

## Synthesis and Characterization of Al-Pillared Bentonite Clay Minerals

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**Abstract:** Aluminum pillared material was synthesized from natural bentonite mineral using  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  solution as pillaring agent. The pillared products were characterized using X-Ray powder Diffraction (XRD), Atomic Absorption Spectrophotometer (AAS), Fourier Transform Infra-Red (FTIR) spectroscopy and surface area-pore volume measurements. The d-spacing for the intercalated and pillared bentonites is 13.0 and 18.0 Å, respectively. The intensity of the bands assigned to Si-O and Al-O framework vibrations were slightly reduced on pillaring. The decrease in intensity is due to the process of dehydration and dehydroxylation involved during pillaring. The specific surface areas of pillared and unpillared bentonite are 49.86 and 29.99  $\text{m}^2 \text{g}^{-1}$ , respectively. These fundamental results are of importance in developing novel heterogeneous catalysts and adsorbents.

**Key words:** Bentonite, Al-pillared bentonite, synthesis, characterization, dehydroxylation, Nigeria

### INTRODUCTION

Pillared clays are considered to be interesting two-dimensional zeolite-like, shape selective molecular sieves and have been widely used as catalysts or catalyst support in the petroleum and petrochemical industries due to their pore size and enhanced acid sites properties, (Auer and Hofmann, 1993; Ratti *et al.*, 2010). The principle behind clay pillaring originates from the insertion of voluminous or oligomeric inorganic metal hydroxycations between the layers of clays in order to keep them apart. On calcination, the metal hydroxycations are decomposed into oxide pillars which create interlayer and interpillar spaces (Okoye and Obi, 2011). The term pillared and pillaring originated from the research of Vaughan and Lussier (1980) on smectite-type clay minerals. These researchers discovered that thermally stable inorganic moieties can be intercalated between the individual clay lamellar sheets. The resulting materials were therefore, calcined to give the metal oxide acting as pillars. The pillared materials were demonstrated to have an increased interlamellar distance, an increased pore volume and were accessible by molecules within a specific size range (Fatma and Suna, 2008).

In general the pillaring process can be described according to the diagram shown in Fig. 1. The sodium bentonite clay is used as a starting material. A solution containing the aluminium polycation is mixed with the clay suspension for ion exchange and intercalation. After

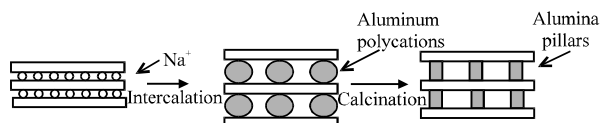


Fig. 1: Preparation of al-pillared bentonite: intercalation of aluminum polycation followed by calcinations to generate the pillar

intercalation with the polycation, the sample is washed, dried and calcined to give the metal oxide pillar in the clay interlayer.

The pillared structure has been suggested to produce acid sites through dehydration and dehydroxylation of the metal cations at high temperatures (Schoonheydt *et al.*, 1999). The number and strength of the acid sites present the clay sample are important factors for catalytic applications. Bronsted and Lewis acids are two types of acid sites which have generally been reported to exist in pillared clays (Fatma and Suna, 2008). Lewis acid sites have been found to be correlated with the number and nature of the pillars whereas the Bronsted acid sites are located within the clay sheets (Auer and Hofmann, 1993). The pillared clays have also been found to have more Lewis acid sites than Bronsted acid sites (Kurian and Sugunan, 2003) and were said to contain total surface acidity that varies with the pillaring agents. The acidity of the pillared clay can be studied by IR spectroscopy using pyridine adsorption-desorption

process. It was shown via IR studies that as the clay mineral is dehydrated with increasing temperature, its Lewis acidity increases and becomes more important than its Bronsted acidity (Lambert and Poncelet, 1997; Tyagi *et al.*, 2006).

The main objective of this work is to investigate the possibility of synthesizing a thermally stable and wide pore Al-pillared bentonite catalyst from natural clay deposit. Furthermore, it aims to characterize the structures of these Al-pillared smectites in order to establish their catalytic properties and applications.

## EXPERIMENTAL

**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 at 110°C for 2 days.

**Al-pillared synthesis:** The transformation of natural clay mineral into pillared clay requires the use of a pillaring solution prepared by adding slowly a basic solution of 0.2 M NaOH to 0.1 M Al(NO)<sub>3</sub>·9H<sub>2</sub>O under constant stirring. The pillaring solution was left overnight at room temperature under constant stirring. There after, the pillaring solution was added dropwise to about 2.5 g of the clay in 250 mL suspension with constant stirring and aged overnight at room temperature. Afterwards, the pillared clay suspension was filtered and washed with distilled water. The pillared clay was air-dried at ambient temperature and at 105°C for 4 h and then calcined at 200°C for 2 h (Jone and Purnell, 1994). The resulting product is Aluminum Pillared Clay Mineral (Al-PILC).

