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Preparation and characterization of Fe_2O_3/mesoporous clay composite from Nigerian local bentonite clay

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Abstract

Clay obtained from a deposit in Itu, Nigeria, was used to prepare mesoporous clay-iron (II) oxide composite. Characterization of the prepared composite was performed to ascertain its physicochemical and textural properties. The effect of HCl treatment by hydrothermal process on the pore structure of the clay material and ferric oxide modification were also studied by nitrogen adsorption/desorption at -196°C, X-ray diffraction of the crystal structure, Fourier Transformed Spectroscopy (FTIR) of surface functionalities and Scanning electron microscopy (SEM) of the surface morphology. The results revealed evolution of mesopores and an increase in surface area following acid treatment and subsequent Fe_2O_3 inoculation. The resulting mesoporous clay composites showed prominent peaks typical of alumino-silicate materials which attenuate upon acid treatment and subsequent ferric oxide impregnation. FTIR results confirm the surface structural bands in alumino-silicate materials which have undergone dehydroxylation and dealumination, leading to aggregation of particles

1. Introduction

Clay is a naturally occurring alumino-silicate material formed by weathering of rocks over a long time in the presence of dilute carbonic and other inorganic acids. The major components of clay are alumina and silica tetrahedrons (Al_2O_3 and SiO_2). Clay has found applications in many industrial processes such as catalysis, adsorption and as support materials. The use of clay in heterogeneous catalysis as solid acid catalyst is almost as old as the catalysis concept itself [1-3]. Among the earliest heterogeneous catalysts were acid activated bentonites and clay. Despite the actual dominant use of microporous materials such as zeolites, there are great advantages associated with the use of mesoporous materials. As obtainable with other porous materials, the pore dimension of clays can be tuned. The modified clays not only are economical, but also their modified structure and dimension of their pores facilitate diffusion in and out of active sites [4]. The industrial utilization of clay is also closely associated with its reactivity and surface properties, which also depend strongly on surface modification. Several methods have been suggested in literature to improve the surface properties of clay materials to increase its efficiency for various applications. Examples of such methods include mechano-chemical activation, intercalation, thermo-chemical treatment and chemical activation [5].

Acid activation of clay has been widely studied as a chemical treatment for the improvement of the surface and catalytic properties of bentonites, fibrous and montmorillonite clays, and the most commonly used methods for surface modification of clay are hydrothermal treatment and acid leaching [6]. Steam treatment of mordenite to improve its catalytic properties has been reported; however, the steam treatment is known to have major drawbacks such as partial amorphization of the clay framework [7]. The relative crystallinity of the material drops with an increase in the severity of the treatment, leading to fewer active sites. Also, during the process part of the micro and mesopores are filled with debris leading to partial blocking of active sites. Another side effect of steaming is that the number and nature of the acid sites is changed by the extraction of aluminum [8].

Acid leaching can be used in combination with steaming process or as an alternative method of treatment of clay to improve its surface and catalytic properties [9]. The main purpose of acid leaching can be the removal of non-framework material created during hydrothermal treatment and can also facilitate direct creation of mesopores. A mild acid-leaching step with either inorganic acid such as dilute nitric acid or an organic (complexing) acid such as oxalic acid dissolves any extra framework materials resulting in formation of higher mesopore volumes compared to untreated clay materials. The method has been found to be effective in treatment of mordenite as it generates large mesopores and improves its catalytic properties [9]. The acid treated clays are composed of a mixture of non-attached clay layers and hydrous amorphous and partially protonated silica phase. These high surface area silica gels are competitive in different uses and very promising as sorbents and catalyst supports [10]. It is found that the solubility of clay in acids varies with the nature of the acid, the acid-clay ratio, temperature and duration of the treatment [10, 11]. Previous studies on Nigerian clays focused on their modification for adsorption of chemical pollutants from aqueous media. Modified clays suitable for this application must be amorphous with larger pore size and availability of enough acid and metal sites. The Nigerian industrial sector especially the petroleum industry is in urgent need of indigenous technology at best possible cost. Therefore, the objective of this research was to develop a modified clay composite from Nigerian local clay by chemical modification to enhance its surface properties and functions.

