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SPECIFIC SURFACE AREA OF HEAT TREATED ILLITIC MINERAL CLAY

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Abstract

Pristine clay samples were characterized by X-ray diffraction, differential thermal analysis and gravimetric thermal analysis, as well as by nitrogen adsorption/desorption method for specific surface area determination. The samples were thermally treated at different temperatures, up to 1200°C, and for different periods of time, up to 8 hours, in order to investigate the effect of heat treatment parameters on their porosity. The heat treatment applied for 2 hours at 1200°C leads after cooling to dark brown blackish colour, glassy structure and negligible specific surface area.

Key words: Illite mineral clay, specific surface area, heat treatment effects.

Introduction

The illite, a hydrated potassium-iron-aluminum silicate, is one of the major component of clays used for the production of traditional ceramics, the understanding of its high temperature transformations is of paramount importance for the knowledge of the structural and micro structural properties of fired ceramic products [1]. Illites have their origin in micas, usually muscovite, which is inherited in the soil sequence from the source materials from witch the soil is formed. Most of the general studies describing illite genesis in this manner show large mica flakes breaking into smaller particles until they become clay-sized.

In studies of soil genesis, the illites occurring in the soil are often found to be unstable. This transformation of illites in other less potassic minerals is observed in various types of soil-forming environments. Nevertheless, illite is sufficiently abundant in some cases to warrant a place in soil classification and terminology [2]. Illite clays are also investigated for their potential applications for microbial reduction of iron [3]. Other interesting studies are focussed on the role of microbes in the smectite-to-illite transformation based on a bioreaction [4].

Clay materials with controlled porosity found applications in the water treatment by the membrane separation techniques. According to their diameters of the pores, they can be used either as membranes of microfiltration or like supports for membranes of ultrafiltration [5].

In this work we investigate panonian age illite clay from Odorheiul Secuiesc region used to obtain the traditional Marginea black-ceramic, with respect to the changes in surface area induced by increasing heat treatment temperature and duration.

Experimental

The samples are natural clays extracted from the soil from Transylvania, Odorheiul Secuiesc region. The samples were modeled in biscuit forms and cured at different temperatures. After curing the samples were crushed until we obtained a fine powder. Before curing it was made X-ray diffraction analysis (XRD), differential thermal analysis (DTA) and DTG curves. The samples were heat treated at temperatures ranging between 700^{o}C and 1100^{o}C for 2, 4 and 8 hours, as well as at 1200^{o}C for 5 minutes and for 2 hours. Specific surface areas of the pristine and thermally treated samples were determines using BET (Brunauer, Emmett and Teller) method.

BET theory is a well-known rule for the physical adsorption of gas molecules on a solid surface, that is basis for an important analysis technique for the measurement of the specific surface area of a material [6]. The concept of the theory is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption, to multilayer adsorption with the following hypotheses: (a) gas molecules physically adsorb on a solid in layers infinitely; (b) there is no interaction between each adsorption layer; and (c) the Langmuir theory can be applied to each layer. The resulting BET equation is :

$$\frac{1}{v[(P_0/P)-1]} = \frac{c-1}{v_m \cdot c} \cdot \frac{P}{P_0} + \frac{1}{v_m \cdot c} \qquad (1)$$

where P and P_0 are the equilibrium and the saturation pressure of adsorbates at the temperature of adsorption, v is the adsorbed gas quantity (for example, in volume units), and v_m is the monolayer adsorbed gas quantity, c is the BET constant expressed by:

$$c = \exp(\frac{E_1 - E_L}{RT}) \qquad (2)$$

E_1 is the heat of adsorption for the first layer, and E_L is that for the second and higher layers and is equal to the heat of liquefaction [6].

The XRD spectra were recorded with a Shimadzu XRD-6000 diffractometer, using Cu K_α radiation (λ=1.5418 Å), with Ni-filter. The measurements were performed at a scan speed of 7 ^{o}/min.

The differential thermal analysis (DTA) and gravimetric thermal analysis (GTA) were performed on Shimadzu analyzer DTG-60H witch simultaneously measures TG and

DTA, in air, using alumina crucibles, with hitting rate of 10 ºC/min, from room temperature to 1300 ºC.

The Specific Surface Area measurements were made with a Qsurf 9600 Series Surface Analyzer, working on the single point BET principle, using a single gas mixture 30% N_2 in helium equilibrium.

