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INVESTIGATION INTO THE PROPERTIES OF CLAY DOPED WITH SILVER ION FOR USE AS A CATALYST.

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ABSTRACT

The work on the investigation into the properties of clay doped with silver ion for use as a catalyst has been carried out. The clay sample from Ilorin from Ilorin, Kwara State, Nigeria was ground, sieved and calcined in a furnace at a temperature of 550-600°C for a period of 6hrs. The sample was doped with silver ion using 0.2M of NaOH/NaCl Solution with 0.2M $AgNO_3$ in a ratio 2:1. The sample was than analyzed using X-ray fluorescence equipment (XRF) [Cement X –ray spectrometer, PW 1660, Philips X-ray Analyser) with a monitor. The following results were obtained 33.44% SiO_2, 23.11% Al_2O_3, 9.87% Fe_2O_3, 3.86% CaO, 1.98% MgO, 0.01% SO_3, 0.87% K_2O, 0.71% Na_2O, 8.61% L.O.I, 3.03% L.S.F, 1.01S/R and 2.34% A/R for the calcined sample. While that of the doped samples are 33.15% S_1O_2, 22.10 Al_2O_3, 9.23%Fe_2O_3, 4.44% CaO, 1.99% MgO, 0.04% SO_3, 0.96% K_2O, 8.10 L.O.I, 3.55 L.S.F, 1.06 S/R and 2.39 A/R. These results when compare with samples having catalytic properties was found to be suitable for use as a catalyst.

Keywords: Clay, Doped, Silver Ion, IRF Analysis

INTRODUCTION

Clays are solid acidic catalysts which can function as both Bronsted and Lewis acids in their natural and Ion exchanged form. They are also known to act as radical catalysts (Wentworth, 1992). Clay minerals are the most important chemical weathering product of the soil. They are formed by alteration of the existing minerals or by synthesis from elements when minerals weather to their elemental form. Since clay are crystalline, the atoms in clay minerals are arranged in a regular order. Clay minerals are part of larger class of silicate minerals called Aluminosilicates (Velde, 1995). Aluminosilicates is a three dimensional framework structure of silicate mineral in which the silicon atoms are replaced by aluminium atoms and the framework must be negatively charged and also, there must be other Cations uniformly distributed through it (Albert, 1987). Treatments of Clay involve subjecting clay to various treatments so as to modify the properties for the intended purpose. Such treatments include doping. Doping is the act of adding impurities to a substance such as clay in order to modify its properties. Hence modifying the properties of clay by incorporating different metal cations (such as silver ion), molecules, or complexes can lead to a catalyst that are useful in effecting even more varieties of reactions and higher selectivity in product structure and yield. The ranges of reactions that have been usefully performed on clay catalyst include addition elimination, addition-elimination, and substitution (Johnson and Blake (1987). However, the characteristics common to all clay minerals derive from their chemical composition, layered structure and size (Blatt and Murray, 1980) include their physical features: They are sticky and plastic when moist, but hard and cohesive when dry. Structurally, they are crystalline hydrous Alumionsilicates and also contains various other cations. Their chemical composition and crystal structure are basis on which they are divided into four main groups such as Kaolinite, Ulite, Smectite and Chlovite. Among these, the one that is found to be 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. (Johnson and Blake, 1987). Clay has many uses today including Pottery, ceramics, and linings for landfills, computer chips, cosmetics and pharmaceuticals. They are also important in soils because of the negative charge they contribute for Cations exchange. (Velde, 1995). An important industrial application of clays can be found in petrochemical processing. 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 that increases the octane number. However, this research work has investigated into the properties of clay doped with silver ion for use as catalyst and as adsorbents of aqueous solutions. Clay is loosely defined as fine-grained sheet silicates. Generally, clays are earthy, fine grained materials which develop plasticity when mixed with water. Clays are composed essentially of the elements silicon, aluminium, oxygen and hydrogen. Thus, it can be described as hydrous Aluminosilicates. Aluminosilicates are a class of silicates minerals in which some of the silicon atoms are replaced by aluminium atoms in a three dimensional framework structure and the framework must be negatively charged and there must be other cations uniformly distributed through it (Albert, 1987). Aluminosilicates are among the most diverse, widespread and useful silicate minerals in nature. Many synthetic Aluminosilicates can be made and several are manufactured industrially for use as an ion exchangers (when wet) and molecular sieves (when dry). Examples of Aluminosilicates are Feldspars, zeolites and ultramarine (Glinka 1986). Clays are rarely found separately and usually mixed not only with other clays but with microscopic crystals of carbonates, feldspars, micas and quartz (Johnson and Blake,1987). However, their chemical composition and crystal structure are basis on which they are divided into four main groups such as Ulite, Smactite, Vermiculite and Kaolite. Among these, the one that is found to be the most useful to the organic chemist as a catalyst is a sub-group of the Smectite clay called Montmorillonite, which is the main constituent to Bentonites and fuller's earth. (Leonard and Herbert, 1990). Catalyst could be a simple or complex, synthetic or neutral chemical, which are capable of making an otherwise impracticable reaction to occur under the mildest possible conditions. An important family of catalyst that has received considerable attention in recent times is derived from the soil, the most note worthy ones being clays and zeolites. (Leonard, and Herbert, 1990).

