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Thermogravimetric Investigation of the Dehydration Kinetics of KSF, K10 and Turkish Bentonite

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The kinetic parameters for the dehydration of bentonite from Turkey, KSF and K10 were determined by using dynamic TG techniques. The Ozawa method is better for the dehydration of the clay samples than the first order equation of Coats and Redfern. The former function calculates consistently higher activation energies than the latter. The mean values of the activation energies in the α range 0.1-0.7, are 56-66 kJ mol⁻¹ in the Ozawa method.

Key Words: Dehydration kinetics, Bentonite, KSF, K10, Ozawa method, Coats-Redfern method

Introduction

The Ozawa method^{1,2} and the methods of Coats and Redfern³ were used in this study. The derivations of the methods are outlined in the original papers. Here the uses of the final operative equations are investigated and given below.

The Ozawa Method

$$\log \beta = \log(AE/R) - 2.315 - 0.4567(E/RT) - \log g(\alpha) \quad (1)$$

where β is the heating rate (K min⁻¹), A is the pre-exponential factor (min⁻¹), R is the gas constant (8.314 Jmol⁻¹K⁻¹) and

$$g(\alpha) = (AE/\beta R)P(x) \quad (2)$$

$$x = E/RT \quad (3)$$

α is the fraction reacted.

$$\alpha = (W_o - W_t)/(W_o - W_f) \quad (4)$$

where W_o is the initial mass of the sample, W_t is the mass of the sample at temperature t and W_f is the final mass at a temperature at which the mass loss is approximately unchanged.

In this method, plots of $\log \beta$ versus $1/T$ give parallel lines for each α value. The slope of these lines gives the activation energy, as seen from equation 5,

$$\text{Slope} = -0.4567(E/R) \quad (5)$$

The next step in the analysis is the determination of A and reaction order n . For this reason, the theoretical curves of $(1-\alpha)$ against $\log g(\alpha)$ should be found before the calculation, as given in reference 1.

The Method of Coats and Redfern

This method, as reviewed by Johnson and Gallagher⁴ is an integral method that assumes various orders of reaction and compares the linearity in each case to select the correct order. The equations are given below;

By plotting the appropriate left-hand side of the below equations versus $1/T$, the slope equals $-E/2.303R$.

$$\log \left[\frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right] = \log \frac{AR}{\beta E} \left[1 - \frac{2RT}{E} \right] - \frac{E}{2.303RT} \quad \text{for } n \neq 1 \quad (6)$$

$$\log \left[\frac{-\log(1 - \alpha)}{T^2} \right] = \log \frac{AR}{\beta E} \left[1 - \frac{2RT}{E} \right] - \frac{E}{2.303RT} \quad \text{for } n = 1 \quad (7)$$

E and A values can be calculated from these equations.

The hydrations of natural and acid activated montmorillonite have also been determined by using a rising temperature program technique. The TG data were evaluated in a four-step mechanism. The dehydration activation energies of natural and acid activated montmorillonite samples were calculated⁵. The effect of thermal treatment on some of the physico-chemical properties of the bentonite was also investigated⁶.

In this study, our aim was to calculate the activation energy of dehydration of a Turkish bentonite sample in comparison with two commercial bentonites.

Experimental

Materials

Thermal analysis was performed on three bentonites: one from the Resadiye-Tokat region of Turkey, and two from Fluka, KSF (Fluka No. 69866) and K10 (Fluka No. 69867). The chemical composition of the samples is given in Table 1^{7,8}. The samples KSF and K10 are based on calcium-bentonite, which is found in the region of Mainburg-Landshut in Germany. Their compositions can therefore vary from batch to batch.

