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Sulfuric Acid Dealumination of Metakaolin as a Scalable Precursor Route for the Synthesis of High-Surface-Area γ-Alumina

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ABSTRACT

The growing demand for high-purity γ-alumina and the declining availability of high-grade bauxite have stimulated interest in alternative alumina feedstocks derived from abundant clay minerals. This study investigates the suitability of Ikere-Ekiti kaolin, Nigeria, as a low-cost precursor for the synthesis of high-surface-area γ-alumina through beneficiation, thermal activation, and sulfuric acid dealumination. Raw kaolin was subjected to mechanical scrubbing, particle size classification, and gravitational sedimentation to enhance alumina content and remove siliceous and metallic impurities. The beneficiated kaolin was thermally activated at temperatures between 550 and 850°C for 15 and 120 minutes to produce reactive metakaolin. Structural transformation was evaluated using X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR), while chemical evolution during beneficiation and dealumination was monitored using X-ray fluorescence (XRF). Complete dehydroxylation and amorphization of kaolinite were achieved at 550°C after 120 min, yielding highly reactive metakaolin suitable for acid extraction. Sulfuric acid leaching conducted at 3, 5, and 7 M H_2SO_4 resulted in dealumination efficiencies of 76.8%, 86.7%, and 89.6%, respectively. The progressive increase in residue Si/Al molar ratio from 1.0 to 17.0 confirmed selective aluminum dissolution and the formation of an aluminum-rich, silicon-depleted leachate favorable for γ-alumina precursor recovery. Beneficiation increased the Al_2O_3 content from 24.9 wt.% in the raw clay to 47.6 wt.% in the refined fraction, demonstrating the effectiveness of the upgrading strategy. Among the investigated conditions, 5 M H_2SO_4 provided the most favorable balance between dealumination efficiency, precursor purity, impurity control, and reagent economy. The results establish sulfuric acid dealumination of metakaolin as a technically viable and scalable route for producing high-purity γ-alumina from indigenous Nigerian kaolin resources, thereby promoting sustainable mineral beneficiation and value addition.

***Keywords*— Aluminum sulfate leachate, γ-Alumina, Metakaolin, Kaolin beneficiation and Sulfuric acid dealumination**

I. INTRODUCTION

Gamma-alumina is a high-surface-area nanomaterial with a characteristic spinel structure, widely employed as a tunable support to stabilize and disperse active metal species in heterogeneous catalysis [1]. The vast technological utility of aluminum oxide is rooted in its structural diversity. The material exists as a series of metastable polymorphs (γ, θ, η, δ, κ) each offering distinct physicochemical properties before culminating in the stable alpha-Al2O3 state [2]. Gamma-alumina is recognized as an exceptionally important phase in catalysis, particularly within the petroleum and automotive industries [1]. Its role as a high-surface-area catalyst support is critical for processes like hydrotreating and emission control due to its abundance of Lewis acid sites and chemical stability [3]. Furthermore, its structural integrity at high temperatures makes it a preferred material for thermal wear coatings and advanced composites in spacecraft. A key breakthrough in alumina research is the understanding of its phase stability at the nanoscale. While alpha-alumina is the most stable bulk phase, gamma-alumina becomes thermodynamically stable relative to alpha-alumina once it reaches a critical surface area [4].

The industrial production of commercial-grade alumina is historically dominated by the Bayer process. This hydrometallurgical route involves the alkaline digestion of bauxite (hydrated aluminum oxides) with sodium hydroxide to yield a concentrated sodium aluminate solution. Subsequent controlled hydrolysis precipitates aluminum hydroxide, which serves as the precursor for the final calcination stage to produce anhydrous alumina. The diminishing global supply of high-grade bauxite, coupled with a growing demand for aluminum, has forced the industry to look for new ways to produce alumina from low-grade minerals [5]. [6] synthesized gamma alumina from alum for catalytic application using yeast cell as pore forming agent. Gamma alumina had been synthesized from other low-cost sources such as Propane Dehydrogenation [7], kaolin [8].

Nigeria possesses extensive kaolinite reserves distributed across diverse geological terrains, yet the transformation of these deposits into high-value industrial commodities remains largely unrealized, representing a significant missed opportunity within the broader context of sustainable mineral resource utilization. The Ikere-Ekiti deposit in Ekiti State exemplifies this untapped potential, offering a regionally accessible aluminosilicate feedstock amenable to systematic upgrading and value chain integration. Realizing this potential, however, demands rigorous beneficiation, encompassing mechanical disaggregation, hydraulic classification, and particle size fractionation, to achieve selective removal of deleterious phases including quartz, iron oxyhydroxides, feldspars, and micaceous minerals, each of which can adversely compromise the structural reactivity, phase evolution behaviour, and ultimate purity of downstream alumina precursors.

