2 h, while increase in pore size was equally observed in Figure 2, the observations were attributed to the coalescing of the nuclide of the product which resulted in loss of surface area and increase in pore size. From 2 h of soaking time to 3 h, an increase in surface area and decrease in pore size were observed which could be as a result of rearrangement of the atoms of the material and hence the formation particles with smaller pores, which resulted in higher surface area. From 3 h to 4 h of soaking time, about 10% decrease in specific surface area was observed. The pore volumes of the calcination products obtained were in the range of 0.22 cm³/g to 0.41cm³/g (Figure 2).

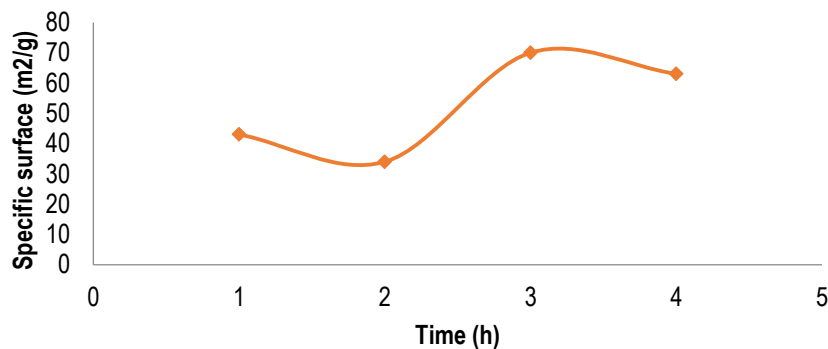


Figure 1: Specific Surface Area with Variation in Soaking Time at 800°C

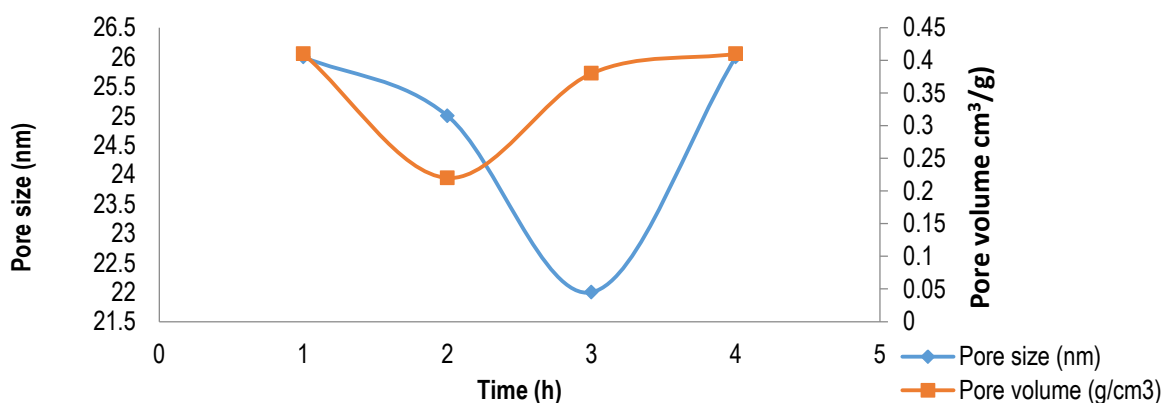


Figure 2: Pore Size and Pore Volume with Variation in Soaking Time at 800°C

Specific surface area was observed to generally increase from 20 m²/g to 155 m²/g as temperature increased from 700°C to 900 °C as shown in Figure 3. A rapid increase in specific surface area was observed between 800 °C and 850°C (i.e. from 70 m²/g to 166 m²/g) which

accounted for 137% increase in specific surface area. This value gave an indication of the development of a new material with high surface area which was confirmed by the XRD patterns to be gamma-alumina.