Table 1. Chemical Composition of the Clays, wt %

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	MgO	CaO	Na ₂ O	K ₂ O	Sulphate	Ignition	Total
Bentonite	58.8	19.2	3.6	0.4	2.1	4.2	2.7	1.4	-	7.5	99.9
KSF	55.0	18.0	4.0	-	3.0	3.0	<0.5	1.5	5.0	10.0	100
K10	69.0	14.0	4.5	-	2.0	1.5	<0.5	1.5	-	7.0	100

Techniques

All thermal analysis work was done using a Shimadzu TGA 50 thermal analyzer at various heating rates in a stream of nitrogen ($10\text{cm}^3\text{ min}^{-1}$). TG and DTG data were determined by a Shimadzu CR4A Unit with TAPAC 50 Software. By using this program, one can easily determine all of the mass losses at each temperature on the thermograms with a simple cursor. Then, using equation 4, α can be calculated and plotted against $1/T$. In this device, a weight of 20 mg is read to a precision of $10\ \mu\text{g}$ by a precision balance.

Results and Discussions

Thermogravimetry of Samples

The thermograms were obtained at four different heating rates: 5, 10, 15 and $20^\circ\text{C min}^{-1}$. TG and DTG thermograms of bentonite, KSF and K10 at a heating rate of $10^\circ\text{C min}^{-1}$ are given in Figure 1. Analysis of these curves estimates the mass loss associated with the processes of dehydration and dehydroxylation. The former is estimated from mass loss up to 300°C and the later between 300 and 800°C . Dehydration is usually exhibited in a single wave, whereas dehydroxylation appears in the form of overlapping waves. The data in Table 2 give the mass losses that occurred through the dehydration and dehydroxylation of the samples at different heating rates.

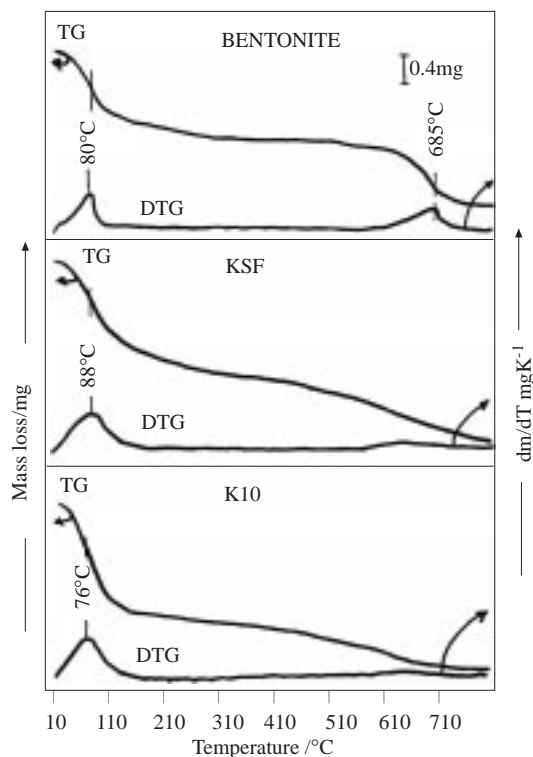


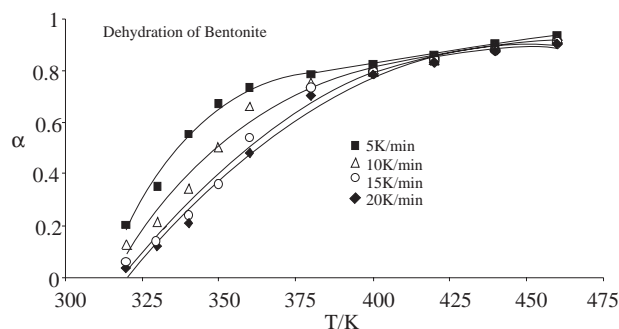
Figure 1. TG and DTG thermograms of bentonite, KSF and K10

Table 2. Mass loss in the dehydration and dehydroxylation regions of TG (%)

