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THE THERMAL DECOMPOSITION KINETICS OF THE REŞADİYE (TOKAT / TURKEY) BENTONITE AND ITS FRACTIONS

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ABSTRACT

The untreated bentonite was separated into three fractions by subsequent precipitations from its suspension, during different periods. One fraction remained in suspension during infinite period. Hence, a total of four fractions were separated. The activation energies, and pre-exponential factors for the dehydration, dehydroxylation and calcination, of a total of five samples, comprising the untreated bentonite were determined by the Coats – Redfern procedure, using the thermogravimetric data. The decompositions were thought to obey a first order rate law. Their rate equations were written by using the determined quantities.

INTRODUCTION

Besides one or some of the clay minerals such as kaolinite, montmorillonite, illite, chlorite, sepiolite and attapulgite, clays contain also one or some of the non-clay minerals such as quartz, amphibol, α-cristobalite, tridymite, opal-A, opal-C, opal-CT, feldspar, gibbs, alunite, correndum, calcite, magnesite and dolomite. In some clays, trace amounts of organic matter are also encountered. Clays are used either directly or after purification in more than hundred application areas [1].

The sheets formed of $SiO_4{}^{4-}$ tetrahedrons (T) and the sheets formed of $AlO_6{}^{6-}$ octahedrons (O), which are the building blocks of clay minerals, are packed in the order of TOT to form a 2:1 unit layer of the montmorillonite mineral [2]. TOT layers are packed one on top of the other to form montmorillonite particles, and these particles agglomerate randomly to form the minerals [3]. Montmorillonite and clay minerals such as bidellite, nontronite and saponite, derived from montmorillonite by isomorphic ion exchange compose the smectite group. In order to maintain charge equality, only the 2 / 3 of the octahedron centers, which form the O sheets in the TOT layers, contain Al^{3+}. The smectites of this character have dioctahedral structure. The structure in which all of the octahedron centers, which form the O sheets in the TOT layers, contain Mg^{2+} is trioctahedral [4,5].

An excess of negative charge appears if ions such as Al^{3+} or Fe^{3+} replace some of the Si^{4+} ions that are in the centers of the tetrahedrons, which form the T sheets of the TOT layers. The same condition occurs if ions which have smaller oxidation numbers such as Fe^{2+}, Mg^{2+}, Zn^{2+} and Li^{+} replace some of the Al^{3+} ions which are in the centers of the octahedrons which form the O sheets. The excess of negative charge is balanced by the ions such as K^{+}, Na^{+} and Ca^{2+} which enter between the TOT layers together with some water and electroneutrality is provided. These ions which exist naturally in water are called *exchangeable cations* since they can exchange all kinds of organic and inorganic cations [6-10]. The montmorillonites whose exchangeable cations are mainly Na^{+} are called sodium montmorillonite (NaM), whose exchangeable cations are mainly Ca^{2+} are called calcium montmorillonite (CaM) and those which contain equal amounts of Na^{+} and Ca^{+} exchangeable cations are called meta montmorillonites (NaCaM). Although the NaMs give everlasting aqueous suspensions, the NaCaM and CaMs flocculate after a while from their aqueous suspensions [11-13]. As a result of this property montmorillonite minerals can be separated from eachother. The ideal chemical formulas of NaM and CaM are respectively represented as follows

$$Si_8\,(Al_{3.3}\,Mg_{0.67})\,O_{20}\,(OH)_4\,Na^{+}_{0.67}.n\,H_2O$$
$$Si_8\,(Al_{3.3}\,Mg_{0.67})\,O_{20}\,(OH)_4\,Ca^{2+}_{0.33}.n\,H_2O$$

