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SOME THERMAL CHARACTERISTICS OF A MINERAL MIXTURE OF PALYGORSKITE, METAHALLOYSITE, MAGNESITE AND DOLOMITE

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An industrial raw material taken from Sivrihisar (Eskişehir, Turkey) region was heat-treated at different temperatures in the range of 100–1000°C for 2 h. The volumetric percentage of the particles having a diameter below 2 μm after staying in an aqueous suspension of the material was determined as 67% by the particle size distribution analysis. The mineralogical composition of the material was obtained as mass% of 32% palygorskite, 10% metahalloysite, 35% magnesite, 20% dolomite and 3% interparticle water by using the acid treatment, X-ray diffraction and thermal analysis (TG, DTA) data.

The temperature ranges were determined for the endothermic dehydrations for the interparticle water as 25–140°C, for the zeolitic water as 140–320°C, and for the bound water as 320–480°C, in the palygorskite. The temperature range for the endothermic dehydroxylation and exothermic recrystalization of the palygorskite is 780–840°C. The temperature range for the endothermic dehydroxylation of the metahalloysite and calcinations of magnesite are coincided at 480–600°C. Dolomite calcined in the temperature range of 600–1000°C by two steps. The zig-zag changes in the specific surface area (S/m^2 g^{-1}) and specific micro and mesopore volume (V/cm^3 g^{-1}) as the temperature increases were discussed according to the dehydrations in the palygorkskite, dehydroxylation of palygorskite and metahalloysite, and calcinations in magnesite and dolomite.

Keywords: *dehdyration, dehydroxylation, metahalloysite, palygorskite, thermal analysis, XRD*

Indroduction

In general, an industrial raw material is a mixture of minerals [1]. The application areas of the raw material were determined according to their chemical and mineralogical compositions [2]. Monomineralic materials are seldom found in the nature [3]. Clays, used over hundred areas, are among the most important industrial raw materials [4–6]. Many clays are the mixture of the clay and nonclay minerals [7]. One or more clay and nonclay minerals can be found in any clay [8–11].

The clays with the major clay mineral palygorskite or sepiolite include generally carbonates such as magnesite ($MgCO_3$), calcite ($CaCO_3$) and dolomite ($MgCO_3$, $CaCO_3$) as nonclay minerals [12]. Fibrous and other types of clay minerals are seldom found together in the clays. For example, few clays contain palygorskite and metahalloysite together as fibrous and layer types of clay minerals, respectively.

Several structural models for palygorskite (attapulgite) have been discussed in [13–19]. The theoretical half unit-cell formula of palygorskite is given as $Si_8O_{20}Mg_5(OH)_2(OH_2)_4{\cdot}4H_2O$ [20]. Palygorskite is 2:1 type phyllosilicate and derived from talc-like tetrahedral-octahedral-tetrahedral (T–O–T) ribbons, expanded infinitely along the z-direction of the fibrous crystal, with a width of two pyroxene chains. The $8Si^{4+}$ and $5Mg^{2+}$ cations are located at the tetrahedral and octahedral positions of each ribbon. Some of the Mg^{2+} cations are replaced principally by Al^{3+} and Fe^{3+} cations. Palygorskite has di- or trioctahedral character depending on the divalent/trivalent cation ratio, distribution of cations, and occupancy of the octahedral sites [21, 22]. Two hydroxyls are bonded to the third Mg^{2+} among the $5Mg^{2+}$ cations of each palygorskite ribbon. The ribbons are connected to each other by Si–O–Si bridges by each four corners to form continuous tetrahedral sheets and discontinuous octahedral sheets. The discontinuity of the octahedral sheets allows to form of rectangular channel-like nanopores with the cross-section of 0.37·0.64 nm.

Four water molecules are bonded two per two to the first and the fifth Mg^{2+} cations at the both ends of each ribbon and located in nanochannels. These molecules are called bound (structural or crystal) water in palygorskite [23]. Furthermore, four water molecules per half-unit cell are located two per two with in the nanocahannels in the both side of each other ribbon. These water molecules in hydrogen bonded with bound water and each other are called zeolitic water. One water molecule per half-unit cell of palygorskite formed from two hydroxyls on the third Mg^{2+} cation

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is called dehydroxylation water. The theoretical content of the zeolitic water (ZW), bound water (BW), and dehydroxylation water (DW) in the palygorskite are calculated stochiometrically in mass% of 8.53, 8.53 and 2.13%, respectively. The molar and mass ratios of ZW:BW:DW=4:4:1 must be constant according to the proportion law in chemistry. The moisture water located interparticle is exchangeable and not shown in the chemical formula of palygorskite.

Halloysite is a kaolin polytype which is often tubular or spherical instead of being platy [24–27]. The ideal chemical formula of halloysite is $Al_2Si_2O_5(OH)_4 \cdot nH_2O$. The open structure of 1.0 nm halloysite allows intercalation of nH_2O molecules [28]. After dehydration of the intercalated water at about 180°C, collapsing of halloysite layers from 1.0 to 0.7 nm occurs [29–33]. Halloysite occurring without intercalated water molecules is called metahalloysite (MH). The structure of metahalloysite is more disordered than the structure of halloysite [34].

The aim of this study is the examination of thermal behaviour of a mineral mixture of palygorskite, metahalloysite, magnesite, and dolomite by using particle size, chemical, X-ray diffraction, thermal and nitrogen adsorption analyses.

Experimental

An industrial raw material taken from Sivrihisar (Eskişehir/Turkey) region was examined in this study. The natural rock was suspensed in water by stirring time to time and was held for 24 h at room temperature to obtain fine particles without any destruction. The volumetric particle size distribution (PSD) of the suspensed samples after 10 min and 24 h were determined by using a Mastersizer Instrument (Malvern, Micron Model, UK). The precipitate in the suspension after staying 24 h was separated by a centrifuge (Rotofix 32, Typ 1205, Hettic), air dried, ground gently, and stored in a plastic bottle to use next experiments.

A sample of 10 g taken air dried material was heated at 100°C for 2 h in an oven (Binder, IP 20) and its moisture was determined by weighing. The rest of this sample was calcined at 1000°C for 2 h in a furnace (Alser, Protherm, PLF 12077) and its loss on ignition (LOI) was determined by weighing. For the chemical analysis, approximately 0.25 g calcined sample was weighed and put in a platinum crucible. The mixture obtained after addition of 3 g LiB_4O_7 (Merck) in this sample was digested at 1000°C for 1 h and cooled to the room temperature. The crucible was inserted in a beaker of 100 mL HCl 10% solution. The system was heated at 90°C by stirring until the precipitate in the crucible was solved. The solution was diluted to 250 mL in a volumetric flask. The chemical analysis was determined by Hitachi Z-8200 Atomic Absorption Spectrophotometer. The results were calculated as the mass% of the metal oxides.

Thermal gravimetric analyses (TG) and differential thermal analyses (DTA) curves of the air dried sample were recorded using a Shimadzu Apparatus (DTG-60H). Approximately 20 mg of a sample was placed in a platinum crucible on the pan of the microbalance and heated in the range 25–1000°C using α-Al_2O_3 as inert material. Analysis was performed under flowing nitrogen with the rate of 100 mL min^{-1} and a heating rate of 10°C min^{-1}.

The air dried samples, each having a mass of 10 g, were heated in 100°C intervals up to 1000°C and were thermally treated by maintaining at each temperature for 2 h by using a furnace (Alser, Prothem, PLF 12077).

The X-ray diffraction (XRD) patterns of the natural and heat-treated samples were obtained from random mounts using a Rikagu D-Max 2200 Powder Diffractometer with CuK_α radiation and a Ni filter.

