

THE EFFECT OF THERMAL TREATMENT ON SOME OF THE PHYSICOCHEMICAL PROPERTIES OF A BENTONITE

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Abstract—A white calcium bentonite (CaB) from the Kütahya region, Turkey, contains 35 wt. % opal-CT and 65 wt. % Ca-rich montmorillonite (CaM). Samples were heated at various temperatures between 100–1300°C for 2 h. Thermal gravimetric (TG), derivative thermal gravimetric (DTG), and differential thermal analysis (DTA) curves were determined. Adsorption and desorption of N₂ at liquid N₂ temperature for each heat-treated sample was determined. X-ray diffraction (XRD) and cation-exchange capacity (CEC) data were obtained. The change in the *d*(001) value and the deformation of the crystal structure of CaM depend on temperature. Deformation is defined here as changes of the clay by dehydration, dehydroxylation, recrystallization, shrinkage, fracture, etc. The activation energies related to the dehydration and dehydroxylation of CaB calculated from the thermogravimetric data are 33 and 59 kJ mol⁻¹, respectively. The average deformation enthalpies, in the respective temperature intervals between 200–700°C and 700–900°C, were estimated to be 25 and 205 kJ mol⁻¹ using CEC data and an approach developed in this study. The specific surface area (S) and the specific micropore-mesopore volume (V) calculated from the adsorption and desorption data, respectively, show a “zig zag” variation with increasing temperature to 700°C, but decrease rapidly above this temperature. The S and V values were 43 m² g⁻¹ and 0.107 cm³ g⁻¹, respectively, for untreated bentonite. They reach a maximum at 500°C and are 89 m² g⁻¹ and 0.149 cm³ g⁻¹, respectively. The XRD data clearly show that, at 500°C, where the irreversible dehydration is completed without any change in the crystal structure, the porosity of CaM reaches its maximum.

Key Words—Adsorption, Bentonite, Cation-Exchange Capacity, Dehydration, Dehydroxylation, Montmorillonite, Pore Volume, Surface Area, Thermal Analysis.

INTRODUCTION

Bentonites, which contain high percentages of smectite, are greatly effected by thermal treatment. For example, physicochemical properties, such as strength, swelling, plasticity, cohesion, compressibility, particle size, cation-exchange capacity (CEC), pore structure, adsorptive properties, and catalytic activity as well as the chemical composition of the particles and the mineralogy can change considerably depending on thermal effects (Bradley and Grim, 1951; Brindley, 1978; Mozas *et al.*, 1980; Reicle, 1985; Ceylan *et al.*, 1993; Sarıkaya *et al.*, 1993; Joshi *et al.*, 1994). Bentonites are used as industrial raw materials in more than 25 applications (Murray, 1991). The major uses of bentonites are iron ore pelletizing, pet adsorbents, drilling fluids, bleaching of edible oils, and applications in civil engineering and the foundry industry. Bentonite may be subjected to high temperatures when used in these applications. In addition, before construction of bridges and buildings on smectitic soils, the ground below the foundations may be heat-treated to <600°C to harden the soil and to reduce the swelling characteristics of the clay (Wang *et al.*, 1990). Because of these effects, the investigation of the variation of the physicochemical properties of bentonites as a function of temperature is of great importance.

Variations in the chemical composition, mineralogy and physicochemical properties after thermal treatment, acid activation, or soda activation of most of the

bentonites of Turkey have not been investigated systematically. Bentonite from Kütahya, Turkey, in addition to its present application, may be used as a powder catalyst in the gasification, liquefaction, and desulfurization process of solid fuels, such as lignites and bituminous coals. The physicochemical properties of this bentonite need to be examined at 100–800°C, because the mineralogy and the pore structure must not be destroyed at the process temperature. Therefore, the purpose of this study is to investigate the mineralogy, pore structure, and cation-exchange capacity as a function of thermal treatment of the Kütahya bentonite from Turkey. This bentonite contains Ca-rich montmorillonite and opal-CT.