Against this background, the present investigation provides a comprehensive characterization of the chemical composition, mineralogical assemblage, and structural transformations undergone by Ikere-Ekiti kaolin across successive stages of beneficiation, thermal activation to metakaolin, and selective sulfuric acid dealumination. Particular attention is directed toward explaining the mechanistic relationships between each processing stage and the material attributes that govern phase-selective γ-Al_2O_3 formation, with the overarching objective of establishing a scientifically grounded and resource-efficient processing pathway from indigenous raw clay to catalyst-grade alumina.

The study is specifically focused on establishing clear structure–property–processing relationships that underpin the controlled synthesis of γ-Al_2O_3 from this indigenous, low-cost aluminosilicate resource.

II. MATERIALS AND METHODS

A. Primary Beneficiation and Particle Classification

(i) Scrubbing and size fractionation

Raw kaolinite clay was collected from the Ikere-Ekiti deposit in Ekiti State, Nigeria. Compositional analysis by X-ray fluorescence (XRF) confirmed the major constituents as SiO2 (68.13 wt.%), Al2O3 (24.91 wt.%), Fe2O3 (1.74 wt.%), TiO2 (2.05 wt.%), and minor oxides (< 1 wt. % each). In order to ensure maximum disaggregation of the mineral clusters, the raw composite kaolin underwent an initial 24-hour hydration period in deionized water. This was followed by intensive mechanical attrition using a Crypto Peerless Agitation Mixer for 3 hours at 300 rpm. This stage is critical for liberating the kaolinite fraction from the robust mineral matrix.

A cut-off threshold of 63 µm was utilized to isolate the clay fraction from grit and accessory minerals like quartz and feldspar. Eliminating these coarser impurities is essential, as their presence can increase the Si/Al ratio [9]; [10]. The resulting slurry was wet-sieved, decanted, and subjected to a two-stage drying process; initial ambient air-drying followed by 24 hours in an HS 61A drying oven at 105 °C. The processed material was categorized as Scrubbed Kaolin (SK).

(ii) Refined sedimentation via gravitational flux

To enhance the purity of the aluminosilicate precursor, the SK fraction underwent secondary refinement via controlled gravitational sedimentation. This process utilized the principles of Stokes' Law to differentiate particles based on their terminal settling velocities within a fluid column according to Equation 1:

$$t = \frac{18\eta h}{d^2 g(\rho - \rho_o)} \quad (1)$$

Where t represents settling time, η is the dynamic viscosity of the aqueous phase, ρ and ρo are the densities of the particle and solvent respectively, and g is gravitational acceleration.

The raw clay (SK) was dispersed in deionized water at a 1:4 (w/w) ratio. To ensure complete particle deagglomeration, sodium hexametaphosphate (NaHMP, 1.5 wt. %) was incorporated as a deflocculant [10]. Following 10 minutes of vigorous mechanical agitation, the suspension was diluted to a total volume of 1,000 mL (equivalent to a 30 cm hydraulic head). Aiming for a cut-off diameter of < 2 µm (ASTM C 837), a 24-hour sedimentation period was determined. The resulting fine-fraction supernatant was siphoned, dehydrated at 60 °C, and categorized as Refined Kaolin (RK). The chemical evolution and phase purity across the scrubbing and refinement stages were rigorously monitored via XRF, XRD, SEM/EDX, and FTIR spectroscopy

B. Thermal Activation (Metakaolinization)

Metakaolin (Al2O3.2(SiO2) represents the anhydrous, amorphous transition phase derived from the calcination of kaolinite and serves as the essential reactive precursor for gamma alumina production. In its native state, kaolinite consists of stable Si-O tetrahedral and Al-O octahedral layers that exhibit negligible chemical reactivity [11]. Controlled thermal dehydroxylation is necessary to collapse this ordered crystalline lattice, generating a disordered state with significantly increased surface energy and reactivity, as represented by Equation 2.

$$Al_2Si_2O_5(OH)_4 \xrightarrow{\Delta} Al_2\,Si_2O_7 + 2H_2O \quad (2)$$

Clay minerals are sensitive to local mineral impurities and degree of crystallinity [1], therefore, four discrete temperatures were evaluated; 550, 650, 750, and 850 °C. This range was strategically mapped to the thermochemical evolution of the mineral. The kinetic impact of thermal exposure was assessed using residence times of 15 and 120 minutes. All treatments were conducted in a standard air atmosphere, as the dehydroxylation of aluminosilicates is a non-reductive oxidative process.