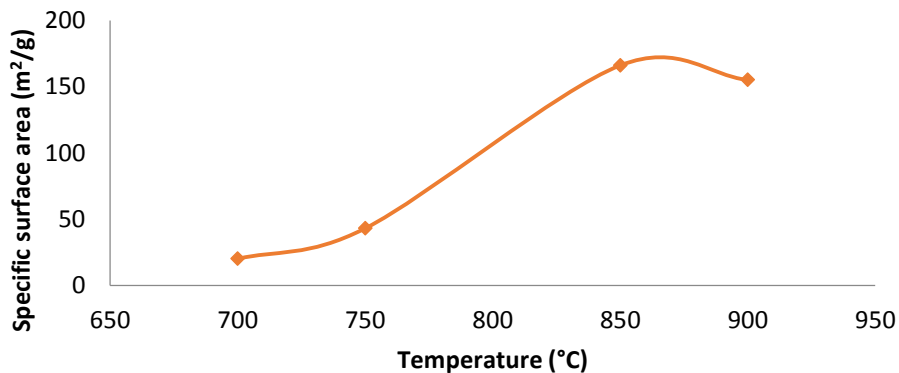


Figure 3: Specific Surface Area with Variation in Calcinations Temperature for 3 h

Heat treatment at 850°C and 900°C produced gamma-alumina with large specific surface area values of 166 m²/g and 155 m²/g respectively. It has been reported that porous materials having a surface area value above 100 m²/g is considered having a high surface area and is a potential material for catalyst support (Wefers, 1987). Calcination temperature of 850°C for 3 h gave the highest specific surface area (Figure 3). The products obtained had relatively large pore sizes

ranging from 20 nm to 30 nm as shown in Figure 4. Resistance to mass flow in and out of the pores will be negligible when in use, owing to relatively smaller pore size of zeolite being about 0.74 nm (Figure 4). The pore size of the gamma-alumina was found to be about 27 times that of zeolite Y, which agrees with Čejka (2010). Figure 4 shows that large pore volume was observed at calcination temperature of 850°C and 900°C.