2. Materials and Method

2.1 Materials Collection

Clay was collected from local farmlands at Ikot Ebom-Itu, Akwa Ibom State. It was sun-dried and later dried at 40˚C in the oven overnight. Concentrated hydrochloric acid (HCl) and iron (III) oxide (Fe_2O_3) were supplied by Sigma Aldrich. Distilled water, hydrochloric acid and iron (III) oxide were used for the preparation of the clay composites.

2.2 Hydrothermal Treatment of Clay

Mesoporous clay (LCC1) was prepared by hydrothermal process as described by van Donk et al. [12]. In this process, 50 g of the dried sample was added to a 200ml conical flask containing 100cm^3 of distill water. The mixture was then heated at 150°C with constant stirring using magnetic stirrer for 1 h. The mixture was then filtered and oven dried at 120 °C.

2.3 Acid leaching of mesoporous clay

The dried mesoporous clay (50g) prepared in the previous step was added to a 200ml conical flask containing 100ml of 11% HCl. The mixture was heated electrically at 150 °C with constant stirring using magnetic stirrer for 1 h and filtered; and the residue was washed with distilled water until it showed negative chloride test with dilute silver nitrate. The acidified mesoporous clay was then oven dried at 120 °C for 1 h and calcined at 550 °C for 5 h in a muffle furnace. After cooling to room temperature, the sample was collected and labeled as LCC2.

2.4 Preparation of mesoporous clay-Fe_2O_3 modification

The acidified mesoporous clay obtained from the acid leaching step was used to form a composite with Fe_2O_3 (ferric oxide) according to a previous method [13]. Fifty grams (50g) of LCC2 was taken into 200ml conical flask containing 50ml of deionized water. Five grams (5g) of red oxide was added into the flask. The mixture was heated to 150°C with constant stirring using magnetic stirrer and filtered. The mixture was then oven-dried at 120°C for 1 h. The dried mesoporous clay composite was further calcined at 550°C for 5 h in a muffle furnace and labeled as LCC3.

2.5 Characterization

The three samples (LCC1, LCC2 and LCC3) were characterized using Nitrogen adsorption, X-ray Diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR) and Scanning electron microscope (SEM). Nitrogen adsorption–desorption measurements were performed on the samples at liquid nitrogen temperature (−196 °C) with Micromeritics ASAP 2020surface area and porosity analyzer. The analysis procedure is automated and operates with the static volumetric technique. Before each measurement, the samples were first degassed at 300 °C for 3h [14]. The surface area was calculated by the BET method. Pore volume was calculated at relative pressure of 0.98. The pore size was calculated by BJH method. The bulk structures of both parent clay and the modified clay composites were examined by the XRD (Rigaku Corp., Japan) using the Cu K_α radiation following the standard procedures. The determination of the surface functional groups was carried out using FTIR spectrophotometer (Fisher Thermoscientific, USA) following standard procedures. The spectra were recorded using KBr wafers in the range 4000-650cm^{-1}. The surface morphology of samples was determined by SEM (SEM: JSM-5310LV Microanalyzer, JEOL Co.).

3. Result and Discussion

The physical and textural properties of hydrothermally treated clay (LCC1), acid treated clay (LCC2) and ferric oxide modified clay (LCC3) are shown in Table 1. By physical observation, there was not much difference in the colour between LCC1 and LCC2. However, LCC3 showed marked colour change from brown to brick red due to presence of the iron (III) ions in the framework of the catalyst.

Table 1. Physical and textural properties of clay samples

catalyst	BET surface area(m^{2}g^{-1})	Pore size (nm)	Pore volume (cm^{3}g^{-1})	Colour	Density	Particle size (nm)
LCC1	18.8	20.6	0.099	Brown	2.58	15.1
LCC2	166.1	14.0	0.586	Light brown	2.26	12.5
LCC3	145.8	15.2	0.552	Brick red	2.30	3.6

The N_2 adsorption–desorption isotherms of the LCC1, LCC2 and LCC3 presented in Figure 1 can be classified as type II isotherm which are typical of mesoporous structures according to IUPAC nomenclature. Their hysteresis loop is similar to type H1, typical of agglomerates of plate-like particles containing slit-shaped pores commonly found in silica and alumina containing catalyst materials [15]. The isotherms revealed the presence of mesopores with hysteresis loop at P/P_o of 0.64–1.0 for the LCC2 and 0.72–1.0 for LCC3.The mesopore volume increased from 0.099 in LCC1 to 0.586 in LCC2 and drops to 0.552cm^{3}g^{-1} in LCC3 due to slight blockage of some pores by the Iron (III) oxide catalyst precursor. The textural properties of the three samples are presented in Table 1.