where n H_2O represents the water between the TOT layers, Na^{+} and Ca^{2+} represent the exchangeable cations and OH groups represent the hydroxyls bonded to the octahedrons. NaM and CaM can be transformed to eachother reversibly, by cation exchange [14-17]. As the temperature rises between 50 – 500 °C the elimination of water between the layers is called dehydration and when the temperature is between 600 –700 °C the elimination of the OH groups which are bonded to the octahedrons, by the production of water is called dehydroxylation [19]. Clays whose major mineral is montmorillonite or one of the other smectites are called bentonites. The bentonites whose major minerals are NaM, CaM and NaCaM are represented respectively as NaB, CaB and NaCaB [18]. Natural bentonites may contain between 10 – 40 % non-smectite clay minerals and non-clay minerals. Around 800 °C, the decomposition of carbonates such as calcite, magnesite and dolomite which are among the non-clay minerals, is called calcination. As the temperature rises above 900 °C, the interfusion of the new solid phases which are produced from the decomposed clay minerals is called sintering. Bentonites are used as binders in foundry and ceramic production since they produce muds of high plasticity, with water. Both productions are realized at high temperatures therefore decompositions such as dehydration, dehydroxylation and calcination of the clay and non-clay minerals take place [20,21]. The optimum decomposition rates for the production of casting moulds and ceramics without fracture, can be reached by regulating the heating rate. As in the cases of other chemicals, the decomposition rates of minerals are also determined by thermal analysis [22-24]. The temperature intervals for the thermal decompositions are determined by differential thermal analysis (DTA) curves. The thermal decomposition rates are determined by using the thermogravimetric (TG) data in these intervals [25-26].

The aim of this study was to determine the thermal decomposition rates of the events such as dehydration, dehydroxylation and calcination observed in Reşadiye bentonite and its fractions.

MATERIALS AND METHOD

A Wyoming type bentonite taken from the Reşadiye (Tokat / Turkey) region (R0), and samples which precipitated in 15 minutes (R1) in 3 days (R2) and in one week (R3), from the aqueous suspension and a sample which remained unprecipitated as an aqueous suspension (R4) were chosen as the material. The chemical analysis, mineralogical analysis, cation exchange capacities, pore structures of these samples were reported previously [27,28]. It was determined that R0 contained 25 % R1, 18 % R2, 7 % R3 and 50 % R4, represented in mass percents. R1 contained a large amount of clinoptilolite as well as illite, opal-CT, amphibol, quartz, calcite and dolomite. R2 contained 38 % (in mass) NaCaM, clinoptilolite and opal-CT. R3 contained 97 % (in mass) NaCaM as well as a small amount of and opal-CT. It was ascertained that the R4 fraction contained NaM in which there was a trace amount of opal-CT. As a result, it was concluded that R0 contained 50 % (in mass) NaM, 11 % (in mass) NaCaM and 39 % (in mass) other minerals.

The TG and DTA curves of the samples R0, R1, R2, R3, and R4 were determined by a Netzsch Simultaneous TG-DTG-DTA Instrument Model 429, at a heating rate of 10 K min $^{-1}$. α-Al_2O_3 was used as an inert material.

RESULTS AND DISCUSSION

A decomposition factor, represented by α is defined as the ratio of the decreases in mass at each increase of 10 K, to the decrease in mass which remains constant at 1000°C.Since the mass percent of the substance which is not decomposed is $(1-\alpha)$, an equation for the decomposition rate defined as $d\alpha / dt$ can be written as follows

$$d\alpha / dt = k\ (1-\alpha)^n = A\,e^{-E/RT}\ (1-\alpha)^n \qquad (1)$$

where t is the time, k is the decomposition constant, n is the order of the decomposition reaction, E is the activation energy of the decomposition, A is the pre-exponential factor which is equal to the rate constant for the decompositions whose activation energy is zero, T is the absolute temperature and R is the universal gas constant. After integrating the above equation by making some approximations, the following equation is obtained, if 1 is substituted for the value of n.

$$\ln \{ [-\ln(1-\alpha)] / T^2 \} = -(E/RT) + \ln[(AR/\beta E)(1-2RT/E)] \qquad (2)$$

This equation is known as the Coats – Redfern Equation where, $\beta = dT / dt$ is the heating rate in the thermogravimetric analysis and $(AR / \beta E)(1 - 2RT / E)$ is unitless and nearly constant.

The temperature intervals at which the dehydration, dehydroxylation and calcination took place were determined from the DTA data, the decomposition factors were determined from the TG data and the thermal decomposition rates in the original bentonite fractions were obtained as follows.

