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Characterization of some selected Ghanaian clay minerals for potential industrial applications

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The aim of this work was to study five (5) selected local raw clay materials from Ghana using different characterization techniques such as Thermogravimetric/Differential Thermal Analysis (TG/DTA), X-ray diffraction (XRD), Fourier Transform Infra-red Spectroscopy (FTIR), Scanning Electron Microscopy equipped with Energy Dispersive X-ray Spectroscopy (SEM-EDX) and Nitrogen Desorption (Brunauer-Emmett-Teller, BET) specific surface area analysis. The clay samples studied are; Nkroful kaolin (NK), Amanfrom kaolin (AK), Ball clay (BC), Akyem Feldspar (AF) and Akwatia silica (AS). SEM and EDX show the morphological features of the five clay samples and also confirm the presence of some dominant elemental compositions such as aluminium and silicon in all the samples. FTIR show that the vibrations spectra in the region around 3,600-3,700 cm^{-1} and 700-800 cm^{-1} are due to M-OH groups and that at 900-1000 cm^{-1} corresponds to Si-O-Si modes. BET analysis gives specific surface area of the clay samples as NK (4.6 m^2/g), AK (21.9 m^2/g), BC (25.50 m^2/g), AS (0.79 m^2/g) and AF (0.49 m^2/g). X-ray diffraction pattern confirm the presence of quartz as the major reflection in all the samples analysed and only kaolinite reflections appeared in three of the samples (NK, AK and BC). All the kaolinite clays (NK, AK and BC) are suitable starting materials for the fabrication of electroporcelain insulators, catalytic converters and diesel particulate filters.

Keywords: Clay, Specific surface area, Electro-porcelain.

Introduction

Clay refers to the finest fraction of sediments that consist of accumulations of different minerals such as quartz, feldspar and many more which is formed by the weathering of silicate minerals in/on the earth's crust [1]. Clay has many vast benefits in medicine and industrial purposes which has gained extensive research interest due to its abundance and low cost [2]. In Africa, clay is mainly used in making pots for storing water or food and earthen ware bowls for cooking. Prehistoric practices such as geophagy, which is the practice of ingesting earth materials or substances such as clay [3, 4] to augment a scanty mineral deficient diet (for example; iron, copper, calcium, zinc and manganese) [5], as part of a culture, or to stimulate a healing response to sooth an infected and inflamed gastrointestinal lining [6] is still prevalent in the 21st century.

Clays such as smectites, kaolinite and fibrous clay minerals have been applied widely for drug delivery systems because of their large specific surface area, pore volume and uniform porosity for sustained release [7]. Smectites in particular are frequently used as substrate, because it can retain large amounts of drug due to its cation exchange ability [7]. Others such as palygorskite, kaolinite and talc are extensively used in pharmaceutical formulations because of their high specific surface area, good rheological properties, chemical inertness, low toxicity and good biocompatibility which is highly suitable for patients [8]. The adsorptive properties of some clay materials such as high pore volume, fine particles size and cation ion exchange allows the removal of oils, toxins and contaminants from the skin, which makes clay suitable for formulations in the cosmetic industry [6, 9, 10]. Therapeutic uses of clay includes mixing variable amounts of clay with different sea or salt lake mineral waters to form pastes for fighting chronic rheumatism and bone muscle diseases [9, 11-13]. Many studies have proven that clays can be used for biomaterials and other medical devices such as biosensors [14-18]. In agriculture, sepiolite and palygorskite clay suspensions have been used as a tool to reduce the amount of cadmium (Cd) concentration in the soil. This was done to solve the pollution of soil by this heavy metal. It has also been used as fertilizer because of its nutrients content, thereby increasing crop yield [19].

Kaolin is widely used in the paper industry to coat the surface of paper for brighter colors, as filler in many composite materials to add strength and to improve the abrasion resistance, and rigidity to both natural and synthetic rubber products at a low cost. It is also used in the ceramic industry as an insulator and paint industry due to its high covering power, low cost and

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high resistance to chemical attack [20-24].