Sample	Heating rate $^{\circ}\text{C min}^{-1}$	Sample weight mg	Total loss $< 800^{\circ}\text{C}$	Dehydration $< 300^{\circ}\text{C}$	Dehydroxylation $300-800^{\circ}\text{C}$
Bentonite	5	15.77	12.36	6.81	5.55
	10	17.26	12.32	6.66	5.66
	15	19.57	12.32	6.80	5.52
	20	16.60	12.39	6.67	5.72
Average			12.35	6.74	5.61
KSF	5	17.63	17.28	10.28	7.00
	10	15.48	17.24	10.48	6.76
	15	19.30	16.19	10.01	6.18
	20	18.32	16.34	10.04	6.30
Average			16.76	10.20	6.56
K10	5	17.26	14.77	10.82	3.95
	10	16.16	14.67	10.56	4.11
	15	17.11	14.16	10.10	4.06
	20	13.20	13.10	9.04	4.06
Average			14.18	10.13	4.05

As can be seen from Table 2, the heating rates had no effect on mass losses. The averages of total losses were in the order of KSF, K10 and Bentonite. The values are 16.76, 14.18 and 12.35 percent, respectively.

The TG curves were divided into two parts: the first covering the range up to 300°C and the second covering the range from 300 to 800°C . The former curves were transferred into decomposition curves plotted in the form of fractions decomposed as a function of temperature (as in Figure 2). For the analysis of the dehydration curves, two methods were used.


Figure 2. Thermograms of bentonite at different heating rates

The Ozawa Method

α and $(1-\alpha)$ values were found for each heating rate from these TG curves. Then α was plotted against temperature. The absolute temperature determined from these curves for each $(1-\alpha)$ in which there is a 0.1 difference between each one and the curves is plotted as $\log\beta$ versus $1/T$ (Figure 3). The activation energies (E) determined from the slope of each line are listed in Table 3. It was found that the mean values of the activation energies were 56.1, 65.5 and 60.2 for bentonite, KSF and K10 respectively.