**Characterization of Al-pillared sample:** The elements, Si, Al, Fe, Na, Ca and Mg were analyzed using atomic absorption and emission spectrophotometry. Nitrogen adsorption-desorption isotherm were determined at -196°C in an Autosorb-I (Quan-Tachnome). Samples of 0.2302 g were out gassed at 180°C under vacuum. The Specific Surface Area (SSA) was determined based on BET (Branauer *et al.*, 1938) 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 0.808 g mL<sup>-1</sup>. The micropore size distribution was analysed using the methods proposed by Horvath and Kawazoe (1983) and modified by Saito and Foley (1991).

Powder X-Ray Diffraction (PXRD) patterns were recorded using a Philips APD 1700 instrument with quartz plate CuK $\alpha$  radiation of wavelength 1.5406 Å (Ckwoksi and Joshi, 2007). The vibrational framework of the clay samples was studied using FTIR spectroscopy.

Scanning electron microscope (LEO SUPRA 50VP-FIELD EMISSION SEM, Carl Zeiss, Germany) was used to observe the surface morphology of the pillared clays.

## RESULTS AND DISCUSSION

**Chemical composition of the clay samples:** The chemical composition of both pillared and unpillared bentonite clay is shown in Table 1. The results indicate that the natural bentonite contains silica, alumina, magnesia, iron (III) oxide and sodium oxide as major constituents while traces of calcium and potassium oxides exist as impurities.

On pillaring, the aluminium content increased while other metals decreased significantly due to ion exchange and washing several times with water. The decrease in the amount of exchangeable metal cations (K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>3+</sup>) upon pillaring is clearly seen because apart from washing, the entrance of Al-pillar metal replaces exchangeable cations.

**XRD pattern:** The XRD patterns of the natural, Al-Intercalated and Al-pillared bentonites are shown in Fig. 2. The XRD pattern of the natural bentonite exhibits a peak at  $2\theta = 6.9^\circ$  commonly assigned to the basal (001) plane. The d-spacing for the aluminum-intercalated and pillared bentonites is 13.0 and 18.0 Å, respectively.

The shift in  $2\theta$  value of 100 planes and thus the increase in d-spacing upon pillaring are evident (Klopprogge, 1998). The natural intercalated and pillared clays 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.

**Surface area and porosity:** Table 2 shows the total BET and micropore surface areas, pore volumes and average pore diameters for both pillared and unpillared bentonites. In the case of pillared sample, the BET surface area (ca. 49.99 m<sup>2</sup> g<sup>-1</sup>), the micropore surface area (ca. 3.3 m<sup>2</sup> g<sup>-1</sup>),

Table 1: The chemical compositions of unpillared and Al-pillared bentonite clay minerals

Metal oxides (wt%)	Unpillared bentonite (wt%)	Al-pillared bentonite (wt%)
SiO <sub>2</sub>	74.12	71.20
Al <sub>2</sub> O <sub>3</sub>	0.50	16.99
Fe <sub>2</sub> O <sub>3</sub>	7.88	3.42
CaO	0.02	0.01
MgO	0.23	0.15
Na <sub>2</sub> O	0.04	0.02
TiO <sub>2</sub>	Nil	Nil
K <sub>2</sub> O	0.11	0.01

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

Samples	BET surface area ( $\text{m g}^{-2}$ )	Micro pore surface area ( $\text{m g}^{-2}$ )	Micro pore vol. ( $\text{cm g}^{-3}$ )	Total pore volume ( $\text{cm g}^{-3}$ )	Average pore diameter ( $\text{\AA}$ )
Al-pillared bentonite	49.86	3.30	0.0014	0.013	16.20
Unpillared bentonite	29.99	2.70	0.0011	0.010	14.80

the total pore volume ( $0.013 \text{ cm}^3 \text{ g}^{-1}$ ) and the average pore diameter are significantly higher than that of the unpillared sample due to the presence of micropores created by aluminium pillar in the interlayer regions. The average pore diameter is within the range typical of smectite clays (Narsito and Wijaya, 2011).