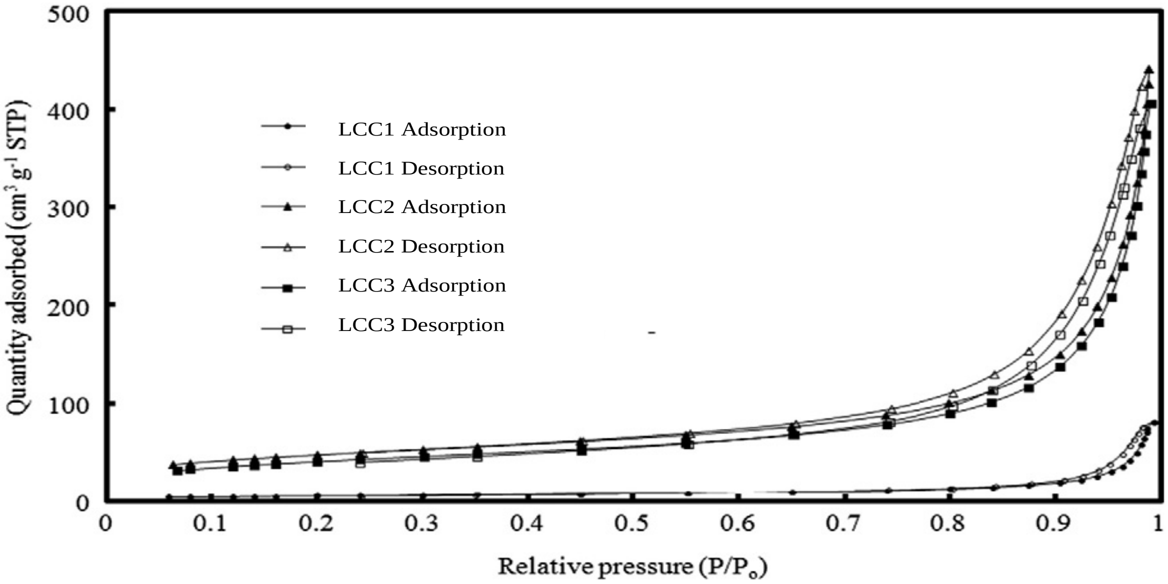

Figure 1: Nitrogen adsorption/ desorption plot of clay samples

The surface area of the LCC1 increased from 18.76 to 166.14 in LCC2 after acid treatment, but it reduced to 145.8m^{2}g^{-1} after Fe_2O_3modification probably due to partial blockage of the pores by the intercalating ions as suggested in a similar study [15]. The result from the XRD (Fig. 2) reveals the changes in the framework structure of the treated clay samples (LCC2 and LCC3) with well-defined reflections at 2theta values of 26^0 for quartz phase, which is a characteristic peak for clay materials [16]. The peaks at 2theta around 24.1, 33.2, 35.6, 40.3, 49.5 and 54.1^0 are used to determine the particle size of the clay material (Table 1). Upon acid treatment, the peak intensities of LCC2 were found to decrease progressively. This is due to disorder in the crystalline structure that may have occurred during the acid treatment. Further deceases in peak intensities were observed in the ferric oxide modified clay composite (LCC3). This reduction may be attributed to the partial amorphization and loss of framework Al atom as suggested in a study previously reported [17]. In the literature, partially amorphized clay materials are used as a catalyst component for heavy hydrocarbon cracking, petrochemicals and in production of fine chemicals [17, 18], therefore, LCC3 can find applications in these industries. The used of acid treated mesoporous zeolite from Indonesian natural zeolite for catalytic pyrolysis of waste plastics into liquid fuel has also been reported [19].