Recently, research has shown that archeological clay obtained in Komaland, from the Northern Region of Ghana has prospects to enhance human fetal osteoblast cells growth *in vitro* [25]. Also, other research has shown that treated kaolin from natural clay using chemical and thermal reactions inhibit Hela cervical cancer cells in vitro [26]. Some modified clay minerals with lidocaine and silver have been exploited in burn wounds and antisepsis respectively [27]. In Africa, several kaolin deposits are not utilized effectively and may serve as assets in economic gains and research opportunities [28]. Natural clay has been inadequately exploited to know their chemical composition, their characteristics and applications as compared to those that are modified, synthetic or refined. In Ghana, although the clay industry is huge, the properties that inform their usage are limited.

This work seeks to explore various clay deposits from five different geographical locations, that is; Amanfrom Kaolin (AK), Ball clay (BC), Nkronful Kaolin (NK), Akyem Feldspar (AF), and Akwatia silica (AS) and characterize them using techniques such as TGA/DSC, XRD, FTIR, SEM equipped with EDX and BET so as to better understand their characteristics for future industrial applications such as electroporcelain insulators, diesel particulate filters and as washcoat materials in catalytic converters.

Materials and Methodology

Sources of the raw materials

The raw materials for this study were collected from kaolin deposits in Ghana located in the Western and Central regions.

Powder preparation and analysis

Powder samples were prepared for this study using a 400 g quantity of lumpy kaolin deposits, Nkroful and Amanfrom, which were first ground using a Thomas grinding machine to break up the agglomerates. The samples were each further milled for 13 h in a cascading ball mill using alumina balls to obtain fine powders. These were sieved through a gradient sieve with aperture size of 63 μm.

Specific surface area analysis

The specific surface area of the clay materials was determined using BET method with a MICROMERITICS ASAP 2010 apparatus.

FTIR Analysis

Fourier transformed infra-red spectroscopy (FTIR) was carried out with a Shimadzu spectrophotometer (FTIR-8400S) scanning between 4,000 and 500 cm^{-1}. Each clay sample was finely ground in a mortar and then mixed with potassium bromide (KBr) powder. The powder mixture was put in a mould and pressed at high pressure to form thin pellets. In order to minimize the amount of water adsorbed, the pellets were heated in a furnace overnight at 130 ºC.

XRD experiments and degree of crystallinity

XRD analyses were performed using a Philips diffractometer (PANalytical, X'pert Pro MPD model) with a Bragg-Brentano configuration with voltage of 45 kV and current of 40 mA. The measurement was done at room temperature using a filtered Cu Kα (λ = 0.15418 nm) radiation and scanning from 10 to 70 degrees with scan speed of 0.042°/sec.

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) measurements

The morphology and microchemical features of the clay samples were observed with a Field Emission Scanning Electron Microscope (FE-SEM Philips XL30) equipped with an energy dispersive x-ray spectroscope. Particles images were obtained with a secondary detector.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA)

Thermal analyses were carried out with a TGA/DSC apparatus, SDT Q600 by TA Instruments. 15 mg of solid samples were heated over the temperature range from ambient to 1,000 ºC at a heating rate of 5 ºC/min in air atmosphere with a 100 $mL{\cdot}min^{-1}$ flow rate. Samples were analyzed in alumina crucibles and the reference was an empty alumina pan.

Results and Discussions

TGA/DSC Analysis

The results for the TGA/DSC curves for all the samples (AK, BC, & NK, AF, and AS) are given in Fig. 1 for the temperature range 0-1000 ºC. As evident in the TGA/DSC peaks, there is some weight losses observed in the samples.

For samples AK & BC, weight loss occurred in the temperature ranges of 200-700 ºC which are 2.5%, 5.9% & 3.3%, 5.4% respectively. After 700 ºC, the weight loss in AK and BC are 0.5% and 0.4% corresponding to total weight loss of 8.9% & 9.1% respectively. The difference in mass loss between the two samples is about 0.2% which is an indication of similar heating pattern (i.e, AK & BC) as seen in their TGA/DSC curves, while NK gave a total mass loss of 6.1% at 700 ºC. The endothermic peak at 200 ºC indicated the removal of water and other hydroxylated functional groups attached to the clay minerals. As temperature is increased to 700 ºC, α-β quartz transition occurs without further mass loss which is in agreement with earlier reports for quartz transitions [29]. For AS and AF, total weight losses are relatively insignificant