Beneficiated kaolin (BK) was distributed into alumina crucibles at a uniform depth to prevent local thermal gradients. Calcination was performed in an SXL GALLENKAMP muffle furnace with a linear ramp rate of 10 °C min^{-1}. Following the prescribed dwell time, the resulting metakaolin (MK) was cooled within the sealed furnace and transferred to a desiccator to preserve its anhydrous state.

C. Metakaolin Dealumination

Dealumination was performed to produce an alumina-rich leached solution with an adjusted Al/Si molar

ratio. This modification is critical for the synthesis of high-purity gamma alumina. Based on XRD analysis that indicated maximum amorphization, the sample calcined at 550 °C for 120 minutes was selected for leaching.

The chemical extraction was executed using sulfuric acid (H2SO4) at concentrations of 3 M, 5 M, and 7 M, maintaining a constant solid-to-liquid mass ratio of 1:5. The leaching was conducted at a steady 80 °C within a reflux-stabilized Pyrex assembly to prevent evaporative loss, with continuous magnetic stirring to ensure uniform acid-solid contact for 120 minutes. Thereafter, the suspensions were allowed to reach ambient temperature before solid-liquid separation via centrifugation

III. RESULTS

A. Chemical Characterization of Ikere-Ekiti Kaolin and Assessment of Precursor Suitability for γ-Al_2O_3 Synthesis

The chemical composition of the Ikere-Ekiti kaolin across the three processing stages; Sourced, Scrubbed, and Refined, as determined by X-ray fluorescence (XRF) spectrometry is presented in Table 1. The discussion that follows focuses primarily on the Sourced material as a baseline characterization of the raw clay feedstock, before evaluating the compositional evolution induced by beneficiation and acid treatment in the context of precursor suitability for high-purity γ-Al_2O_3 synthesis.

(a) Primary oxide composition of the sourced kaolin

The Sourced Ikere-Ekiti kaolin is dominated by two major oxide constituents; SiO_2 at 68.135 wt. % and Al_2O_3 at 24.913 wt. %, which together account for approximately 93.0 wt. % of the total chemical composition. This binary dominance is characteristic of naturally occurring kaolinite-bearing clays, in which the aluminosilicate mineral kaolinite ($Al_2Si_2O_5(OH)_4$) constitutes the principal phase, with the theoretical SiO_2/Al_2O_3 molar ratio for pure kaolinite being 2.0. The measured SiO_2/Al_2O_3 mass ratio in the Sourced material is approximately 2.74, which is notably higher than the stoichiometric kaolinite ratio of 1.18 on a mass basis. This excess silica is attributable to the co-presence of free quartz (SiO_2) and/or other siliceous gangue minerals, including alkali feldspars and amorphous silica, within the raw clay matrix, consistent with the geological setting of sedimentary kaolin deposits in southwestern Nigeria where quartz contamination is commonly reported. The relatively modest Al_2O_3 content of 24.913 wt. % in the Sourced material, compared to the theoretical value of 39.5 wt. % for pure kaolinite, further corroborates the diluting effect of siliceous gangue and confirms that the raw clay requires significant upgrading before it can serve as a viable precursor for alumina synthesis.

From the perspective of γ-Al_2O_3 synthesis, the Al_2O_3 content of the Sourced kaolin is insufficient in its raw state to guarantee phase-pure alumina formation upon acid dealumination and subsequent calcination. At 24.9 wt. % Al_2O_3, the aluminum concentration in the leachate generated by H_2SO_4 treatment would be comparatively dilute, reducing process efficiency and increasing the acid consumption per unit mass of recoverable aluminum. Furthermore, the high SiO_2 content of 68.1 wt. presents the risk of substantial silicon co-dissolution at higher acid concentrations, introducing siliceous contamination into the aluminum sulfate leachate that would ultimately manifest as amorphous SiO_2 inclusions or mullite ($3Al_2O_3•2SiO_2$) impurities in the calcined alumina product. These considerations collectively establish that beneficiation of the sourced kaolin is not merely advisable but chemically necessary prior to dealumination.