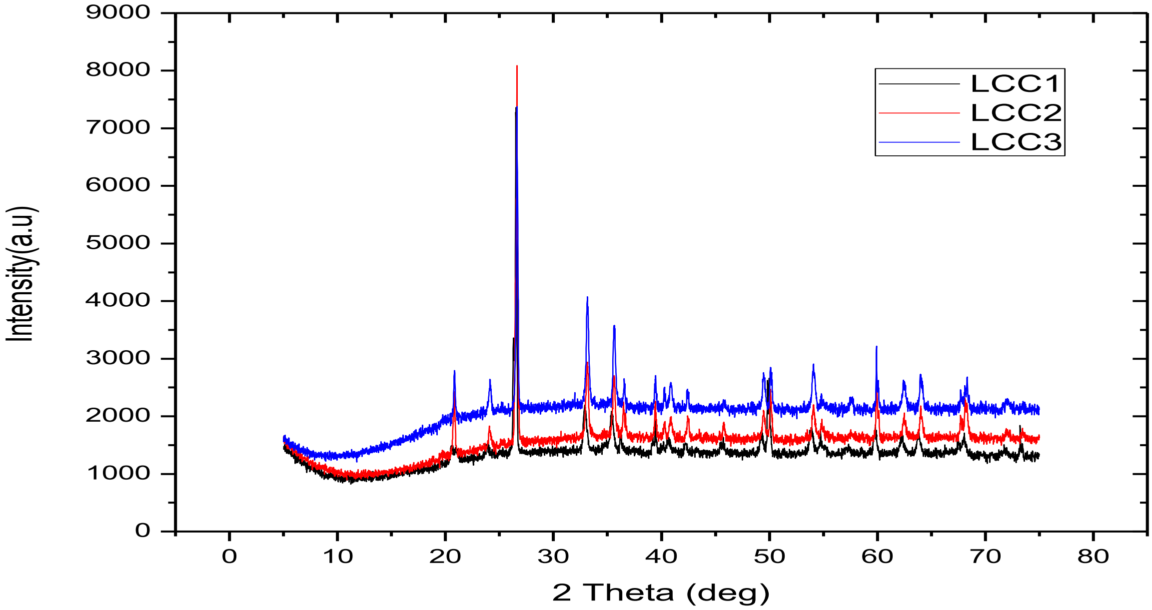

Figure 2: X-ray Diffraction analysis ofclaysamples

The FTIR results for the hydrothermally treated clay (LCC1), acid treated clay (LCC2) and iron (III) oxide modified clay (LCC3) are shown in Figure 3. The LCC1 shows prominent absorption bands at 3455 cm^{-1} which corresponds to Al-OH stretching typical of clay materials; however, the peak became broadened for LCC2 and LCC3. This band broadening could result from partial penetration of cations into the clay mineral layer and attack to the structural hydroxyl group resulting in dehydroxylation and subsequent leaching of the aluminum ions from the octahedral layer as suggested in a similar report [19]. The bands appearing at 3060, 2960 and 2920 for all samples are characteristic bands for structural hydroxyl groups in the stretching region. However, the changing patterns in these bands are as a result of dehydroxylation and distortion of the framework structure due to modifications. These bands were found to be absent in case of the untreated clay due to structural disintegration which has been explained by Wu and Williams [20]. In the bending mode region, all the clay materials, LCC1, LCC2 and LCC3 show a series of absorption bands with peak maxima at 1644, which indicated the presence of OH bending of inner surface hydroxyl groups. This peak also became broadened in the acid treated clay due to loss of some amount of absorbed water. Consequent upon modification of the material with the iron (III) oxide precursor, this peak was further broadened showing distortion in the H-O-H bonds. The peak at 1434 cm^{-1} is quite intense in the modified samples and can be attributed to the bending vibration mode of physiosorbed water on the surface of free silica produced by leaching [21]. The characteristic asymmetric stretching vibrations of Si–O–Si bonds are shown by the IR band at 1060 cm^{-1} whilst the symmetric stretching vibrations are shown by the band at 790cm^{-1}. This later band was absent for LCC3, which can be attributed to amorphous silica in the modified samples and can be a direct result of leaching [21]. The IR bands at 805,755 and 541cm^{-1} can be assigned to the Al–Al–OH, Al–Mg–OH and Si-O-Al vibration of the clay sheet. This clearly points to the fact that during the modification, the de-alumination process is facilitated by acid treatment and the subsequent modification [21-23].

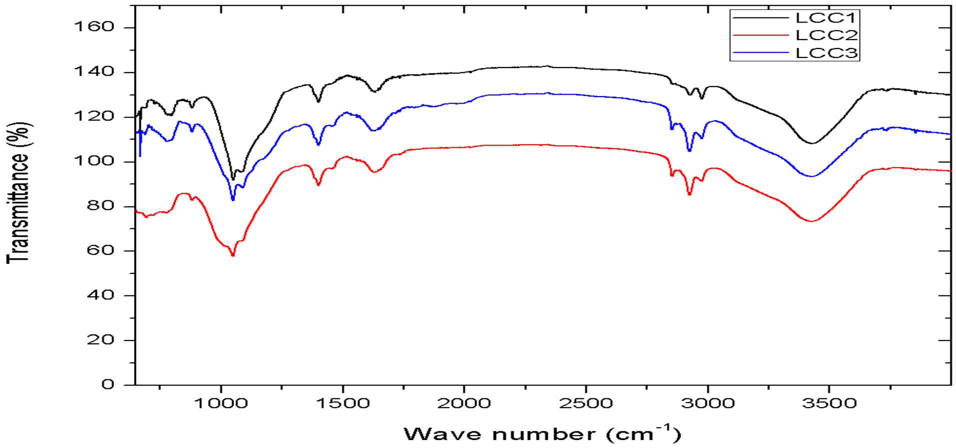

Figure 3: FTIR analysis of clay samples

The scanning electron micrographs of the untreated clay (LCC1) and intercalated clay (LCC3) composites reveal their surface morphologies. The SEM micrograph of the parent clay reveals presence of large particles stacked together in form of agglomerates. The SEM image for the modified clay shows well bonded aggregates rather than detached particles. This implies that some crystalline impurities have been removed by the acid treatment and subsequent modification [24, 25].

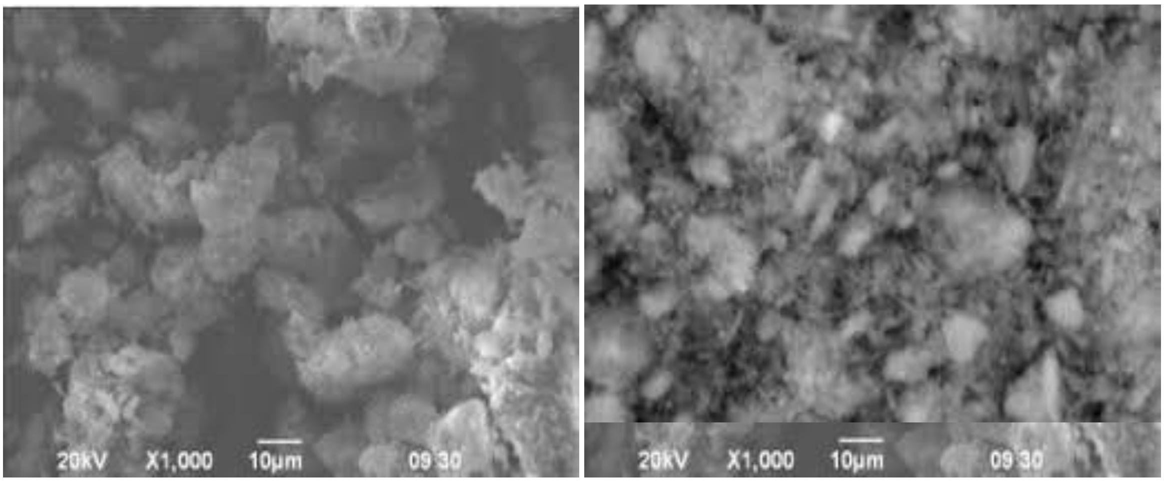

Figure 4 Scanning electron micrographs of untreated clay (LCC1) and intercalated clay composites (LCC3)

Conclusion

In this work, preparation and characterization of catalyst composites from the Nigerian local clay and the effect of different modifications on the structural framework and pore structure of clay were studied. Nitrogen adsorption/desorption analysis of the samples indicated increases in surface area and pore volume with acid treatment and subsequent modification. From the result, mesopore volume increased from 0.099 for LCC1 to 0.586 cm^3g^{-1} in LCC2 and drops to 0.552 cm^3g^{-1} in LCC3 due to slight blockage of some pores by the ferric oxide catalyst precursor, with corresponding increases in surface areas. This increase in pore size and volume provides the catalyst with superior diffusion properties. The distortion in the framework of the catalyst is due to partial amorphization and dealumination of the material resulting from the acid treatment and subsequent modification of the ferric oxide precursor; thus, making the synthetic composite a potential mesoporous silica-alumina based material for diverse potential industrial applications.

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