The Acidic Character of Clay

Organic reactions that take place under acid catalysis can be very efficiently carried out using clay catalysts that may function as Bronsted or Lewis acids or both. A variety of organic reaction that are catalysed by Bronwsted acids or Lewis acids here been shown to take place in clays especially montmorillonite, more efficiently i.e. under milder conditions, with greater selectivity, better yield, and shorter reaction times. Moreover, the work up and purification procedures are simpler as the catalyst is separated easily from the reaction mixture. Because of these reasons and the fact that the catalyst can be reused or regenerated, the entire synthetic activity is not only economical but also environmentally friendly. The ranges of reactions that have been successfully performed on clay catalyst include addition, elimination, addition – elimination, substitution, rearrangement, Diels-Alder reactions, and oxidation-reduction. (www.ias.ac.in/resonance/jan2002/pdf/Jan2002 pgs 64 - 77.pdf).The Lewis acidity is due to Al^{3+} and Fe^{3+} at the crystal edges, and can be further enhanced by exchange of the interlayer cations Na^+ and Ca^{2+} by Al^{3+} ions on treating the clay with $AlCl_3$ solution. Lewis acids include $AlCl_3$, $TiCl_4$, and $FeCl_3$ .The bronsted acid character of clay arises mainly due to the dissociation of the intercalated water molecules coordinated to cations. higher levels of Bronsted acidity are achieved by exchanging highly polarised ions such as Cr^{3+} for Na^+, Ca^{2+} present in neutral clay, and water content is low. Besides the total acidity, the surface area and pore volume in the clay structure also add to the efficiency of the catalyst. Bronsted acids include H_2SO_4, HCl, and HNO_3 with general reaction of type: $[M(H_2O)n]^{3+} \leftrightarrow [M(H2O)^{n-1}OH]^{2+} + H^+$.

