Thermal Decomposition Studies of Clays from Odukpani, South-South Nigeria by Differential Thermal and Thermogravimetric Analytical Techniques

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ABSTRACT: Thermal decomposition pattern of clays obtained form Odukpani, South-South Nigeria were investigated on the temperature range of 100-1000oC by simultaneous thermoanalytical methods, DTA and TGA. Occasionally, they were completed by energy dispersive analysis of X-ray (EDAX) as well as by methods of chemical analysis. The decomposition processes of the clay samples were carried out on nitrogen atmosphere. The thermo-analytical data obtained from this study yielded thermograms that provided valuable informations on the purity of the clay materials and mode of the reactions.

Keywords: Thermal decomposition, DTA, TGA and Odukpani clays.

Paper Type: Research paper

INTRODUCTION

In the literature, no analytical data are available relating to the thermal analysis of Odukpani clays and their analogues. Thermal analysis techniques have been used extensively for studying the thermal transition of a substance upon heating (Maiti *et al.,* 1974; Stucki *et al.,* 1990 and Kotoky *et al.,* 2006). Differential thermal analysis (DTA) technique have proven to be very valuable for the elucidation of some mechanistic problems in inorganic and organic Chemistry. This technique allows not only the choice of the optimal reaction conditions but also the confirmation of the formation of intermediates and the evaluation of their stabilities (Anikin and Dugacheva, 1973). Beside x-ray diffraction (XRD), differential thermal analysis (DTA) has proven to be suitable for the identification of kaolinitic group of minerals in clay samples.

Various Investigators have obtained DTA thermograms of kaolinites which are characterized by strong endothermic deflection between 530 to 720^{0}C due to the dehydration and decomposition of the

structure of the kaolin and middle strong exothermic effect between 940 to 1020^{o}C representing the crystallization of the spinel phase. A semi-quantitative determination of kaolinite in sample by the DTA technique is possible by measuring the peak area to width at half-height of the endothermic deflection (Smykatz-Kloss, 1974; Brindly, 1961).

Information on kaolinite-potassium acetate complex have been documented by Ruiz-Cruz and Franco-Duru (1999). Recently, however, there have been some studies on the adsorption layers on material surfaces by thermogravimetry (TGA) technique (Staszozuk and Planta, 2001).

Nurchol *et al.* (1997) studied the mineralogical and chemical properties of manganese nodules in Java clay soils from different parent materials. The results obtained revealed that the predominant soil clay minerals in all samples were koalinites; mixture of minerals, thermal analysis may be difficult if the reaction of different minerals overlap and if those typical of a single mineral mixtures are changed by solid state reactions. It is therefore, necessary to supplement DTA and TGA with other techniques such as IR, XRD and EGA (Smith, 1972, Reyoids and Walker, 1993). The mineral assemblage of clays help in understanding and management of flood and erosion related problems (Kotoky, *et al.,* 2006).

Clays and clay minerals are geologically, industrially and agriculturally important. They are important in the construction of tunnels, road cuts, fills and dams (Oden *et al.,* 2001). Most clay are grey or white in color. They have good covering or hiding power when used as pigment extender in coating and filling applications and have low conductivity of both heat and electricity (Ekosse, 1994). Depending on the physical and chemical characteristics, clays have varying uses in a number of industries such as plastics, paints, ceramics, ink, catalyst, pharmaceuticals and fiber glass among others (Murray, 1980b; Emufurieta, 1992). For some uses, the clay, must meet such specifications as particle size, color, brightness and viscosity although for some other uses, the clay do not need any particular specification. For example, cement clinker manufacture, the only requirement is light colour and chemical composition which serve to introduce SiO_2, Al_2O_3 and Fe_2O_3 into the reaction mixture (Halle *et al.,* 1974). Brick forming properties of Odukpani clay deposits, mainly physical, chemical and mineralogical studies have been investigated (Attah *et al.,* 2001). Osabor *et al.* (2009) characterized Odukpani's clays with Atomic adsorption spectrophotometer (AAS), X-ray Diffractometer (XRD), Infrared (IR) and Energy Dispersive

analysis of X-ray (EDAX). The results obtained from the study revealed that Odukpani clay deposit is mainly koalinite.

The present paper deals with the application of DTA and TGA techniques for the study of thermal transformations of Odukpani clays and their analogues.

MATERIALS AND METHODS

MATERIALS

Fresh clay samples were collected from ten (10) different locations within the Ikot Omin clay deposits at Odukpani, South-South Nigeria (Fig.1). The samples were collected along a pit sank in the clay deposit and at a depth intervals of 10cm with the aid of a shovel and digger and hand-picked to minimize the possibility of contamination. About 2.0kg of each sample was collected and placed on small polythene bags. 1.0kg of each sample was dried, pulverized and sieved before analysis.