To separate clay minerals from carbonate rocks in the natural material, an acid treatment was conducted. After mixing, 1.2243 g material was dried at 100°C for 2 h and a sodium acetate-acetic acid solution buffer at pH=5, 0.1 N hydrochloric acid solution was added drop by drop in the mixture until the disappearing of the carbon dioxide bubbles. The precipitate was separated, washed until being free of chloride and acetate ions, and dried at room temperature. The mass of the dried sample at 100°C for 2 h was weighed as 0.5795 g. The difference of two masses gives a total mass of the carbonates found in the sample before the acid treatment.

The adsorption and desorption of N_2 at liquid N_2 temperature for the natural and heated samples were determined by a volumetric adsorption instrument, of Pyrex glass, which was connected to high vacuum [35].

Results and discussion

Particle size analysis

The PSDs of the material held in aqueous suspension for 10 min and 24 h are shown in Fig. 1, as volumetric percentages *vs*. particle diameter (Vol.%–*D*) curve and its derivative [d(Vol.%)/d*D*–*D*] curve. The volumetric percentages of the particles having *D* below 2 μm for the samples held in aqueous suspensions for 10 min and 24 h are read from Fig. 1 as 13 and 67%, respectively. Also, their outer surface areas are measured by PSD measurements as 2.5 and 6.3 $m^2\ g^{-1}$ respectively. The exact distribution of clay mineral particles below 2 μm in water takes long time such as

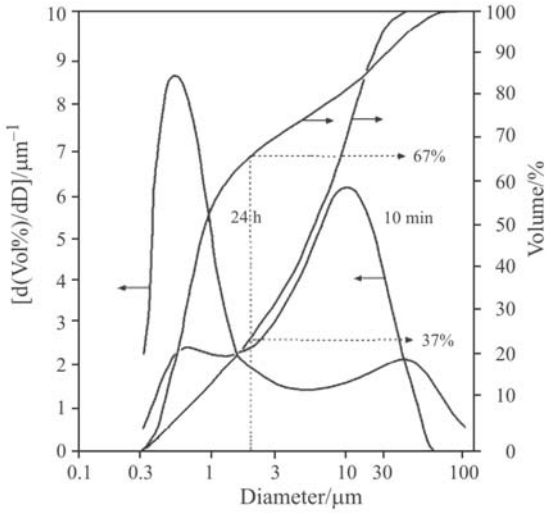

Fig. 1 Particle size distribution curves of the natural rock staying in its aqueous suspension for 10 min and 24 h

24 h. Particle sizes of nonclay minerals in water are generally larger than 2 μm. Clay minerals can be separated easily from nonclay minerals based on the PSDs in aqueous suspensions.

XRD analysis

The XRD patterns are obtained from random mount of the natural rock and its heated samples are represented in Fig. 2. In the XRD patterns of the natural rock, four sharp strong reflections at 1.050, 0.644, 0.289 and 0.275 nm are due to the palygorskite (P), metahalloysite (MH), dolomite (D), and magnesite (M) [11]. The other small reflections belong to palygorskite and metahalloysite. Therefore the natural rock contains palygorskite and metahalloysite as clay minerals, and also magnesite and dolomite as nonclay minerals.

There is not any significant change in the XRD patterns of the heated samples up to 400°C as seen in Fig. 2. However, the small decrease in intensity and increase in the width of the reflection at 1.050 nm show that a little reversible folding in palygorskite structure and its nanochannels by heating up to 400°C.

The loss of reflections at 1.050 and 0.741 nm shows an irreversible folding of sepiolite and metahalloysite structures, while the heating temperature reaches to 500 and 600°C, respectively [28]. Absence of reflection at 0.275 nm shows exactly the calcinations (decarbonation) of magnesite up to 600°C. The reflections at 0.334 and 0.289 nm show the formation of quartz (Q) and calcite (C) respectively as the temperature rises to 600°C. Calcite originates from the first step calcination of dolomite. The second step calcination of dolomite is the calcination of the previously formed calcite completed exactly up to 1000°C.

