Effects of Dealumination on the Physio-Chemical Properties of Clay for Industrial Applications

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Abstract

The physiochemical properties of natural clay and its modified form were investigated for use as catalyst. The clay samples were from Ukpor, in Nnewi in Anambra state, south eastern Nigeria. The particle size of 2mm was used. A known weight of the natural clay was mixed with a 36 N sulphuric acid at a molar ratio of 1: 5. The mixture was heated in a furnace at 500°C, ramped at 5oC/min for one hour. The resulted clay was calcined at 600oC for 6 hours. The natural clay and its treated samples were characterized using X-ray fluorescence equipment (XRF), X-ray diffraction (XRDP) powder patterns, Scanning Electron Microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Energy Dispersive X-ray (EDX). The results of the treated clay revealed it's amorphous, 67% increase of silicon. The EDX revealed 36.5% Si, 2.4% Al. No significant change in the O_2 of both samples. Surface area was 500 m^2/g. The Si/Al ratio was raised to 15.0 for the treated clay. Using a 36 N sulphuric acid showed greater influenced on the physiochemical properties compared to aqueous HCl, $NaHSO_4$ and H_2SO_4. This opens up higher possibility of controlling the degree of alumina and silica by choice for different industrial applications.

Keywords: Clay; Beneficiation; Dealuminated clay; Dissolution; Sulphuric acid

1.1 Introduction

The creation of powerful new materials for innovative applications is one of the big technical and scientific challenges in our day. Clay, an aluminisilicate material can be a good source of silica. High purity silica is used in a variety of industrial applications. It is used as a filler, a catalytic support, in optical glasses, in fused silica wares, and as a waveguide. Also, clays are solid minerals that can function as both Bronsted and Lewis acids in their natural and Ion exchanged form. Ion exchange is the property of clays to adsorb certain anions and cations as well as their capacity to retain them in exchangeable state. In other words, the adsorbed ions are exchanged for other anions and cations in an aqueous solution, however, such exchange reaction can also take place in non-aqueous medium. The exchangeable ions are held around the outside of the silica-alumina clay structural units, and the exchange reaction generally

does not affect the structure of the silica-alumina packet (Carlson, 2004). A well-known example of the ion exchange reaction is the softening of water by the use of zeolites. Clay minerals are the most important chemical weathering products of aluminium rich rocks. Generally, clay is crystalline, the atoms are arranged in a regular order. The character of the clay mineral found in a given soil depends on the nature of the parent material, climate, topography, vegetation and time during which these factors have operated (Grim, 1992). Aluminosilicates is a three dimensional framework structure of silicate mineral in which the silicon atoms are replaced by aluminium atoms in a negatively charged framework with other cations uniformly distributed through it (Obaje *et al*., 2013).

Treatments of clay involve subjecting clay to various treatments so as to modify the properties for the intended purpose. Such treatments include doping, desilication, dealumination, etc. Modifying the properties of clay can lead to variety of catalysts that are useful in effecting more different reactions and higher selectivity in product structure and yield. Their chemical composition and crystal structure are the basis on which clay is divided into groups, such as Kaolinite, Ulite, Smectite and Chlorite. Among these, the most useful as a catalyst is a sub-group of the Smectite clay called Montmorillonite which is the main constituent of bentonites and Fuller's earth. (Arata and Hino 2011). Clay is important in the construction industry both as a building material and as a foundation for structures. An important industrial application of clays can be found in petroleum and petrochemical processing. Others include ceramic, electrical, pharmaceutical, paint, paper, nuclear energy and textile industries, respectively, etc. Pillared clays which are more stable at higher temperatures (>200°C) are used in petroleum cracking, catalytic reforming and isomerisation of n-alkanes to branched chain alkanes. Many synthetic aluminosilicate can be made and several are manufactured industrially for use: as an ion exchanger and molecular 'sieves, examples are feldspars and zeolites (Fernando and Joan, 2007). The authors studied the dealumination of kaolin using sodium potassium hydroxide during gel formation for the synthesis of zeolite X. A variety of organic reaction that are catalysed by Bronsted acids or Lewis acids have been shown to take place in clays especially montmorillonite, more efficiently under milder conditions, with greater selectivity, better yield, and shorter reaction times.

