THERMAL BEHAVIOR OF A MINERAL MIXTURE OF SEPIOLITE AND DOLOMITE

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An industrial raw material taken from Beypazarı (Ankara, Turkey) region was heated at different temperatures in the 100–1100°C interval for 2 h. The volumetric percentage of particles having diameter below 2 μm in an aqueous suspension of the material held 24 h were determined as 85% by the particle size distribution analysis. The mineralogical composition of the material was obtained as mass% of 81% sepiolite, 15% dolomite, and 4% interparticle water by using the X-ray diffraction (XRD) and thermal analysis (TG, DTA) data. The temperature ranges were determined for the dehydrations of the interparticle water and the zeolitic water as 25–340°C, for the dehydration of the bound water as 340–580°C, and for the dehydroxylation of the hydroxyls as 800–833°C in the sepiolite. 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}) with the temperature increases were discussed according to the dehydrations and dehydroxylation of the sepiolite.

Keywords: dehydration, dehydroxylation, sepiolite, surface area, thermal analysis, X-ray diffraction

Introduction

Many clays contain different nonclay minerals besides major and minor clay minerals [1]. The clays with the major clay mineral sepiolite include mainly carbonates with dolomite ($MgCO_3 \cdot CaCO_3$), magnesite ($MgCO_3$), and calcite ($CaCO_3$) as nonclay minerals [1–5]. The theoretical half-unit cell formula of sepiolite is given as $Si_{12}O_{30}Mg_8(OH)_4(OH_2)_4 \cdot 8H_2O$ [6, 7]. Sepiolite 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 crystal. The $12Si^{4+}$ and $8Mg^{2+}$ cations are located at the tetrahedral and octahedral positions, respectively. Four hydroxyls are bonded by two per two the third and sixth Mg^{2+} among the $8Mg^{2+}$ cations of each sepiolite ribbon. The ribbons are connected 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 sheet allows to form of rectangular channel-like nanopores with the cross section of 0.37×1.06 nm [8, 9].

Four water molecules are bonded by two per two the first and eight Mg^{2+} cations at the both ends of each ribbon and located in nanopores. These molecules are called bound (structural or crystal) water in sepiolite [10–13]. There are 8 water molecules per half-unit cell, four per four within the nanopores located both side of each ribbon. These 8 water molecules are in hydrogen bonding with bound water and each are called zeolitic water. The theoretical content of the zeolitic water (ZW), bound water (BW), and dehydroxylation water (DW) in the sepiolite are calculated stoichiometrically in mass% of 11.10, 5.56 and 2.78%, respectively. The molar and mass ratios of ZW:BW:DW= 4:2:1 must be constant according to the proportion law in chemistry. The moisture water adsorbed and condensed interparticle is exchangeable and not shown in the chemical formula of sepiolite.

Sepiolite has been used as industrial raw material over hundred applications [14–20]. Many of the technological applications are based on the adsorptive and catalytic properties of sepiolite [21–28]. Sepiolite has also been used for the fabrication of all-inorganic ultrafiltration membranes recently [29, 30].

Sepiolite occurrences have been reported in USA, Kenya, Spain, Portugal, Turkey, Saudi Arabia, Great Britain, Marocco, and elsewhere [31–33]. Turkish sepiolites have been found in Eskişehir, Konya, Bolu and Ankara regions located in the north-west of Anatolia [2–5, 34–37]. There are few studies about the heat and acid treatments, and also porosity of the Turkish sepiolites [24, 25, 28, 38–41].

Many of the physicochemical properties of these sepiolites have not been investigated extensively. Therefore, the aim of this study is to investigate some physico-chemical properties such as chemical composition, mineralogy, particle size distribution, thermal behavior and adsorptive properties of a sepiolite containing dolomite.

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Experimental

A commercially mined rock was taken from Beypazarı (Ankara, Turkey) region to use as a material in this study. The rock was suspended in water by stirring time to time and stayed there for 24 h at room temperature to obtain fine particles without destruction. The volumetric particle size distribution (PSD) of the samples stayed in water for 24 h and 10 min were determined by using a Mastersizer Instrument (Malvern, Micron Model, UK). The precipitate in the suspension held 24 h was separated by a centrifuge (Rotofix 32, Typ 1205, Hettich), air dried, ground gently, and stored in a plastic bottle to use in the following experiments.

