Original Article

Synthesis and Characterization of Titanium Pillared Bentonite Clay Mineral

Okoye, I. P and Obi, C.
Department of Pure and Industrial Chemistry, University of Port Harcourt, P.M.B. 5323 Choba,
Port Harcourt, Nigeria.
Email: chidexcom@yahoo.com

ABSTRACT

Titanium-pillared clay was synthesized using titanium chloride as the precursor. The pillared product was characterized using Atomic Absorption/ Emission Spectrophotometer (AAS), X-ray diffraction (XRD), BET Nitrogen adsorption, Fourier Transform Infra-Red (FTIR) and Scanning Electron Microscopy (SEM). The results revealed that a significant improvement was achieved on the pillared product. A mesoporous material was obtained in contrast with the classical microporous pillared structure. The characterization indicated an increase in the basal spacing (d_{001}).The introduction of titania on the bentonite (parent) broadens the bands due to the presence of more OH groups of the pillar, which is interpreted as an effect of pillaring. The decrease in intensity is due to the process of dehydration and dehydroxylation involved during pillaring. The BET specific surface area and micropore volume of the pillared clay are 68.40 m^2/g and $9.0 \times 10^{-3} cm^3/g$. These fundamental results presented showed that synthesized Nigerian clay minerals are eco-friendly and good heterogeneous catalysts/adsorbents for removal of industrial pollutants and the production of fine chemicals.
KEYWORDS: *Nigerian Bentonite, Ti-Pillaring, Synthesis, Characterization.*

INTRODUCTION

The synthesis of a solid heterogeneous catalyst and adsorbent has become indispensable owing to the geometric increase in pollution index in most developing countries. In fact, catalysis serves as a blue print in environmental pollution control, with selective catalytic routes replacing stoichometric processes (which are not cost effective) that generate waste problems [1]. There are large deposits of bentonite clay minerals across the parts of the country. These minerals are not yet exploited for commercial purposes. Clays have been used as acidic catalysts in petroleum cracking and several other organic reactions. To enhance performance, research is now focused on the synthesis of pillared clays (PILCs), which posse's larger two-dimensiona pores [2]. Pillaring is achieved by the insertion of voluminous inorganic metal hydroxycation between layers of the clay in order to keep them apart. On thermal treatment, the metal hydroxycations are transformed into pillars which are responsible for the acidity [3, 4, 5]. The surface of the pillars posses both Lewis and Bronsted acid sites [5, 6, 7]. The Bronsted acidity is attributed to the separation of the clay interlayer by pillaring and consequent surface exposure of the sylanol groups. On the other hand, the pillars contribute mainly to Lewis acidity. Several investigations have focused strongly on the use of transition metals such as Al, Zr, Cr, Ti, and mixed metals such as Cr-Fe, Cr-Al, Cr-Ti, etc, as pillars in order to produce a desired pillared product [8].

In Nigeria, the obscured relationship between synthesis and characterization of these pillared products are not quite clear and not well documented for future use, hence the need for this study. It is important to evaluate the suitability of the Nigerian clay resources in pillared clay synthesis.

Titanium pillared bentonite has a considerably larger interlayer spacing in comparison with other metal oxide pillared clay minerals and shows high adsorption ability [9].

Therefore, the aim of this study is to transform clay which is a locally available raw material into fine solid catalyst. The pillared product showed uniformity and reproducibility at the pilot scale. Several analytical techniques were employed in the characterization including XRD, BET surface area analysis, vibrational framework studies by FTIR spectroscopy, morphology of the pillared clay by SEM, and the metal oxide composition using Atomic Absorption Spectrophotometer (AAS).

MATERIALS AND METHODS
Clay Source and Sampling

Sample of the natural clay was collected from the open clay deposit in Ezinachi, Okigwe Local Government Area, Imo state, Nigeria. The clay sample was washed and dried under sunshine for two days.