1.2   Experimental Procedure

The clay sample was pre-treated and sieved to 2mm. Dealumination of kaolin was carried out according to Iyakwari *et al*. (2016). A known weight of the natural clay was mixed with a standard analytical-grade 36 N sulphuric acid (H_2SO_4) solution at a molar at a ratio of 1: 5. Aliquot of the mixture was placed in open quartz crucible. It was heated in a furnace at 500°C, ramped at 5°C/min for one hour. Once the reaction time and temperature was reached the crucible was left in the furnace for 6 h. The physio-chemical properties of the resulted material were analysed. The catalytic surface areas of the catalysts were obtained from N_2 adsorption isotherms determined at 77K using the Coulter^{TM} (SA 3100^{TM} series). The samples were outgassed under high vacuum for 2 h at 200°C prior to the analysis. The pore size was determined using ImageJ software with SEM images. The crystallite size of the modified sample was calculated using data from X-ray diffractogram and X'pert data viewer software in the Scherrer's formula.

1.3   Results and Discussion

The textural properties and elemental analysis of the natural and the dealuminated clay are given in Table 1. For convenience clay is designated as 'C' and its modified form as 'DC'.

Table 1: Result of Physical Analysis

Parameter	Natural clay (C)	Dealuminated clay (DC)
Specific surface area, m^2/g	100	500
Particle size, μm	250	250
Particle density, kg/m^3	1120	850
Pore-volume, m^3/g	0.25	0.40
Porosity	0.34	0.45

The XRPD pattern of the clay was crystalline with three mineral phases identified (kaolinite, quartz and mica) however, the quartz and mica were minor. In the X-ray diffraction pattern of dealuminated clay, there were no kaolinite crystalline peaks. The disappearance of these major peaks gave way to amorphous material with a very broad band within the low-range angle 15-35° 2θ as in shown in Figure 1Figure. Rosenberg and Anderson (2012) described the broad band as an amorphous phase of silica (SiO_2).
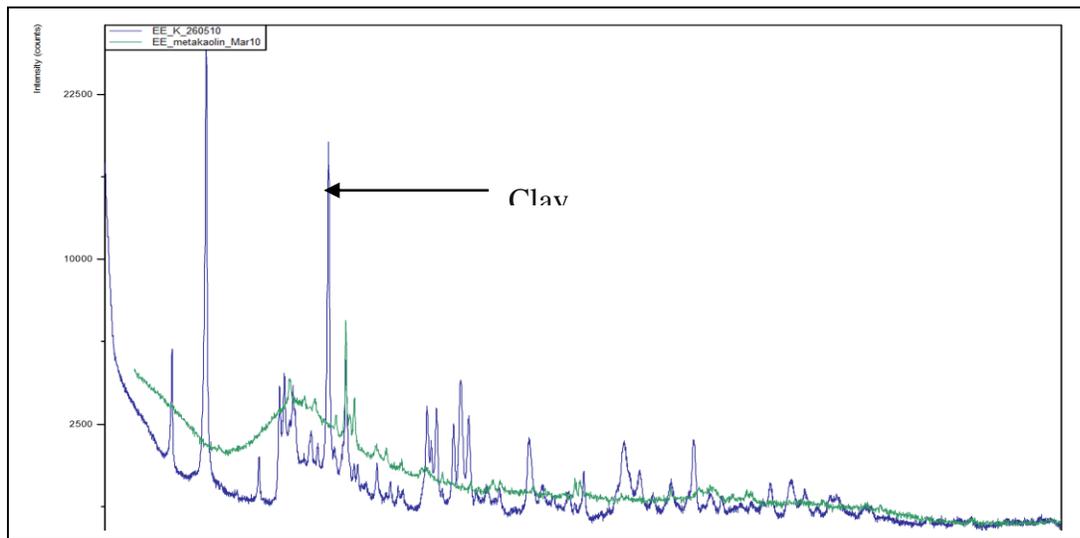

Figure 1: XRPD patterns of clay (blue) and dealuminated clay (green)

The elemental analysis shows that the aluminium content was reduced by 86% and the silicon increased by 69% (Table 2). However, the level of oxygen remained relatively constant. The

presence of 0.9 wt% sulphur in the dealuminated clay is due to the sulphuric acid that was used during the dealumination of the clay.

Table 2: Textural and Elemental Composition of clay and dealuminated samples

Catalyst	Crystallite size (nm)	Elemental analysis (EDX) (wt%)					
		O	Si	Al	P	Fe	S
C (clay)	42.06	57.8	21.5	18.0	1.9	0.9	-
DC (dealuminated clay)	-	57.3	36.5	2.4	2.9	-	0.9

The dealumination was clearly successful, as the SiO_2/Al_2O_3 ratio of the clay, which was initially 1:2 increased to 15.0 (EDX analysis in Table 3). The modified clay has more silica and less alumina than the natural clay.