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

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

The air dried samples, each having a mass of 10 g, were heated from with 100 to 1100°C and were thermally treated by maintaining at each temperature for 2 h by using a furnace (Protherm, PLF 12077, Alser).

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$_\alpha$ radiation and Ni filter.

The adsorption and desorption of N_2 at liquid N_2 temperature for natural and heat treated samples were determined by a volumetric adsorption instrument, of Pyrex glass, which was connected to high vacuum [42].

Results and discussion

Particle size analysis

The PSDs of the material held in aqueous suspension for 10 min and 24 h were represented in Fig. 1, as volumetric percentage *vs.* particle diameter (Vol% − *D*) curve and its derivative [d(Vol.%)/d*D* − *D*] curve. The vol.% of the particles having *D* below 2 μm are read from Fig. 1 for the samples held in aqueous suspensions of 10 min and 24 h are read from Fig. 1 as 13 and 85%, respectively. Since only particles of clay minerals distributed spontaneously in water below 2 μm, 85% may be taken as clay minerals percentages in the natural rock. Furthermore, the exactly distribution of clay mineral particles below 2 μm in water takes long time such as 24 h. The white color, softness, light mass, and high water adsorption capacity of the natural rock show that the clay mineral within may be sepiolite or palygorskite.
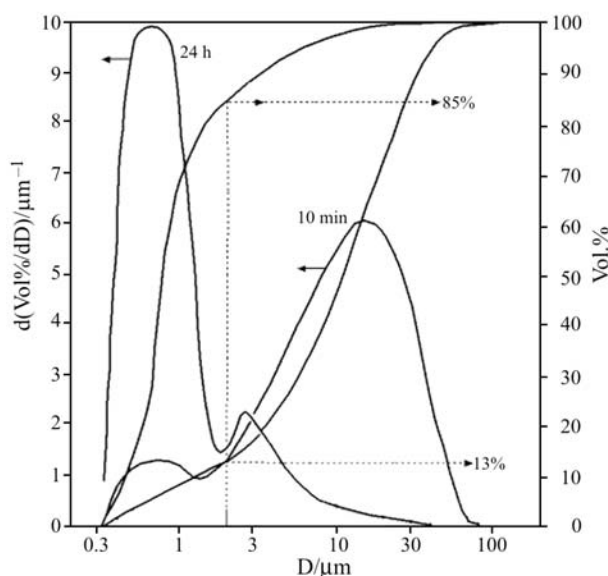

Fig. 1 Particle size distribution curves of the sepiolite and dolomite mixture staying in its aqueous suspension for 10 min and 24 h, respectively

XRD analysis

The XRD patterns obtained from random mount of the natural rock and its heated samples are shown in Fig. 2. In the XRD pattern of the natural rock, two sharp and strong reflections at 1.205 and 0.289 nm are characterized sepiolite (S) and dolomite (D) minerals, respectively [1]. The other reflections in same pattern belong to the sepiolite. Therefore, the natural rock contains sepiolite and dolomite as clay and nonclay minerals respectively.

There is not any significant change in the XRD patterns of the heated samples up to 600°C. However, the intensity decreases and width increases slightly of
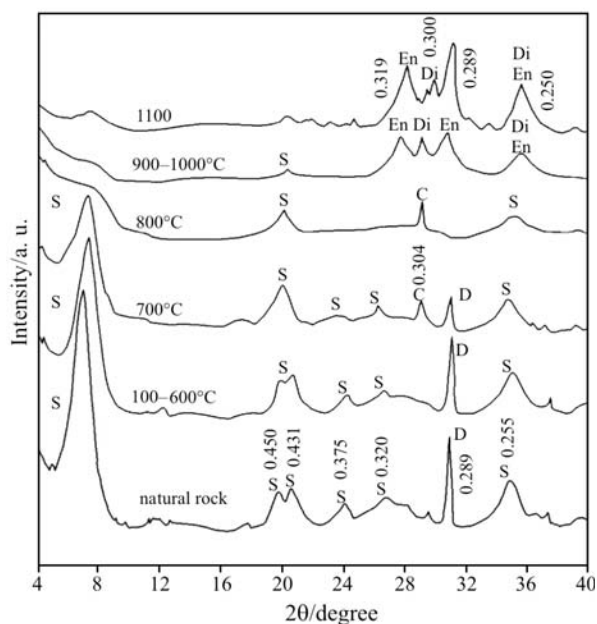
Fig. 2 X-ray diffraction patterns of the natural rock and its heat treated samples at different temperatures in the range 100–1100°C; S – sepiolite, D – dolomite, C – calcite, En – enstatite, Di – diopside