METHODS

A sub-sample of 1.0g from each of the dried samples was digested in a sterilized polypropylene bottle using a mixture of concentrated HCl and HF acids (Analar grade) in a ratio of 7:1, respectively. The mixture was heated in a thermostated water bath at a temperature range of 50-60^{0c} for 2h. The resulting milky solution was cooled in tightly covered bottles under tap and 10ml of saturated boric acid (Analar grade) solution was added. The sample solution was securedly covered and returned to the water bath that was preheated to about 70^{o}C. Heating continued until clear sample solution was obtained. The solution was finally made up to 250ml with distilled water in a plastic volumetric flask. The diluted clear digest were used to establish the relationship between intensity and concentration (Mann *et al.,* 1974; Underwood and Day, 1988; Emufurieta *et al.,* 1992). Another set of sample solutions were prepared with a dilution factor of 100. Some of the samples were duplicated and analyzed to ascertain precision and accuracy. The recommended, standard methods of A.O.A.C. (1990) were used to obtain the elemental concentrations. Sodium and potassium levels were determined using flame analyzer Jenway PFP-F and atomic absorption spectro-photometer model 1233; while oxy-acetylene flame was used to analyze for iron, manganese, calcium, magnesium, silicon, aluminium, titanium and phosphorous.

A mettler vacuum Toledo TG 850 thermo-analyzer was used which enabled us to record TGA and DTA curves simultaneously. The thermoanalytical investigations were carried out on high purity dried nitrogen gas with a flow rate of 5.01/h under vacuum at 10^{-5} torr between 0-1000^{oe}. The heating rate was 10^{o}C/min. Al_2O_3 was used as a reference material.

The energy dispersive analysis of X-ray (EDAX) was carried out on the samples using a scanning electron microscope (SEM) fitted with a link 1515 spectometer. For elemental analysis, the sample film was placed firmly in a waxed and gold plated. The EDAX patterns were obtained with the help of a computer attached to the instrument.

For each experimental condition, 2 to 3 measurements were performed to estimate the reproducibility. The reproducibility was quite good and the data presented reflects the results obtained beyond experimental error.

RESULTS AND DISCUSSIONS

RESULTS

Thermal decomposition pattern of clays from Odukpani, South South Nigeria have been investigated by simultaneous DTA-TGA methods. The results of the simultaneous DTA and TGA of Odukpani clays are presented in Table 1 and Fig. 2.

Fig. 3 represents the EDAX pattern of the clay samples studied. Energy dispersive analysis of X-ray (EDAX) analysis shows a ratio of Al: SI of 1:2 as depicted in the thermogram. However, the particle size distribution of the samples was 0.046□m

Table 2 show the results obtained from the clay samples analyzed using atomic absorption spectrophotometer and flame photometer. The obtained results revealed that aluminium and silicon are the predominant elements in the clay samples.

DISCUSSION

Fig. 2 represents the simultaneous DTA-TGA thermogram of the clay samples investigated. Table1 contains the thermoanalytical data for the clay samples studied. The DTA thermogram showed three peaks, (one exothermic and two endothermic between 0 and 1000^{0}c. The first endothermic peak was asymmetric occurred at 520^{0}c, the second peak occurring at 200^{0}C informed of the removal of the

last traces of OH^- in the form of H_2O which can exist in the lattice even above 600°C (Szabo *et al.,* 1974). At 905°C a broad exothermic peak appeared thereby pointing to a new spinel-type phase. The samples contain about 1% total organic carbon, 1.5%, organic matter and 2.3% pyrite. It can be concluded that organic materials decomposed at this temperature range. The thermogravimetric analysis (TGA) was carried out in a flowing N_2 atmosphere. The results obtained revealed a single broad loss of mass in the region of 400 to 550°C (T°C on set is 400°C).

The loss of mass of 13.59% corresponds to the removal of the water molecules in kaolinite groups (calculated loss of mass of 13.95%). This result compared favorably well with 13.80% reported by Szabo *et al.,* (1974) for Georgian koaline. Within this temperature range occurs the dehydroxylation of kaolinite. No loss of weight was observed above 550°C indicating a complete separation of the structural water associated with kaolinite clays. The inflection point of the TGA thermogram was 503.99°C.

The temperature listed above provide a thermogravimetric method of analyzing clays, indeed prolonged heating of clays gives a weight loss due to evolution of CO_2 (Pekene and Sharp, 1974).

