THE STUDY OF THERMAL EFFECT ON THE SURFACE PROPERTIES OF GAMMA-ALUMINA SYNTHESIED FROM KANKARA KAOLIN.

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ABSTRACT

Gamma alumina is a good material for catalyst support and its surface properties is of great importance. In this study the gamma-alumina (γ-Al_2O_3) synthesized to be used as catalyst support for zeolite catalyst was obtained by calcination of ammonium alum an intermediate product prepared from kaolin which was sourced from Kankara, Katsina, Nigeria. The surface properties were determined using BET technique. BET specific surface area of gamma alumina produced at 825°C for soaking time of 3h was 120m²/g while at 850°C for soaking time of 4h the surface area was 140m²/g. The pore size and pore volume range from 15nm to 25nm and 0.5cm³/g to 0.8cm³/g respectively. The XRD pattern obtained at 825°C and 875°C calcination temperatures conformed to the standard pattern of gamma-alumina, having the strong peaks at Bragg angles of 67, 46, 39 and 38°. The SEM image showed clearly the plate-like structure of gamma alumina. Thus kankara kaolin is a promising material for the production of gamma alumina.

Keywords: *Gamma-alumina, kaolin, catalyst, support.*

1. INTRODUCTION

Alumina is widely used as basic material of catalytic support because of its high chemical inertness, strength and hardness. Gamma-alumina possesses excellent surface area owing to the small particle size, which results in high activity of the surface for a catalyst support [1]. Mesoporous alumina has excellent properties such as highly uniform channels, large surface area and narrow pore size distribution. It has been widely used as adsorbents, catalysts support, and other ceramic applications [2]. Alumina is an important material that can be prepared from bauxite or kaolin in several different phases. The most stable form of alumina is α-alumina, which is employed as a ceramic material. Other phases of alumina, known as transitional aluminas are widely used as catalysts, catalytic supports or adsorbents. Among the transitional aluminas, gamma-alumina is the most employed one for applications in catalysis and adsorption, because of its high surface area and good porosity parameters [3, 4]. Catalyst support is the material, usually a solid with high surface area to which catalyst is affixed. Typical supports include various kinds of carbon, alumina and silica. The reactivity of heterogeneous catalysts and nanomaterial-based catalysts occurs at the surface atoms. Consequently great efforts are made to maximize the surface area of a catalyst by distributing it over the support. Kaolin contains 33-39wt.% of alumina, therefore, it can be suitable material for production of gamma-alumina because of its abundance and having considerable content of alumina in kaolin structure. More so, the non-availability of commercial deposit of bauxite being alumina rich mineral in Nigeria led to use of kaolin as the starting material for this study. The two vital parameters in the production of gamma-alumina are the calcination temperature and soaking time. This paper sought to investigate the effect of these two parameters on the textural properties of the gamma-alumina produced. It has been reported that porous materials having a surface area value above 100m²/g is considered having a high surface area and is a potential material for catalyst support [5, 6, 7].

Single alum (Aluminium sulphate) was produced from Kankara kaolin which was associated with difficulties in filtering the crystals form and the process involved external heating source [8]. The difficulties of filtering the alum crystal forms fromed was overcome by the use of excess acid in the reaction medium and was

reported [9]. Partial dealumination techniques using novel method had been carried out for the synthesis of zeolite from Kankara kaolin as reported by previous studies [10]. In that studies the filtrate of the dealumination being alum was discarded as waste material. Gamma alumina was synthesized at a single temperature from Kankara kaolin [11]. Precipitation of Al (hydr)oxide with ammonia from acid-leachates of calcined kaolin [12].

Despite all the reported studies on Kankara kaolin, no work had been reported on the details surface parameter analysis as dependent on temperature and time being the key parameters in heat treatment reaction. As such, this study sough to establish the effect of temperature and soaking time on the thermal treatment of ammonium alum produced from Kankara kaolin through novel method (which does not involve external heating) on the surface parameters which is a unique property of a porous material.

The Brunauer-Emmett-Teller (BET) equation can be used to determine volume of gas required for monolayer coverage, for surface parameter determination of porous material, v_m for cases of multilayer adsorption. The surface area is calculated by multiplying by a monolayer packing constant for the adsorbed gas. For a porous material, the surface area determined experimentally depends on the size of the adsorbed molecule relative to the size of the pores. The specific surface area per unit mass S_M is given by:

$$S_M = \frac{N_A v_m A_m}{V_{mol} M_s} \tag{1}$$

where N_A is Avogadro's number, A_m is the area occupied by one adsorbate molecule (16.2×10^{-20}m^2 for N$_2$ and 19.5×10^{-20} m^2 for Kr), V_{mol} is the volume of mole of gas at STP of V_m, and M_s is the mass of the sample [13].

