



ALUMINA PHASE TRANSFORMATION FROM THERMAL DECOMPOSITION OF AMMONIUM ALUM SYNTHESIZED FROM KANKARA KAOLIN

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ABSTRACT

Thermal stability of transitional alumina phases produced from ammonium alum using Kankara kaolin as starting material was studied. Wet beneficiation method was employed to purify the starting material, after which it was calcined and dealuminated with sulphuric acid. The elemental composition, mineralogical, and physiological analyses were carried out using X-ray fluorescence (XRF), X-ray diffraction (XRD) and Brunauer-Emmett-Teller (BET) techniques respectively. The ammonium alum was thermally treated by varying the calcination temperature from 700 to 1200°C and varying the time of calcination from 1 to 4 h. The formation of gamma alumina began at calcination temperature of 825°C for calcination time of 3 h, which was found to be lower than reported works of 900°C. It was found to be stable at higher temperature of 1125°C, above which phase transformation to alpha alumina was observed. The observed wide range of thermal stability of the gamma alumina phase gives it good advantage to be used for high temperature applications, such as support for catalyst promoters. Alpha alumina phase formation began at 1150°C and was fully formed at 1200°C. BET specific surface area of 166 m²/g was obtained for the gamma alumina phase which was high enough for its application as support for catalyst, catalyst and adsorbent.

Keywords: Kaolin, ammonium alum, gamma alumina, alpha alumina

1. INTRODUCTION

Alumina is one of the major components used as catalyst support, which is especially important with regard to precious-metal catalysts [1]. High surface area aluminas with porous structure have gained importance due to their potential applications as catalysts and catalyst supports as well as adsorptive materials in separation processes. Transitional alumina especially gamma-alumina, has been a major catalytic support in automotive and petroleum industries, as well as in adsorption technology. Micro and nanocrystalline aluminas are commonly used for Al₂O₃-based ceramics [2]. Alumina remains a very important material used as a support for metal catalyst and zeolite catalysts which are used for processing petroleum, gas, petrochemicals and for other applications in the chemical processing industry [3, 4]. Alumina is one of the most used and advanced ceramic materials with applications ranging from spark plugs to catalyst materials [5]. Currently and for the foreseeable future, the most important types of nanoparticles which possess high specific surface area are simple oxides such as Al₂O₃, which are used in established applications [6], and for sapphire crystal growth [7]. Presently, alpha-alumina (α-Al₂O₃) has many

uses in traditional and advanced ceramics. It is an important substrate for the growth of the superconductors and semiconductors by molecular beam [8]. Alumina exists both in the transition or metastable and stable forms. Alpha (α) alumina is the only stable phase of alumina while the metastable phases include, chi (χ) phase, eta (η) phase, kappa (κ) phase, theta (θ) phase, delta (δ) phase, and gamma (γ) phase [6, 9]. Transitional aluminas may also be formed by pyrolysis of crystalline hydrates of aluminum salt such as sulphate, nitrate, ammonium alum and chloride [8]. Conventional methods for synthesizing α-Al₂O₃ involve solid state thermally driven transformations from the hydrates of aluminum oxide. The extent and total conversion to the corundum structure, which depends on the temperature and the time of thermal treatment occurs on heating above 1230°C [6]. Bauxite has been widely used in industry to produce alumina via the Bayer process, while nonbauxitic materials which are more abundant in many countries, have been processed in attempts to develop alternative technologies for alumina production. Examples of such nonbauxitic raw materials include: alunite, sillimanite, and alusite, kyanite, kaolin, mica and fly ash [10]. Due to the decline in bauxite reserve (both

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qualitatively and quantitatively) and the need to explore the use of locally sourced raw materials, various research works had been carried out and it has been shown that kaolin clay (which is next to bauxite in alumina content), can be used for alum production [11] and alumina [12]. Ammonium alum $(NH_4)_2 SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$, a white crystalline double sulphate of aluminum is used in water purification, vegetable glues, porcelain cements, natural deodorant and in fire proofing textiles. Ammonium alum $(NH_4Al(SO_4)_2 \cdot 12H_2O)$ is a potential starting material for preparation of high purity reactive alumina [13]. Several works that had been reported on Kankara kaolin include, single alum that had been produced from Kankara kaolin clay and met industrial requirements [14], preliminary investigation of alumina production from single alum [15], production of double alum from Kankara kaolin [11], extraction of alumina from ammonium alum [13, 16], gamma alumina from aluminum hydroxide prepared from Kankara kaolin [17].