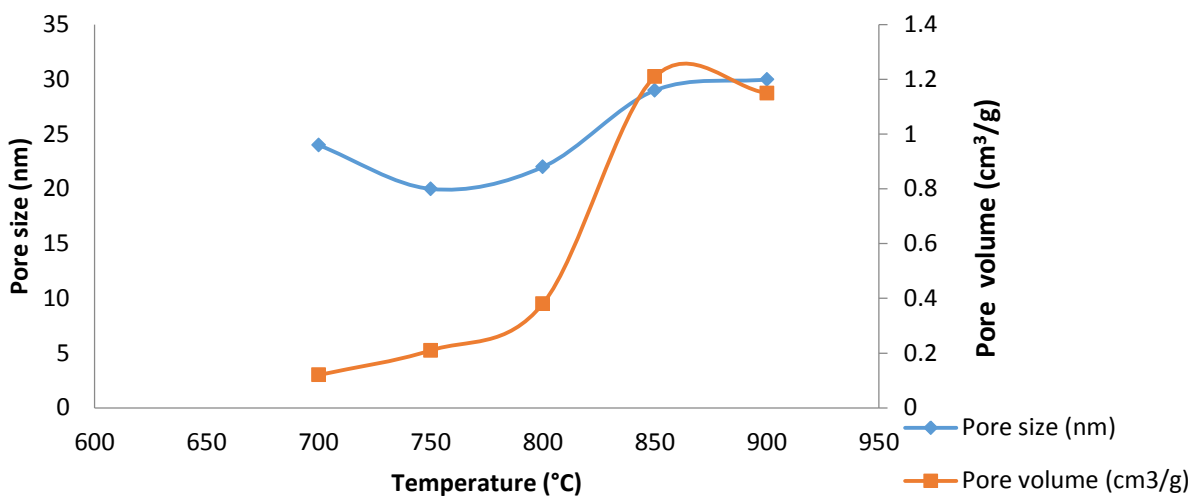


Figure 4: Pore size and Pore Volume with Variation in Temperature for 3 h

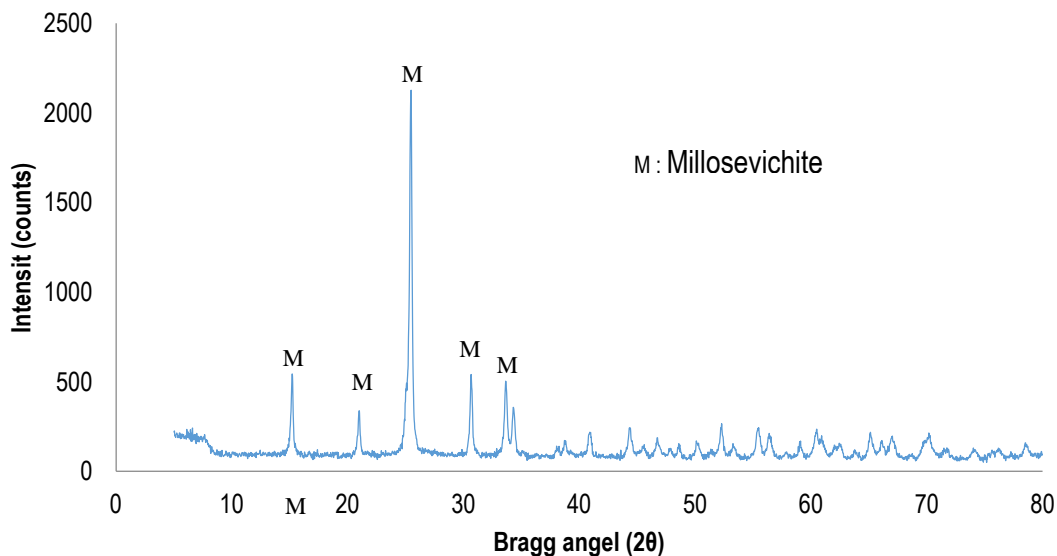


Figure 5: X-ray Diffraction Pattern of Aluminum Sulfate

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Millosevichite, a crystal phase of aluminium sulfate was obtained when the ammonium alum was calcined at 800°C for 3 h as shown in Figure 5. The indicated peaks of milosevichite are in accordance with comprehensive work done on mineral identification (Chen, 1977). Gamma-alumina was obtained at 850°C after 3 h soaking

as shown in Figure 6. The XRD pattern for this sample showed broad peaks at d-spacing of 1.43Å, 1.99Å and 2.43Å which largely matched with the commercial and standard XRD pattern of gamma-alumina and conformed with earlier reports (Santos, 2000; Aderemi, 2011).

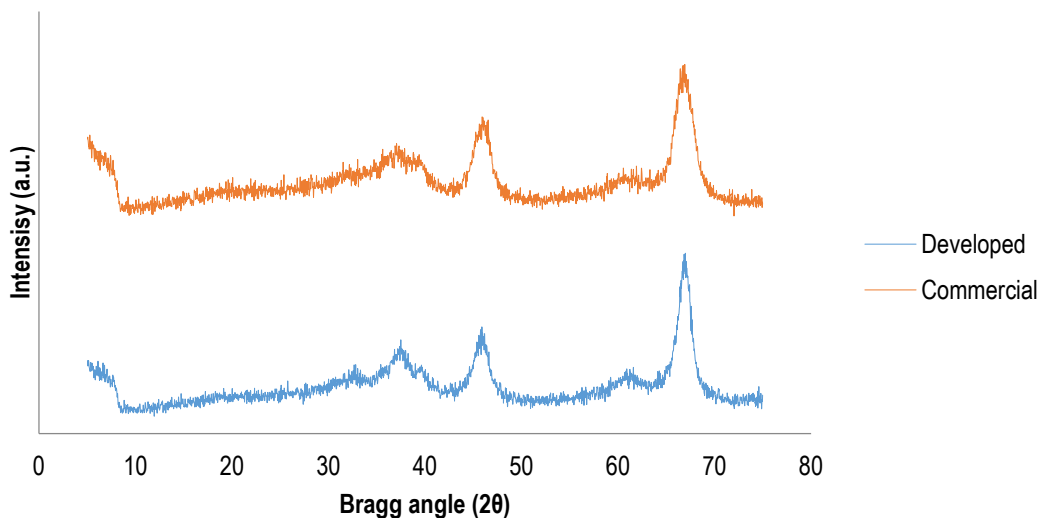


Figure 6: X-ray Diffraction Pattern of Gamma-Alumina

The chemical composition of the gamma-alumina obtained from the XRF analysis (Table 1) showed that the Al₂O₃ content was 85.02% with

4.76% SO₃ and 5.16% loss on ignition. This suggested that there were SO₃ and water still left in the structure.