$$v_m = \frac{1}{S + I} \tag{2}$$

Where S is the slope   I is the intercept

2. MATERIALS AND METHODS

The starting material was kaolin sourced from Kankara town of Katsina state, Nigeria. A well-established method of wet beneficiation process [9 11 14] was employed to obtain purified kaolin. The beneficiated kaolin was calcined at 750°C for 2 hours to activate the kaolin as reported in previous studies [9, 14]. For a run of dealumination step of 50g metakaolin 185ml of water was added and stir to form metakaolin slurry, 167ml of 96wt% was added. After about 15mins 288ml of distilled water was added to

quench the reaction. The solution obtained during dealumination was filtered with high vacuum pump. Ammonium sulfate was used as the salting agent to crystallize the ammonium alum at 0°C for 6hrs. The ammonium alum crystals were filtered from the mother liquor and then dried at 250°C for 6hrs. The ammonium alum was calcined at a constant soaking time of 3 hrs for 825°C, 850°C and 875°C. And at constant calcination temperature of 850°C soaking time of 1, 2, 3, and 4 hours were varied. The specific surface area, average pore size and pore volume were determined using the Brunauer-Emmett-Teller (BET) technique by N$_2$ adsorption at -196°C using Tristar 3000 micrometrics equipment. at the University College London (UCL). The X-ray diffraction patterns were obtained using Empyreal, PANalytical diffractometer employing Cu Kα radiation (λ=0.154nm). at the National Geoscience Research Laboratories (NGRL), Kaduna. The Scanning Electron Microscopy (SEM) image of the gamma alumina at 850°C and soaking time of 3h was carried out. Minipal 4 machine was used to ascertain the chemical compositions of the gamma alumina through XRF analysis.

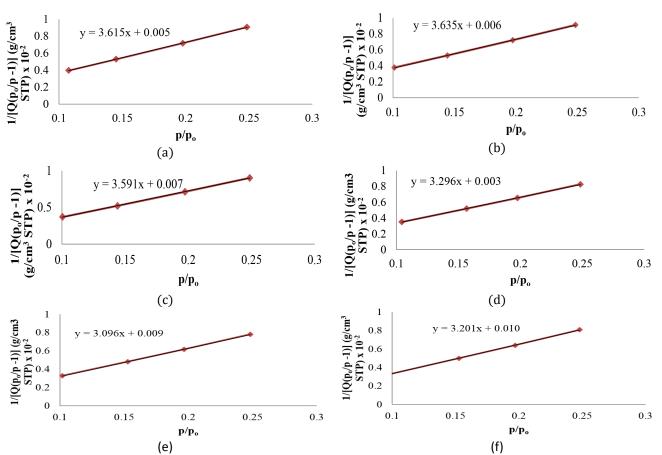*Table 1: Chemical composition of as-synthesized and commercial gamma alumina*

Oxides	Gamma-alumina	
	As-synthesized	Commercial
Al$_2$O$_3$	85.02	89.80
SO$_3$	4.76	2.54
SiO$_2$	ND*	0.03
Fe$_2$O$_3$	2.67	0.17
LOI	5.16	5.21
Other oxides	2.19	2.25

*ND: Not detected

3. RESULTS AND DISCUSSION

The gamma-alumina was lower in alumina content when compared with the commercial alumina by 4.78% as shown in Table 1. The silica content in the prepared gamma-alumina was below detection while it was detected in the commercial gamma-alumina. The Fe$_2$O$_3$ in the prepared gamma-alumina was higher in value when compared to the commercial alumina, this might be attributed to the source of the product being a natural mineral.
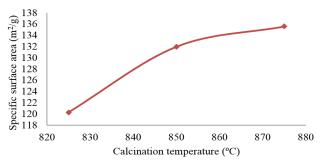
BET isothermal plots are as shown in Figure 1 (a – f), from the model equations obtained from the plot, the values of the slope and intercept were used to evaluate volume of gas (v$_m$) required for multilayer adsorption as shown in Equation 2 which was in conformity as reported previously [13]. The value of v$_m$ was inserted in Equation 1, to obtain the specific surface area of each of the gamma-alumina obtained at different temperatures and times.
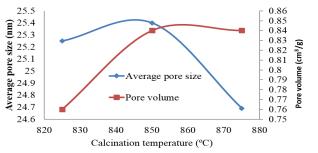
Figure 1: BET isothermal plots, (a) 825ºC for 3 hrs; (b) 850 ºC for 1 hr; (c) 850 ºC for 2 hrs; (d) 850 ºC for 3 hrs (e) 850 ºC for 4 hrs (f) 875 ºC for 3 hrs

At a constant soaking time of 3 hours, as the calcination temperature increased the specific surface area of the gamma-alumina also increased as shown in Figure 2. But the increase was more rapid between 825ºC and 850ºC, beyond which the increase in the specific surface area with respect to the calcination temperature became gradual. The highest specific surface area value of the gamma-alumina was obtained at a calcination temperature of 875ºC. The increase in the surface area as the thermal energy increases could be attributed to the liberation of the SO_3 from the collapse structure of crystalline aluminum sulfate to yield a transitional alumina.