the peak at 1.205 nm. This changes show that the reversible folding in sepiolite crystal and its nano-channels by heating up to 600°C [7, 12].

The significant decrease in intensity, increase in width, and disappearing of the 1.205 nm peak respectively as the temperature rising of 600–900°C intervals are due to the irreversible folding of the sepiolite crystal.

The decrease in intensity of the 0.289 nm peak and the appearing a new 0.304 nm peak represent the first step of calcination of the dolomite to give a calcite (C) while the temperature rising of 600–800°C interval. The formed calcite also calcinated exactly while the temperature rising up to 1100°C as the second step of the dolomite calcination.

Over 900°C, the new peaks appearing at 0.319, 0.300, 0.289 and 0.250 nm show the formation of enstatite (En) and diopside (Di) phases [43]. The chemical formulas of the enstatite and diopside are $Mg_2Si_2O_6$ and $CaMg(Si_2O_6)$, respectively.

Chemical analysis

The bulk chemical analysis of the natural rock (mass%) is: SiO_2, 44.30; Al_2O_3, 1.45; Fe_2O_3, 0.42; TiO_2, 0.09; MgO, 23.36; CaO, 9.24; Na_2O, 0.25; K_2O, 0.24, and loss on ignition (LOI) 20.35. The SiO_2, Al_2O_3, Fe_2O_3, TiO_2, Na_2O and K_2O are only due to the sepiolite. The CaO is originated only from dolomite. The MgO comes both from sepiolite and dolomite. The LOI is due to the dehydration and dehydroxylation of the sepiolite and also the calcination of the dolomite.

The Al_2O_3 and Fe_2O_3 are originated from the isomorphous replacements of Al^{3+} and Fe^{3+} cations with Mg^{2+} cations in the octahedral and Si^{4+} in the tetrahedral chains of the sepiolite [44]. The presence of these trivalent cations in octahedral positions and in tetrahedral positions creates excess of positive and negative charges, respectively. The excess positive charge in the ribbons is compensated partly by the excess negative charge. The rest of excess positive charge in the ribbons is balanced by vacancies, with one vacancy per two trivalent cations. The divalent/trivalent cation ratio depends on the origin of the sepiolite effect to physico-chemical behavior such as acid leaching [45].

Thermal analysis

Thermal analysis in combination with other techniques such as particle size, X-ray diffraction, and chemical analyses is suitable for the quantitative determination of minerals in solid mixtures [46–50]. TG and DTA curves of the natural rock are given in the Fig. 3 for the temperature range of 25–1000°C. Five endothermic changes and one exothermic change are seen in the DTA curves. The temperature interval and maximum rate temperature of these changes are shown on the TG and DTA curves in Fig. 3.

The first and major endothermic mass loss of 9.0% between 25 and 190°C with the maximum rate at 83°C is due to the dehydration of interparticle water (W) known as moisture and one part of zeolitic water (ZW_1). The second endothermic mass loss of 4.5% between 190 and 340°C with the maximum rate at 311°C is due to the dehydration rest part of zeolitic water (ZW_2). The total
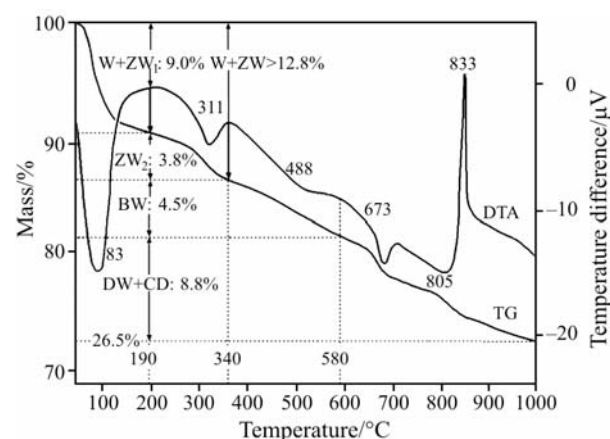