Natural Reşadiye Bentonite (R0)

The $\alpha - t$ curve drawn by using the TG data, for the R0 sample,which was determined to be a Wyoming type bentonite , is given in Figure 1 and the Coats – Redfern straight lines are given in Figure 2. It can be clearly observed in Figure 1 that about 40 % of the total mass loss in R0 during the thermal decompositions, resulted from dehydration (a) and the rest resulted from dehydroxylation (b). The following respective equations for the dehydration (a) and dehydroxylation (b) in R0, were obtained by using the slopes of the straight lines in Figure 2 and the Coats – Redfern Equation.

$$d\alpha_a / dt = 1315\ e^{-3600/RT}\ (1 - \alpha) \quad (3)$$

$$d\alpha_b / dt = 724\ e^{-61000/RT}\ (1 - \alpha) \quad (4)$$

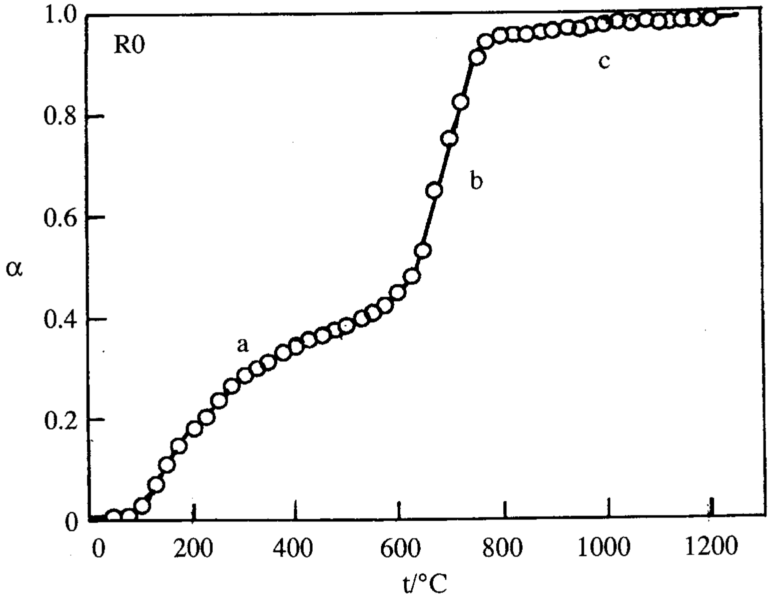

Figure 1. The variation of the decomposition factor of Reşadiye bentonite (R0), as a function of temperature.

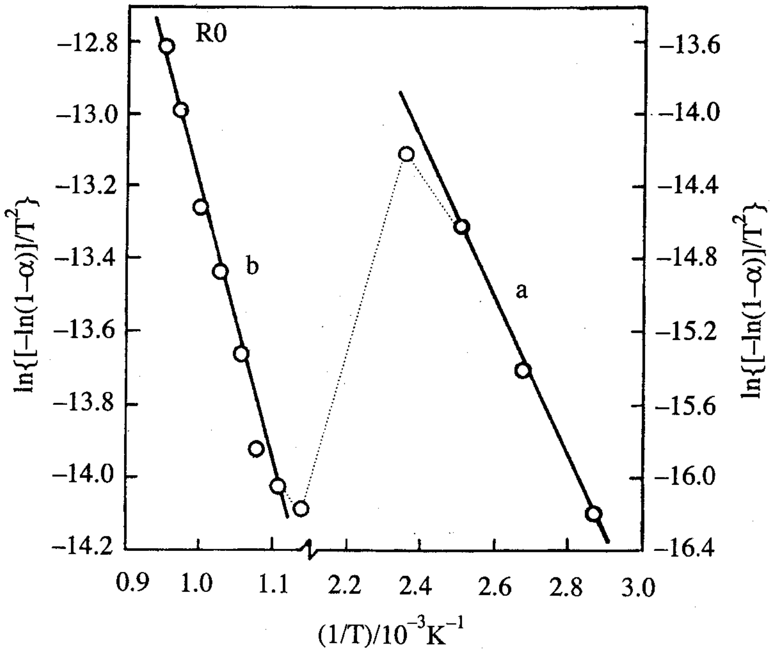

Figure 2. The Coats-Redfern straight lines for the dehydration (a) and dehydroxylation (b) of the untreated Reşadiye bentonite (R0).