MATERIALS AND METHODS

A calcium bentonite (CaB) sample from the Kütahya region, Turkey, was used in the experiments. The rheological properties of the Na₂CO₃ activated samples (Yıldız *et al.*, 1999) and the adsorptive properties of the H₂SO₄ activated samples (Önal *et al.*, unpublished data, 1999) were previously investigated. The bulk chemical analysis of the bentonite (wt. %) is: SiO₂, 75.58; Al₂O₃, 14.72; Fe₂O₃, 0.76; TiO₂, 0.16; CaO, 0.85; MgO, 1.40; Na₂O, 0.39; K₂O, 1.68; and loss on ignition (LOI), 5.04. Analytically pure methylene blue used for the determination of the CEC and 85% ortho phosphoric acid used for the digestion were obtained from Merck Chemical Company.

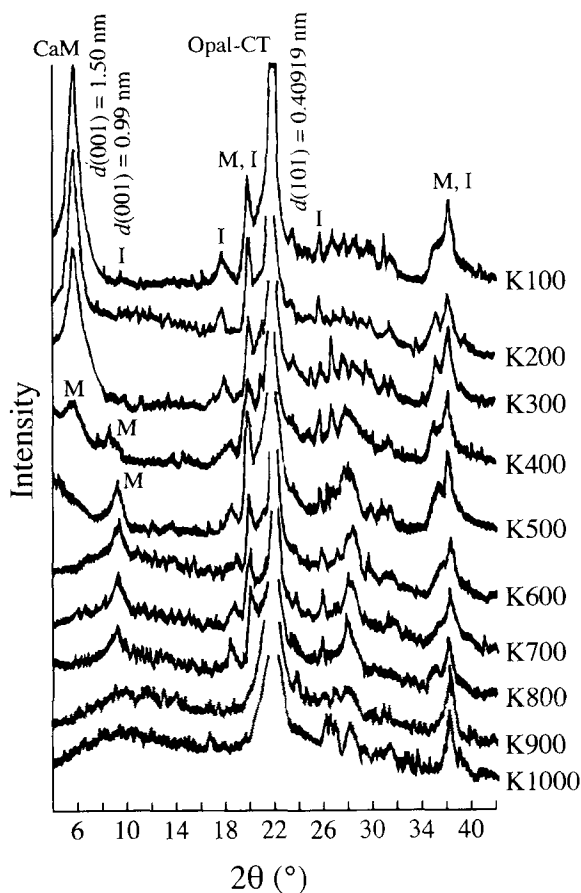


Figure 1. The XRD patterns of untreated and thermally treated bentonite samples. (M = montmorillonite, I = illite).

The bentonite was ground to pass through a 0.074-mm sieve and was labeled as K0. Samples, each having a mass of 20 g, were heated in 100°C intervals to 1300°C and were thermally treated by maintaining at each temperature for 2 h. Samples were then labeled as K100, K200, *etc.*, and stored in polyethylene bags. In addition, a 10% aqueous suspension of K0 was prepared, and the fraction which precipitated in 5 min from this suspension was labeled as K1. K0 was maintained at 1050°C for 2 h and was labeled as K2. Also, a phosphoric acid digestion (Talvitie, 1951; Miles, 1994) was obtained by mixing 2 g of K0 and 100 mL of 85% ortho phosphoric acid (dehydrates to pyrophosphoric acid) and heating the mixture for 12 min at 240°C.

The X-ray diffraction (XRD) patterns of each sample were obtained from random mounts using a Philips PW 1730 powder diffractometer with $\text{CuK}\alpha$ radiation and a Ni filter. A Netzsch Simultaneous TG-DTG-DTA Instrument Model 429, was used at a heating rate (β) of 10 K min^{-1} to determine the thermal gravimetric (TG), derivative thermal gravimetric (DTG), and differential thermal analysis (DTA) curves of the original