Titanium Pillarization

The pillaring agents were prepared following the method described by Lin et al. [10]. Titanium chloride ($TiCl_4$) from Aldrich was mixed with twice the volume of ethanol, and stirred in a solution of glycerol. The total mixture was added drop wise to a calculated amount of clay in 250ml of deionised water and allowed to equilibrate under stirring for 4hours at room temperature. The titanium intercalated clay material was filtered and dried overnight in an oven at 110°C. The intercalated Ti-clay was calcined at 500°C for 4 hours in air to give the Ti-pillared clay (Ti-PILC).

Characterization of Ti-pillared sample

An elemental analysis in natural and pillared clay samples was performed by a gravimetric method and Atomic Absorption/Emission Spectrophotometer. Nitrogen adsorption–desorption isotherm were determined at – 196°C in an Autosorb – I (Quan-Tachnome). Samples of 0.2302g were out gassed at 180°C under vacuum.The specific surface area (SSA) was determined based on BET [11] model. The specific total pore volume was determined from the adsorption at the relative pressure of 0.95, converted to liquid volume assuming a nitrogen density of 0.808g/ml. The micro pore size distribution was analyzed based on the methods proposed by Horvath and Kawazoe, [12] and by Saito and Foley, [13] were used in considering the oxalic character of the surface. Powder X-ray diffraction (PXRD) patterns were recorded using a Philips APD 1700 instrument, with quartz plate CuKα radiation of wavelength 1.5406 Å [14]. The vibrational framework of the pillared sample was studied using FTIR. Scanning electron microscope (LEO SUPRA 50VP-FIELD EMISSION SEM, Carl Zeiss, Germany) was used to observe the surface morphology of the prepared pillared clays used as catalyst.

RESULTS AND DISCUSSION
Elemental Analysis

The result of elemental analysis of the bentonite clay mineral is presented in Table 1. It is shown that the percentage composition of silica is highest in the natural clay while a trace of calcium and potassium exits as an impurity. On pillaring, the titanium content increased whiles other decreased significantly, due to washing and ion exchange.

Table 1. Physicochemical compositions of the natural and Ti-Pillared bentonite clay

Metal oxides (% Weight)	Natural bentonite	Ti-Pillared bentonite
SiO_2	74.12	71.20
Al_2O_3	0.50	0.32
Fe_2O_3	7.88	3.42
CaO	0.02	0.01
MgO	0.23	0.15
Na_2O	0.04	0.02
TiO_2	Nil	12.36
K_2O	0.11	0.01

The XRD patterns of natural, Ti-Intercalated and Ti-Pillared bentonites in the $2\theta = 30°$ range is represented in Figure 1. The XRD pattern of the natural bentonite is used for comparison. The orientation of the interlayers allow the (001) diffraction peak to be more intense. The XRD pattern of the natural bentonite exhibits a peak at $2\theta = 6.9$ Å, commonly assigned to the basal (001) reflection. The d-spacing for the titanium-intercalated bentonite is 15.0 Å. The d-spacing for the titanium-pillared (Ti-PILBe) bentonite calcined at 500°C is 22.0 Å. The shift in 2θ value of 100 planes and thus the increase in d-spacing upon pillaring are evident. Kloprogge, [8] in his work reported that pillared smectites are clays with high permanent porosity obtained by separating the clay sheets by a molecular prop or pillaring agent. Thus, the enhanced porosity and surface area shown in Table 2.