Despite the works carried out on Kankara kaolin, no work has been done to investigate the transitional phases present during the thermal decomposition of ammonium alum prepared from Kankara kaolin. The phase transition temperature from the metastable to stable phase of alumina has not been investigated *via* thermal decomposition of ammonium alum prepared from Kankara kaolin which is thrust of this study. Thus, this study involves preparation of ammonium alum from the filtrate of dealumination of metakaolin. The effect of thermal treatment of the ammonium alum was closely studied as the calcination temperature and time were varied. The alumina phases transformation was also monitored as the thermal conditions were changed.

2. MATERIALS AND METHOD

2.1 Materials

The kaolinite clay was sourced from Kankara town of Katsina State, Nigeria. The reproducibility of the alum from the kaolin at Kankara deposit at different sampling

point had been proven. Industrial grade concentrated sulphuric acid, 96wt% (Johnson Solomon Chemicals, London) was used for the metakaolin dealumination. Ammonium sulphate Analar grade (BDH, Chemicals LTD, England) was used as the salting agent to obtain the ammonium alum crystals.

2.2 Methods

2.2.1 Kaolin purification and calcination

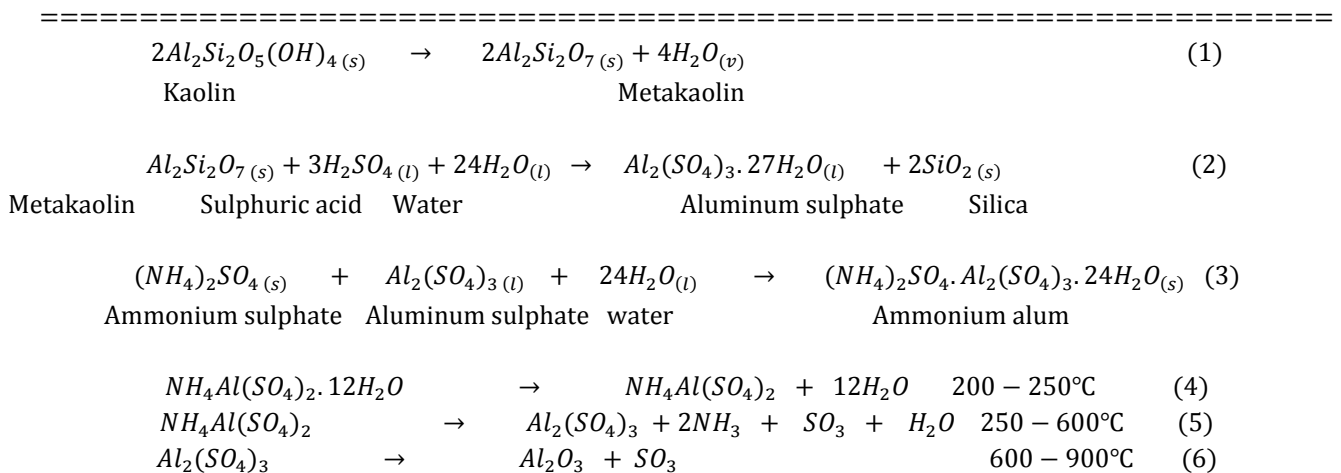
Raw kaolinite clay was purified using the wet beneficiation method [18, 19]. The dried beneficiated kaolin was thermally activated in an exposed electric element furnace (Nabertherm; 30–1400°C) at 750°C for calcination time of 2h to obtain metakaolin [20], the reactive phase of disordered kaolin as shown in Equation (1).

2.2.2 Dealumination

The alumina content of the amorphous metakaolin was leached in the reaction medium of 60wt% sulphuric acid using the novel method approach of dealumination [20, 21]. The dealumination mixture was then filtered using a high vacuum pump (Edwards ES50) filtration set-up. The products obtained was liquid aluminum sulphate and unreacted silica as residue. The reaction is represented in Equation (2).

2.2.3 Crystallization

Prior to crystallization, the mixture was diluted with 288 cm³ of distilled water, reducing the acidic nature of the mixture from 60wt% to 30wt%. This was done to enhance the ease of separation of the excess acid from the alum by taking advantage of the freezing point depression of sulphuric acid solutions on dilution. The filtrate was then cooled at temperature of 0°C for 6 h [22]. Ammonium sulphate was added to the filtrate as a salting agent to produce ammonium alum. Equation (3) shows the crystallization reaction.