Table: 3 Elemental Analysis and Textural Properties of Support

Sample	Si/Al (wt%)	XRD pattern
C (clay)	1.2	Crystalline
DC (dealuminated clay)	15.0	Amorphous

The effect of dealumination on percentage composition of the Si and Al was also shown by XPS analysis. The Al 2p spectra for clay and its dealuminated form at the same binding energy of 74.5eV (Figure2), correspond to aluminium (III) oxide (Moulder *et al.*, 1995; Wagner *et al.*, 2000)
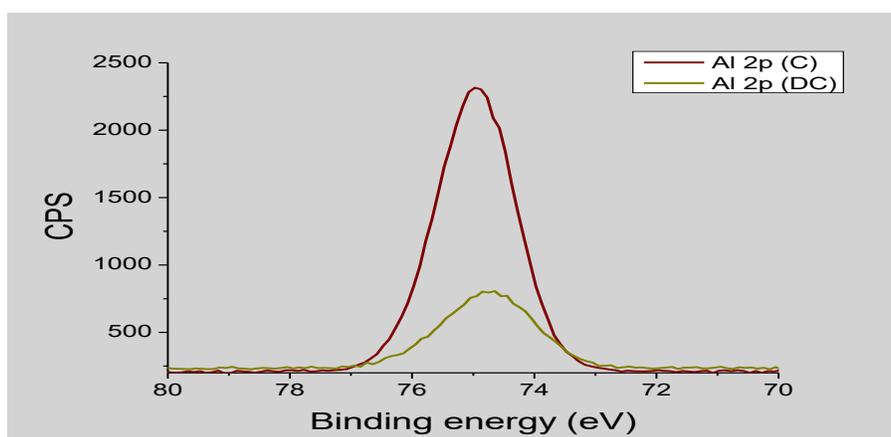

Figure2: XPS Spectra of Al 2p of clay and the dealuminated samples

The silicon (Si 2p) spectra of both samples were very similar around 103.3eV (the binding energy of silicon), as shown in Figure 3, which is a confirmation Si^{4+} in silicon oxide.
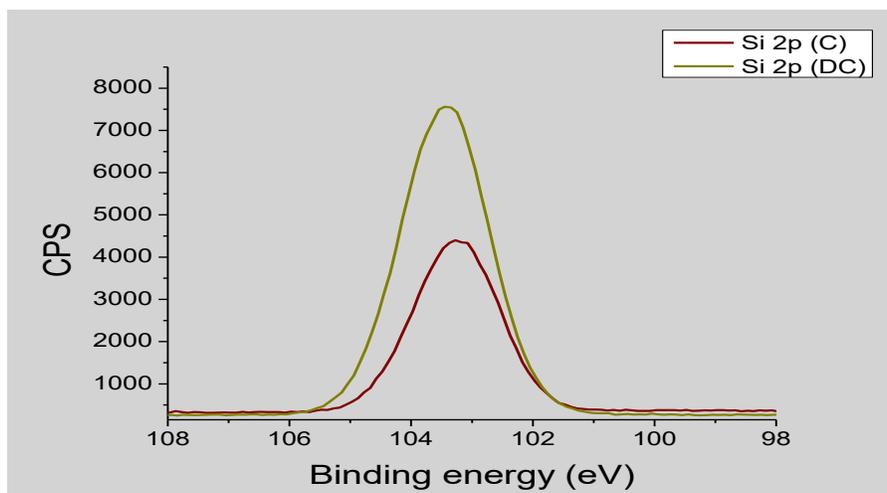
Figure 3: XPS Spectra of Si 2p of both clay and the dealuminated samples

1.4   Conclusion

The process of dealumination showed noticeable change in the properties of the clay. The result showed that the dealuminated clay had increased surface area; generally, it revealed improved physical properties of the treated clay sample. From the results obtained, it was deduced that the chemical composition of the dealuminated clay sample was different from the natural sample. However, the chemical composition was not relatively altered, but the percentages were altered. This research has successfully reduced the Al^{3+} and increase the Si^{4+} of clay via a very simple process. Thereby, increasing the clay's ability for Bronsted acid characteristics if used or doped with metals for various industrial applications. The resulted aluminium sulphate is also an industrial chemical

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