New reflections show the formation of new phases in the range of 800–1000°C. The reflection at 0.398 nm

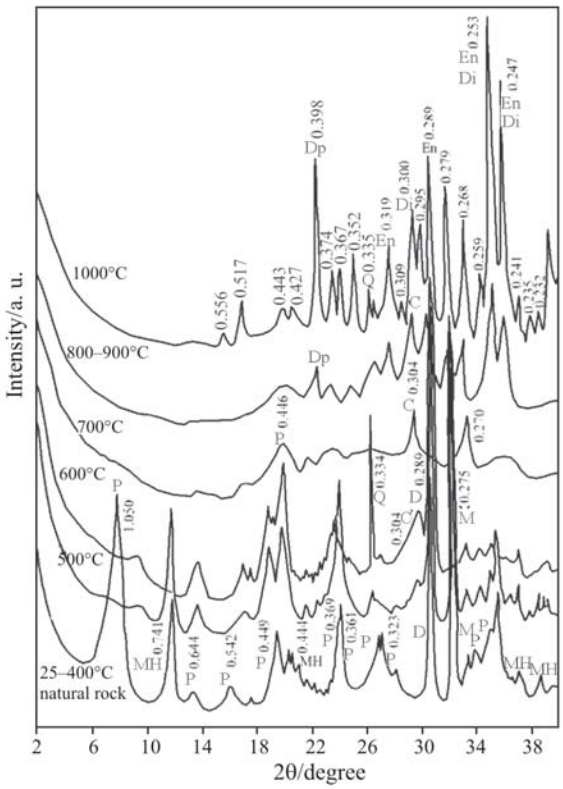

Fig. 2 X-ray diffraction patterns of the natural rock and its heat treated samples at different temperatures in the range 100–1000°C (P: palygorskite, MH: metahalloysite, D: dolomite, M: magnesite, C: calcite, Q: quartz, Dp: diaspore, En: enstatite, Di: diopside)

shows the formation of diaspore (Dp=α-AlOOH) originated from the recrystallization of metahalloysite. Many other reflections seen in the XRD pattern for the heated sample at 1000°C indicate the formation of enstatite (En) and diopside (Di) phases [36, 37]. The chemical formulas of the enstatite and diopside are $Mg_2Si_2O_6$ and $CaMgSi_2O_6$, respectively. They have been formed by the recrystallization of the mineral mixtures, at elevated temperatures.

Chemical analysis

The bulk chemical analysis of the natural rock (mass%) is: SiO_2, 30.36; Al_2O_3, 1.17; Fe_2O_3, 5.49; MgO, 29.39; CaO, 4.75; Na_2O, 0.02; K_2O, 0.08, and loss on ignition (LOI) is 28.71. The SiO_2, Al_2O_3, Fe_2O_3 and one part of MgO contents are originated from palygorskite and metahalloysite minerals. The rest of the MgO content is due to the magnesite and dolomite. The CaO content comes only from dolomite. LOI is due to the dehydration and dehydroxylation of the palygorskite, dehydroxylation of metahalloysite and calcinations of magnesite and dolomite.

There are many isomorphous substitutions among the cations in the palygorskite [21]. The Al^{3+}, Fe^{3+} and Fe^{2+} for Mg^{2+} substitutions in octahedral chains and also

Al^{3+} for Si^{4+} substitutions in tetrahedral chains of the palygorskite may occur. Positive and negative charges arising octahedral and tetrahedral replacement respectively can be largely balanced with each other. Unbalanced excess negative charge is compensated by vacancies, with one vacancy per two trivalent cations or exchangeable cations adsorbed on palygorskite crystal [22]. The divalent/trivalent cation ratio depends on the origin of palygorskite affects to some physicochemical behavior such as acid leaching and thermal treatment [38]. Since the formation of the Fe_2O_3 while the heating temperature rising 1000°C, the gray color of the natural rock is converted to dark brown.

Thermal analysis

Thermal analysis in combination with other techniques such as particle size, X-ray diffraction, and chemical analyses is suitable for the quantitive determination of minerals in solid mixtures [39–44]. The TG and DTA curves of the natural rock are given in Fig. 3 for the temperature range of 25–1000°C. Six endothermic changes and one exothermic change are seen in the DTA curve. The temperature ranges and maximum rate temperature of these changes are shown on the TG and DTA curves in Fig. 3. The changes are evaluated as below [19, 45].

The first endothermic mass loss of 3.1% between 25–140°C with a maximum rate at 94°C is due to the dehydration of interparticle water (W) or adsorbed water known also as moisture.

The second endothermic mass loss of 3.0% between 140–320°C with a maximum rate at 244°C is due to the dehydration of the zeolitic water (ZW). This mass loss must be less than or equal to the theoretical value. Other than this, a part of moisture is mistaken as zeolitic water.

The third endothermic mass loss of 3.0% between 320–480°C with a maximum rate at 329°C is due to the dehydration of the bound water (BW). Bound water molecules are lost in two steps accompanied by reversible structural change similar to sepiolite [23, 46, 47]. The loss about one half of the bound water by the first dehydration step is partially folded the nanochannels. Since the hindrance of these folded channel on the diffusion of the rest bound water molecules by second step causes a decrease in rate and consequently an increase in temperature of the dehydration. The mass losses originated from zeolitic and bound water must be equal to the percentages according to the chemical formula of palygorskite. The mass loss content for bound water must be less than or equal to the theoretical value of 8.53%. Other than this, a part of the zeolitic water is mistaken as bound water. The phase formed after the reversible dehydration of bound water is called palygorskite anhydride with a chemical formula of $Si_8O_{20}Mg_5(OH)_2$.

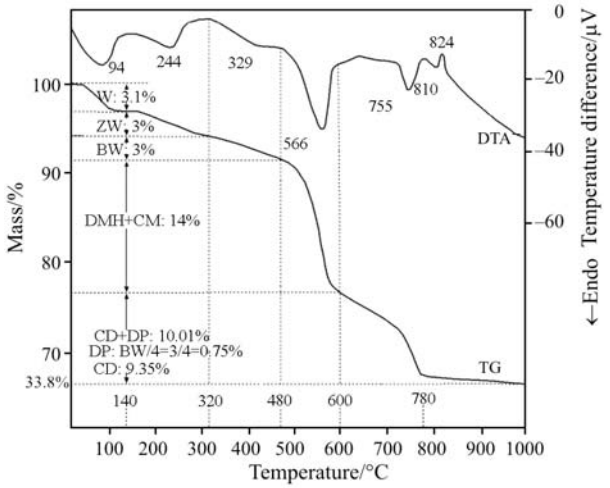

Fig. 3 TG and DTA curves of the natural rock in the temperature range 25–1000°C

The fourth endothermic mass loss of 14.0% between 480–600°C with a maximum rate at 566°C is originated from the dehydroxylation of metahalloysite (DMH) and the calcination of magnesite (CM). The reactions can be represented respectively as below:

$$Al_2Si_2O_5(OH)_4 \rightarrow Al_2O_3 \cdot 2SiO_2 + 2H_2O$$

$$MgCO_3 \rightarrow MgO + CO_2$$

The mass losses came from metahalloysite and magnesite in the same temperature range can not be easily distinguished.

The fifth mass loss of 10.1% between 600–1000°C is due to a maximum rate at 755 and 810°C are originated from the calcination of dolomite (CD) and dehydroxylation of palygorskite (DW) to give enstatite respectively. The reactions can be represented respectively as below:

$$MgCO_3 \cdot CaCO_3 \rightarrow MgO + CaO + 2CO_2$$

$$2Si_8Mg_5O_{20}(OH)_2 \rightarrow 5Mg_2Si_2O_6 + 6SiO_2 + 2H_2O$$

Since the ratio of DW/BW=1/4 according to the chemical formula of palygorskite the mass loss by dehydroxylation must be 3/4=75%. The rest of the mass loss between 600–1000°C such as 10.1–0.75=9.35% is occurred by the calcination of dolomite. There is not any mass loss during the exothermic recrystallization of palygorskite and halloysite above 800°C. Diopside forms according to the reaction:

$$CaO + MgO + 2SiO_2 \rightarrow CaMgSi_2O_6$$

The phase of Al_2O_3 remained from the metahalloysite is diaspore as represented in Fig. 2.

Mineralogical analysis

The mineral content in the natural rock can be determined by using acid treatment, XRD, TG and DTA data as follows. The mass% of moisture in the natural rock is observed from TG curve as 3.1%. The mass% of sepiolite is calculated from the ratio of the bound water content in the rock to its theoretical content as (3.00/8.53)·100=35.2%. The total mass% of magnesite and dolomite is calculated as (1.2243–0.5795)·1000/1.2243=52.7% from the calcination data obtained by acid treatment. The dolomite percentage is calculated stochiometrically according to the constant proportions law in chemistry as (184.392/88)·9.35·100=19.6%. Here 184.392 g mol^{-1} is the molar mass of dolomite and 2·44=88 g represent the mass of carbon dioxide found in one mole of dolomite. The rest of the total mass loss after acid treatment gives the mass% of magnesite as 52.7–19.6=33.1%. The mass% of metahalloysite is the rest of 100% and calculated as 100–(3.1+35.2+33.1+19.6)=9.0%. The composition of the mineral mixture can be given approximately as 3% moisture, 35% palygorskite, 9% metahalloysite, 33% magnesite and 20% dolomite.

Nitrogen adsorption–desorption analysis

The specific surface areas (S/m^2 g^{-1}) of the natural rock and heated samples were determined by the Brunauer, Emmett and Teller (BET) method by using the adsorption data [48]. The specific micro- and mesopore volumes (V/cm^3 g^{-1}) of same samples were calculated from the adsorption capacity as liquid nitrogen volume obtained from desorption isotherm at the relative equilibrium pressure p/p_0=0.96 [49, 50]. The 'zig-zag' changes in S and V by the heating temperature are given in Fig. 4. The values of S and V for the natural rock are 63 m^2 g^{-1} and 0.10 cm^3 g^{-1}, respectively. While the temperature increases at around 200 and 700°C the S and V increase to their maximum values of approximately 120 m^2 g^{-1} and 0.26 cm^3 g^{-1} respectively. The increases are originated from the dehydration of interparticle, zeolitic and bound water of palygorskite, dehyroxylation of metahalloysite, and calcination of magnesite.

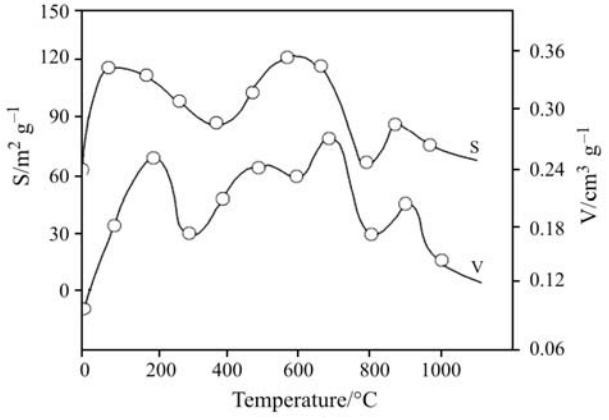

Fig. 4 Variation of specific surface area (S/m^2 g^{-1}) and specific micro- and mesopore volume (V/cm^3 g^{-1}) of the mixture of palygorskite, metahalloysite, magnesite and dolomite by rising temperature

Conclusions

Mineralogical composition of a raw material can be determined by using acid treatment, XRD, TG and DTA data. The mass% of the interparticle, zeolitic, bound and dehydroxylation water in the palygorskite were determined by thermal analysis. The content of zeolitic and bound water in palygorskite is same and must be constant according to the chemical formula. Their value in a mineral mixture is always less than the theoretical values calculated from the formula of palygorskite. The palygorskite content in a mineral mixture can be calculated from the ratio of the bound water content to the its theoretical values 8.53%.

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