2.2.4 Thermal Treatment

The wet ammonium alum was heated to 250°C for 4 h to expel the water of crystallization. The dried ammonium alum was calcined in the electric furnace at various temperature ranging from 700 to 1200°C and calcination time ranging from 1 to 4 h. Single alum decomposition begins at about 700°C and alpha alumina is usually obtained at about 1200°C, these findings informed the choice of the calcination temperatures for this study. Equations (4) to (6), show the step-wise thermal decomposition of the ammonium alum. Physicochemical characterization of the products was carried out *via* different techniques.

2.2.5 Characterization Techniques

The elemental composition (in oxide form) of the starting material, intermediate and final products were determined using the XRF machine (Minipal 4, PANalytical). XRD patterns were obtained using Empyrean, PANalytical diffractometer employing Cu K α radiation with $\lambda=0.154\text{nm}$, the range of the Bragg's angle for the analysis was from 4 to 75°, operated at continuous scanning, scanning speed of 5°/min, generator settings of 10 mA and 40 kV. The textural properties (surface area, pore size and pore volume), of the products were determined using BET method by N₂ adsorption at -196°C using Tristar 3000 Micrometrics equipment.

3. RESULTS AND DISCUSSION

3.1 X-ray Fluorescence

The chemical compositions of Kankara kaolin, beneficiated kaolin, metakaolin and the alumina products obtained at calcination temperature of 800°C are presented in Table 1. The alumina content increases

steadily with beneficiation, which is the aim of the process. silica content was observed to also increase numerically, this was not in the same proportion with the alumina. This implies that the materials removed during the beneficiation process were high in silica content, basically, montmorillonite, mica and quartz. The silica to alumina ratio calculated from the XRF analysis result shown in Table 1 for metakaolin was approximately 2, which agreed with the literature value [23]. It was also an indication that at the calcination temperature of 750°C for 2 h, complete conversion of kaolin to metakaolin had occurred. Thermal decomposition of aluminum sulphate had been reported to commence at 800°C [24]. The maximum alumina content obtained at this calcination temperature was 39% for 3 h calcination time, this low value and high value of the sulphate content of 59% gave an indication that the desired alumina phase was yet to be formed. Calcination time of 3 h, however was used for further thermal treatment, since within experimental error the average alumina content for 3 h and 4 h were same as observed in Table 1.

Steady increase of alumina content was observed from 700°C to 800°C, while a rapid increase was observed between 800°C to 850°C, while the same trend was noticed with the sulphate composition in the opposite direction as seen in Table 2.

This sudden increase was an indication of phase change of the material. As such the thermal decomposition of aluminum sulphate to alumina would have started between 800 and 850°C. The steady increase continued from 850°C to 1200°C with a steady decrease of the sulphate component as shown graphically in Figure 1. The assertion of phase change from aluminum sulphate to alumina was still subject to further verification.

Table 1: XRF analysis for the starting material, intermediate products and preliminary calcination

| Oxides | RK | BK | MK | 800°C | | | |
|---|-------|-------|-------|-------|-------|-------|-------|
| | | | | 1h | 2h | 3h | 4h |
| Al ₂ O ₃ | 33.41 | 37.80 | 42.06 | 30.40 | 29.40 | 39.00 | 38.90 |
| SiO ₂ | 45.10 | 47.48 | 49.90 | 2.20 | ND | ND | ND |
| SO ₃ | ND | ND | ND | 65.02 | 67.44 | 59.21 | 58.97 |
| Na ₂ O | 0.693 | 0.270 | 0.12 | 0.04 | 0.06 | 0.05 | 0.04 |
| K ₂ O | 1.49 | 0.544 | 0.427 | 0.01 | 0.09 | 0.07 | 0.15 |
| MgO | 0.016 | 0.05 | 0.038 | 0.36 | 0.40 | 0.18 | 0.19 |
| CaO | 0.343 | 0.325 | 0.289 | 0.68 | 1.80 | 0.12 | 0.40 |
| Fe ₂ O ₃ | 0.555 | 0.562 | 0.483 | 0.82 | 0.66 | 0.81 | 0.86 |
| Others | ND | ND | ND | 0.43 | 0.23 | 0.28 | 0.49 |
| SiO ₂ / Al ₂ O ₃ | 2.29 | 2.14 | 2.02 | NA | NA | NA | NA |