This occurs due to the presence of titania pillars. Yamanaka et al. [15] equally reported that TiO_2 pillared montmorillonite gave a basal spacing of 23.2Å at room temperature. The basal spacing of the sample is shifted to 22.2Å when calcined at 500°C. Titanium pillaring is found to be very effective for the development of thermally stable porous structure in clays. The natural, intercalated and pillared clays respectively prepared in this present work showed expanded clay layers. Peaks corresponding to 001, 002, 003, and 004 planes were detected. These results reveal that the pillared clay samples have good ordered layers with insertion of alumina pillars, which caused an increase in the clay basal spacing.
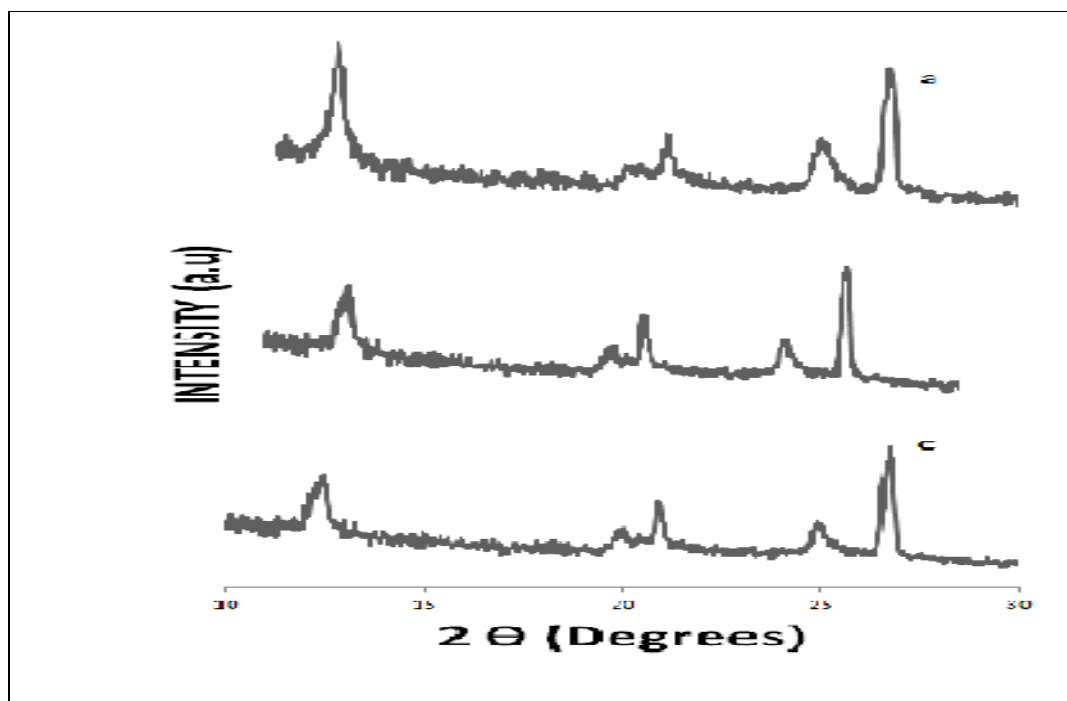

Fig 1. PXRD pattern of Natural, Ti-Intercalated and Ti-Pillared bentonite clay.

The results of surface area also show the pore evolution after pillarization. The BET and micro pore surface areas, pore volume and average pore diameter of the material are listed in Table 1. The BET specific surface of the pillared material increased as a result of pillaring. The porosity of the pillared material is higher than the unpillared as represented in Figure 3. Although an expanded material is obtained, the interlamellar space appears to be blocked, with nitrogen molecules not able to access the interlayer gallery. This is confirmed by the low total pore volume of the sample.

Table 2. BET surface and micro pore areas, micro pore volume and average diameter of Al-pillared bentonite

SAMPLE	BET surface area (m^2/g)	Micro pore volume (m^3/g)	Micro pore area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (Å)
Natural bentonite	29.99	0.0011	2.70	0.0010	14.80
Ti-Pillared bentonite	68.40	0.0090	18.57	0.016	16.2

