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KINETICS OF THE THERMAL DEHYDRATION OF ACID-ACTIVATED MONTMORILLONITE BY THE RISING TEMPERATURE TECHNIQUE

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ABSTRACT

The activation energies of dehydration and combustion of organic materials in a clay sample, and of dehydration of natural and acid-activated montmorillonite have been determined using a rising temperature programme technique. The effect of acid activation of the montmorillonite on the dehydroxylation is discussed.

INTRODUCTION

The thermal dehydration kinetics of clay minerals have been investigated in detail [1–10], but little is known about the kinetics of the thermal dehydration of acid-activated clay minerals [11,12].

The kinetic parameters of dehydration are quite important for the investigation of the probable mechanism of acid activation of clay minerals. For this reason, the activation energies of samples of natural and acid-activated montmorillonite have been calculated from DTA and TG traces of the samples.

In the present work, a sample of clay mineral from the Çanakkale reserve was activated with concentrated sulphuric acid by a dry process [12,13].

Over many years, various methods of thermogravimetric data analysis have been evolved for the evaluation of kinetic parameters such as the energy of activation for solid decomposition reactions [4,10,14].

Most reactions of the type

$$\text{solid} \rightarrow \text{solid} + \text{gas}$$

can be described by the equation

$$d\alpha/dt = A(1-\alpha)^n \exp(-E/RT)$$

where $d\alpha/dt$ is the rate of the decomposition, α is the fraction reacted, n is the order of the reaction, T is the Kelvin temperature, A is the pre-exponential term, R is the universal gas constant, and E is the activation energy.

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The equation $dT/dt = \beta$ is also used, where β is the heating rate (in K min^{-1}).

The dehydration of a clay is a first-order reaction [1,9]. For $n = 1$, integration of the above equation by approximation by series or by partial integration [14,15] results in

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT}$$

As has been reported previously [16], determining the kinetic parameters using the above equation, i.e. by plotting $\ln[-\ln(1-\alpha)/T^2]$ vs. $1/T$, seems to give more accurate results than does the well-known Coats and Redfern equation. In this approach, it has been supposed that

$$\ln\left[\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right)\right]$$

is nearly constant.

EXPERIMENTAL

Samples of clay mineral—a mixed-layer illite–montmorillonite from the Çanakkale reserve [13]—were activated with sulphuric acid under various conditions. The acid-activated sample which had the best bleaching capacity was selected for study.

DTA and TG traces were obtained using a Netzsch DTA and TG simultaneous instrument at a heating rate of 10 K min^{-1} in a static atmosphere, using kaoline heated to 1200 °C as inert material.

RESULTS AND DISCUSSION

DTA and TG plots of the natural and the acid-activated montmorillonite are shown in Figs. 1 and 2.

In a layered clay mineral such as montmorillonite, loss of adsorbed water from the inter-layer space is termed dehydration, and loss of hydroxyl groups from the octahedral sheet of the clay lattice is referred to as dehydroxylation [17].

It can be seen that the position of the peak at 105 °C does not change, and the amount of hygroscopic moisture is approximately equal to that of the natural sample [13].

The small endothermic peak observed for the activated clay sample is due to dehydration of calcium sulphate produced during the sulphuric acid treatment, because the clay is associated with a small amount of calcite

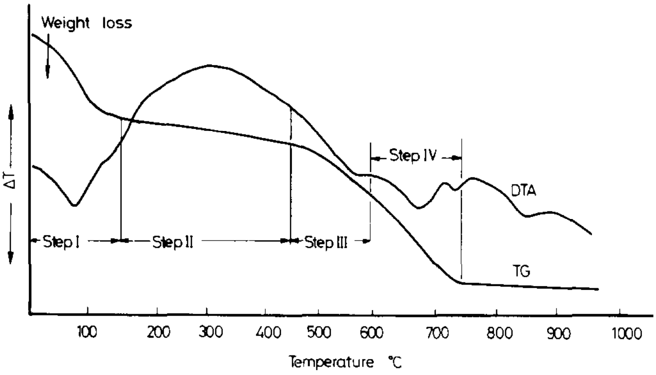

Fig. 1. DTA and TG traces of natural Çanakkale montmorillonite.

[13,18]. The size of the exothermic peak, which is due to the combustion of organic material, decreases after acid activation.

For the acid-activated sample, the peak temperatures shifted from 570 to 515 °C and from 670 to 655 °C respectively, the peak areas decreased, and the peak at 725 °C disappeared completely.

TG data were obtained at a constant heating rate of $\beta = 10$ K min^{-1} for all the samples. The fraction decomposed α was plotted for both natural and acid-activated samples (Fig. 3). The α values at various temperatures were determined from these traces. Values of $\ln[-\ln(1-\alpha)/T^2]$ were then plotted against $1/T$ (Fig. 4). In each curve, the first step is due to dehydration, the second step is due to the combustion of organic material, and the third and fourth steps correspond to dehydroxylation of the natural or the acid-activated montmorillonite.