RK: Raw kaolin BK: Beneficiated kaolin MK: Metakaolin ND: Not detected NA: Not applicable

Table 2: Chemical composition of alumina calcined at higher temperature at 3h calcination time

| | 700°C | 750°C | 800°C | 850°C | 900°C | 950°C | 1000°C | 1050°C | 1100°C | 1150°C | 1200°C |
|--------------------------------|-------|-------|-------|-------|-------|-------|--------|--------|--------|--------|--------|
| Al ₂ O ₃ | 28.40 | 30.10 | 39.00 | 85.02 | 89.20 | 91.90 | 92.30 | 92.60 | 93.10 | 93.50 | 93.90 |
| SiO ₂ | 1.82 | ND | ND | ND | ND | 0.20 | 0.21 | 0.23 | 0.29 | 0.11 | 0.61 |
| SO ₃ | 68.55 | 68.94 | 59.21 | 7.76 | 3.55 | 0.90 | 0.80 | 0.74 | 0.30 | 0.20 | 0.17 |
| Na ₂ O | 0.08 | 0.03 | 0.05 | 0.04 | 0.03 | 0.10 | 0.11 | 0.10 | 0.12 | 0.16 | 0.12 |
| K ₂ O | 0.15 | 0.10 | 0.07 | 0.48 | 0.28 | 0.27 | 0.27 | 0.26 | 0.28 | 0.39 | 0.22 |
| MgO | 0.10 | 0.12 | 0.18 | 0.10 | 0.08 | 0.09 | 0.09 | 0.08 | 0.09 | 0.08 | 0.07 |
| CaO | 0.25 | 0.10 | 0.12 | 0.15 | 0.17 | 0.25 | 0.24 | 0.22 | 0.23 | 0.28 | 0.43 |
| Fe ₂ O ₃ | 0.58 | 0.60 | 0.81 | 2.67 | 2.87 | 3.43 | 2.89 | 2.62 | 2.65 | 1.82 | 1.44 |
| Others | 0.32 | 0.17 | 0.28 | 3.65 | 3.63 | 2.92 | 3.15 | 3.09 | 2.91 | 3.46 | 3.61 |

*ND: Not detected

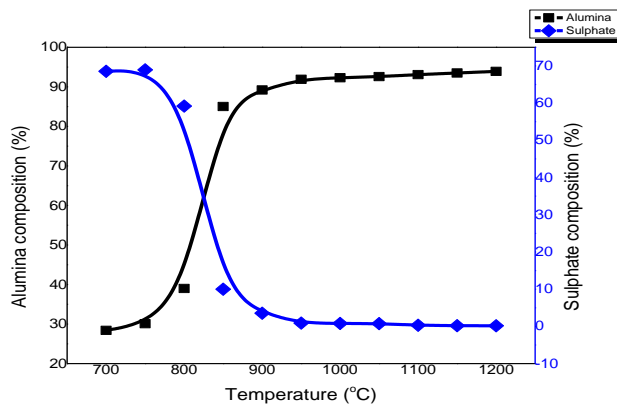


Figure 1: Variation in alumina and sulphur content with temperature of thermally treated ammonium alum