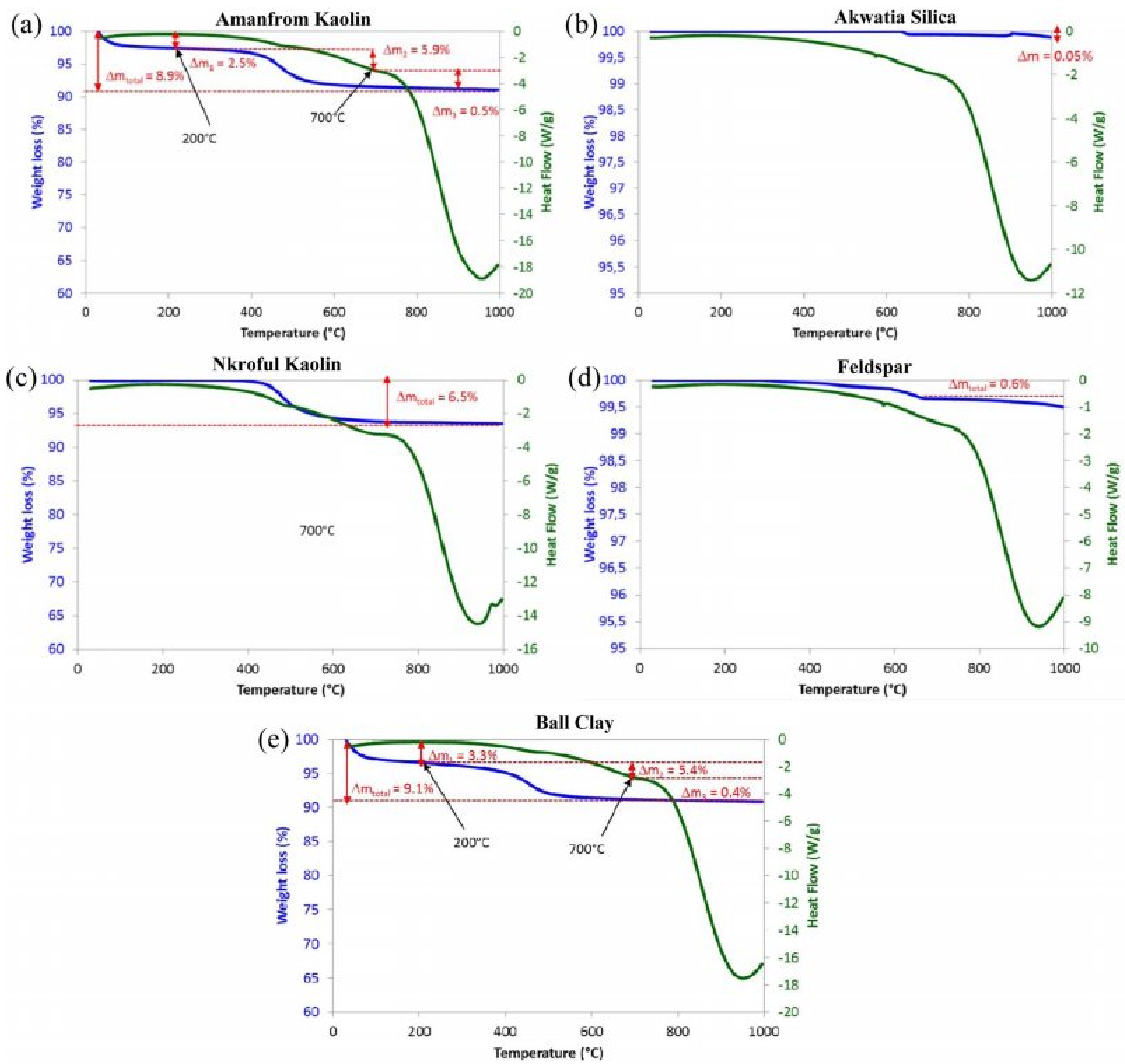

Fig. 1. TGA/DSC curves for (a) Amanfrom kaolin, (b) Akawtia silica, (c) Nkroful Kaolin, (d) Akyem-Akroso Feldspar and (e) Ball Clay.

compare to the three kaolinite materials. Additionally, there appears to be an exothermic peak in all the samples at 980 ºC and this is attributed to the formation of a spinel phase at higher temperatures [17, 26].