**Mid infrared spectroscopy:** 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  $1400\text{--}400 \text{ cm}^{-1}$  which is characteristic of metal bonded silica (Salerno *et al.*, 2001; Trombetta *et al.*, 2000; Kurian and Sugunan, 2003). The FTIR spectra of the parent (natural) bentonite, aluminum intercalated and pillared bentonites are shown in Fig. 3. The spectrum of the natural bentonite (Fig. 3a) shows an intense peak at around  $1400 \text{ cm}^{-1}$  that is due to bending vibrations of water.

The Si-O coordination bands at  $1160$ ,  $1120$  and  $1110 \text{ cm}^{-1}$  are due to the stretching of Si-O in the Si-O-Si groups of the tetrahedral sheet. A medium to strong peak at  $1050 \text{ cm}^{-1}$  is attributed to asymmetric stretching vibration of  $\text{SiO}_2$  tetrahedra. These peaks are noted to decrease in intensity due to the process of dehydration and dehydroxylation involved during pillaring. The observed bands at  $550$  and  $450 \text{ cm}^{-1}$  are due to Al-O-Si groups of the octahedral and Si-O-Si bending vibrations, respectively. The intensities of the peaks were slightly reduced in the pillared bentonite in comparison with the intercalated and natural bentonites. This could be as a result of the large substitution of the clay interlayer cation by Al-ion (Einaga, 1979; Nabivanets and Kudritskaya, 1967; Gil *et al.*, 2000). A small peak in the hydroxyl bending region at  $850 \text{ cm}^{-1}$  assigned to isolated Al-O vibration becomes significant for Al-pillared sample but was completely absent in the spectrum of natural bentonite (Fig. 3c) which clearly suggest that the octahedral cations (Fe, Mg) are being replaced by aluminum. The process of pillaring substitutes a large amount of interlayer cations that generally exist in hydrated forms and thus decreases the hydroxyl ion contents. It has been shown that pillared clays have low amount of adsorbed/co-ordinated water due to dehydroxylation (Kurian and Sugunan, 2003). Bands around  $1000 \text{ cm}^{-1}$  are due to symmetric vibrations of  $\text{Al}^{4+}$  tetrahedral. The doublet at  $800$  and  $780 \text{ cm}^{-1}$  indicates the presence of quartz impurity in the sample in accordance

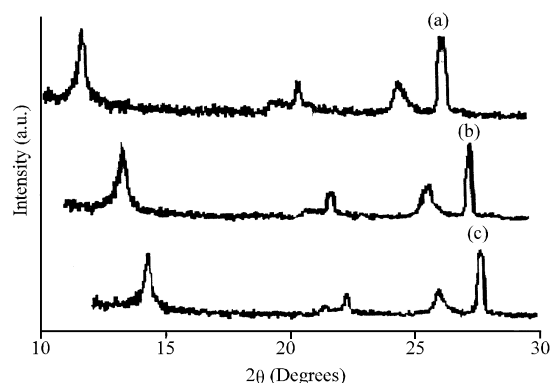


Fig. 2: XRD pattern of a) Natural; b) Al-Intercalated and c) Al-pillared bentonites

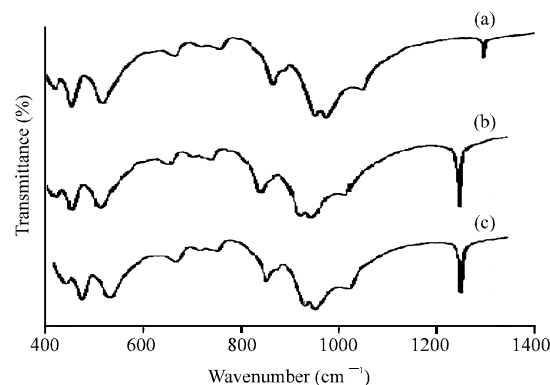


Fig. 3: FTIR spectra of a) natural; b) Al-intercalated and c) Al-pillared bentonites

with the recent report by Madejova *et al.* (1998). These peaks associated with Al-pillared clay are noted to decrease slightly in intensity when compared with unpillared samples. However, the spectral features are similar for the three samples shown in Fig. 3 which clearly indicates that intercalation and pillaring do not destroy the structure of the bentonite.

## CONCLUSION

It was observed that physico-chemical properties of Al-pillared bentonite clay changed as a result of pillaring. The presence of aluminium pillars on bentonite produced materials with higher basal spacing, specific surface area and pore volume as evident from XRD and surface area-pore volume analysis. FT-IR analysis also showed

that intercalation and pillaring did not destroy the structure of the bentonite. The results obtained in this research reveal that the insertion of alumina pillar, props apart the clay layers and produced materials with good ordered layer structures.

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