Mid-infrared spectroscopy is a very important tool for investigating structural changes in pillared clay frameworks. The region of interest for determining structural composition is the frequency region between 1400 - 400 cm^{-1} which is characteristic of metal bonded silica [7]. The FTIR spectra of the parent (natural bentonite), titanium intercalated and pillared bentonites are represented in Figure 2. Peaks at around 1400 cm^{-1} are due to bending vibrations of water. This is comparable to the research done on pillared montmorillonite by Binitha and Sugunan, [16]. The introduction of titania on the bentonite (parent) by pillaring broadens the bands due to the presence of more –OH groups of the pillar, which is interpreted as an effect of pillaring. The decrease in intensity is due to the process of dehydration and dehydroxylation involved during pillaring. The process of pillaring substitutes a large amount of interlayer cations that generally exist in hydrated forms and thus decreases the intensity of –OH peaks. It has been shown that pillared clays have low amount of adsorbed/co-ordinated water due to the non-swellable nature. Thus, pillaring reduces the intensity of the bands around 1400 cm^{-1} as seen in Figure 2. The intensity of the peak was reduced in the pillared bentonite much more than the intercalated and natural bentonites respectively. This could be as a result of the large isomorphous substitution of the clay interlayer cation by Ti^{4+} [10]. The very intense band centred at 1300 cm^{-1} is due to asymmetric stretching vibrations of SiO_4 tetrahedra. Bands around 1000 cm^{-1} are due to symmetric vibrations of Al^{4+} tetrahedral. Bands consisting of peaks of medium intensity at 450 - 550 cm^{-1} are due to bending vibrations of Si-O.
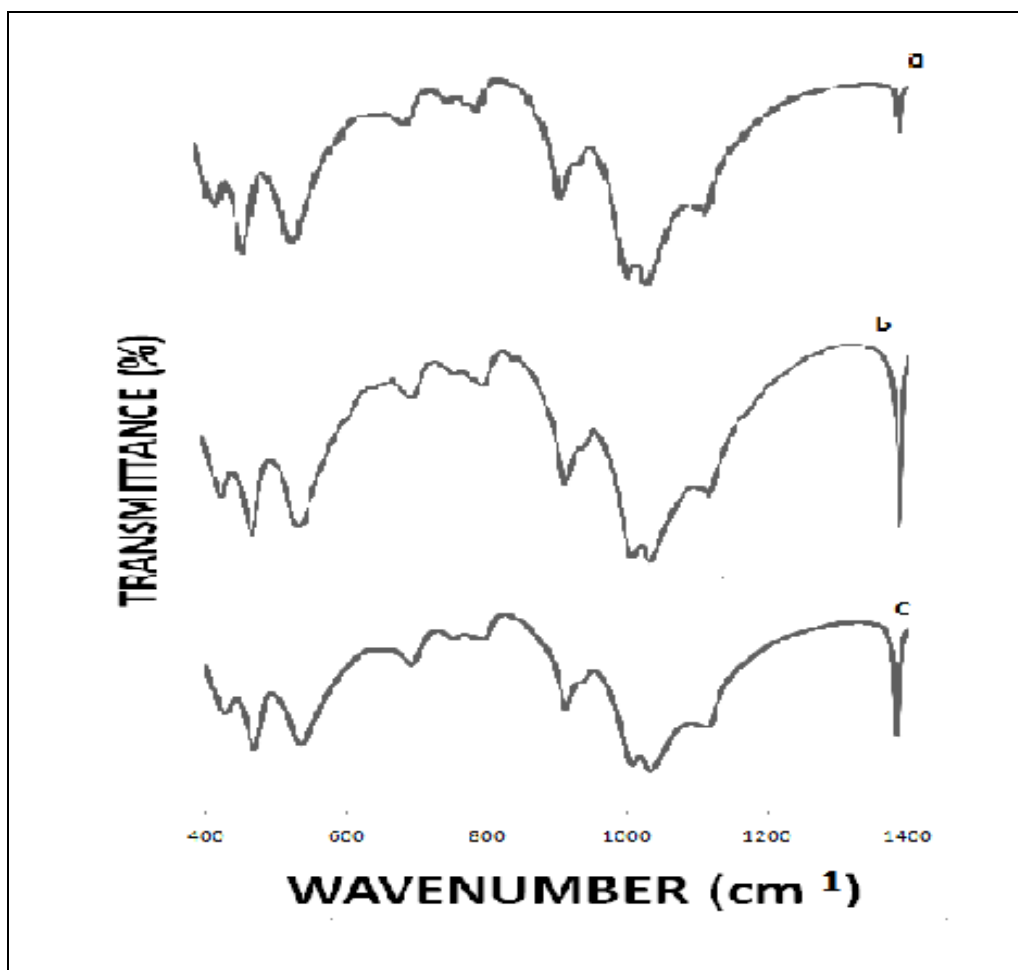