Fig. 3 TG and DTA curves of the natural rock in the temperature range 25–1000°C. Mass loss% occurs each temperature range due to the evolution of volatiles is seen in the figure; W – 3.8% moisture, ZW_1 – 5.2% a part of zeolitic water, ZW_2 – 3.8% the rest part of zeolitic water, ZW – 9.0% total zeolitic water, BW – 4.5% bound (structural or crystal) water, DW+CD – 8.8% total of water and carbondioxide formed by dehydroxylation of sepiolite and calcination of dolomite minerals, respectively

of the two mass losses (W+ZW$_1$+ZW$_2$) up to 340°C is 12.8%. The exactly distinguish of the dehydration temperatures for the interparticle water and zeolitic water is seen almost impossible.

The third endothermic mass loss of 4.5% between 340 and 580°C with the maximum rate at 448°C is due to the dehydration of the bound water (BW). Bound water molecules are lost in two steps accompanied by reversible structure change [7, 12, 13]. 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 channels 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. It is seen that further studies are required to exactly explaining of the two dehydroxylation steps. The mass loss percentage due to the bound water must be less than or equal the theoretical value of 5.56%. Besides, a part of the zeolitic water is mistakenly accepted as bound water. The phase after two reversible dehydration steps is called sepiolite anhydrite with the chemical formula of Si$_{12}$O$_{30}$Mg$_8$(OH)$_4$.

The fourth and the fifth endothermic mass losses of 8.8% after 580 up to 1000°C with the maximum rates at 673 and 805°C cause from both of the calcination of the dolomite and dehydroxylation of the sepiolite. After the irreversible dehydroxylation, the sepiolite anhydrite is transformed into an amorphous phase called meta-sepiolite, by an exothermic change without mass loss with the maximum rate temperature at 833°C.

Calculation of mineral contents in the natural rock

The mineral contents in natural rock can be calculated by different ways using the chemical and thermal analysis data. One of this is used as follows. The ratio of the bound water content obtained from TG curve to the bound water content calculated theoretically from the chemical formula of the pure sepiolite without moisture gives the mass% of the sepiolite in the natural rock as 4.5/5.56=0.81 (81%). Since the according chemical formula, the zeolitic water is two fold of the bound water and the mass% of the zeolitic water of the sepiolite in the natural rock must be 2×4.5=9.0 (9.0%). Therefore, the mass% of the moisture is 12.8–9.0=3.8 approximately 4%. The rest of 15% shows the mass% of the dolomite. Therefore, the natural rock contains 81% sepiolite, 15% dolomite, and 4% moisture.

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) procedure by using the ad-
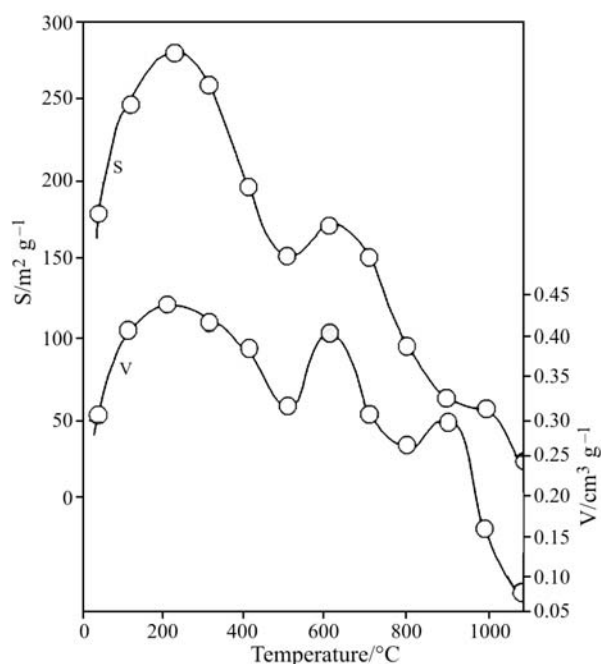