Gradual increase in specific area was observed as the soaking time increased from 1 to 2 h as shown in Figure 3 at a constant calcination temperature of 850ºC. A more rapid steady increase was observed as the soaking time increased from 2 to 4 h. Increase in soaking time translate to increase in the thermal energy in the system as such more of the chemical bonds present in the intermediate product (alum) to liberate SO_3 gas and leaving the solid product, which is alumina. It could be infered from Figure 3, that for the first hour, most of the thermal energy in the form of heat was utilise for weaken of the existing chemical bonds, while one hour soaking time, pronouced liberation of the gaseous product occurred which translated to the increase in the specific surface area.

Figure 4 shows the effect of calcination temperature on the average pore diameter (size) and pore volume of the gamma-alumina developed. The optimum range of the average pore size was obtained between 840ºC and 850ºC. Beyond 850ºC the pore size began to decrease, this may be attributed to the collapse of larger pore particle to smaller pore particle possessing larger surface area. It is generally believed that the smaller the pore sizes of a porous material the higher its surface area. The pore volume of the gaama-alumina increased as the calcination temperature incresed from 825ºC to an optimum temperature of about 850ºC. Decrease in the pore volume was observed after 850 ºC as shown in Figure 4.

Figure 2: Variation of specific surface area with calcination temperature at constant soaking time of 3 h.

Figure 3: Variation of specific surface area with soaking time at constant constant temperature of 850ºC

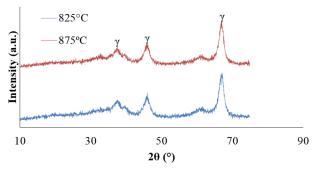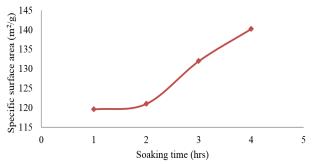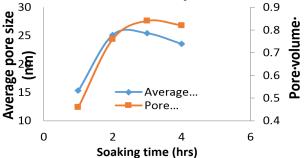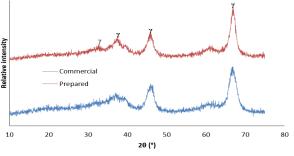*Figure 4: Variation of average pore size pore volume with calcination temperature at constant soaking time of 3h*

Figure 5: Variation of average pore size and pore volume with soaking time at constant temperature of 850ºC

Figure 6: XRD patterns of developed gamma-alumina

Figure 7: XRD pattern of commercial and prepared gamma-alumina
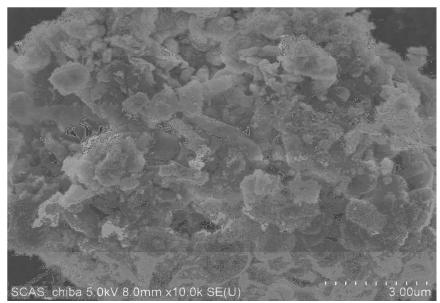

Figure 8: SEM image of gamma alumina synthezied fro Kankara kaolin

Soaking time of 3 hours was the optimum with respect to the pore volume of the gamma-alumina developed. The average pore size of the gamma-alumina developed increased with soaking time between 1 and 2 h as shown in Figure 5. The average pore size began to decrease but in a gradual manner beyond the soaking time of 2 h. The optimum soaking time range is between 2 and 3 h.

From the diffractogram obtained from XRD analysis, it showed that gamma-alumina was produced as shown in Figure 6. The pattern was similar to earlier studies reported [11 12].

A close similarity was observed between the XRD patterns of the developed gamma-alumina and the commercial gamma-alumina produced from bauxite (Figure 7). The standard peaks of gamma-alumina were present in the XRD pattern for both the commercial and developed gamma-alumina which occurred at the same position of Bragg angles.

The morphology of the gamma-alumina synthesized is as shown in Figure 8, it hexagonal shape associated with gamma-alumina was observed. The large surface area recorded must have been due to the clear platelet structure of γ-alumina (Figure 8) as distinct from the other transition aluminas.

4. CONCLUSION

The specific surface area of the gamma-alumina developed from Kankara kaolin was good enough for support materials for metal catalysts such as platinium. Specific surface area of above 100m²/g was obtained. The average pore size is large enough to prevent diffusion resistance of both reactants and products. Calcination temperature of 850ºC for 4 soaking time gave the highest surface area value. The optimum values of the average pore size and pore volume were obtained at calcination temperature of 850 ºC for 3 h soaking time. The gamma-alumina produced was similar to the commercial gamma-alumina.

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