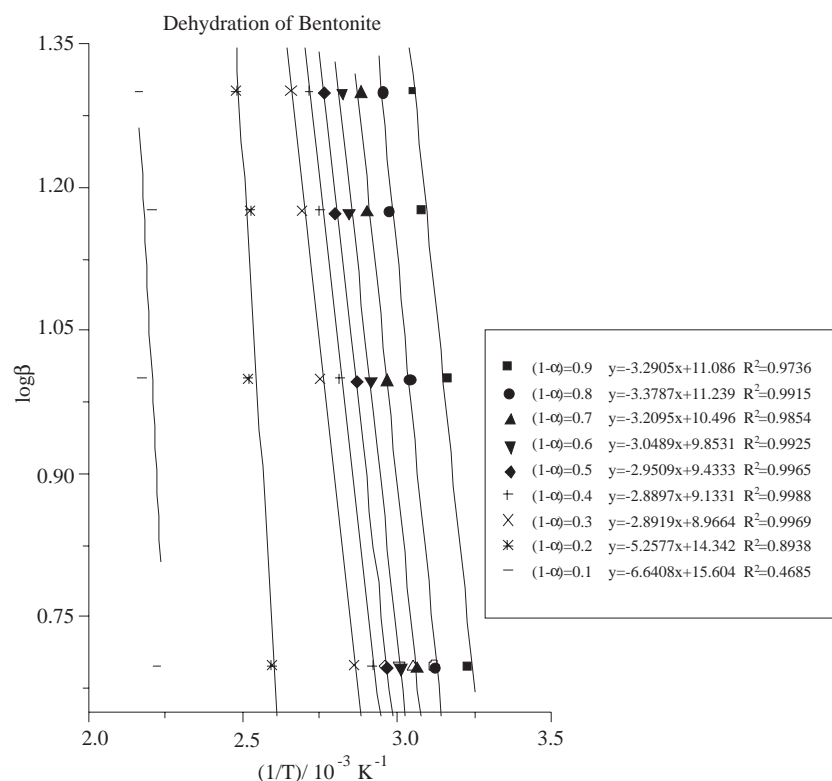


Figure 3. Plots of $\log \beta$ against $1/T$ for bentonite

Table 3. Activation Energies from Ozawa Method

$1-\alpha$	T/K	E/kJmol ⁻¹		
		Bentonite	KSF	K10
0.3	364	52.7	88.8	61.7
0.4	356	52.6	66.2	57.6
0.5	350	53.7	64.1	57.8
0.6	344	55.5	62.4	57.3
0.7	338	58.4	60.0	58.8
0.8	329	61.5	60.4	60.3
0.9	316	58.4	56.5	67.8
\bar{E} ($1-\alpha=0.3-0.9$)		56.1	65.5	60.2

The Method of Coats and Redfern

The left-hand side of equations 6 and 7 versus $1/T$ was plotted and the slope of these lines gave the E values. In testing the present data of dehydration of the samples, equations 6 and 7 expressing the orders 0, 1/2 and 1 were plotted. The first order equation was found to fit better. The straight line plots for bentonite are given in Figure 4, and the calculated activation energies are cited in Table 4.

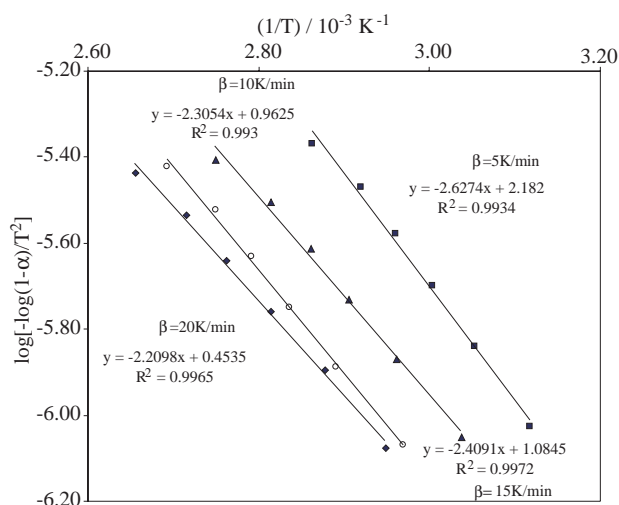

Figure 4. Coats-Redfern plots of bentonite

Table 4. Activation Energies from Coats-Redfern Method

Sample	Heating rate $^{\circ}\text{C min}^{-1}$	T_{max} /K	E/kJmol^{-1}
Bentonite	5	339	51.2
	10	353	44.1
	15	361	46.1
	20	366	42.3
	\bar{E}		45.9
KSF	5	381	22.9
	10	361	24.8
	15	372	26.0
	20	378	25.9
	\bar{E}		24.9
K10	5	326	33.4
	10	349	36.4
	15	359	33.5
	20	369	33.8
	\bar{E}		34.3

Discussion and Conclusions

In general, the Ozawa method is better for the dehydration of the clay samples than the first order equation of Coats and Redfern³. Moreover, the former function calculates consistently higher activation energies than the latter. Comparison of the data in Tables 3 and 4 indicates the following:

1. The mean values of the activation energies in the α range 0.1-0.7 are 56-66 kJ mol^{-1} in the case of the Ozawa method.
2. The mean activation energy values in Table 4 are somewhat different from the values in Table 3. There is no correlation between them. The values are 45.9, 34.3 and 24.9 kJ mol^{-1} for bentonite, KSF and K10 respectively.
3. The estimated mean values of E in the Ozawa method are not very different from the published values⁹.

In conclusion, the three different bentonites seem to show similar activation energies as far as the Ozawa method is concerned. Activation energies of 60 kJ mol^{-1} seem reasonable estimates for the dehydration of interlayer physically adsorbed water as well as from the hydration shells of the exchangeable cations. The thickness of this adsorbed and shell water usually depends on the pretreatment, the kind of exchangeable cation and the locality of the raw material.

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