METHODOLOGY

The raw clay was collected in Ilorin, Ilorin-south local government of Kwara state It was ground and sieved using mortar and pestle to a size of 250 μm mesh size.300g of the sample was weighed and calcined in a furnace at a temperature between 550-600°C for a period of 6hrs. It was removed and allowed to cool, after which it was reweighed and the weight loss calculated. After calcinations, both reduction in weight and the colour change from whitish-black to brown was observed. The clay was doped by preparing sodium hydroxide solution that was added to a sodium chloride solution where the calcined clay of 150g had already been dispersed. The pH of the clay suspension was monitored until it reached a value of 9. This pH value was maintained by gradual addition of sodium hydroxide in the ratio 1:1. The metal-doped clay was then obtained by adding silver nitrate solution to a suspension of NaOH/NaCl clay in a ratio of 1:2 while all solutions were 0.2M. It was then dried for a period of 24hrs at a temperature of 32°C.The chemical composition of calcined and doped samples were determined using X-ray fluorescence method. 20g of each of the calcined and doped sample were weighed and added to 0.4g of stearic acid. The mixture was ground for 60 seconds. The milled sample, were put into a 50mm external diameter steel container. This was transferred into a compressing machine, with a range of pressure between 10 kN-40 kN to form pellets. The pellets were mounted onto iron source holder of X-ray fluorescence equipment (cement X-ray assessed spectrometer, PW 1660, Phillips X-ray Analyser) with IBM computer monitor and a reset time of 3000seconds for iron source for every sample was used, after which characteristic peaks were displayed and conversion to equivalent concentration value was done through appropriate software.

RESULTS AND DISCUSSION

The result obtained during the experiment on the investigations into the properties of clay doped with silver ion for use as a catalyst are shown on the table 1.0 and 2.0 below.

Table 1: Chemical Analysis for the Calcined Sample

S_1O_2	Al_2O_3	Fe_2O_3	CaO	MgO
33.44%	23.11%	9.87%	3.86%	1.98%
SO_3	K_2O	Na_2O	L.O.I	
0.01%	0.87%	0.71%	8.61%	
L.S.F	S/R	A/R		
3.03%	1.01	2.34		

Table 2: Chemical Analysis for the Doped Sample

S_1O_2	Al_2O_3	Fe_2O_3	CaO	MgO
33.15%	22.10%	9.23%	4.44%	1.99%
SO_3	K_2O	Na_2O	L.O.I	
0.04%	0.96%	0.87%	8.10%	
L.S.F	S/R	A/R		
3.55%	1.06	2.39		

Table 3: Result of Physical Analysis

Parameter	Calcined clay	Doped clay
Specific surface area, m^2/g	1,700	2,100
Particle size, μ m	250	250
Particle density, kg/m^3	1120	1180
Pore-volume, m^3/g particle	0.36	0.40
Porosity	0.430	0.444
Surface acidity (mole H^+/g sample)	6.60×10^{-8}	6.38×10^{-6}

DISCUSSION

Table 1.0 shows the various chemical composition of the calcined clay. The result shows that the calcined sample comprises of 33.44% S_1O_2, 23.11% Al_2O_3, 9.87% Fe_2O_3, 3.86% CaO, 1.98% MgO, 0.01% SO_3, 0.87% K_2O, 0.71% Na_2O and the L.O.I, L.S.F, S/R and A/R are 8.61%, 3.03%, 1.01 and 2.34 respectively. Table 2.0 shows the various chemical composition of the doped sample, from which, we have 33.15%, S_1O_2, 22.10% Al_2O_3 9.23% Fe_2O_3, 4.44% CaO, 1.99% MgO, 0.04% SO_3, 0.96% K_2O, 0.87% Na_2O and L.O.I, L.S.F, S/R, A/R were found to be 8.10%, 3.55%, 1.06, 2.39 respectively. From the results obtained, it could be deduced that the chemical composition of the calcined samples was different from the doped sample. Since, most of the constituents of the doped sample contains higher percentages than the calcined samples such constituents include CaO, MgO, SO_4, K_2O, Na_2O, L.S.F, S/R and A/R. this shows that the chemical composition of the doped sample has been altered, hence, the structural arrangement has been modified. This is in agreement with theory, that is,when sample such as clay are modified (using cations such as silver ion), they could be used as a catalyst. Although the XRF analysis of the doped sample is not exhaustive for use as a catalyst, further analysis such as porosity, surface area, pore volume, surface acidity, were determined and the results showed the possibility of the material being used as macro porous material.

CONCLUSION

The results of the chemical analysis obtained for this work has revealed that the doped clay sample contains most of the constituent in higher percentages when compared to the calcined sample. This is because the doped sample has been structurally modified, and hence could be used as a catalyst.

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