Table 1: Chemical composition of sourced, scrubbed and refined Ikere Kaolin samples

Oxides	Sourced	Scrubbed	Refined
SiO_2	68.135	55.200	50.297
Al_2O_3	24.913	37.277	47.628
Cr_2O_3	0.012	0.022	0.010
MnO	0.060	0.044	0.063
Fe_2O_3	1.748	2.928	1.628
CO_3O_4	0.002	0.006	0.001
NiO	0.010	0.006	0.019
CuO	0.081	0.040	0.059
Nb_2O_3	0.024	0.019	0.024
MoO_3	0.005	0.002	0.005
WO_3	0.509	0.509	0.000
P_2O_5	0.127	0.233	0.288
SO_3	0.509	0.193	0.509
CaO	0.127	0.290	0.288
MgO	0.000	0.000	0.000
BaO	0.097	0.467	0.312
Ta_2O_5	0.164	0.234	0.365
V_2O_5	0.152	0.144	0.134
TiO_2	2.057	0.028	1.014
ZnO	2.057	1.891	1.014
Ag_2O	0.028	0.009	0.025
Cl	0.022	0.009	0.021
ZrO_2	0.414	0.248	0.188
SnO_2	0.007	0.000	0.000
K_2O	0.097	0.312	0.467

(b) Iron oxide content and its significance

The Fe_2O_3 content of the Sourced kaolin is 1.748 wt%, representing the most significant impurity oxide after SiO_2 and Al_2O_3. Iron contamination in kaolin-derived alumina precursors is a well-documented challenge, given the tendency of Fe^{3+} to isomorphously substitute for Al^{3+} in the γ-Al_2O_3 spinel-type defect structure owing to the comparable ionic radii of Fe^{3+} (0.645 Å) and Al^{3+} (0.535 Å) in octahedral coordination [12]; [13]; [14]. Such substitution introduces paramagnetic centres into the alumina lattice, imparts undesirable reddish-brown colouration to the product, reduces the density of catalytically active surface acid sites, and may promote undesired redox reactions in catalytic applications. For catalyst support applications, particularly in hydrotreating and reforming where strict metal specifications apply, iron contamination at the level of 1.748 wt. % in the precursor feedstock is a critical concern that must be substantially reduced through beneficiation before the material can be considered suitable. The iron-bearing phases in Ikere-Ekiti kaolin are likely goethite (α-FeOOH) and hematite (α-Fe_2O_3), which are commonly associated with tropical lateritic weathering profiles in Ekiti State and are amenable to selective removal by reductive bleaching with sodium dithionite or by magnetic separation [15]

(c) Titanium dioxide content and its significance

TiO_2 is present at 2.057 wt. % in the Sourced kaolin, a concentration that is elevated relative to many commercial kaolin deposits and reflects the geological association of the Ikere-Ekiti clay with titaniferous accessory minerals, most probably anatase (TiO_2) and ilmenite ($FeTiO_3$), which are characteristic of weathered basement complex lithologies in Nigeria [16]. In the context of γ-Al_2O_3 synthesis, TiO_2 at this level is a significant concern for two reasons. First, upon calcination of the alumina precursor, residual titanium would crystallize as anatase or rutile, introducing detectable impurity reflections in the XRD pattern and compromising phase purity. Second, TiO_2 has a markedly different acid dissolution behaviour from Al_2O_3 under H_2SO_4 conditions, at moderate concentrations and temperatures, titanyl sulfate ($TiOSO_4$) forms as a soluble species but hydrolyses readily upon dilution or heating to reprecipitate $TiO_2 \bullet nH_2O$, creating the risk of titanium re-entrainment in the recovered aluminum sulfate intermediate. The dramatic reduction of TiO_2 to 0.028 wt% in the Scrubbed stage, followed by a partial re-emergence to 1.014 wt. % in the Refined stage, is consistent with exactly this hydrolytic re-precipitation mechanism and underscores the need for a dedicated titanium removal step, such as controlled hydrolysis at pH 1.5–2.0 or complexation with H_2O_2, in the process flowsheet.

(d) Zinc oxide content and its significance

ZnO is recorded at 2.057 wt. % in the Sourced material, a concentration that is unusually high for a naturally occurring kaolin clay and warrants specific comment. Natural kaolinite typically contains trace

ZnO (< 0.05 wt. %), and the elevated zinc level in Ikere-Ekiti kaolin may reflect either localized geochemical enrichment from sphalerite (ZnS)-bearing basement rocks in the Ekiti region, or anthropogenic contamination from agricultural or industrial activities in the vicinity of the deposit. Irrespective of origin, ZnO at 2.057 wt. % in the precursor clay is a substantive impurity: zinc cations occupy tetrahedral sites within the γ-Al_2O_3 spinel-like framework, modifying the surface Lewis acid site distribution and potentially altering the catalytic selectivity of the product in ways that are difficult to predict or control without precise stoichiometric management [17]. For high-purity γ-Al_2O_3 synthesis, the zinc content must be substantially reduced. Given the moderate solubility of ZnO in dilute H_2SO_4, zinc is expected to co-dissolve during dealumination and partition into the aluminum sulfate leachate; selective removal from the leachate by sulfide precipitation (as ZnS) or solvent extraction with organophosphate reagents would be required to prevent zinc carryover into the calcined alumina