The activation energies of dehydration of the natural and the acid-activated montmorillonite samples are very similar, and the combustion energies are also nearly equal.

The activation energies of dehydroxylation in the third step are also very similar (Table 1), because the dehydroxylation reactions occur between the

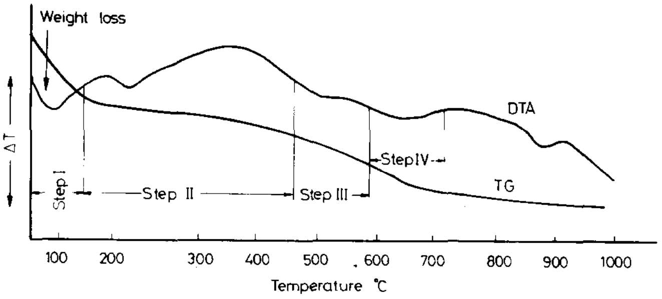

Fig. 2. DTA and TG traces of acid-activated montmorillonite.

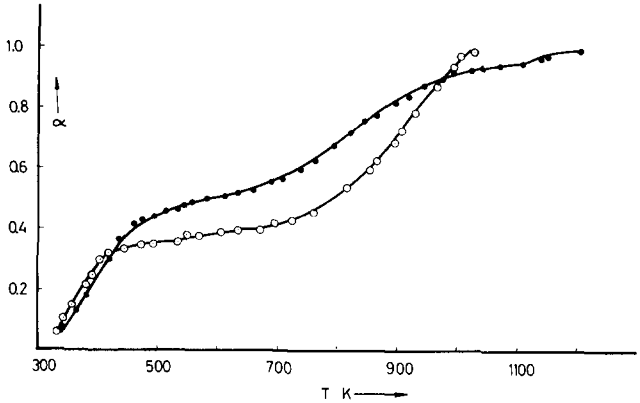

Fig. 3. Plots of α vs. T for (○) natural and (●) acid-activated montmorillonite.

surface hydroxyl groups for both the clays.

$$OH^- + OH^- \rightarrow H_2O + O^{2-}$$

The dehydroxylation reaction is related to the combination of –OH groups within the lattice of the natural clay in the fourth step, but the same reaction can take place between –OH groups of the Si–OH created during acid activation. These groups undergo dehydroxylation much more readily than do the octahedral –OH groups within the lattice [19]. The activation energy of the acid-activated montmorillonite is therefore found to be much lower than that of the natural montmorillonite in the fourth step.

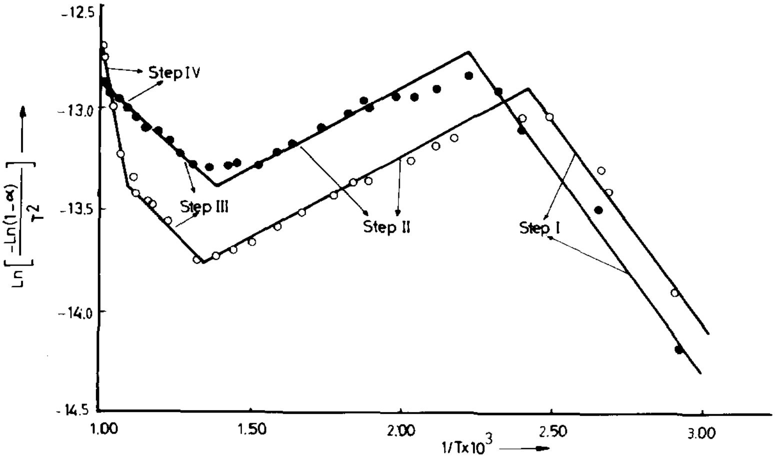

Fig. 4. Plots of $\ln[-\ln(1-\alpha)/T^2]$ vs. $1/T$ for (○) natural and (●) acid-activated montmorillonite.

TABLE 1

Activation energies of natural and acid-activated montmorillonite

Clay	Temperature range (K)	Activation energy (kJ mol^{-1})	Regression coefficient	Reaction
Natural montmorillonite	303–418	14.72	0.97	Dehydration
	418–723	−6.43	0.98	Combustion
	723–853	9.80	0.99	Dehydroxylation
	853–963	50.74	0.98	Dehydroxylation
Acid-activated montmorillonite	303–433	16.63	0.99	Dehydration
	433–738	−4.99	0.97	Combustion
	738–863	9.98	0.98	Dehydroxylation
	863–993	13.00	0.99	Dehydroxylation

These findings will be of value to further explorations of the probable mechanism of acid activation of clay minerals.

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