It can be observed that the activation energy of the dehydration, which is a physical event is smaller than that of the dehydroxylation, which is a chemical event. The dehydration occurs through the elimination of water which exists, respectively, in the TOT layers of the smectite minerals in R0, in the pores of opal-CT ($SiO_2.xH_2O$), which is a semi-crystal, in the pores of clinoptilolite which is a natural zeolitic mineral. The dehydroxylation occurs through the elimination of the hydroxyl groups which exist in the smectite and illite minerals of R0, by a chemical reaction which produces water.

The c part of the α – t curve in Figure 1 shows that the decomposition factor increases around 5 % during the calcination, indicating that the amounts of calcite and dolomite which exist in R0 are very small. It was not possible to obtain a Coats-Redfern equation in this temperature interval, where the increase in the decomposition factor was small, therefore, the calcination rates of the carbonates contained in R0 were not determined.

R1 Fraction

The α – t curve of this sample, which was plotted by using the TG data, is given in Figure 3. The Coats-Redfern straight lines are given in Figure 4. Half of the mass loss of this fraction is due to dehydration (a) and the other half is due to calcination (c). By using the Coats-Redfern equation and the slopes of the straight lines given in Figure 4, the dehydration (a) and calcination (c) rates were determined, respectively, as follows

$$d\alpha_a / dt = 711\ e^{-34000/RT} (1 - \alpha) \tag{5}$$

$$d\alpha_c / dt = 1.46 \times 10^{18}\ e^{-145000/RT} (1 - \alpha) \tag{6}$$

It was observed that the activation energy of calcination was bigger that of deydroxylation, although both of these were chemical decompositions. The dehydration was due to the elimination of a large amount of water from the pores of clinoptilolite and opal-CT contained in R1. The calcination was due to thermal decomposition of a large amount of calcite contained in R0, by the production of carbon dioxide.

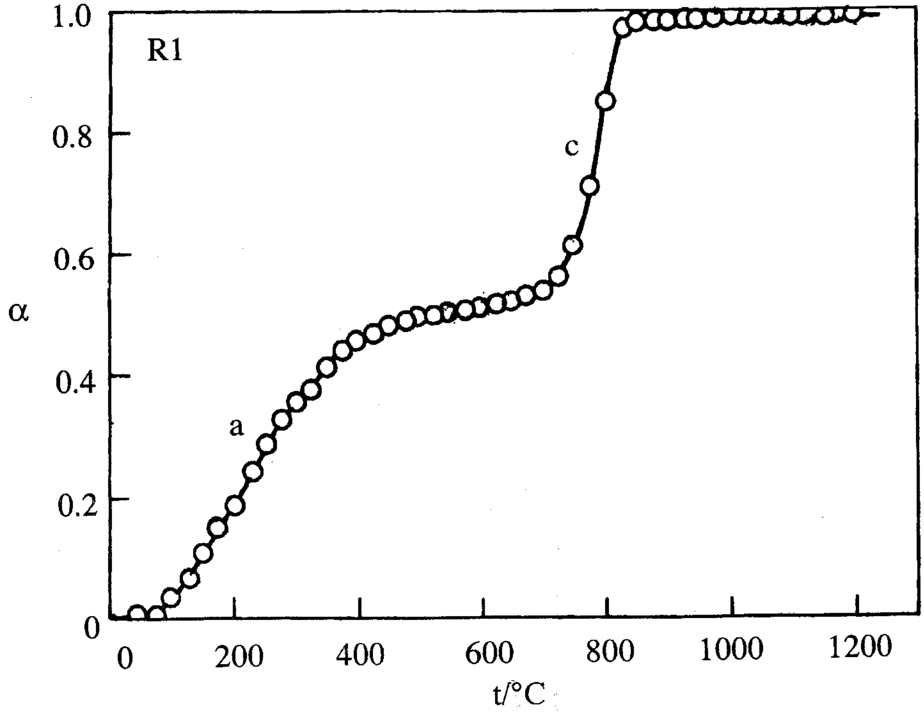

Figure 3. The variation of the decomposition factor of the R1 fraction, as a function of temperature.