Results and discussions

The XRD pattern shown in Fig. 1 indicates that the pristine sample consists in a mixture of illite quartz and muscovite crystals [7]. The DTA curve (Fig. 2) exhibits three endothermic peaks at 53.88 ºC, 689.53 ºC and 1201.16 ºC. The first one is due to water physisorbed on the clay and it is accompanied by a weight loss peak in the DTG curve. The second peak indicates the destruction of illite by dehydroxylation [1, 8], this peak gives a weight loss in the range of 440–740°C. The third peak represents the melting of the sample.

To follow the change of materials porosity during heat treatment, the specific surface area (SSA) was measured. The illite-based materials were treated at different temperatures: 700ºC, 800ºC, 900ºC, 1000ºC, 1100ºC, 1200 ºC, each for different period of time: 2 hours, 4 hours and 8 hours, except for the sample treated at 1200ºC, because this temperature is the melting temperature of the sample as sown in the DTA curve. At this temperature the sample was treated 2 minutes and 2 hours. The measured SSA for untreated and heat treated samples are presented in Table 1.

The specific surface area obtained for the de pristine clay is 16.1950 m^2/g. The data show a tendency for SSA to decrease with temperature of heat treatment. According to the values summerised in Table 1, by heat treatment at 700ºC the clay looses more than a half of the specific surface area, and SSA decreases from 16.1950 m^2/g to 6.9855 m^2/g. The higher the firing temperature the smaller the specific surface area becomes and with that the denser and less porous the material becomes, and it were more and more difficult to ground. The sample treated at 1200ºC for 2 hours has a dark brown blackish colour after cooling, it achieves a glassy structure and an insignificant specific surface area, as can be seen in Table 1. Another sample was heat treated at 1200ºC only for 5 min. After cooling it has a blackish colour too, contains lot of holes and looks like a hard sponge.

The colour of the samples depend on heat treatment temperature. The pristine clay was gray, after treatment at 700ºC it changed the colour to reddish orange, like oxidized iron, and for higher treatment temperatures the samples became darker, to almost black for heat treatments applied at 1200ºC.

Conclusions

The primary clay consists in a mixture of illite quartz and muscovite crystals. Its melting temperature is close to 1200ºC. The increase of heat treatment temperatures up to 1200^oC changes the specific surface area of pristine clay, 16.1950 m^2/g, to the midget value of 0.0585 m^2/g, denoting a very low porosity of high temperature heat treated clay samples. The colour change from gray to black proves that the Marginea ceramic is obtained under high temperature firing conditions of the clay ore.

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Tables and figures caption

Table 1. Specific surface areas obtained with nitrogen adsorption BET method

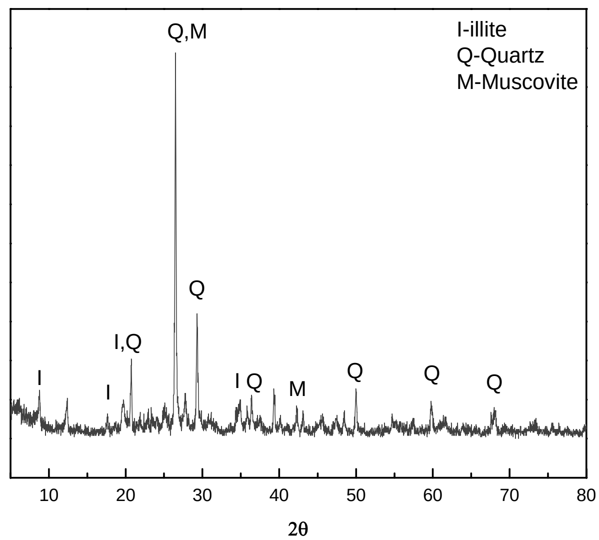
Figure 1 XRD spectrum of the pristine clay sample.

Figure 2 DTA/DTG curves of the pristine illite sample.

Figure 3 Dependence of specific surface area on heat treatment temperature.