FTIR Analysis

FTIR spectroscopy has been used extensively to characterize clay and clay based minerals [30, 31]. Fig. 2 is the FTIR for the various samples used in this study. The stretching and bending vibrations found in the region of 3,600-3,700 cm^{-1} and 700-800 cm^{-1} respectively are due to M-OH groups [32]. Also, the weak band around 1,600-1,631 cm^{-1} is ascribed to the bending modes of physisorbed water molecules with other OH groups present in the clay minerals. These stretching and bending vibrations occurs in all the kaolinites (AK, NK & BC) but not observed in the silica-based, AS and AF as shown in Fig. 2. The bands around 900-1,000 cm^{-1} are attributed to Si-O-Si stretching vibrations, see Fig. 2. Additionally, the appearance of medium intensity bands around 500-650 cm^{-1} is attributed to the presence of quartz in all the samples, (showing intense band for AK and AF). The sharp peaks observed in the spectra for NK & AK, suggest a well order kaolinite phases in these two clay samples. The FTIR analysis closely agrees with the studies of S. Mahmoudi et al. on clay materials from Cameroon [33].

XRD Analysis

The minerals structure in clays can successfully be determined through the use of X-ray diffraction. This can also be used to validate FTIR analysis. XRD was

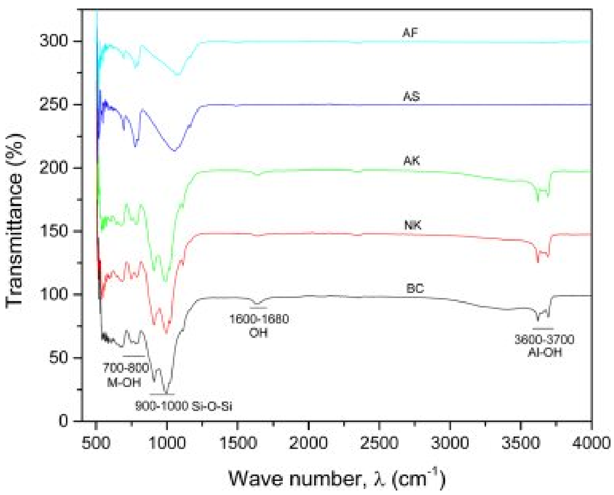

Fig. 2. FTIR analysis for Ball clay (BC), Nkroful (NK), Amanfrom (AK), Akwatia Silica (AS) and Akyem Feldspar (AF).

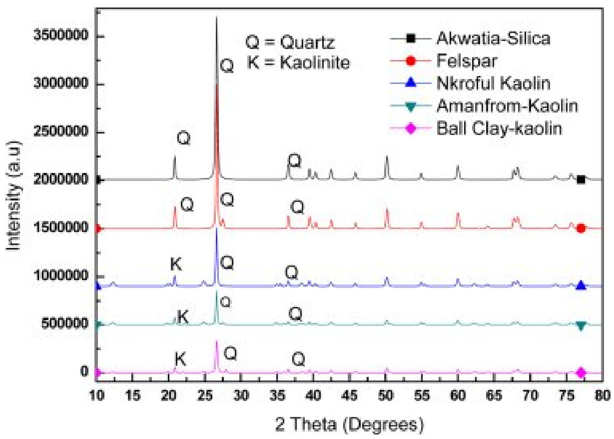

Fig. 3. X-ray diffraction patterns of the various samples.

used to identify the structural phases present in the samples. The XRD patterns for the AS and AF are very similar with the dominant phase present being SiO_2, whereas that of NK, AK and BC contains $Al_2Si_2O_5(OH)_4$ and Na (Al Si_3 O_8) as major components in addition to some traces of SiO_2 as shown in Fig. 3 and also in Table 1. Furthermore, AF was found to contain some traces of potassium, hydrogen and sulphur suggesting that, it is a potash feldspar (see Table 1). This also goes

Table 2. BET studies on various samples.