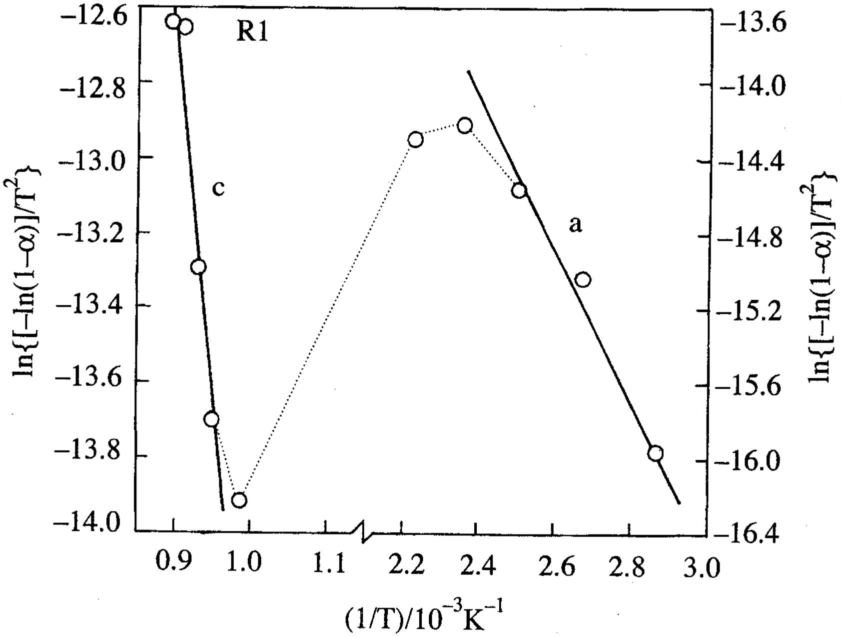

Figure 4. The Coats-Redfern straight lines for the dehydration (a) and calcination (c) of the R1 fraction.

R2 Fraction

The $\alpha - t$ curve of this fraction, which was plotted by using the TG data is given in Figure 5 and the Coats-Redfern straight lines are given in Figure 6. It was clearly observed from Figure 5 that 75 % of the mass loss of R2 was due to dehydration (a) and the rest was due to dehydroxylation (b). By using the Coats-Redfern equation and the slopes of the straight lines given in Figure 6, the dehydration (a) and dehdroxylation (b) rates were determined, respectively as follows

$$d\alpha_a / dt = 4\, e^{-15000/RT} (1 - \alpha) \qquad (7)$$

$$d\alpha_b / dt = 12\, e^{-32000/RT} (1 - \alpha) \qquad (8)$$

It was observed that the activation energies of the dehydration and dehydroxylation of R2 were about half of those of R0. This situation was related to the catalytic effect of large amounts of opal-CT contained in R2.