(e) ZrO_2, V_2O_5, Ta_2O_5, and other trace oxides

Several additional minor and trace oxide constituents are detected in the Sourced kaolin, each with distinct implications for downstream processing. ZrO_2 (0.414 wt. %) is notable as zirconia is highly refractory and virtually insoluble in dilute to moderate H_2SO_4, meaning it will concentrate in the leach residue rather than contaminating the aluminum sulfate leachate; however, its presence in the residue may affect the valorization potential of that stream as a silica co-product. V_2O_5 (0.152 wt. %) is of environmental and regulatory concern in catalyst applications, as vanadium species are known to exhibit cytotoxicity and are subject to restrictions in food-contact and pharmaceutical catalytic processes [18]. Ta_2O_5 (0.164 wt%), although present at low levels, is a high-value critical mineral whose enrichment to 0.365 wt. % in the Refined stage suggests that systematic recovery from the process streams could contribute to the economic viability of the overall operation, a consideration of increasing relevance given global supply chain pressures on tantalum. P_2O_5 (0.127 wt%) is significant as phosphate ions are known to strongly adsorb onto alumina surfaces, blocking active hydroxyl sites and reducing the effective surface acidity of the γ-Al_2O_3 product; its progressive increase across processing stages (0.127 → 0.233 → 0.288 wt%) suggests accumulation through preferential dissolution of phosphate-bearing accessory phases and warrants monitoring.

(f) Alkali and alkaline earth oxides

The Sourced kaolin contains modest levels of K_2O (0.097 wt.%), CaO (0.127 wt. %), and BaO (0.097 wt. %), with MgO below the detection limit. These alkali and alkaline earth cations are commonly associated with feldspar inclusions (for K and Ca) and barite (for Ba) in kaolin deposits and are generally mobilized under acid leaching conditions. Their low levels in the Sourced material do not pose immediate concerns

for γ-Al_2O_3 purity, though the progressive enrichment of K_2O to 0.467 wt. % and BaO to 0.467 wt. % in the Scrubbed and Refined stages respectively suggests selective concentration during processing that should be monitored. Alkali metals incorporated into the alumina lattice are known to suppress surface acidity by neutralizing Brønsted acid sites, while calcium and barium can form sulfate precipitates ($CaSO_4$, $BaSO_4$) of low solubility during the H_2SO_4 leaching stage, potentially co-precipitating with the aluminum sulfate product and compromising its purity.

(g) Absence of MgO and very low concentrations of NiO, CuO, and Co_3O_4

The complete absence of MgO across all three processing stages is noteworthy, as it excludes smectite and chlorite contamination, clay minerals commonly associated with kaolin of hydrothermal origin, and supports the interpretation of Ikere-Ekiti kaolin as a sedimentary, weathering-derived deposit of relatively homogeneous mineralogy. The trace levels of NiO (0.010 wt. %), CuO (0.081 wt. %), and Co_3O_4 (0.002 wt. %) in the Sourced material are below the threshold of concern for most catalytic and adsorption applications, though in fine chemical or pharmaceutical alumina applications their presence would require verification against applicable purity standards.

Considered in totality, the chemical composition of the Sourced Ikere-Ekiti kaolin presents a mixed but ultimately encouraging picture for γ-Al_2O_3 synthesis. On the positive side, the combined SiO_2 and Al_2O_3 content of 93.0 wt. % confirms that the material is mineralogically dominated by kaolinitic phases with limited contamination from carbonate or organic matter. The absence of MgO and very low levels of NiO, Co_3O_4, and heavy metal oxides reduce the remediation burden for most catalytic applications. The Al_2O_3 content, while low at 24.9 wt. % in the raw state, responds well to beneficiation, rising to 37.3 wt. % after scrubbing and 47.6 wt. % after refining, confirming that the deposit is amenable to meaningful alumina upgrading through the proposed processing sequence.