Table 1

Sample code	Curing temperature (ºC)	Curing time (hours)	SSA (m^2/g)
01	0	0	16.1950
1-A	700	2	6.9855
1-B		4	7.7043
1-C		8	7.3863
2-A	800	2	5.6312
2-B		4	5.8263
2-C		8	4.8590
3-A	900	2	2.2342
3-B		4	1.8862
3-C		8	2.2984
4-A	1000	2	2.3874
4-B		4	1.2874
4-C		8	0.8934
5-A	1100	2	0.5553
5-B		4	0.2977
5-C		8	0.1864
6-A	1200	0.1	0.1094
6-B		2	0.0585



Q,M
I-illite
Q-Quartz
M-Muscovite
Q
I,Q
I
I
I Q
M
Q
Q
Q
10
20
30
40
50
60
70
80
2θ

Figure 1

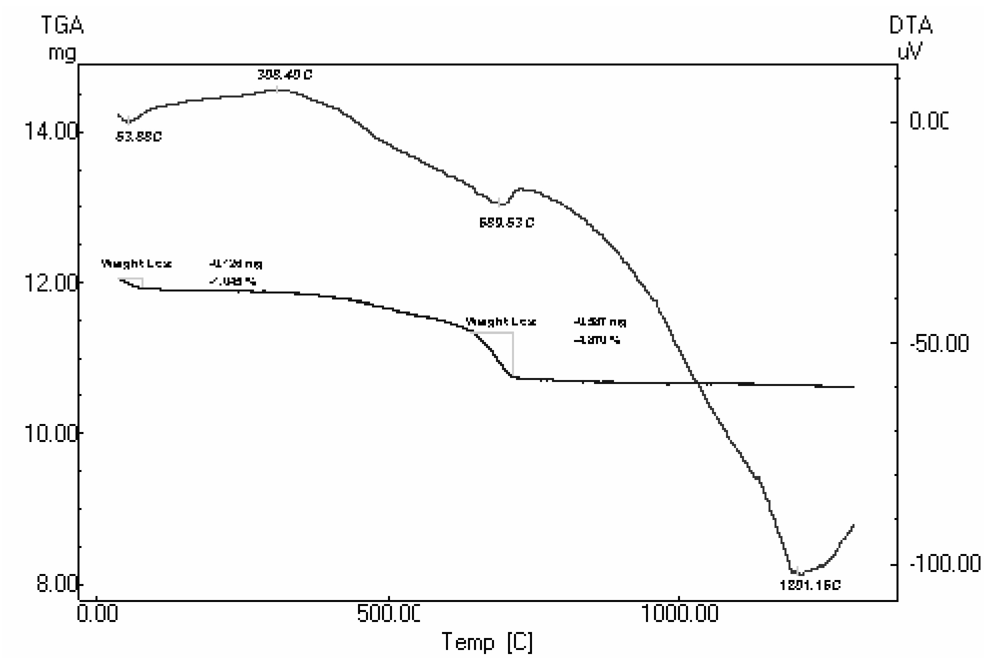

TGA
mg
DTA
uV
308.40 C
53.88C
689.53 C
1201.15C
14.00
12.00
10.00
8.00
0.00
-50.00
-100.00
0.00
500.00
1000.00
Temp [C]

Figure 2

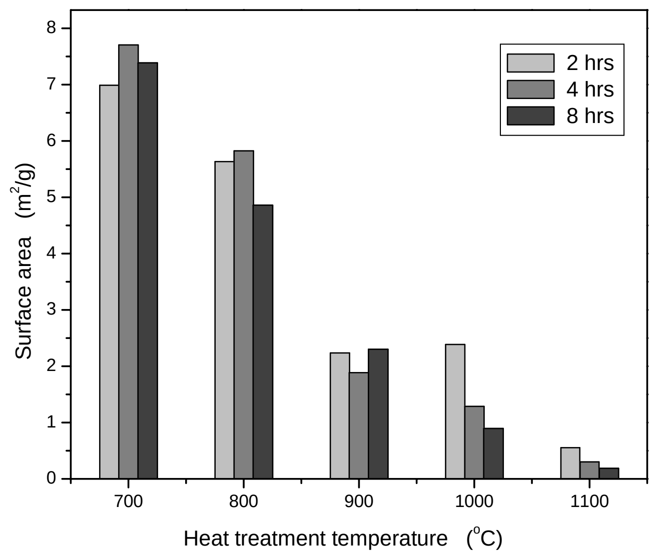

2 hrs
4 hrs
8 hrs
Surface area (m2/g)
0
1
2
3
4
5
6
7
8
700
800
900
1000
1100
Heat treatment temperature (oC)

Figure 3