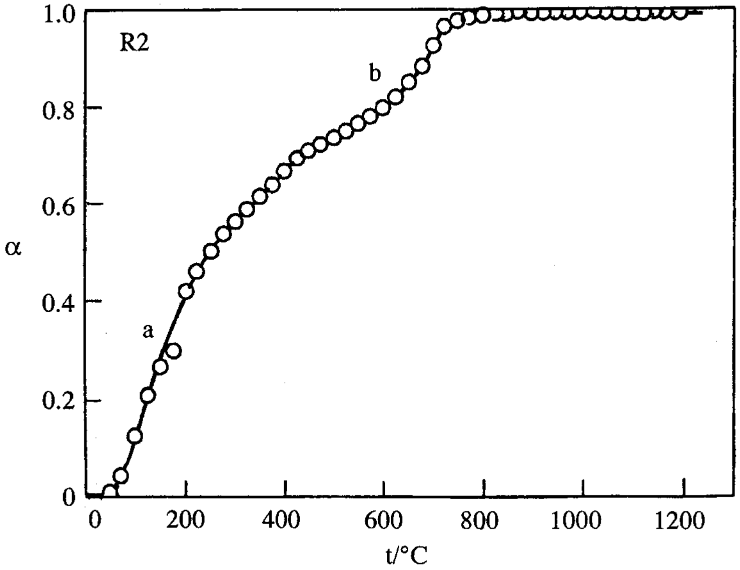

Figure 5. The variation of the decomposition factor of the R2 fraction, as a function of temperature.

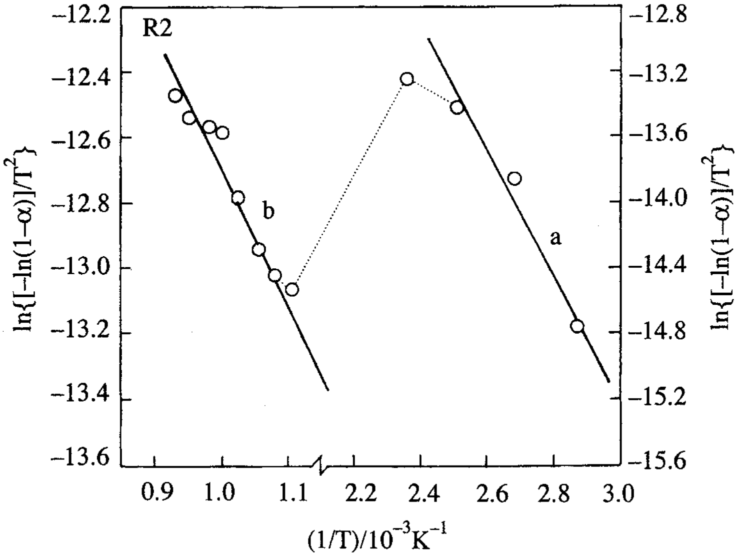

Figure 6. The Coats-Redfern straight lines for the dehydration (a) and dehydroxylation (b) of the R2 fraction.

R3 Fraction

The $\alpha - t$ curve of the R3 fraction, which was plotted by using the TG data is given in Figure 7 and the Coats-Redfern straight lines are given in Figure 8. It was clearly observed from Figure 7 that 65 % of the mass loss of R3 was due to dehydration and the rest was due to dehydroxylation. By using the Coats-Redfern equation and the slopes of the straight lines given in Figure 8, the dehydration (a) and dehydroxylation (b) rates were determined, respectively as follows

$$d\alpha_a / dt = 7580\, e^{-37000/RT}\,(1 - \alpha) \tag{9}$$
$$d\alpha_b / dt = 1664\, e^{-67000/RT}\,(1 - \alpha) \tag{10}$$

The dehydration and dehydroxylation originated from the large amounts of NaCaM contained in R3.

