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Porosimetry and thermal analysis of lateritic clay minerals-Ag-TiO₂ nanocomposite as ceramic photocatalyst material

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Silver nanoparticle doped titanium oxide photocatalyst material is intercalated into chemically activated lateritic clay (CLY) minerals using sol-gel technique for the preparation of powder ceramic nanocomposite photocatalyst. The photocatalyst nanocomposites were sintered at high temperature to induce thermal reaction and crystalline growth between the constituents via Oswald ripening. Physical and thermal characterizations of intercalated (STOX-C) and sintered-intercalated (STOX-CS) samples were studied using BET (N₂ adsorption-desorption analysis), differential scanning calorimetry (DSC/DTA), and scanning electron microscopy (SEM). Microstructural examination of Ag-NPs doped TiO₂ revealed evenly distributed uniform nanocrystallites after the sol-gel synthesis. The micrograph of the clay mineral samples indicated transition from a combination of rod-like and platelet phases to aggregates of spherical crystallites after intercalation and sintering. The natural structure of the clay mineral changed after sol-gel intercalation with Ag-TiO₂ nanoparticle. Nitrogen adsorption-desorption analysis of the samples revealed that nanoparticle intercalation does not really affect the particle surface area, however isothermal sintering after intercalation caused remarkable reduction in crystallites surface area (37.912 m²/g to 8.971 m²/g). Meanwhile, the pore sizes increased after sintering from 17.47 nm to 24.42 nm. Changes from hysteresis loop to a near-reversible isotherm behaviour were observed after photocatalyst nanoparticle sintering. The thermal analysis revealed transition reactions of lateritic mineral functional structure by between Ag-TiO₂ intercalation.

Key words: Sol-gel, Adsorption-desorption, Nanocomposite, Sintering, Lateritic clay.

Introduction

Laterite is a soil and rock type rich in iron and aluminium, and is commonly considered to have formed in hot and wet tropical regions of the world. Laterite is a common soil type in Nigeria and other parts of Africa. Nearly all laterites are of rusty-red coloration, because of high concentration of iron oxide, with kaolinite as the predominant clay mineral [1-3]. Lateritic clay minerals develop by rigorous and longlasting weathering of the underlying parent rock. Tropical laterization is a prolonged process of chemical weathering which produces a wide variety in the thickness, grade, chemistry and ore mineralogy of the resulting soils. The majority of the land area containing laterites is between the tropics of Cancer and Capricorn. The combination of natural geologic mineral matrices and chemicals compounds often exhibits interesting and unique properties [4, 5]. From a physico-chemical point of view, it permits the formation of bi or multi-

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functional materials, combining the chemical and physical properties of the two partners [6-9]. This synthesis often leads to the modification of the physicochemical properties of the support mineral such as properties of surface properties, property of adsorption, hydrophobicity, etc. In addition, functional chemical species can be immobilized and stabilized on suitable natural substrates. Among these nanohybrid materials, clay mineralsphotocatalyst nanocomposites constitute a versatile area of investigation, which is due specifically to the abundant availability of natural clay minerals and the possibility to intercalate a large variety of functional molecules into their microstructure [10-15]. Most clay minerals, especially, aluminosilicates are abundant and widely available. For instance, kaolinite clay is characterised by a dioctahedral structure [16], and there is a strong interactions between the tetrahedral and the octahedral sheets through H-bonds. Naturally, different clay minerals have been applied in environmental remediation. They are also used in other sectors not directly related to remediation, such as photocatalysis, agriculture, food protection and manufacturing. Initial laboratory studies have shown that laterite is capable of 99% removal of phosphorus from solution. A pilotscale experimental filtration bed containing laterite

achieved 96% removal of phosphorus [17]. Ordinarily, clay minerals often contain different impurities which hinder their performance and applications as functional materials. However, in many cases the clay mineral particles can be chemically activated to modify its surface structure [18-21]. Laterite is a hydrated mixture of Al, Fe and Titanium (Ti) derived from the decomposition of aluminosilicate bauxite rocks and the subsequent loss of alkalis, lime, magnesia and silica. Eyles [22] reports an advanced lateritized sample containing 6.9% SiO₂, 39.8% A1₂O₃, 26.7% Fe₂O₃ and 3.6% TiO₂. Lateritic clay mineral dissolved in acid and precipitated at pH > 6.0 was found to be effective in removing organic matter and heavy metals from effluents. This led to its use as ferric aluminium sulphate, for decolourising drinking water [23].