Table 1: Chemical composition of products obtained (XRF analysis)

| Oxides | Al ₂ O ₃ | SiO ₂ | SO ₃ | LOI | Other Oxide |
|----------|--------------------------------|------------------|-----------------|------|-------------|
| 800°C/3h | 39.00 | ND* | 59.51 | ND** | 1.51 |
| 850°C/3h | 85.02 | ND* | 4.76 | 5.16 | 5.05 |

ND* Not detected ND** Not determined

The morphology of the gamma-alumina is presented in Figure 7. Each lump represents a macrostructure consisting of agglomerated particles with irregular particle shapes. Therefore, it could be deduced from the images that the gamma-alumina possessed a lumpy anhedral morphology (Salahudeen, 2014), this further

shows the amorphous nature of the gamma-alumina produced as already shown by the XRD result. The structural morphology was a flake-like euhedral morphology, which is in agreement with reported works (Aderemi and Hameed, 2011; Salahudeen *et al.*, 2014).

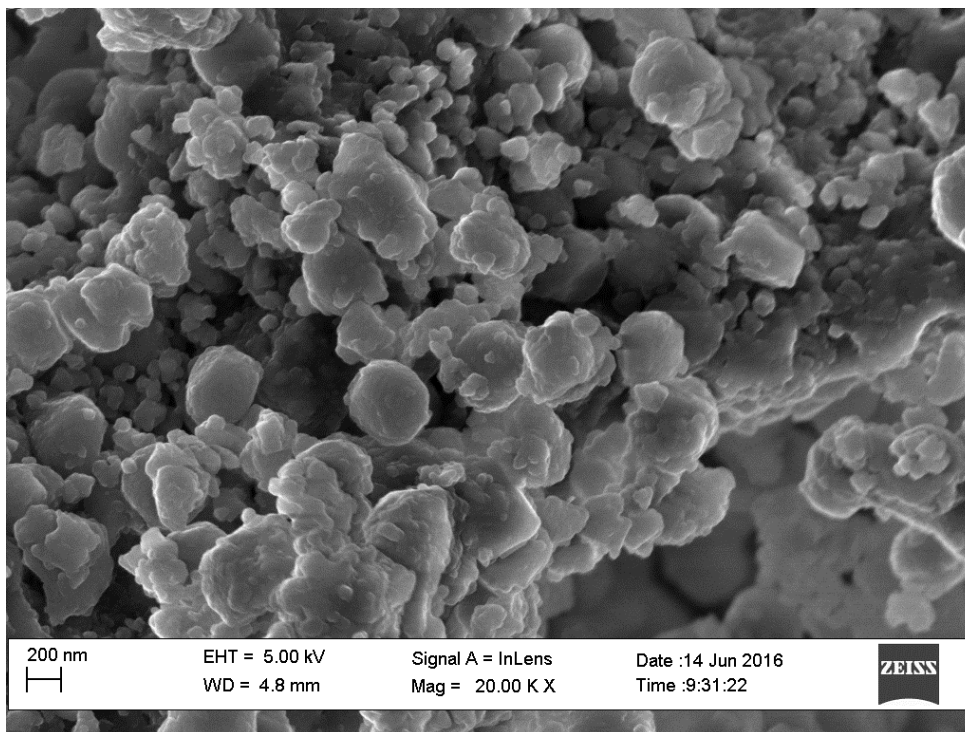


Figure 7: SEM Image of Gamma-Alumina Synthesized from Kankara Kaolin

CONCLUSION

It may be concluded from the investigations that gamma-alumina with large specific surface area ($166\text{m}^2/\text{g}$) was developed from Nigerian Kaolin, which may find application as catalyst support material. Thermal decomposition of ammonium alum at 800°C and below did not yield alumina rather crystalline aluminum sulfate was obtained.

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This studies shows that Kankara Kaolin is a promising material for the production of gamma-alumina.

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