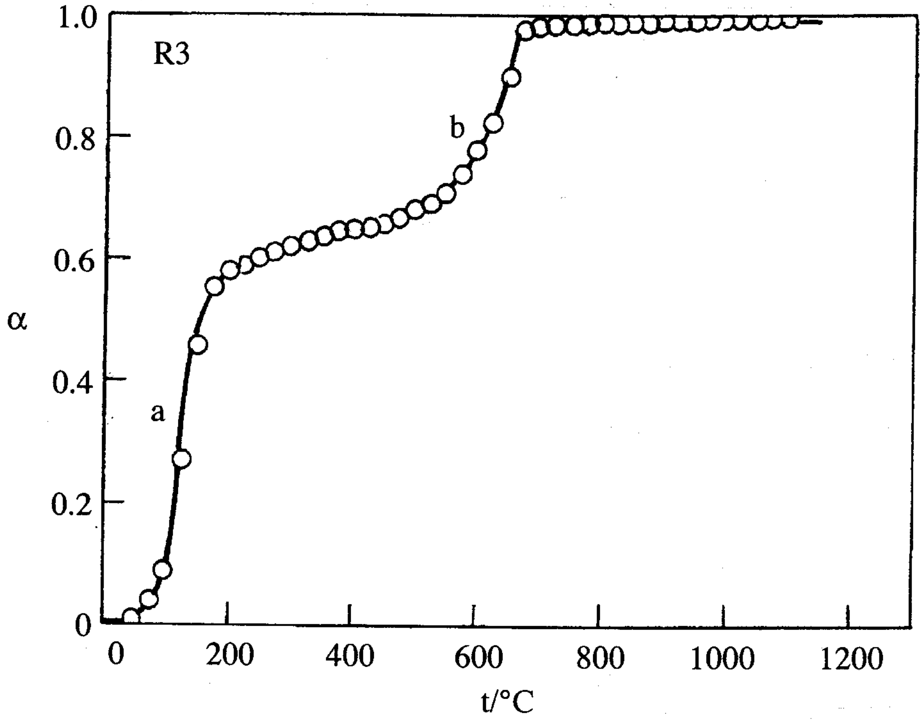

Figure 7. The variation of the decomposition factor of the R3 fraction, as a function of temperature.

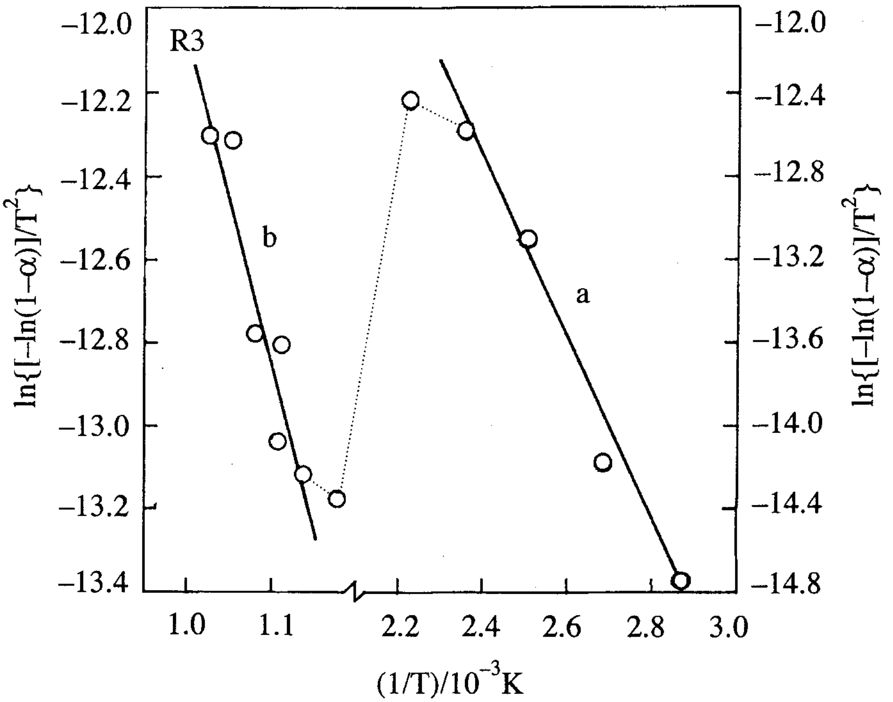

Figure 8. The Coats-Redfern straight lines for the dehydration (a) and dehydroxylation (b) of the R3 fraction.

R4 Fraction

The $\alpha - t$ curve of the R4 fraction, which was plotted by using the TG data is given in Figure 9 and the Coats-Redfern straight lines are given in Figure 10. It was clearly observed from Figure 9 that 45 % of the mass loss of R4 was due to dehydration and the rest was due to dehydroxylation. By using the Coats-Redfern equation and the slopes of the straight lines given in Figure 10, the dehydration (a) and dehydroxylation (b) rates were determined, respectively as follows

$$d\alpha_a / dt = 1318\, e^{-34000/RT} (1 - \alpha) \qquad (10)$$

$$d\alpha_b / dt = 484\, e^{-67000/RT} (1 - \alpha) \qquad (11)$$

The dehydration and dehydroxylation originated from NaM which existed around 100 % in R4. It was observed that the activation energies of the dehydration and dehydroxylation of smectites such as NaCaM and NaM were very close to eachother.