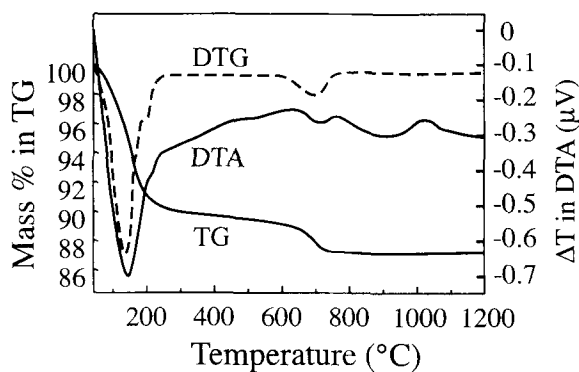


Figure 2. The TG, DTG, and DTA curves of the bentonite.

bentonite. $\alpha\text{-Al}_2\text{O}_3$ was used as an inert material. The CEC, defined as the milliequivalents of exchangeable cations per 100 g of clay or clay minerals was determined by the methylene blue standard procedure (Hang and Brindley, 1970; Rytwo *et al.*, 1991). The adsorption and desorption of N_2 at liquid N_2 temperature for each sample was determined by a volumetric adsorption instrument, of pyrex glass, which was connected to high vacuum (Sarkaya and Aybar, 1978).

RESULTS

The XRD patterns of ten thermally treated K0 samples are given in Figure 1. The patterns show that the Kütahya bentonite contains Ca-rich montmorillonite (CaM) as the major clay mineral, a trace amount of illite (I), and a large amount of opal-CT. XRD analysis of the K0 and K1 samples showed that illite settled from the aqueous suspension in 5 min and could be largely eliminated. Specimens where illite was not removed were used in thermal treatments and therefore, illite peaks are observed in the XRD patterns given in Figure 1. The XRD analyses do not show interstratified CaM-I phases. Phosphoric-acid digestion dissolved the bentonite completely. The K2 sample produced an XRD pattern (not given here) with the characteristic opal-CT peak, $d(101) = 0.40929$ nm. After heating at 1050°C for 24 h the peak became narrower, shifted, and intensified at least two times. The results clearly showed that α -cristobalite, whose characteristic XRD peak can be easily confused with that of opal-CT (Elzea *et al.*, 1994), was not present. By comparing bulk analysis of the bentonite to the ideal chemical formula of smectites (Grim and Güven, 1978) the amount of opal-CT in the bentonite is estimated at 35 wt. %.

TG, DTG, and DTA curves of the untreated bentonite are given in Figure 2. In the DTA curves, the endothermic peak which results from dehydration is observed at 100–400°C. The endothermic peak which results from dehydroxylation and the exothermic peak which results from recrystallization are observed at

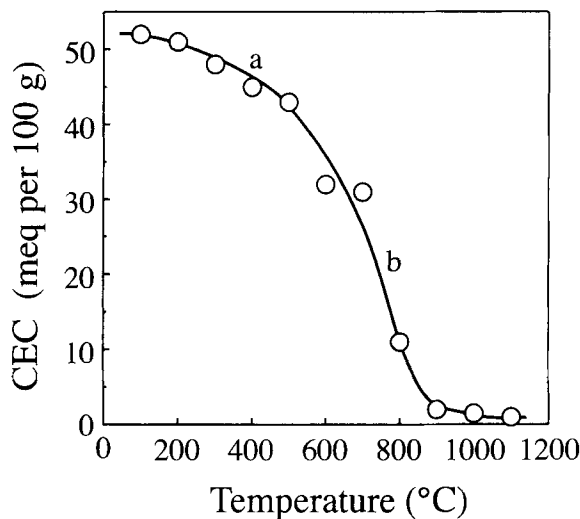


Figure 3. Variation of the cation-exchange capacity of untreated bentonite vs. the thermal-treatment temperature.

600–800°C. The exothermic peak resulting from the loss of the crystal structure of the 2:1 layers of CaM and recrystallization is observed at 950–1050°C.

The variation of CEC by thermal treatment is given in Figure 3. Note that the CEC decreases slowly with increasing temperature to 600°C (slope a) and then decreases rapidly and approaches zero at 900°C (slope b).