Sample	Sp (m^2/g)
Akwatia (AS)	0.79
Amanfrom (AK)	21.90
Ball Clay (BC)	25.51
Akyem Feldspar (AF)	0.49
Nkroful (NK)	4.95

to confirm the identification of the stretching frequencies observed in the FTIR in which similar vibrations frequencies were found for the three kaolinite groups at about 3,600-3,700 cm^{-1} and that of the silica and feldspar also having same frequency.

Specific surface area analysis

Table 2 shows the BET specific surface area measurements for the various samples. It is clear that, BC has the highest surface area of 25.51 m^2/g which explains why it can absorb large amount of water making it plastic because of large pore volumes and its finer particle sizes. Similarly, AK has surface area of about 21.90 m^2/g but is not as plastic as ball clay. Nkroful kaolin has a surface area of 4.9 m^2/g making it the least of the kaolinite groups which becomes hard when dry. The other silica-based have the least surface area; AF with 0.49 and AS 0.79 m^2/g respectively, which have nearly similar pores and show why they are non-absorbers and have a larger particle size than the others.

The high specific surface area of BC and AK can be applied in the areas of wash-coat materials for catalytic converters used in purifying exhaust gasses from internal combustion engines [30]. The catalyst wash-coat is a carrier for the catalytic materials, which is used to disperse catalyst materials over a high surface area. The catalytic materials are suspended in the washcoat before application to the core body and the washcoat have rough, irregular surface to increase surface area, which helps to maximize the catalytically active surface available to react with the engine exhaust gasses.

SEM Analysis

The SEM images and EDX analysis of the samples are given in Fig. 4. Morphological features show that,

Table 1. Identified crystalline phases from X-ray diffraction studies on the five (5) clay samples.

Compound name	Chemical formula	Crystal system	Clay
Silicon Oxide	SiO_2	Hexagonal	All
Aluminum Silicate Hydrate	$Al_2Si_2O_5(OH)_4$	Triclinic	NK, BC, AK
Titanium Oxide	TiO_2	Tetragonal	AF
Sodium Aluminum Silicate	$Na(AlSi_3O_8)$	Triclinic	AF
Potassium Hydrogen Sulfide	KHS	Rhombohedral	AF
Calcium Aluminum Silicate	$CaAl_2Si_2O_8$	Triclinic	NK, BC, AK
Potassium Aluminum Silicate	$KAlSi_3O_8$	Triclinic	AF
Sodium Calcium Aluminum Silicate	$(Na,Ca)Al(Si,Al)_3O_8$	Triclinic	All