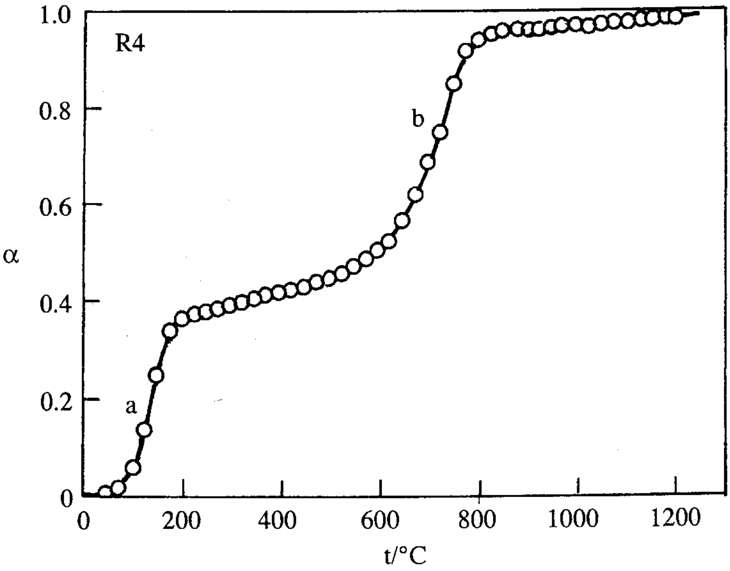

Figure 9. The variation of the decomposition factor of the R4 fraction, as a function of temperature.

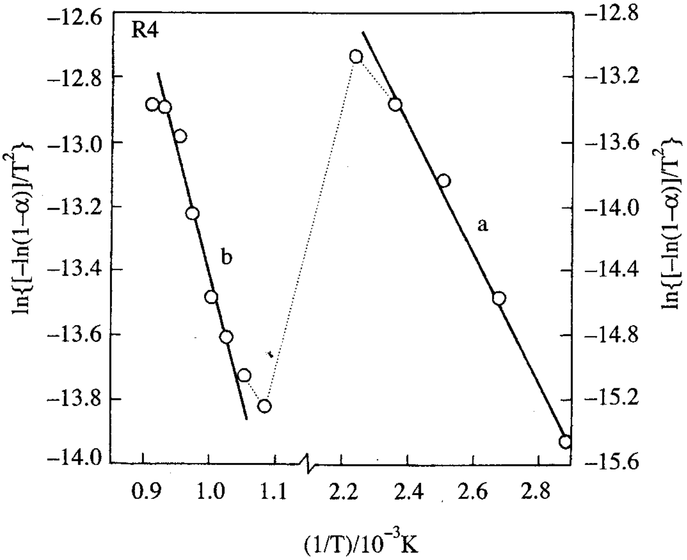

Figure 10. The Coats-Redfern straight lines for the dehydration (a) and dehydroxylation (b) of the R4 fraction.

CONCLUSION

It was shown that it was possible to determine the activation energies of the thermal decompsitions (i.e. dehydration, dehydroxylation, calcination) of the minerals contained in the untreated bentonite and its fractions, by using the TG data and the slopes of the straight lines plotted according to the Coats-Redfern equation. It was observed that the activation energies increased in the order of dehydration, dehydroxylation and calcination. The pre-exponential factor is equal to the decomposition rate constant at the instant the activation energy is zero. Big differences were observed in the values of pre-exponential factors from one sample to another. It was not possible to explain these differences. It was understood that opal-CT,which has a semi-crystal structure catalysed the dehydration and dehydroxylation of smectite minerals. It was also understood that, although the exchangeable cations contained in the smectite minerals had no effect on the activation energies of the dehydration and dehydroxylation, they changed the amount of water eliminated by the dehydration. It was concluded that it is necessary to investigate the dehydration and dehydroxylation kinetics of the smectite minerals in further detail by using the TG data which will be obtained at different heating rates.

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