On the challenging side, the elevated SiO_2 (68.1 wt. %), Fe_2O_3 (1.748 wt. %), TiO_2 (2.057 wt. %), and ZnO (2.057 wt%) in the Sourced material collectively define a four-component impurity problem that must be systematically addressed through beneficiation, selective leaching chemistry, and leachate purification before catalyst-grade γ-Al_2O_3 can be reliably obtained. The data confirm that the Sourced kaolin, in its unprocessed state, is not directly suitable for high-purity γ-Al_2O_3 synthesis; however, the substantial compositional improvement demonstrated across the Scrubbed and Refined stages establishes a technically credible processing pathway from raw clay to a precursor with Al_2O_3 approaching 48 wt. % and progressively diminishing impurity burdens. Realizing the full potential of this deposit for γ-Al_2O_3 production will require an integrated process strategy combining optimized beneficiation, controlled

H_2SO_4 dealumination, targeted leachate purification for iron and titanium removal, and a two-stage thermal decomposition protocol, a framework whose scientific basis is developed in the subsequent sections of this work.

B. X-Ray Diffraction Analysis of Metakaolin

The XRD patterns of calcined Ikere kaolin at different temperatures are presented in Figure 1. It largely showed the disappearance of kaolinite peaks across all temperatures safe sample treated at 550^0C for 15 minutes which showed kaolinite peaks at 2-theta degree 12.41 and 24.93. These peaks indicate incomplete transformation of all kaolinite phases at that temperature and time. The XRD pattern also showed diffused big humps between 20^o and 30^o 2θ which suggests transformation to amorphous materials (metakaolin) obtained as a result of the thermal treatment of the kaolin [19].