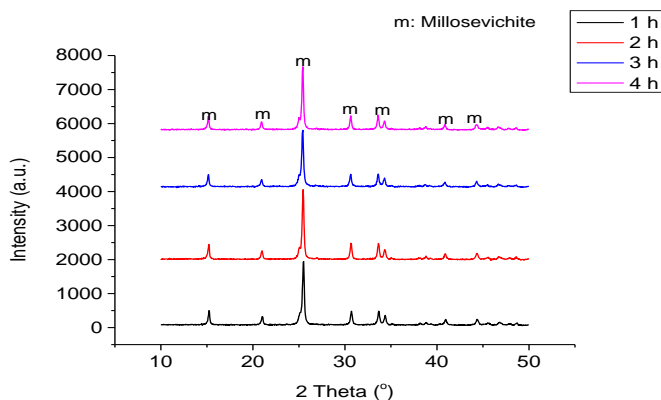


Figure 3: Ammonium alum calcined at 800°C for varying calcination time

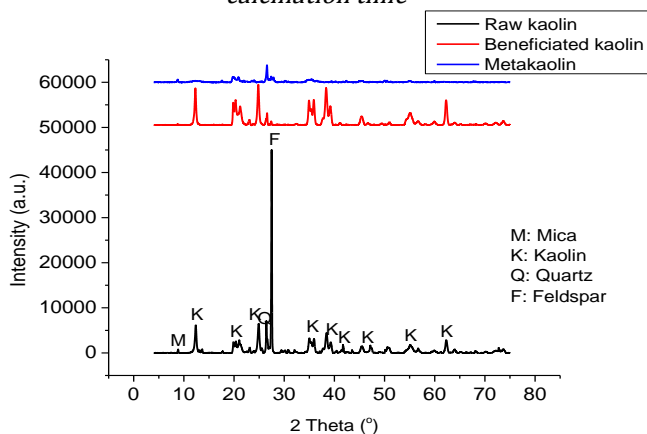


Figure 2: XRD pattern for Kankara kaolin, beneficiated and metakaolin

3.2 XRD Analysis

The XRD pattern of the raw Kankara kaolin was crystalline as evident by its high intensity counts as seen in Figure 2. The high peak at Bragg angle of about 27.5° was an impurity. It was found to be Microcline a potassium rich alkali feldspar. It was not strange because feldspar is one of the impurity that is associated with kaolin among several others. But it was soluble as was observed from the high reduction of the peak after wet beneficiation process, as shown in Figure 2. This was also confirmed by the decrease of the Na₂O and K₂O contents from the raw to the beneficiated kaolin, from the XRF analysis. From the XRD patterns shown in Figures 2, the characteristics peaks of kaolinite [18, 25] were found which occur at Bragg's angle of 12.35, 19.89, 20.38, 24.88, 35.02, 35.95, 36.06, 38.35, and 62.37°. The XRD pattern of metakaolin was observed to be amorphous, owing to the low intensity counts as well as broad peaks (Figure 2). The observation was as expected due to collapse of the structure by the OH group that is in-between the plate-like nature of the kaolin, which led to disorderly arrangement. But the fine quartz was still present as seen by its characteristic peak at Bragg's angle of 26.6°. Mica was as an impurity, found in the raw kaolin but also decreased after beneficiation of the raw kaolin.

No phase transformation occurred during the thermal treatment of the ammonium alum at 800°C for different calcination time, which was in agreement with the observation of the XRF analysis in Table 1. The product obtained was found to be Millosevichite mineral (anhydrous form of aluminum sulphate), which was crystalline as evident by the sharp peaks and high intensity counts, revealed by the XRD pattern as can be seen in Figure 3. The XRD patterns were similar depicting same product obtained.

Further calcination to 825°C confirmed the formation of gamma alumina phase, with its characteristic broad peaks at Bragg's angle of 37.7, 46.1 and 66.7°, which was amorphous. This observation showed that, the transformation of crystalline aluminum sulphate to gamma alumina began at 825°C as observed in Figure 4, which was lower than 900°C earlier reported [10, 17, 24]. Since gamma alumina is not the only transitional

phase of alumina, calcination at higher temperature was done to investigate the presence of other transitional phases of alumina, but from the XRD pattern which is one of the indicative measures to note other transitional phases did not reveal the formation of any other phase other than the gamma alumina. Among other transitional phases of alumina obtained from thermal transformation of aluminum hydroxide from bauxite [8], gamma alumina has shown good properties especially in terms of the specific surface area, as such it is the most widely used transitional phase of alumina for catalytic applications. Its stability over thermal treatment is of great importance and added advantage.

It was observed from the XRD pattern presented in Figure 4, that the gamma alumina phase was stable up to the calcination temperature of 1125°C which was higher than reported value of 1030°C [10]. New peaks were observed at temperature of 1150°C corresponding to Bragg's angle of 25.6, 35.2, 37.9, 43.4, 52.6, 57.6, 66.5 and 68.3°, which was fully developed at 1200°C. The XRD pattern at the calcination temperature of 1200°C showed a complete phase transformation into the alpha alumina phase [5, 6, 8, 25].