The specific surface areas (S) of each sample were determined by the Brunauer-Emmett-Teller (BET) procedure by using N_2 adsorption data. The specific micro- and mesopore volumes (V) were calculated from the desorption data (Gregg and Sing, 1982; Sevinç *et al.*, 1991). The variation of V and S by thermal treatment is given in Figure 4.

DISCUSSION

XRD analyses

In Figure 1, the 001 peak of CaM decreases in intensity while maintaining its position after thermal treatment between 100–300°C. At 400°C it becomes significantly smaller and splits into two peaks. The splitting is related to incomplete dehydration at 400°C. The pattern of K500 shows that this peak changes its position from $d(001) = 1.50$ nm to $d(001) = 0.99$ nm and remains constant in position between 500–800°C. The variation of the $d(001)$ value for CaM by the thermal treatment is given in Figure 5a. The H_2O contained between the 2:1 layers of CaM was lost reversibly below 400°C, but at higher temperatures the loss was irreversible.

The ratios of the 001-peak areas of other samples to the 001-peak area of the K100 sample is defined here as the relative area (RA). The RA of the K400 sample was calculated by using the sum of the areas

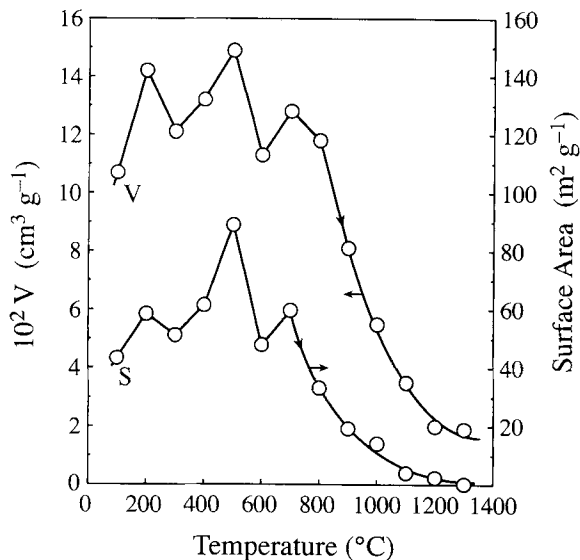


Figure 4. The variation of the specific surface area and the specific micropore and mesopore volume as calculated from the adsorption and desorption data of N_2 at liquid N_2 temperature vs. the thermal-treatment temperature.

of the split 001 peak. The variation of the RA as a function of the thermal-treatment temperature is given in Figure 5b. Based on this figure, the major change in the crystal structure of CaM occurs between 300–500°C.

Thermal analyses

Changes of the clay by dehydration, dehydroxylation, recrystallization, shrinkage, fracture, loss of crystal structure, and sintering, which occur as a result of increasing temperature, can be defined as “deforma-

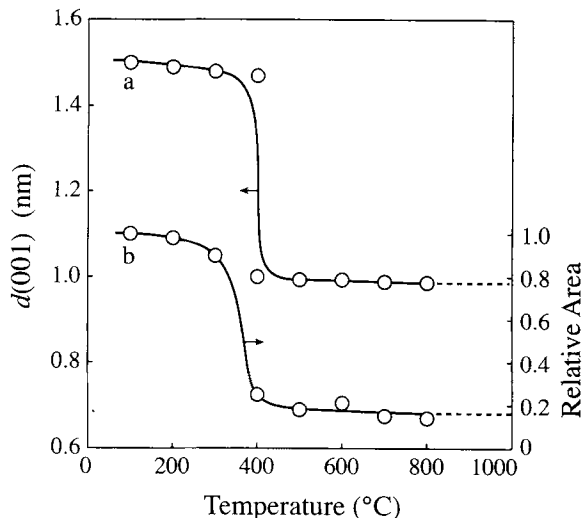


Figure 5. The variation of a) $d(001)$ of CaM and b) the relative area by thermal treatment of CaM in the bentonite.

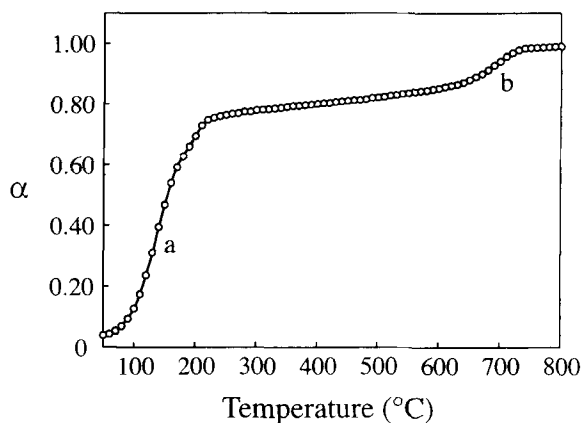


Figure 6. The variation of the deformation fraction, where α is defined as the ratio of the mass loss during each 10 K increase of temperature as obtained from the TG data of the bentonite, to the mass loss at 1000°C vs. temperature.

tion". The mass loss during each 10 K increase of temperature was taken from the TG data. The ratio of this mass loss to the total mass loss after heating to 1000°C was defined as the "deformation fraction" represented by α . The variation of α by temperature follows the curve in Figure 6. On this curve, the first slope shows dehydration (a) and the second slope shows the dehydroxylation (b). The straight lines a and b (Figure 7) are plotted according to the Coats and Redfern (1964) equation given below, which describes approximately a first-order reaction such as solid (1) \rightarrow solid (2) + gas, (i.e., as dehydration, dehydroxylation, and calcination):

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

The slope and intersection of the straight lines are $-E/R$ and $\ln[(AR/\beta E)(1-2RT/E)]$, respectively (Güler and Sarier, 1990). Here, T is the temperature (K), β is the heating rate ($K \text{ min}^{-1}$), R is the universal gas constant, E is the activation energy, and A is the pre-exponential factor. E values were calculated from the slopes of these lines as $E_a = 33 \text{ kJ mol}^{-1}$ and $E_b = 59 \text{ kJ mol}^{-1}$. These results show that the dehydration is a physical event where water is lost without structural loss, whereas the dehydroxylation is a chemical event that invokes decomposition.

The evaluation of the CEC data

The decrease in the CEC is a measure of the deformation related to the CaM layers. As the temperature increases to 500°C, CEC decreases slightly because of reversible dehydration. As the temperature increases above 500°C, the space between the 2:1 CaM layers is reduced and swelling decreases gradually because of irreversible dehydration and dehydroxylation. CEC decreases rapidly because it becomes increasingly dif-

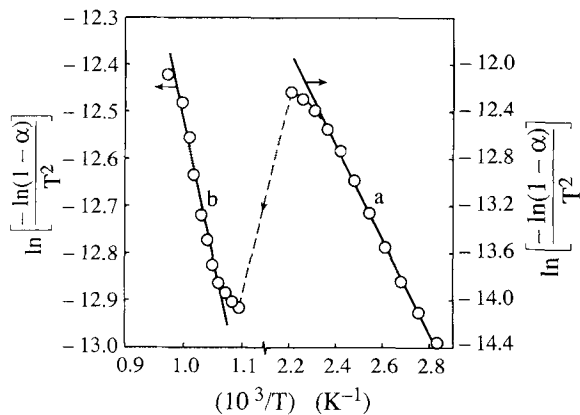


Figure 7. The straight lines obtained by the Coats-Redfern equation used to determine the activation energies related to a) dehydration and b) dehydroxylation of the bentonite.

icult for the methylene blue cations in aqueous solution to enter the interlayer of CaM because the interlayer is partially collapsed. According to this concept, the relative decrease of the CEC at any temperature with respect to the CEC at 100°C is defined as the "deformation" fraction (x) with $K = x/(1-x)$. Although this deformation factor is not equal to the thermodynamic equilibrium constant, it shows a parallel variation. In other words, the variation of the deformation factor and the thermodynamic equilibrium constant vs. temperature are the same. If these relationships are valid, then the graph of $\ln K$ versus $1/T$ should give straight lines with slopes that are different over certain temperature intervals (Figure 8). According to the van't Hoff equation, the slope of these lines must be $-\Delta H/R$, where ΔH is the enthalpy change, which remains constant over the given temperature intervals.