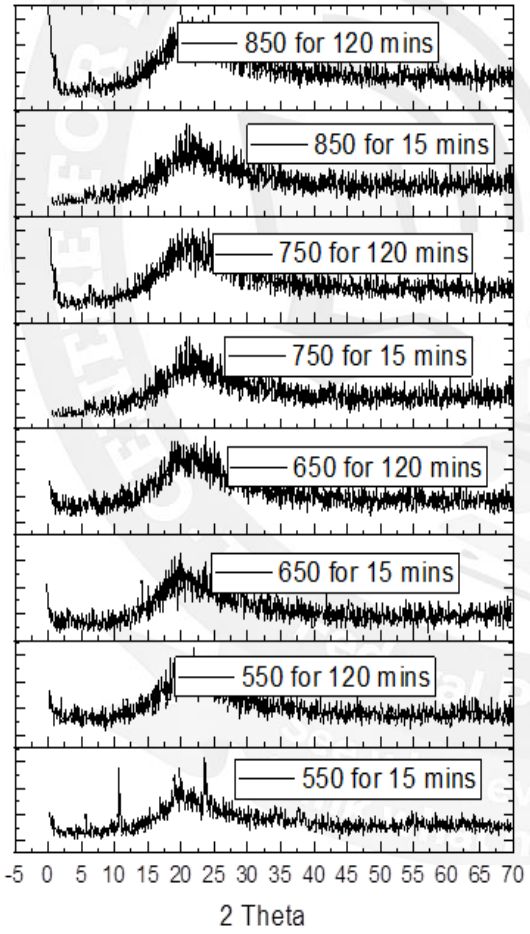

Figure 1: XRD of metakaolin at 550, 650, 750 and 850°C for 15 and 120 minutes

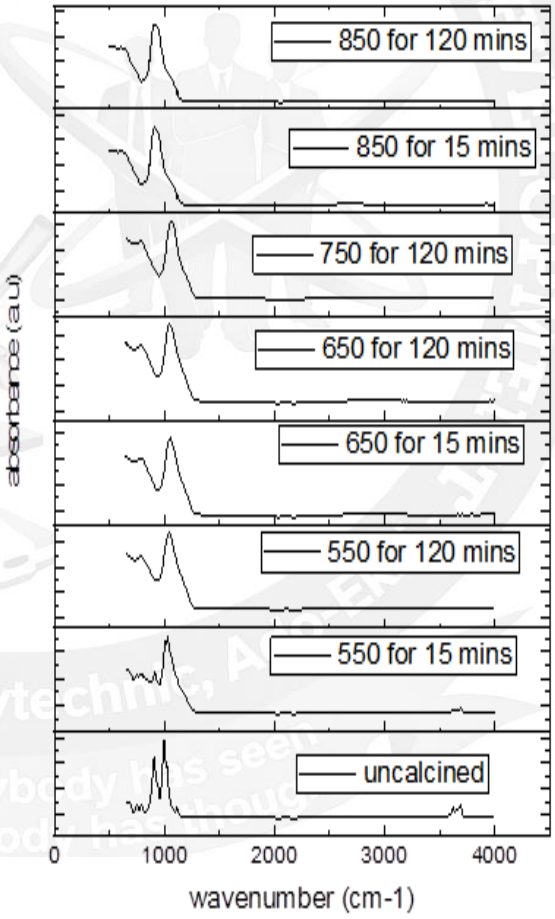

Figure 2: FTIR of metakaolin at 550, 650, 750 and 850°C for 15 and 120 minutes

C. FTIR analysis of the metakaolinized samples

Figure 2 (a-h) shows the FTIR spectra of Ikere kaolin calcined at varied temperatures and durations. The raw kaolin displayed characteristic hydroxyl stretching bands at 3697 cm^{-1} (inner-surface OH) and 3622 cm^{-1} (inner OH), confirming its structural hydroxylation. The main infrared bands in all the IR spectra of the calcined kaolin are found at 1000-1050 (Figure 2 a-e) which represent the silica peak (stretching vibrations of Si-O) due to metakaolinization [19], 715-738 cm-1 due to Si-O from quartz and bands at 1010-1047 cm-1 represent amorphous aluminosilicate stretching vibrations due to metakaolinization [20]. Sample heated at 550oC for 15 minutes retained Al-OH stretching at 3619.25cm-1 which signify an incomplete dehydroxylation. This agrees with XRD result that showed kaolinite peaks at 2 theta value 12.41 and 24.93. However, these bands disappeared progressively with increasing temperature and duration, confirming conversion to metakaolin.

D. Chemical Composition of Acid-Leached Metakaolin Residues and Dealumination Efficiency

The XRF compositional data of the metakaolin and its acid-leached residues at 3 M, 5 M, and 7 M H_2SO_4, presented in Table 3, provide a comprehensive and quantitative account of the selective dissolution behaviour of the constituent phases during sulfuric acid dealumination. The most immediately striking feature of the dataset is the dramatic and progressive depletion of Al_2O_3 from 41.061 wt% in the untreated metakaolin to 9.543 wt. % at 3 M, 5.452 wt. % at 5 M, and 4.264 wt% at 7 M H_2SO_4, occurring in direct correspondence with a systematic enrichment of SiO_2 from 53.137 wt% to 75.027, 81.035, and 85.495 wt% respectively. This inverse Al_2O_3–SiO_2 relationship across the leaching series constitutes the definitive chemical signature of selective dealumination. Sulfuric acid progressively dissolves aluminum from the disordered metakaolin framework as soluble $Al_2(SO_4)_3$, while the silica backbone, being largely resistant to acid attack at the concentrations and temperatures employed, remains in the solid residue and consequently dominates the residue composition with increasing acid strength. The progressive nature of this enrichment across three acid concentrations confirms that dealumination in this system is a concentration-dependent, surface-reaction-controlled process consistent with the proton-mediated cleavage of Al-O-Si linkages in the amorphous metakaolin network, as previously established for analogous aluminosilicate systems treated with mineral acids [21]; [22].

It is important to note that the compositional values in Table 3 represent the solid leach residue, not the leachate, and therefore reflect what remains undissolved after each leaching treatment. The increasing SiO_2 enrichment is thus not a consequence of silica dissolution but of matrix dilution, as aluminum is extracted into solution, the residual solid becomes progressively silica-dominated, and the reported wt. %

values of all other components are recalculated on the basis of a shrinking, silica-enriched matrix. This distinction is critical for the correct interpretation of the impurity oxide trends discussed in subsequent subsections.

E. Quantitative assessment of the degree of dealumination

The degree of dealumination (DA) at each acid concentration can be estimated from the Al_2O_3 mass balance between the metakaolin feed and the leached residue. Assuming a fixed initial mass of metakaolin and accounting for the mass loss during leaching, the Al_2O_3 content decreased from 41.061 wt% in the metakaolin to 9.543, 5.452, and 4.264 wt. % at 3 M, 5 M, and 7 M H_2SO_4 respectively. On a relative basis, these residue values correspond to approximate dealumination efficiencies of 76.8% at 3 M, 86.7% at 5 M, and 89.6% at 7 M H_2SO_4, calculated as the percentage reduction in Al_2O_3 content of the solid residue relative to the metakaolin feed. These values indicate that even at the lowest acid concentration studied (3 M), the majority of aluminum was successfully extracted from the metakaolin framework, and that increasing acid concentration from 5 M to 7 M yielded only a marginal additional improvement of approximately 3 percentage points in dealumination efficiency. This diminishing return at higher acid concentration is characteristic of a system approaching dissolution equilibrium, where the remaining aluminum is structurally incorporated within increasingly silica-encapsulated domains that become progressively less accessible to acid attack as the leaching reaction proceeds and a passivating silica gel layer accumulates on the particle surface.

Therefore, for γ-Al_2O_3 synthesis, the high dealumination efficiency, particularly at 5 M and 7 M H_2SO_4, is highly favourable, as it implies that the aluminum sulfate leachate generated under these conditions carries the vast majority of the available aluminum from the metakaolin feed, maximizing the yield of recoverable precursor for subsequent crystallization and thermal decomposition to γ-Al_2O_3. The residual Al_2O_3 content of 4.264–5.452 wt. % in the leached solids at 5–7 M represents the irreducible aluminum fraction locked within the silica-rich residue, which is not practically recoverable under the conditions studied without resorting to more aggressive treatment.

F. The Si/Al molar ratio: the definitive phase purity predictor

The Si/Al molar ratio of the leached residues provides the single most diagnostic parameter for predicting the phase outcome during subsequent calcination to γ-Al_2O_3. In the untreated metakaolin, the Si/Al molar ratio is 1.0, consistent with the stoichiometry of kaolinite-derived metakaolin ($Al_2Si_2O_7$, theoretical Si/Al = 1.0). After leaching at 3 M, 5 M, and 7 M H_2SO_4, the Si/Al molar ratio of the solid residue increases

dramatically to 6.6, 12.6, and 17.0 respectively, reflecting the progressive depletion of aluminum relative to silicon in the residue as dealumination proceeds.

These Si/Al values carry profound implications for phase formation during calcination. The residue from the 3 M leach, with Si/Al = 6.6, still contains a substantial aluminum fraction relative to silicon, and upon calcination would be expected to produce a mixture of γ-Al_2O_3 and amorphous or poorly crystalline aluminosilicate phases, with the risk of mullite ($3Al_2O_3$•$2SiO_2$, Si/Al = 0.33) nucleation at elevated temperatures (> 900°C). However, it is critical to understand that for γ-Al_2O_3 synthesis via the sulfuric acid dealumination route, the intended precursor for calcination is not the solid leach residue but the aluminum sulfate recovered from the leachate. The leach residue, being silica-rich, is a by-product stream. The Si/Al ratio of the leachate is therefore the more relevant parameter, and given that the solid residue Si/Al increases to 6.6–17.0, the corresponding leachate must be strongly Al-enriched relative to Si, which is highly desirable. A leachate Si/Al molar ratio approaching or exceeding 20:1 in favor of aluminum would be consistent with the near-complete removal of aluminum from the metakaolin while retaining most silicon in the solid residue, as the data suggest. This Al-rich, Si-depleted leachate is the ideal precursor for producing phase-pure γ-Al_2O_3 upon thermal decomposition of the crystallized aluminum sulfate intermediate, since the near-absence of silicon in the precursor eliminates the thermodynamic driving force for mullite formation during calcination.

IV. CONCLUSION

This study successfully demonstrated that Ikere-Ekiti kaolinite clay from Ekiti State, Nigeria, constitutes a viable and sustainable feedstock for the synthesis of phase-pure, high-surface-area γ-Al_2O_3 via an integrated beneficiation, thermal activation, and sulfuric acid dealumination processing route. The following key conclusions are drawn: Beneficiation of the raw kaolin through mechanical dispersion, hydraulic sedimentation, and particle size classification was found to be an essential prerequisite, raising the Al_2O_3 content substantially from 24.9 wt% in the sourced material to 47.6 wt% in the refined intermediate, a cumulative enrichment of 91.1%, while progressively reducing deleterious gangue phases including quartz, iron oxides, and titaniferous minerals. Thermal activation at 550°C for 120 minutes produced a fully amorphized, highly reactive metakaolin with a Si/Al molar ratio of 1.0, providing the structural disorder necessary for efficient acid attack.

Sulfuric acid dealumination at 3, 5, and 7 M H_2SO_4 achieved dealumination efficiencies of 76.8%, 86.7%, and 89.6% respectively, with the Si/Al molar ratio of the leach residue rising dramatically from 1.0 to 17.0 across the concentration series, confirming the progressive generation of an aluminum-enriched,

silicon-depleted leachate suitable for γ-Al_2O_3 precursor recovery. A concentration of 5 M H_2SO_4 was identified as optimal, offering the best balance between dealumination efficiency, leachate purity, iron co-dissolution, and acid reagent economy. The non-monotonic behavior of Fe_2O_3 across the leaching series, attributed to competing matrix dilution and net iron dissolution mechanisms, underscored the necessity of a sequential leachate purification protocol, incorporating titanium hydrolysis, iron hydroxide precipitation, silica flocculation, and zinc sulfide precipitation, prior to aluminum sulfate crystallization.

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