As a further check of the methods described above independent analyses were carried out by Atomic Absorption spectrophometer (AAS), flame photometer (FP) and Energy dispersive analysis of X-ray (EDAX). A typical chemical analysis result of Odukpani clay samples is presented in table 2. The result revealed high percentages of silica and alumina. It was also observed from table 2 that the predominant components of clay (SiO_2, Al_2O_3 and H_2O) clearly defined them as hydrated alumino-Silicate type. Table 2 also reveals that the average silica+alumina + intergranular water (SiO_2 + Ai_2O_3+H_2O) contents in the clay samples constitutes about 88.76% (made up of SiO_2, 47.53%, Al_2O_3, 34.08% and H_2O, 7.20%). Potassium oxide (K_2O, 0.61%) Ferric oxide, (Fe_2O_3, 2.29%) and sodium oxide (Na_2O, 1.79%) are the major significant impurities found in this clay samples. The results obtained from this investigation compares favourably well with values obtained by Oden *et al.,* (2001). The percentages of other oxides such as calcium oxide (CaO, 0.038%), magnesium oxide (MgO, 0.19%), manganese oxide (MnO, 0.000%) phosphorus pentaoxide (P_2O_5, 0.27%) and Titanium oxide (T_1O_2, 0.001%) are comparatively lower than aluminium and silicon contents. The approach adopted in this study was based on previous works in the literature (Szabo *et al.,*

1974). The most readily applicable simplest analysis was provided by Thermo gravimetry and differential thermal Analysis and the reliability of the results was compared and confirmed from literature data.

CONCLUSION

In conclusion, Differential Thermal Analysis DTA and Thermogravimetric Analysis Techniques had provided relevant information on the processes taken during the Thermal treatment of clays Thermal decomposition of Odukpani clays take place as depicted in the thermogram. The temperature interval at which the transition occurs during thermal treatment has been determined. On the basis of the present study, the characteristic thermal effects of Odukpani clays have been confirmed. DTA and TGA techniques are useful tools for the studies of clays. Both techniques are used for the determination of phase compositions and interpretation of other processes taking place in clays on heating.

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Table 1: Results of DTA and TGA analysis for Odukpani clay Samples

						DTA			TGA	
S/N	ATM	Heating rate Oc/min	Max. Temp. (Oc)	Weight of sample (mg)	Weight loss (%)	Peak endo.	Peak endo	Peak exo		Peak
1	N_2	5	1000	27.52	-	530	620	900	-	-
	N_2	5	1000	3.7389	13.6134	-	-	-		480
2	N_2	5	1000	27.50	-	520	630	900		
	N_2	5	1000	3.8389	13.5862	-	-	-		500
3	N_2	5	1000	28.30	-	540	625	910		-
	N_2	5	1000	3.6758	13.7253	-	-	-		490
4	N_2	5	1000	27.13	-	542	630	908		-
	N_2	5	1000	3.6720	13.7422	-	-	-		520
5	N_2	5	1000	27.50	-	533	610	920		-
	N_2	5	1000	3.6720	13.6820	-	-	-		500
6	N_2	5	1000	28.00	-	520	600	915		-
	N_2	5	1000	3.6720	13.6420	-	-	-		502
7	N_2	5	1000	27.6620	-	520	625	900		-

	N_2	5	1000	3.6821	13.7214	-	-	-	504
8	N_2	5	1000	28.50	-	500	610	920	-
	N_2	5	1000	3.6520	13.8230	-	-	-	490
9	N_2	5	1000	27.63	-	490	600	920	-
	N_2	5	1000	3.6521	13.6201	-	-	-	496
10	N_2	5	1000	27.65	-	520	610	900	-
	N_2	5	1000	3.6221	13.8210	-	-	-	506

ATM = Atmosphere

DTA = Differential thermal analysis

TGA = Thermogravimetric analysis

Table 2: chemical analysis of Odukpani clay samples

Deposit		Odukpani Clays						
%Oxides	Mean	Range	a	b	c	d	e	f
S_1O_2	47.52	46.79-49.51	45.57	52.92	57.67	46.88	63.20	50.08
Al_2O_3	34.05	32.32-35.37	38.45	9.42	24.00	37.65	25.61	20.60
Fe_2O_3	2.29	2.15-2.62	0.75	3.65	3.23	0.88	1.52	0.80
MgO	0.19	0.11-0.23	0.05	0.08	0.30	0.13	0.05	0.00
CaO	0.04	0.00-0.06	-	1.91	0.70	0.03	0.10	0.00
Na_2O	1.79	0.54-2.69	-	0.03	0.20	0.21	0.29	1.70
K_2O	0.61	0.32-0.69	0.06	0.98	0.50	1.60	1.75	0.30
T_1O_2	0.001	0.00-0.02	0.01	1.18	-	0.09	0.00	0.50
P_2O_5	0.27	0.01-0.61	-	0.02	-	-	0.23	0.00
MnO	0.00	0.00-0.00	-	-	-	-	0.01	0.00
H_2O^+	12.55	12.55-13.50	-	10.18	10.50	12.45	8.00	10.00
Total organic carbon.	99.33							
Organic matter	1.23	0.86-1.92						

(a) Floride non active Kaolinite (Huber, 1985)

(b) Floride active Kaolinite (Haber, 1985)

(c) Plastic Fire Clay St. Louis M. O. (Huber, 1985).

(d) China Clay GTY (Huber, 1985)

(e) Ibadan Residual Kaolin (average of samples) (Emufurieta, 1988).

(f) Oza-Nagogo Sedimentary Kaolin (average of 20 samples) Emufurieta, 1988).

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