Fig. 4 Variation of specific surface area (S/m^2 g^{-1}) and specific micro- and mesopore volume (V/cm^3 g^{-1}) of the heated mixture of sepiolite and dolomite by rising temperature

sorption data in the relative equilibrium (p/p^0) of 0.05–0.35 [51]. The specific micro- and mesopore volumes (V/cm^3 g^{-1}) of the same samples were calculated from the desorption data at the p/p^0=0.96 [52, 53]. The zig-zag changes in S and V by the heating temperatures are given in Fig. 4. The values of S and V for the natural rock are 174 m^2 g^{-1} and 0.297 cm^3 g^{-1}, respectively. As the temperature increases to about 300°C, the S and V increase to their maximum values of 261 m^2 g^{-1} and 0.434 cm^3 g^{-1}, respectively. The S and V values decrease by the effect of the partially reversible folding of the nanochannels after dehydration of the zeolitic water as the temperature increases to 500°C. The other reversible folding by the dehydration of the bound water up to 600°C cause small increases in the S and V with the maximum values of 172 m^2 g^{-1} and 0.406 cm^3 g^{-1}, respectively. The irreversible folding of the sepiolite and the calcination of the dolomite also cause some little increase in the S and V values. They reach to the minimum values of 26 m^2 g^{-1} and 0.078 cm^3 g^{-1} at the heating temperature of 1100°C.

Conclusions

Mineralogical composition of a raw material can be determined by using XRD, TG and DTA data. The dehydration temperatures of the interparticle water and zeolitic water in the sepiolite cannot be distinguished absolutely by the thermal analysis. The temperature range for the dehydration of the bound

water in sepiolite and its content are determined exactly by the thermal analysis. The mass% of the bound water in the sepiolite found in a mineral mixture must be less than the theoretical value of 5.56%. The sepiolite content in a mineral mixture can be calculated from the ratio of the bound water content to the theoretical bound water content.

Acknowledgements

References

1 D. M. Moore and R. C. Reynolds Jr., X-Ray Diffraction and the Identification and Analysis of Clay Minerals, Oxford University Press, Oxford 1997.

2 A. Akbulut and S. Kadir, Clays Clay Miner., 51 (2003) 279.

3 H. Yalçın and Ö. Bozkaya, Clays Clay Miner., 43 (1995) 705.

4 H. Yalçın and Ö. Bozkaya, Clays Clay Miner., 52 (2004) 227.

5 N. Karakaya, M. Ç. Karakaya, A. Temel, Ş. Küpeli and C. Tunaoğlu, Clays Clay Miner., 52 (2004) 495.

6 A. Preisinger, Clays Clay Miner., 6 (1959) 61.

7 M. R. Weir, W. K. Kuang, G. A. Facey and C. Detellier, Clays Clay Miner., 50 (2002) 240.

8 A. J. Dany, J. Chem. Soc. A, (1971) 2383.

9 R. Prost, Spectrochim. Acta, 31A (1975) 1497.

10 H. Nagata, S. Shimoda and S. Toshio, Clays Clay Miner., 22 (1974) 285.

11 J. L. Ahlrichs, C. Serna and J. M. Serratosa, Clays Clay Miner., 23 (1975) 119.

12 C. Serna, J. L. Ahlrichs and J. M. Serratosa, Clays Clay Miner., 23 (1975) 452.

13 T. Kiyohiro and R. Otsuka, Thermochim. Acta, 147 (1989) 127.

14 R. H. S. Robertson, Chem. Ind., (1957) 1492.

15 A. Preisinger, Clays Clay Miner., 10 (1963) 365.

16 G. P. C. Chambers, Silicates Industrials, (1959) 181.

17 H. H. Murray, Appl. Clay Sci., 5 (1991) 379.

18 H. H. Murray, Clay Miner., 34 (1999) 39.

19 H. H. Murray, Appl. Clay Sci., 17 (2000) 207.

20 E. Galán, Clay Miner., 31 (1996) 443.

21 A. J. Dandy, J. Phys. Chem., (1968) 334.

22 A. J. Dandy and M. S. