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Thermal analysis of a white calcium bentonite

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Abstract A white calcium bentonite (CaB) taken from Çamlıdere (Ankara, Turkey) region was heated at various temperatures between 100 and 1100 °C for 2 h. The mineralogy of the CaB was determined as calcium smectite (CaS), metahalloysite (MH), opal-A (OA), opal-CT (OCT), quartz (Q), feldspar (F), and calcite (C) using the X-ray diffraction patterns of the natural CaB and its heated samples. Besides the XRD patterns, the thermogravimetry, differential thermal analysis, and low-temperature nitrogen adsorption (N_2-AD) data show that the CaS lose adsorbed and hydration water up to 300 °C, dehydroxylation takes place between 300 and 750 °C, and then the 2:1 layer structure completely collapses above 900 °C. The activation energies for the dehydration and dehydroxylation were calculated as 7636 and 48838 J mol^{-1}, respectively, from the TG data using Coats and Redfern method. The specific surface area (S) and specific micro–mesopore volume (V) obtained from N_2-AD data were 44 m^2 g^{-1} and 0.100 cm^3 g^{-1} for the natural CaB. S and V reach their maxima of 105 m^2 g^{-1} and 0.155 cm^3 g^{-1}, respectively, at 300 °C, remain approximately constant as the temperature increases up to 700 °C and then decrease almost in parallel with each other, reaching their minima at 900 °C. This indicates that the S and V values increase gradually during dehydration and dehydroxylation of the CaS.

Keywords Activation energy · Bentonite · Dehydration · Dehydroxylation · Pore volume · Surface area

Introduction

Bentonitic clays, currently in use in over a hundred areas, are among the most important industrial raw materials [1–4]. The color of bentonites may be white, gray, green, blue, yellow, pink, and brown, depending on their mineralogical and chemical compositions. White bentonites are rare and are usually consumed for the production of ceramics, paper, detergents, paint, cosmetics, and clarification of wine [5, 6]. Principal clay minerals of bentonites are smectites such as montmorillonite, beidellite, saponite, nontronite, hectorite, and laponite [7]. Bentonites are predominantly consists of montmorillonite rather than other smectites. Bentonites may also contain other clay minerals and nonclay minerals as impurities [8]. One or more of the other clay minerals such as kaolinite, halloysite, illite, and chlorite may be present as impurities at various extents. The most common nonclay minerals in bentonites are silica polymorphs, zeolites, feldspars, carbonates, gypsum, and pyrite.

A smectite is a 2:1 layer clay mineral and has two silica tetrahedral (T) sheets bonded to a central alumina octahedral (O) sheet [7]. Smectites are described either dioctahedral or trioctahedral depending upon whether the octahedral cations are predominantly trivalent or divalent, respectively. The net negative electric charge of the 2:1 (TOT) layers arising from the natural isomorphic substitution of Al^{3+} with Fe^{2+} and Mg^{2+} in the octahedral sites and Si^{4+} with Al^{3+} in tetrahedral sites is balanced by the exchangeable cations such as Na^+ and Ca^{2+} located between the layers and surrounding the edges. The equivalent amount of exchangeable cations

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per kilogram smectite or clay minerals is defined as cation exchange capacity (CEC). The mineral is named Na-smectite (NaS) or Ca-smectite (CaS), as the exchangeable cation switches from Na^+ to Ca^{2+}. A clay which contains NaS or CaS as dominant mineral is called Na-bentonite (NaB) or Ca-bentonite (CaB). The Na^+ and/or Ca^{2+} cations are hydrated between the 2:1 layers of smectite. Generally, NaS has one, and CaS has two water layers in the interlayer space. As the X-ray diffraction (XRD) patterns indicate, the basal spacing, d(001), of the air-dried NaS and CaS are 1.26 to 1.54 nm, respectively [9]. This value for the anhydrous NaS and CaS is approximately 1.0 nm.

Each particle in a smectite rock or powder is an agglomerate form by large numbers of 2:1 layers. Relatively large size smectite agglomerates can be turned into smaller particles of sizes below 2 μm by keeping in water for a long time 24 h [10]. Agglomerates in smectite cause voids of different sizes. The voids whose widths are smaller than 2 nm, between 2 and 50 nm, and greater than 50 nm are called micropores, mesopores, and macropores, respectively [11]. Recently, all these pores are called as nanopores [12]. The radius of a pore, assumed to be cylindrical, can be taken as half of the pore width. The volume of pores in 1 g of solid is defined as the specific pore volume. The area of the inner and outer walls of the pores located within and among particles in 1 g solid is taken as specific surface area [13]. The pores within an air-dried natural smectite fill up with water. The content of water in macropores that can be removed by heating up to 100 °C for a long time is called moisture of smectite or bentonite. The remaining water located in mesopores, micropores, and interlayer of smectite evaporates completely when heated up to 300 °C [14].

Bentonites and their major clay minerals smectites may be used both naturally and after some physicochemical treatments such as acid activation, ion exchange, and heating as applicable for the area of use [9, 15]. In some of these areas, the bentonite may experience high temperatures [16–19]. Such thermal treatment can affect properties such as strength, swelling, adsorptivity, CEC, porosity, surface area, surface acidity, and catalytic activity [20–30]. Thermal behaviors of a bentonite vary greatly depending on its mineralogy, smectite content, and crystal structure of smectite. Accordingly, details of the thermal modification of each bentonite may better be investigated separately before deciding its value for a specific application area. The aim of this study is to find the changes in mineralogy, crystal structure, surface area, and porosity of a white bentonite by heat treatments between 25 and 1000 °C. Activation energies for dehydration and dehydroxylation of the smectite, the major clay mineral, are estimated from thermal analysis data.

Experimental

A white calcium bentonite (CaB) taken from Ankara region, Turkey, was used in the experiments after grinding to pass through a 0.074-mm (200 mesh) sieve. The bulk chemical analysis of the dried CaB at 105 °C for 4 h is as mass%: SiO_2 72.08, TiO_2 0.08, Al_2O_3 14.77, Fe_2O_3 0.80, MgO 1.63, CaO 2.15, Na_2O 0.43, K_2O 1.05 and loss on ignition (LOI) 6.98. The CEC (by the methylene blue method) is 0.78 equiv kg^{-1}.

The bentonite samples, each weighing 10 g, were heated to 1100 °C in 100 °C intervals with a rate of 10 K/min and were thermally treated by keeping at each temperature for 2 h in a furnace (Protherm, PLF 12077, Alser). The XRD patterns of natural and thermally treated samples were recorded from random mounts prepared by glass slide method using a Rikagu D-Max 2200 Powder Diffractometer, operating at 40 kV and 30 mA, using N-filtered CuK_α radiation having 0.15418 nm wavelength, at a scanning speed of 2° 20 min^{-1} [8].

The differential thermal analysis (DTA) and thermogravimetry (TG) curves of the air-dried and dried (105 °C, for 4 h) CaS samples were recorded by a Shimadzu Apparatus (DTG-60H). For this purpose, approximately 20 mg of sample was placed in a platinum crucible on the pan of the microbalance and was heated in the range 25–1000 °C using α-Al_2O_3 as an inert material. Analysis was performed under flowing nitrogen (with a flow rate of 100 ml min^{-1}) using a heating rate of 10 K/min.

The adsorption and desorption data of N_2, at liquid N_2 temperature, on the natural and thermally treated samples were obtained by a volumetric adsorption instrument of Pyrex glass connected to a high vacuum system [4, 31]. Before each measurement, the samples were outgassed at 150 °C for 4 h under a vacuum of 10^{-3} mmHg. Gas adsorption monometry was used for the determination of the amount of the nitrogen adsorbed [13, 32].

Results and discussion

Mineralogy of the bentonite

The XRD patterns of the natural and all thermally treated bentonite samples were examined, and representative ones, are given in Fig. 1. The minerals in the bentonite were identified by their characteristic XRD-peaks [8]. Thus, the bentonite contains smectite (S) and metahalloysite (MH) as the major and minor clay minerals, respectively, as indicated on the XRD-pattern of the natural bentonite. The value of the basal spacing, d(001) = 1.5771 nm, indicates a calcium-rich smectite (CaS) as major clay minerals in the

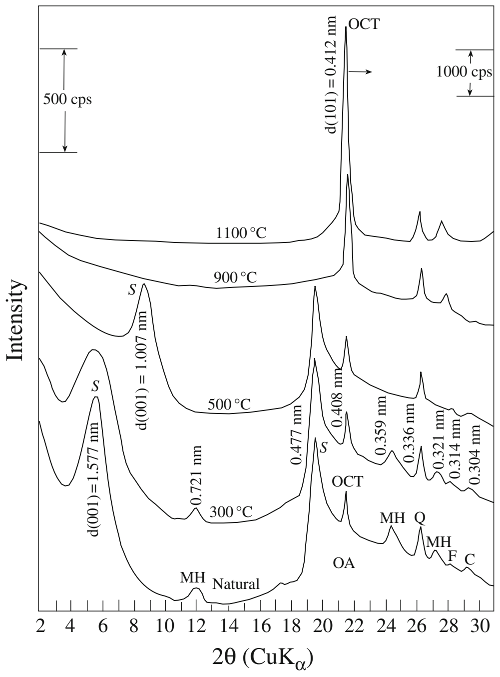

Fig. 1 The XRD patterns of the natural and some acid-activated bentonite samples (*S* smectite, *MH* metahalloysite, *OA* opal-A, *OCT* opal-CT, *Q* quartz, *F* feldspar, *C* calcite)

bentonite and the clay is a calcium bentonite (CaB). The white color of the CaB is originated from the less iron content as seen in chemical analysis. The less amount metahalloysite is a kaolin group mineral and formed after dehydration of the intercalated water of halloysite.

The nonclay minerals in the bentonite are opal-A (OA), opal-CT (OCT), quartz (Q), feldspar (F), and calcite (C). According to the XRD peak intensities, the amount of OCT, Q, F, and Q seem to be too small. The large area of the diffuse XRD-band centered at 2θ of 18–25° indicates the abundance of the OA. The OA and OCT are the amorphous and paracrystalline silicas ($SiO_2 \cdot nH_2O$), respectively, while Q is crystalline silica (SiO_2) [33].

Thermal changes in the CaB

As seen in Fig. 1, the 001 peak of the CaS decreases in intensity and increases in width while maintaining its position after heating from 25 to 300 °C. The position of the 001 peak shifted to right and d(001) value decreased from 1.577 to 1.007 nm after heating between 300 and 500 °C, and than disappeared at 900 °C. The shifting indicates the collapse of the interlayer spaces after the dehydration of water coordinated to the exchangeable cations is complete. The disappearance shows the collapse of the 2:1 (TOT) layer structure of the CaS.

Thermal changes in the OA and OCT

As seen in Fig. 1, while the decrease in the intensity of the 101 XRD-peak for opal-CT is slow up to 900 °C, it diminishes rapidly up to 1100 °C. The position of the 101 peak shifted to left after heating 1100 °C and d(101) value increased from 0.408 to 0.412 nm after heating up to 1100 °C. The increase in the intensity and d(101) value represent the increase in paracrystallinity of the opal-CT [34, 35]. The increase in the intensity of the 101 peak may also be due to the conversion of amorphous OA in bentonite to paracrystalline OCT and creation of new opal-like material from the decomposition of the smectite at the temperatures above 900 °C [36, 37].

Thermal changes of the other minerals in the CaB

The loss of the peaks at 0.721, 0.359, and 0.321 nm shows an irreversible folding of MH structure, while the heating temperature reaches to 500 °C [38]. Absence of the peaks at 0.314 and 0.304 nm indicates the decomposition of the F and calcinations of the C, respectively, up to 900 °C. The unchanged intensity and width of the peak at 0.336 nm represent that the crystallinity of the Q is not affected by the heating process up to 1100 °C.

Thermal analysis

Thermal analysis combined with other techniques such as chemical analysis and XRD is suitable for the examination of clays and their derivatives, as with other materials [39–46]. TG and DTA curves of the natural CaB sample (dried at 105 °C for 4 h) are given in the Fig. 2 for the temperature range of 25–1000 °C. Four endothermic and one exothermic change are seen in the DTA curve. The temperature interval, maximum rate temperature, and mass loss of these changes are shown on the TG and DTA curves in Fig. 2.

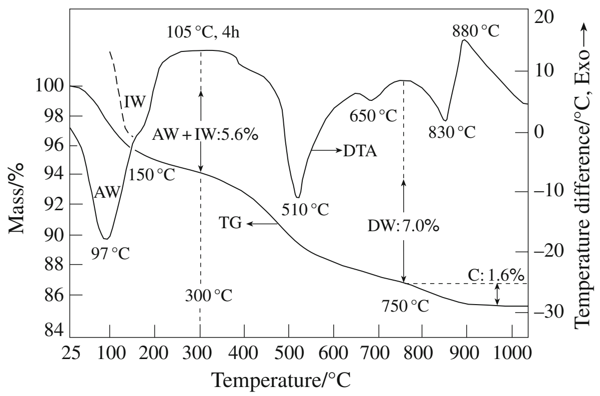

Fig. 2 The TG and DTA curves of the natural bentonite dried at 105 °C for 4 h (*AW* adsorbed water, *IW* interlayer water, *DW* dehydroxylation water)

The first and dominant endothermic peak between 25 and 300 °C is due to the dehydration of adsorbed water (AW) and interlayer water (IW) with the maximum rate at 97 and 150 °C, respectively. The mass loss by the dehydration is 5.6%. This percentage is subject to change depending on preheating temperature and time before thermal analysis. For example, it is 14.6% for air dried natural CaB. The difference $14.6 - 5.6 = 9.0\%$ gives the moisture (W) of the sample. However, the W, AW, and IW cannot be strictly distinguished from each other. The interlayer spaces collapse after complete dehydration. Dehydration causes changes in the porosity, surface area, surface acidity, CEC, and hydrophilic behavior of smectites [29, 30, 47, 48].

The mass loss of 7.0% between 300 and 750 °C is due to the evaporation of dehydroxylation water (DW) from the CaB and MH which are the major and minor clay minerals, respectively. Two endothermic peaks at 510 and 650 °C are due to the dehydroxylation from the *trans*-vacant (tv) and *cis*-vacant (cv) 2:1 layers of the CaS, respectively [49–52]. The peak intensities show that the tv 2:1 layers are more dominant than the cv 2:1 layers. The content of tv and cv 2:1 layers cannot be differentiated exactly. The tv and cv 2:1 layers can be transformed into each other by heating. Dehydroxylation destroys the layer structure of trioctahedral smectites. Inversely, the layer structure of dioctahedral smectites is preserved on dehydroxylation [53, 54]. As seen in the chemical analysis, the low MgO% and high Al_2O_3% show that the CaS in the examined CaB is a dioctahedral smectite. Some physicochemical properties of smectite such as CEC, porosity, surface area, and surface acidity decrease to zero above the dehydroxylation temperature [29, 30].

The endothermic mass loss of 1.6% between 750 and 1000 °C with a maximum rate at 830 °C mainly originates from the calcinations of the trace amount of calcite ($CaCO_3$) in the CaB. The exothermic change without mass loss with a maximum rate at 880 °C shows the recrystallization of the dehydroxylated CaS.

Activation energies for the dehydration and dehydroxylation

Several methods have been used to evaluate activation energy of solid-state reactions involving mass loss by TG [27, 55, 56]. Some solid-state reaction such as dehydration and dehydroxylation can be shown as, solid (1) → solid (2) + gas. The activation energy (E) for this reaction can be calculated from the Coats and Redfern equation as follows [57, 58]:

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

here, α is the dehydration or dehydroxylation fraction calculated from TG data, T is the temperature (K), R is the universal gas constant, A is the frequency factor, and $\beta = \mathrm{d}T/\mathrm{d}t = 10\ \mathrm{Ks}^{-1}$ is the heating rate. Despite the temperature dependence, the second term in this equation is nearly constant.

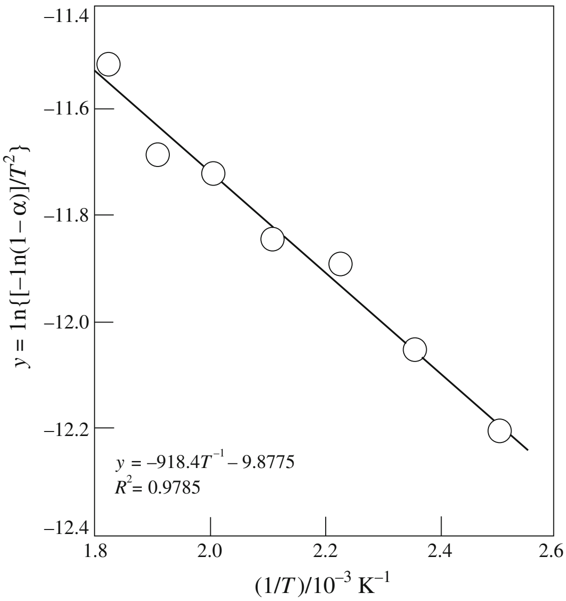

Fig. 3 Coats–Redfern straight line for the dehydration of the smectite

The ratio of a mass loss at each temperature below 300 °C to the total mass loss at this temperature is defined as dehydration fraction (α_1). The Coats–Redfern straight line for the dehydration is obtained using the calculated α_1 values and reciprocal of absolute temperatures ($1/T$) and given in Fig. 3. The activation energy for the dehydration is calculated from the slope of this straight line as $E_1 = 7636\ \mathrm{J\ mol}^{-1}$.

The ratio of a mass loss at each temperature between 300 and 750 °C to the total mass loss at this temperature is defined as dehydroxylation fraction (α_2). The Coats–Redfern straight line for the dehydroxylation is given in Fig. 4. The activation energy for the dehydroxylation is calculated from the slope of this straight line as $E_2 = 48838\ \mathrm{J\ mol}^{-1}$.The activation energy of the dehydroxylation is found to be higher than that of the dehydration.

Surface area and porosity

The specific areas (S) of the natural and heated CaB samples were determined by the Brunauer, Emmett, and Teller (BET) method using the nitrogen adsorption data from the relative equilibrium pressure interval 0.05–0.35 [59]. The specific micro- and mesopore volumes (V) of same samples were calculated from the adsorption capacity as liquid nitrogen volume obtained from desorption isotherm at the relative equilibrium pressure 0.96 [11, 13, 60]. The changes in S and V by the heating temperature are given in Fig. 5. The values

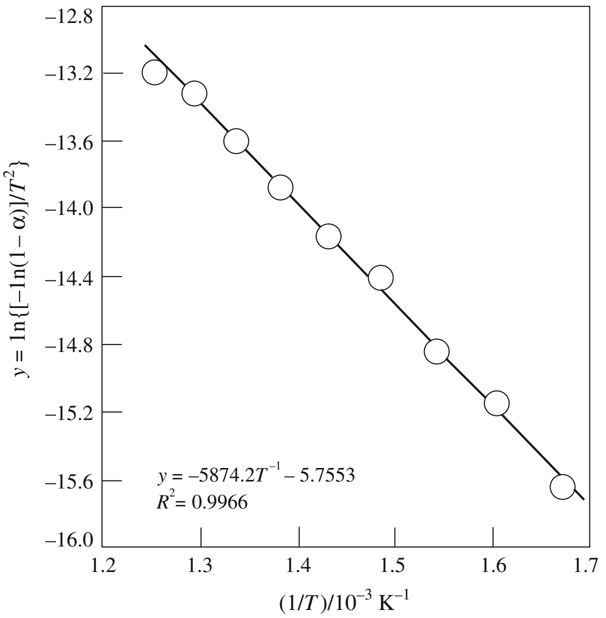

Fig. 4 Coats–Redfern straight line for the dehydroxylation of the smectite

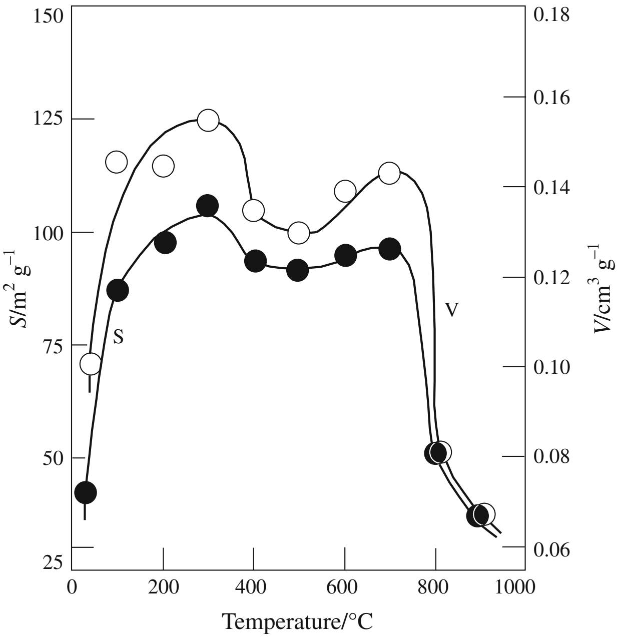

Fig. 5 The changes in specific surface area (*S*) and specific micro–mesopore volume (*V*) of the smectite with the heat treatment temperature

of *S* and *V* for the natural CaB are 44 $\mathrm{m}^2\ \mathrm{g}^{-1}$ and 0.100 $\mathrm{cm}^3\ \mathrm{g}^{-1}$, respectively. While the temperature increases at around 300 °C, the *S* and *V* increase to their maximum values of 105 $\mathrm{m}^2\ \mathrm{g}^{-1}$ and 0.155 $\mathrm{cm}^3\ \mathrm{g}^{-1}$, respectively. The increases are due to the dehydration of adsorbed and interlayer water of the smectite mineral in the CaB. This result agrees well the XRD, DTA, and TG data. The *S* and *V* show a gradual decrease between 300 and 600 °C and their second maxima at 700 °C, which is the maximum rate temperature for the dehydroxylation. These maxima originate from the opening new pores during the dehydroxylation. In turn, the rapid decrease in *S* and *V* at the temperatures above 700 °C is due to the collapse of the 2:1 (TOT) layer structure and thereby closure of the pores of the CaS. This finding is also supported by the XRD, DTA, and TG data.

Conclusions

The crystal structure of the clay and some nonclay minerals are greatly affected by the thermal treatments in the temperature range of 25–1100 °C. The temperature interval, mass loss, and activation energy for the dehydration and dehydroxylation of smectite, the major clay mineral of bentonite, may be estimated from the TG and DTA data. The best temperature range for the thermal activation of bentonite samples was established to be 300–700 °C. The changes in porosity of a bentonite upon heating are the most important structural changes for adsorbents, catalyst supports, catalysts in chemical industry. Furthermore, before construction of the foundation may be heat-treated up to 600 °C to hinder swelling by water uptake and harden the soil in civil engineering.

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