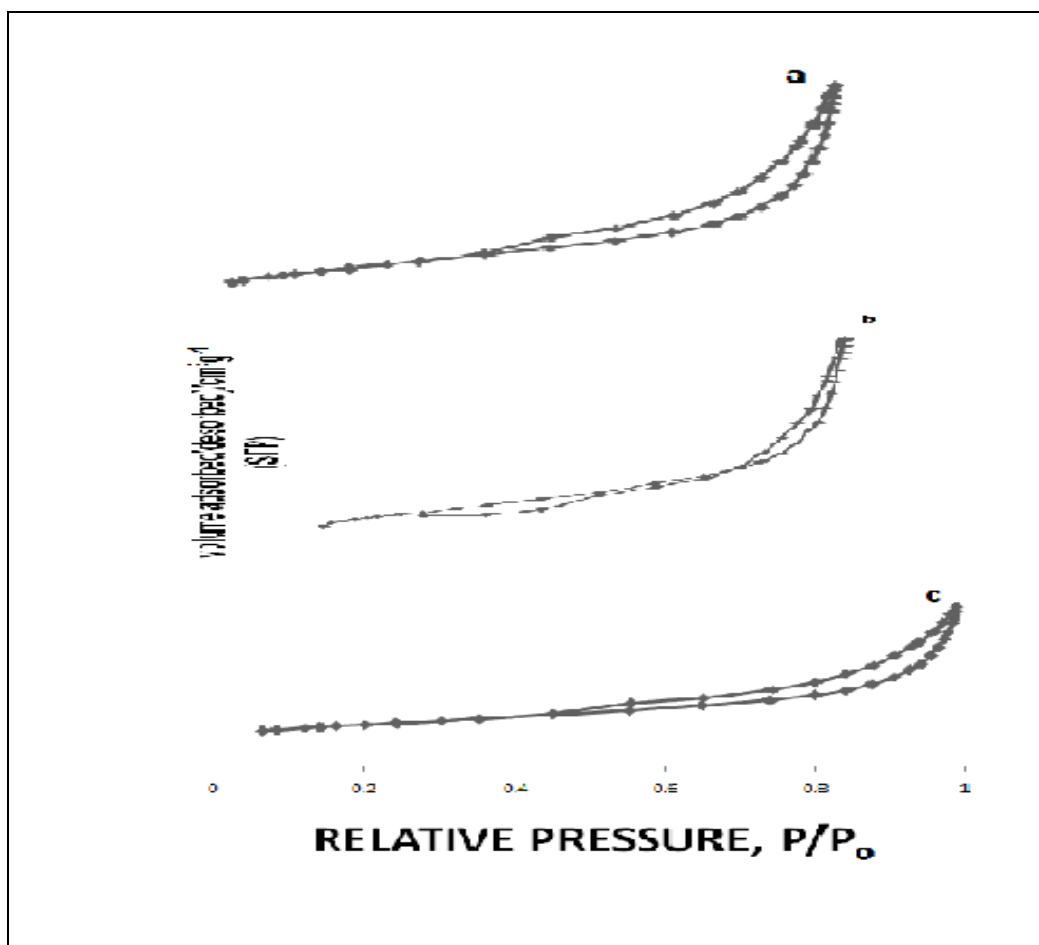**Figure 2**. FTIR spectra of (a) Natural, (b) Ti-Intercalated and (c) Ti-Pillared bentonite clay

Figure 3. N2 adsorption isotherm of (a) Natural, (b) Ti-Intercalated and (c) Ti-Pillared bentonite.