From the slopes of these lines, the enthalpy changes were calculated at $\Delta H_a = 25 \text{ kJ mol}^{-1}$ and $\Delta H_b = 205 \text{ kJ mol}^{-1}$. Because the ΔH_a value is close to the enthalpy change common to physical events, it is clear that the 2:1 layers of CaM do not undergo a loss of structure between 100–600°C. Because the ΔH_b value is close to the enthalpy change in chemical events, the 2:1 layers of CaM undergo chemical deformation between 600–900°C. Figures 2 and 5 show that, at the temperature interval where chemical deformation such as dehydroxylation occurs, the $d(001)$ value and RA remain constant. Thus, the chemical change causes a reduction in the CEC without affecting the crystal structure.

Adsorptive properties

As the temperature increases to 700°C, the V and S values show a "zig-zag" increase, the values decrease rapidly afterwards and reach minimum values at 1300°C (Figure 4). The zig-zag change in V and S

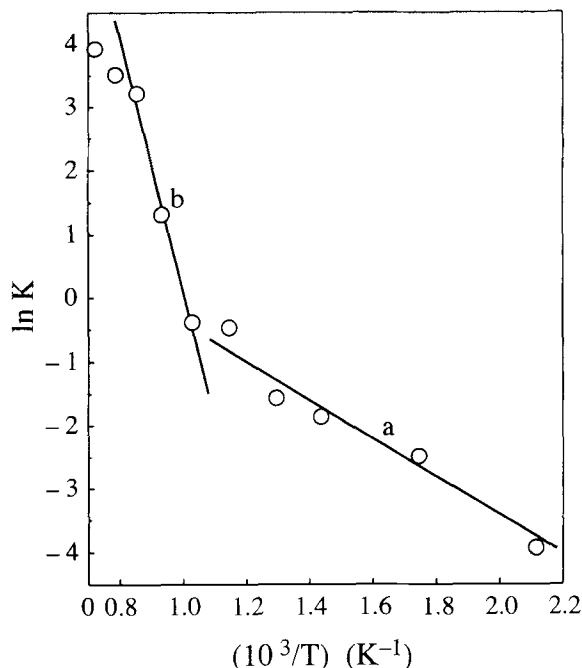


Figure 8. Straight lines show the variation of the natural logarithm of the deformation factor vs. the inverse of the absolute temperature between a) 200–700°C and b) 700–900°C. The deformation factor is defined by assuming that it is proportional to the thermodynamic equilibrium constant.

originates from the dehydration and dehydroxylation of CaM and by the dehydration of opal-CT. As the temperature increases between 700–1300°C, the decomposition of the 2:1 layer of CaM and interpowder sintering cause the rapid drop of V and S.

The kinetics of sintering are obtained by following the variation of V and S values as a function of time, at constant temperature (Sarıkaya *et al.*, unpubl. data, 2000). Similarly, the thermodynamics of sintering are obtained by following the variation of V and S values as a function of temperature, at constant time. At constant-time sintering, where the V and S values are at a minimum, the minimum sintering temperature is determined. Analogously, the minimum sintering time is determined at constant-temperature sintering.

The V and S values, which were $0.107 \text{ cm}^3 \text{ g}^{-1}$ and $42 \text{ m}^2 \text{ g}^{-1}$, respectively, in the untreated sample, reached maximum values at $0.149 \text{ cm}^3 \text{ g}^{-1}$ and $89 \text{ m}^2 \text{ g}^{-1}$, respectively, at 500°C. By considering these results and the results of the CEC and RA, it is concluded that the bentonite investigated here is potentially useful as a powder catalyst for the gasification, liquefaction, and desulfurization process of lignites and bituminous coals in the temperature interval of 100–800°C.

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