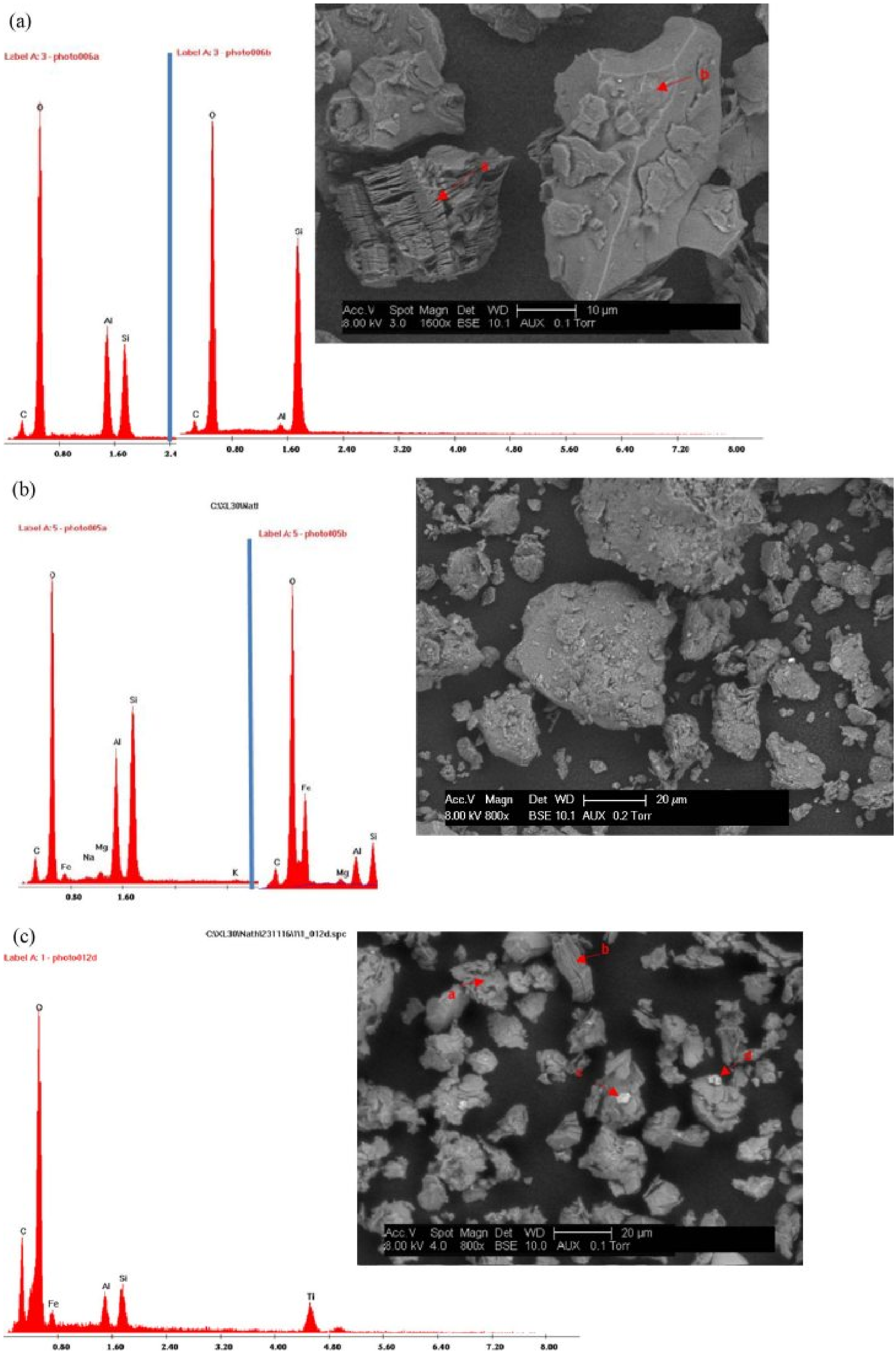

Fig. 4. Scanning electron microscopy images with resolution of 20 µm and EDX spectra for; (a) Nkroful kaolin, (b) Ball clay, (c) Amanfrom, (d) Akwetia silica and (e) Akyem feldspar.