CONCLUSION

The presence of pillars on bentonite produced better materials with uniformity and reproducibility. The material obtained after pillaring showed meso porosity. The results reveal that the pillared clay sample has good ordered layers with insertion of titania pillar, which caused an increase in the clay basal spacing. It was observed that physico-chemical properties of Ti-pillared bentonite clay changed as a result of pillarization process.   Mid-infrared spectroscopy is a very important tool for investigating structural changes in pillared clay framework. The introduction of titanium on the bentonite (parent) by pillaring broadens the bands due to the presence of more –OH groups of the pillar, which is interpreted as an effect of pillaring. Bending vibrations of water, asymmetric stretching vibrations of SiO_4 tetrahedral, symmetric vibrations of Al^{4+} tetrahedral and bending vibrations of Si-O were observed at $1400cm^{-1}$, $1300cm^{-1}$, $1000cm^{-1}$ and $450-550cm^{-1}$. The decrease in intensity is due to the process of dehydration and dehydroxylation involved during pillaring. The process of pillaring substitutes a large amount of interlayer cations that generally exist in hydrated forms and thus decreases the intensity of –OH peaks. These fundamental data generated are of importance in developing novel heterogeneous catalysts and adsorbents. The catalytic activity of esterification reaction using homogenous batch reactor is now being investigated.

REFERENCES

1.   Niemantsverdriet, J.W. (2007). Spectroscopy in Catalysis: An Introduction, Third Edition, published by Wiley-VCH Verlag GmbH & Co. kGaH, Weinheim, pp 1-2.
2.   Fatimah, Is., Narsito and Wijaya, K. (2011). Effect of Aluminium Pillared Montmorillonite on Its Surface Acidity Properties. *ITB J. Sci.,* 43A (**2**), 123-138.

3.   Miguel, A.V, Carolina, B, Mikhail, S, Roman, P.K and Antonio. G. Relationship between the surface properties and the catalytic performances of Al-, Ga-, and AlGa-Pillared saponites, Ind. Eng. Chem. Les., 2009; 48: 406-414.

4.   Binitha, N.N and Sugunan, S. (2006). "Preparation, Characterization and catalytic activity of titania pillared montmorillonite clays".Micr. and Meso. Materials 93, 82-89.

5.   Okoye, I. P and Obi, C. (2011). "The Adsorption Dynamics of Heavy Metal Ions onto Titanium-Pillared and Unpillared Bentonite Clays". *Journal Nig. Environ. Soc.* 5(**5**), 22-28.

6.   Salerno, P., Asenjo, M.B and Mendioroz, J. (2001). "Influence of preparation method on thermal stability and acidity of Al- P1LCs". *Thermochim. Acta,* 379, 101-109.

7.   Gill, A and Gandia, L.M. (2000). Recent Advances in the Synthesis and Catalytic Applications of Pillared Clays. *Catal. Rev-Sci. Eng.,* 42 (**1&2)**, 145-212.

8.   Kloprogge, J.T., Duong, L.V and Frost, R.L. (2005). A review of the Synthesis and Characterization of Pillared Clays and Related Porous Materials for Cracking of Vegetable Oils to Produce Biofuels. *Environ. Geol.,* 47, 967-981.

9.   Kaneko, T., Fuji, M., Kidama, T and Kitayama, Y. (2001). J. Porous Mater., 8, 99.

10. Lin, J.T., Jong, S.J and Cheng, S. (1993). Microporous Mater., Vol.1, 287.

11. Branauer, S., Emmett, P.H and Teller, E. (1938). "Adsorption of gases in multimolecular layers", *J.Am. Chem. Soc.*, 60, 309.

12. Horvath, G and Kawazoe, K. (1983). "Method for the calculation of Effective pore size distribution in molecular Sieve Carbon". *J. Chem. Engn. Jap.,* 16, 470.

13. Saito,A and Foley, H.C. (1991). "Curvature and parametric sensitivity in models for Adsorption in Micropores", AIChE Journal, 37, 429.

14. Ckwoksi, P and Joshi, V. (2007). Adsorption kinetics study for the removal of Ni (II) and   Al (III) from an aqueous solution by natural adsorbents. Desalination, 208, 216-231.

15. Yamanaka, S and Makita, K. (1993). *J. Porous Mater.*, 29.