3.3 BET analysis

Specific surface area is very critical parameter of a porous material when used as a catalyst or catalyst support in which gamma alumina is mostly use. The textural properties (surface area, pore size and pore volume). The highest specific surface area was observed at calcination temperature of 850°C having value of 166 m²/g which was higher than previous reported value of gamma alumina synthesized from the same source but *via* different routes [13, 17]. The specific surface area was gradually being lost as the calcination temperature increases, as can be seen in Figure 5, this could be attributed to gradual internal structural change within the gamma alumina. The low value of the specific surface area of alpha alumina makes it unsuitable for application in catalysis, despite its high stability. The products obtained had relatively large pore sizes (20 nm-30 nm); resistance to mass flow in and out of the pores will be negligible when in use. Large pore volume was observed at calcination temperature of 850°C and 900°C (1.21cm³/g and 1.15cm³/g respectively), as presented in Figure 6. This indicated that diffusion resistance within the pore cavity will not pose a serious challenge.

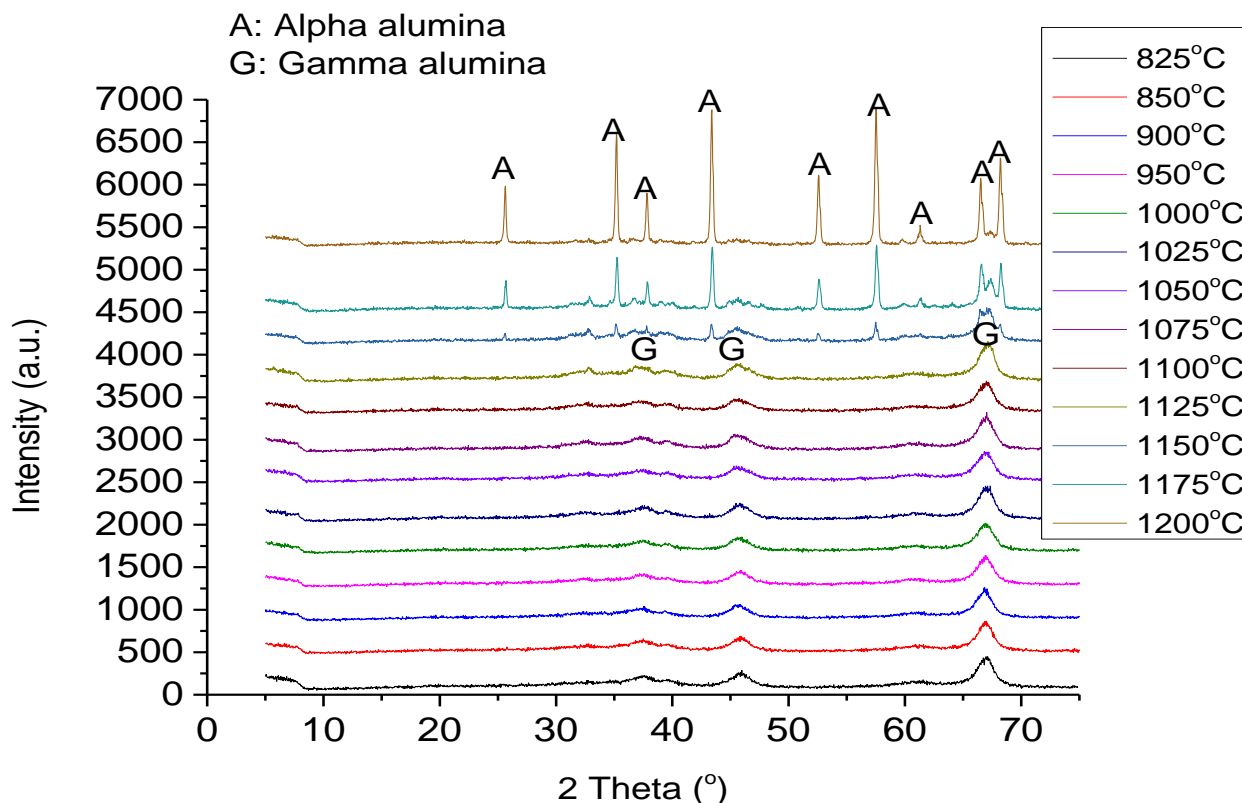


Figure 4: XRD patterns of alumina obtained at various calcination temperature

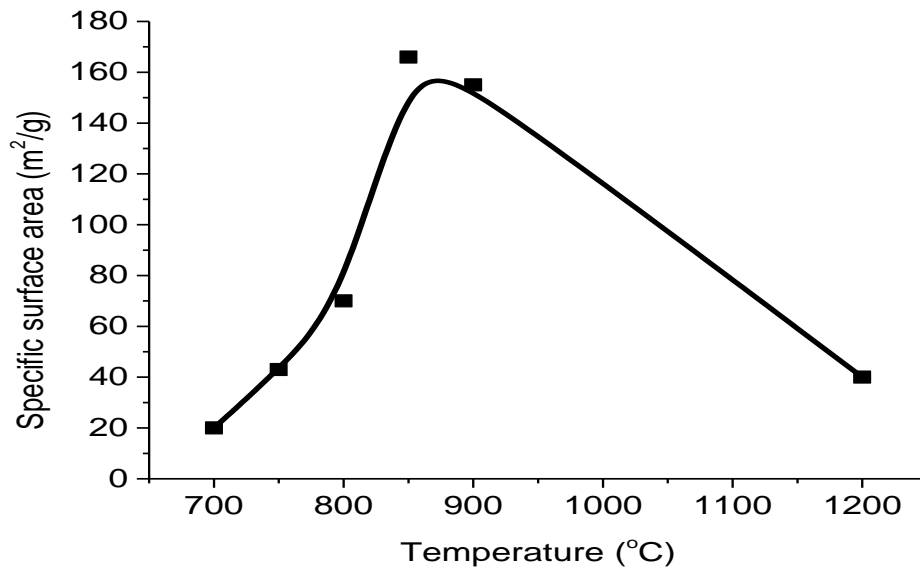


Figure 5: Alumina specific surface area variation with variation of temperature

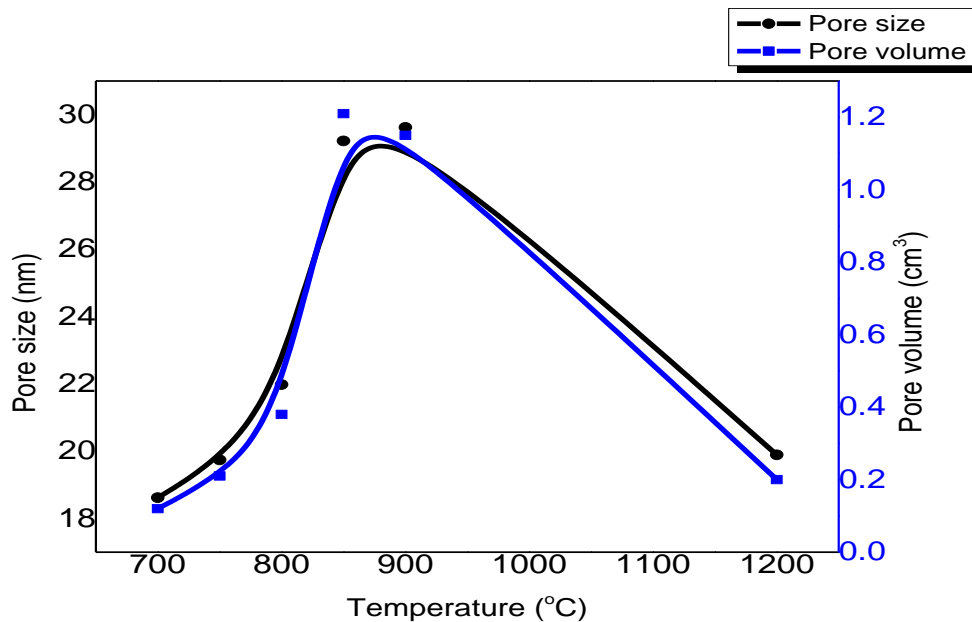


Figure 6: Effect of calcination temperature on alumina pore size and volume

4. CONCLUSION

Pure crystalline phase of aluminum sulphate was observed during calcination of ammonium alum prepared from Kankara kaolin at 800°C, irrespective of the calcination time. The formation of gamma alumina from thermal decomposition of ammonium alum began at 825°C. The best temperature for obtaining gamma alumina from this investigation was 850°C having the highest specific surface area of 166 m²/g. The transformation from gamma to alpha alumina occurs between the temperature ranges of 1125 -1175°C. Fully developed alpha alumina phase was developed at 1200°C. The highest alumina content was 94% found in the alpha alumina phase.

5. ACKNOWLEDGEMENT

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