The surface of a material is the dividing line between it and its surroundings, and naturally for a layered materials, the activation of its surface would enhance its interactions with its surrounding by creating more active sites. We can anticipate therefore, that the nature and amount of surfaces available are an important factor in the behaviour of a solid in adsorption processes. Surface properties affect the performance of catalyst or photocatalysts, cement hydration, adsorption capacity of purifiers. Whenever solid matter is divided into smaller particles new surfaces are created, and similarly, when pores are created within the clay particle interior by dissolution or decomposition by acid, the surface area is increased. Adsorption and degradation of synthetic heavy metal pollutants (Cu2+and Co2+) using acid activated and Ag-TiO2 intercalated kaolinite and diatomaceous minerals have been achieved in earlier studies [26, 27]. With respect to the abundant aluminosilicate clay minerals from laterite sources, more studies, information and analysis of their chemical and physical characteristic after activation and modification with suitable photocatalysts are still highly desirable. Hence, the main objectives of this work were to study the effect of the intercalation of Ag-TiO₂ photocatalyst on surface, microstructural and thermal properties of lateritic clay minerals for degradation and removal of heavy metal pollutants from effluents.

Materials and Methods

Materials

The lateritic clay minerals was extracted from laterite soil obtained as raw from locations in Ile-Ife, Osun State, Nigeria. The samples were first dried to remove surface water in an oven for about two (2) hours, and then cooled to room temperature for further treatment. Analytical grade nitric acid (HNO₃) was used to treat the raw mineral. Silver nitrate (AgNO₃), sodium carbonate (Na₂CO₃), and titanium dioxide (TiO₂) chemicals were purchased and were used with the raw material mineral to prepare the ceramic photocatalyst nanocomposite.

Separation and chemical modification

Lateritic clay mineral sample was obtained from laterite soil/rock matrix by carefully crushing the portion of interest of the raw material, and a clay suspension was prepared by adding the separated mineral particles to distilled water in a 500 mL beaker. The clay material totally soaked in distilled water was left for about 2 hrs to aid dispersion of the clay particles from impurities. The clay solution was stirred mildly for 20 minutes and left standing for about 5 minutes to maintain the finer clay particles in suspension. Then the top coloured sol containing the fine clay suspensions was poured into a separate beaker and centrifuged for separation. The chemical composition of the lateritic clay mineral extracted from laterite soil is given in Table 1 [24]. The physical and chemical properties of lateritic clay mineral was enhanced using 30% dilute HNO3. However, for the preparation of Ag-modified TiO₂ photocatalyst (STOX), 10 g of TiO₂ powder was placed into a 500 ml beaker with 100 ml ethanol as the dispersion medium, and 0.1M solution of AgNO3 with 1% (w/v) solution of sodium carbonate were prepared separately. Hence, 4.6 ml of the prepared silver nitrate solution and 5 ml of sodium carbonate were added to the TiO₂ dispersion. The mixture was stirred vigorously for 2 hrs using a magnetic stirrer to form a slurry solution [25-27]. Meanwhile, acid-activated aluminosilicate lateritic clay minerals (CLY) were prepared from the raw material, and about 25 g was added slowly into the continuously stirred and mildly heated Ag-TiO₂ colloidal solution and left for 2 hours on the hot-plate stirrer. Finally, the intercalated photocatalyst nanocomposite powders designated as STOX-C was recovered from the slurry via centrifugation. The nanocomposite powder was further sintered at a relatively higher temperature (900 °C-1000 °C) for 12 hrs for thermal fusion between constituents and densification.

 Table 1. Chemical compositions of the lateritic clay mineral obtained from laterite soil.

Compound (oxides)	Concentration (wt. %)		
Na ₂ O	3.93		
MgO	0.61		
Al_2O_3	46.16		
SiO_2	45.72		
K ₂ O	0.97		
CaO	0.16		
TiO ₂	0.54		
V_2O_3	0.03		
MnO	0.04		
FeO	1.50		
CoO	0.17		
NiO	0.01		
Cu ₂ O	0.02		
ZnO	0.007		
SrO	0.006		



Fig. 1. SEM micrographs of Ag-TiO2 at low and high magnifications.

The image for sol-gel prepared Ag-TiO nanoparticles (Fig. 1) consist of well-arranged and neatly distributed network of particles of uniform sizes. At higher magnification, each particle is observed to be a coalescence of smaller particles Ag-TiO₂.

Physical and chemical characterizations

The physical characterizations of the activated aluminosilicate clays, sol-intercalated photocatalyst (STOX-C) and sintered photocatalyst nanocomposite (STOX-CS) relating to surface areas, were done by measuring their nitrogen adsorption-desorption isotherms at bath temperature of 77.350 K and ambient temperature of 22.0 °C using BET analyzer (TriStar II 3020 Version 2.00). Changes in texture properties and microstructural information were obtained using scanning electron microscope (SEM, Zeiss DSM-940A). Differential scanning calorimetry (DSC) was to study the thermal and phase transformations of the nanocomposite samples.

Results and Discussion

Microstructural analysis

The micrographs acquired for the samples are shown in Figs. 2(a-c), with noticeable changes in the microstructure and particle distribution depending on treatment. Large bundle of rod-like, flaky aggregates and platelets microstructures are observed for the activated laterite mineral (CLY) after the removal of impurities from within the microstructure by the acid treatments, it is obvious that acid dissolves some of the carbonaceous and other materials, thereby opening more channels and pores especially within the grain boundaries. The treatment prepared the laterite surface for the attachment of photocatalyst nanoparticles as more active sites are provided for attachments. Then, silver doped TiO₂ nanoparticles intercalated are situated on the more active grain surface, as well as within the grain boundaries. For intercalated sample STOX-C, a blobby mixture of plates and rounded grains are seen with nano-sized crystallites of photocatalyst nanoparticles coated on the surface and distributed within the coalesced mineral crystallites. It can be seen that samples CLY and STOX-C are similar microstructurally, as they are still largely an aggregation of smaller grains with larger surface area as induced by the dissolution by







Fig. 2. (a) SEM micrograph of sample CLY, (b) SEM micrograph of sol-prepared STOX-C sample, (c) SEM micrographs of sintered STOX-CS sample.

the acid treatment. Meanwhile, after intercalations with the nanoparticle, the surface area reduced remarkably. This is shown from the physical parameters as determined from the nitrogen adsorption analysis. For sintered nanoparticle intercalated sample STOX-CS, it can be seen that the microstructural characteristic differ noticeably from other samples with relatively larger grains but with well-defined surfaces and crystallite geometry. Aggregations of Ag-TiO₂ nanoparticles is observed to adhere to the lateritic clay crystallites surface after the high temperature heat treatments. Besides, Ag-TiO₂ nanoparticles are also interspersed within the grain boundaries, which acts as bonding layer between the crystallites as can be seen in the micrographs. The microstructural evolutions of the lateritic clay minerals particles indicated diverse effects of chemical and sintering processes on the expected behaviour of the materials in relation to their functionalities.

For instance, it was expected that sintering treatment will lead to the total densification and reduction of pore size of the sintered nanocomposite. Instead of the porosity reducing with sintering due to Oswald ripening, according to the BET result (D_{BET}), the porosity increased drastically. Expectedly, the porosity is accumulated at the grain boundaries. Sintering effect will afford the photocatalyst nanoparticles to be firmly attached on the lateritic clay mineral grains forming a nanocomposite ceramic powder. This will enhance the hydrophobicity of the nanocomposite photocatalyst and help in the selective adsorption or removal of pollutants from water sources. It should be noted that at sintering temperature beyond 600 °C, anatase Ag-TiO₂ nanoparticles transformed to the irreversible rutile phase in the composite. These observations are in agreement with the thermal results.

Physisorption hysteresis loops

In studies, well-defined hysteresis loops onset usually start to appear in the multilayer/capillary condensation range when the pore size is increased to more than a few molecular diameters [28]. Notwithstanding, other forms of hysteresis have been observed at lower P/P° values situated in the normal monolayer range of the isotherm. This behavior has been fully explained in studies [29, 30], based on IUPAC classification [31]. The isotherms and hysteresis loops for the raw, intercalated and sintered nanocomposite samples are shown in Fig. 3. From observations, it is shown that the materials possess both type III and III (H3) isotherm and hysteresis loop respectively. Specifically, this shows the presence of mesopores in the materials and an unrestricted multilayer formation process during adsorption, which indicates strong lateral interaction between adsorbed molecules rather that the adsorbentadsorbate interactions [32]. It should be noted as well that H3 hysteresis loops are typically given by adsorption of non-polar gases on loose assemblage of plate-like particles which forms slit-pores [19]. As shown in the diagram, the loops do not have a plateau at high P/P° values and hence as stated, they are characteristic group III isotherm, with exception of



Fig. 3. Nitrogen adsorption/desorption isotherms for samples CLY, STOX-C and STOX-CS.

sintered nanocomposite with a slight tilt towards a plateau onset. Also, the shapes of the loops also show the non-rigid nature of the aggregated particulates. Relatively, the isotherm for treated raw laterite (CLY) show widest gap between adsorption and desorption branches of the hysteresis loop, while the gap closes with intercalation and sintering. Sample STOX-CS has hysteresis closure point at high P/P (~ 8.0), and complete closure of hysteresis loop, thereby forming a reversible isotherm. The changes in the hysteresis loop and isotherms have implications on the micro-physical characteristics of the materials. From the observed changes in the materials, it can be suggested that the adsorption processes changed from chemisorption to physisorption after high temperature sintering treatments. In chemisorption, the process is irreversible, while adsorption process can be reversible in physisorption [30], and when desorption and adsorption processes follows the same or nearly the same path, the isotherm is termed reversible. Samples CLY and STOX-C isotherms are irreversible while, STOX-CS could be regarded as reversible. The long flat region before the start of the hysteresis loop after sintering shows the presence of sustained multilayer adsorption which is caused largely by the presence of well-defined cylindrical pore channels, which indicates that the pores in the materials were refined after heat treatment. Generally, the changes observed after sintering, is mainly due to the inter and intra-particle densification by heat which caused reduction in surface area (S_{BET}), and an unexpected increase in the average pore size as shown in Table 1.

The slight plateau tilt exhibited by photocatalyst nanocomposite sample STOX-CS indicated the refinement of its grains by sintering action. Findings have shown that well-define plateau are usually given by agglomerates or uniformly spherical particles with cylindrical pore geometry [31]. It shows that sintered lateritic clay nanocomposite consist of agglomerates of spherical particles, which is in strong agreement with SEM results. Hysteresis closure point occur at different relative pressure values for the samples, for instance, it occurred at low P/P_0 (~ 2.0) for CLY, while, the closure points for modified samples shifted to high P/P° (~ 0.7 and ~ 0.9 for STO-C and STOX-CS respectively). In all cases, there is a clear indication of formation of first few multilayers before transiting to the relative high pressure region where hysteresis behaviour shows the functional characteristics of samples based on modification. However, the flat horizontal middle isotherm curve for nanocomposite STOX-CS indicate the sustained multilayer adsorption at intermediate pressure region.

Porosimetry analysis

Caratto, et al., [33] showed that pure catalyst nanoparticles occasionally display lower degradation



Fig. 4. BET surface area plots for CLY, STOX-C and STOX-CS.



Fig. 5. DSC thermogram for samples TOX and STOX.

efficiencies due to self-aggregation problem. Nonetheless, intercalating functional nanoparticles into platelet, on spherical grains, porous scaffolds or substrates may have resultant effects on the matrix porosity, but definitely it enhances the potency of the surfaces acting as the substrate for the nanoparticles. The physical parameters from the nitrogen adsorption-desorption analysis of the samples are presented in Table 2, while the BET surface plots are shown in Fig. 4. The information on the physical properties of raw lateritic clay minerals based on nitrogen adsorption-desorption analysis is rare. However, from the present study, it is observed that acidactivated lateritic clay sample CLY has specific surface area value of $37.9119 \text{ m}^2/\text{g}$ (S_{BET}), much more than values obtained for the samples after intercalation and sintering. Meanwhile, due to the anchoring of the catalyst nanoparticles on the silicate substrates, the surface area of the formed nanocomposite material decreases remarkably typically after sintering $(S_{BET} =$ $8.9707 \text{ m}^2/\text{g}$). This can be attributed to the increase in crystallite size by grain growth and photocatalyst nanoparticles bonding on laterite mineral particles during sintering process. Grain growth process occurs when recovery and recrystallization are accomplished within the material. Since acid activated aluminosilicate surfaces are regions of high energy, they make excellent active sites for the nucleation of photocatalyst nanoparticles and other second phases. In other considerations, reduction in the surface area was shown to be as a result of a reduction in the actual number of grains per volume of photocatalyst material [34, 35]. Densification is another typical effect of sintering on composite material which reduces the total porosity. It is however observed that pore size of photocatalyst-laterite nanocomposite indeed increased after sintering. This can be attributed to the pore accumulation at the grain boundary. As observed from the SEM micrographs, in sample STOX-CS, the photocatalyst NPs are shown to be distributed and attached evenly on the grain surface and bonds between the grains. Moreover, the presence of nanoparticles within the microstructure discouraged direct nucleation between laterite mineral grains, which brought about the unexpected increase in the porosity inspite of sintering process. The larger pores observed in sintered laterite base nanocomposite are mainly located at grain boundaries and between the layered silicate sheets. Since the treated laterite mineral nanocomposite was heated beyond 1050 °C during sintering, the phase must have transform to adjacent phase corresponding to the temperature as shown in thermal analysis spectra. Inspite of the increase in the pore size for nanocomposite, the pore volume is shown to be relatively lowered as compared to others. Easy manipulation of photocatalyst nanoparticles anchored on suitable mineral substrate rather than the pure nanoparticle itself has been established in studies [36, 37].

Thermal analysis

The DSC spectra of TiO₂ (TOX) and sol-gel prepared Ag-TiO₂ (STOX) are shown together in Fig. 5. Both TiO₂ based samples showed an endothermic reaction at the initial stage of the heating process very close to the vaporization temperature of water at 93.4 °C and 94.3 °C respectively. This initial endothermic reaction the release of trapped atmospheric water. Further heating process led to another transformation at 804.2 °C and 866.0 °C (STOX) and 819.1 °C and 883.7 °C (TOX). The doublet endothermic peaks observed for the materials could be

Table 2. Surface area and porosity parameter for kaolinite clay adsorbent.

Samples —	Surface Para	Surface Parameters (m ² /g)		Pore Volume (cm ³ /g)		Pore Size (Å)	
	$\mathbf{S}_{\mathrm{BET}}$	S _{t-MICRO}	V _{Total(SP)}	V _{t-MICRO}	$\mathbf{D}_{\mathrm{BET}}$	D_{BJH}	
CLY	37.9119	0.2739	0.165566	-0.000055	174.6855	169.812	
STOX-C	26.5890	0.3110	0.115344	-0.000101	173.5219	183.228	
STOX-CS	8.9707	0.4435	0.054777	0.000229	244.2454	262.031	



Fig. 6. DTA thermogram and derivative-DTA spectra for acid-treated lateritic clay CLY.