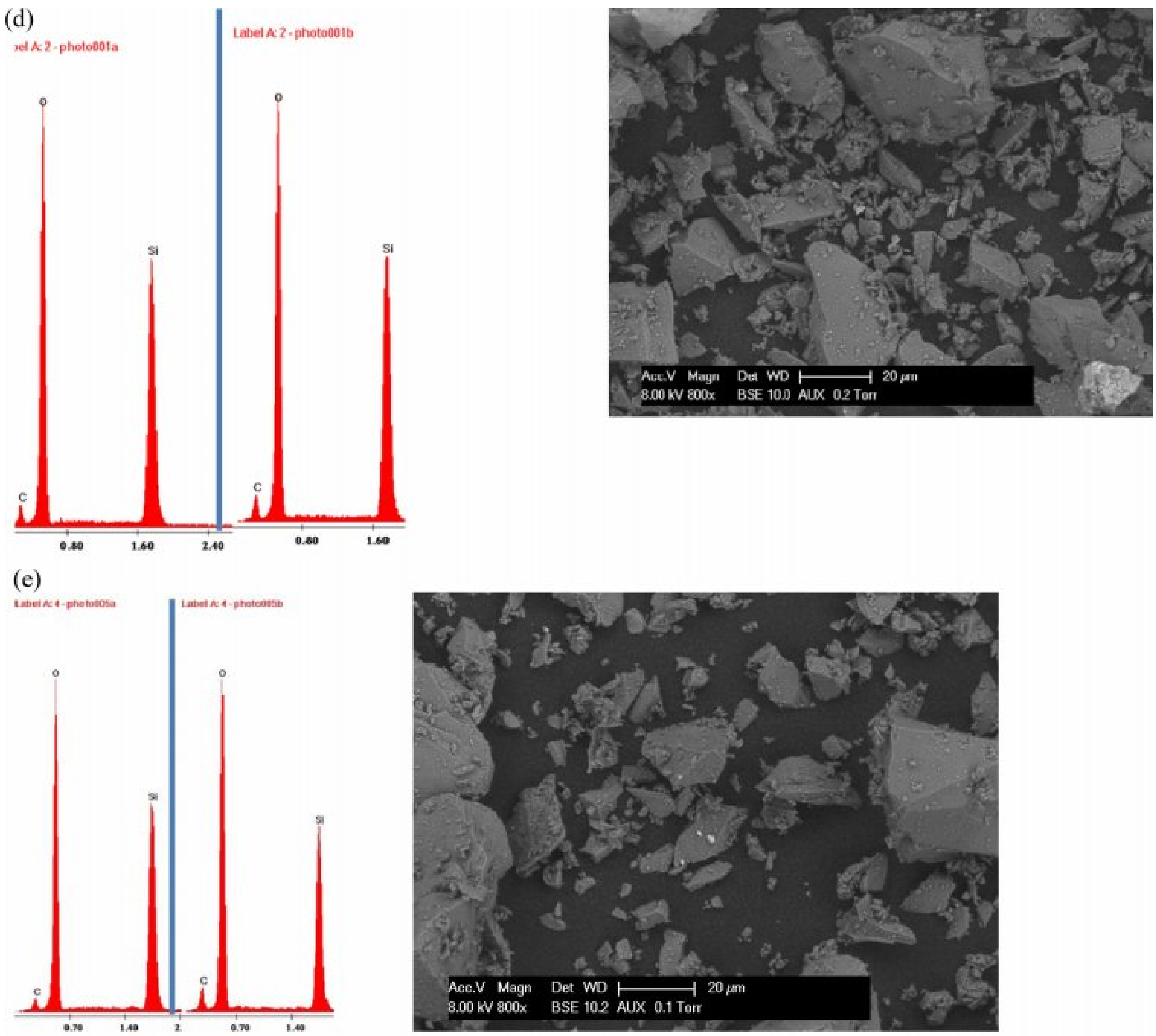

Fig. 4. Continued.

NK is made up of well-developed kaolinite crystals with layered morphology (Fig. 4a). For AK and BC, both show a relatively porous aggregate morphology. The porous aggregates consist of stacks of hexagonal kaolinites plates and some individual crystals (Fig. 4b-c). The EDX analysis of the various peaks also reveals Si & Al as the dominant elements with some traces of other elements which agrees with the FTIR and XRD studies reported earlier. On the other hand, AS and AF show a platelet crystals with their characteristic EDS spectra (see Fig. 4d-e) giving Si as the most dominant elements which is in agreement with the FTIR and XRD studies. The high silica content in AS and AF can be exploited by heating the samples in the presence of a carbon source in an inert or vacuum chamber at high temperatures to form silicon carbide [31]. Since SiC has good oxidation, wear resistance, high hardness and thermal stability it can be used as protective coatings on ceramic components in the aerospace industry [32] and as diesel particulate filter [33].

Conclusion

In this work five types of Ghanaian clays have been evaluated for their potentials in; diesel particulate filters, electroporcelain insulators and catalytic converters. Different characterization techniques such as XRD, SEM equipped with EDX, BET, FTIR and TG-DTA were used extensively to study the clay samples from different locations in Ghana. XRD patterns showed the presence of quartz as the dominant phase in all the samples examined whilst the EDX confirmed the presence of silicon and aluminium as the major elemental compositions. These characterisations have revealed very important features of these minerals that could be tailored towards specific industrial applications.

Conflict of Interest

All authors declare no conflicts of interest in this paper.

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