Fig. 7. DTA and derivative-DTA spectra for photocatalytic Ag- TiO_2 -lateritic nanocomposite STOX-C.

attributed to a successive decomposition and phase transition and recrystallization behavior of the TiO₂ nanoparticles. The left-shift of the doublet endothermic peaks for STOX attributed to the influence of Ag-NP in the material. Metastable anatase and brookite TiO₂ phases usually convert irreversibly to the equilibrium rutile phase upon heating above temperatures in the range 600 °-800 °C [38]. Therefore, it shows with the existence of the endothermic peaks at ~ 800 °C, the pure and doped titanium oxide experience drastic change to form a rutile phase due to the application of heat. A broad exothermic peak observed at 1154.0 °C for pure sample TOX is attributed to phase recrystallization by solid state reaction. Meanwhile, an endothermic reaction at 1175.3 °C for sample STOX, but not observed in sample TOX, could be ascribed to the phase transformation brought by melting of the doping silver nanoparticles in the TiO₂ matrix. Nonetheless, the differential thermal analysis (DTA) spectra for the treated lateritic clay and photocatalyst intercalated nanocomposites (Fig. 6 and 7) are found to exhibit both exothermic and endothermic reactions and transformations at temperature ranges peculiar to their properties, thus showing the purity of the material. A derivative transform spectral is shown together with original spectra in order to show the reactions of the material applied at each peak. That is, a sudden change from the baseline either towards the endothermic side or exothermic side. Water molecules are usually trapped in most aluminosilicate minerals, owing to their open microstructural framework. Therefore, the peak observed at 122.0 °C on thermograms for sample CLY clearly indicated the removal of trapped atmospheric water, however for photocatalyst nanocomposite STOX-C, probably due to the effect of modification, no conspicuous reaction is observed in the main spectrum, but with clear displacement indicated on the derivative spectra, it is concluded there is a similar reaction in the range. The differences in the behaviour of the lateritic clay minerals with heating are clearly identified with other reactions as the temperature further increases. With derivative transform spectrum in Fig. 6, a large displacement is observed for STOX-C at 347.2 °C which may also be attributed to endothermic effect relating to the removal of inner bound or molecular water. As found in other aluminosilicates, a broad endothermic reaction is detected in the 500 °C to 600 °C range for both treated and intercalated laterite mineral samples. After the initial lower temperature reactions, series of reactions and transformations were obtained for the laterite minerals as shown in Fig. 6 and 7. Broad endothermic reactions are observed for both materials between 500 °C and 600 °C, which is consistent with aluminosilicate minerals and this is attributed to the dehydroxylation or the loss of OH groups in the mineral structure. Studies indicates that the main minerals present in the laterite soil are kaolinite, quartz and gibbsite [1,2]. Typically, endothermic dehydroxylation for kaolinite clay usually begins at 550 °C-600 °C to produce disordered metakaolin, $Al_2Si_2O_5$ (OH) $_4 \rightarrow Al_2Si_2O_7 + 2H_2O$, though continuous hydroxyl loss (-OH) is sometimes identified up to 900 °C and this has been attributed to gradual oxolation of the metakaolin [39]. An endothermic peak exhibited by sample STOX-C at 785.0 °C in Fig. 6 shows the influence of intercalation in the material structure, and the reaction could be linked to the photocatalyst Ag-TiO₂ phase transformation between 800.0 °C and 900.0 °C as shown in Fig 5. Exothermic reactions are shown on the thermogram at 965.0 and 966.6 °C for both samples which signifies a major solid state phase transition of the laterite minerals. Fig. 5

Conclusions

Ag-TiO₂-intercalated clay mineral nanocomposite ceramic materials have been prepared from locally available and abundant raw laterite soil/clay minerals. High isothermal sintering was done on the photocatalyst to induce physical and chemical stability of the nanoparticles in the nanocomposite. Remarkable changes in morphology was found after sintering. The adsorptiondesorption isotherm characteristic change from hysteretic process to reversible process. Adsorption hysteresis loops of the nanocomposite were found to be of type III and H3 respectively. The desorption-adsorption processes show a total shift of the hysteresis closure point from low relative pressure (P/P^o ~ 0.3) to high relative pressure (P/ P^o ~ 0.8) after sintering, which indicate the changes in the surface interaction of the nanoparticles with the adsorbates. Generally, the horizontal intermediate relative pressure for sintered photocatalyst showed strong lateral interaction between adsorbed molecules. Sintering treatment induced reversible isotherm characteristic into the materials. With sintered nanocomposite samples having lower surface area, it is due to the adherence of the nanoparticles on the activated lateritic clay particles through Oswald ripening and grain growth phenomena. This further enhances the functionalities of the lateritic clay minerals.

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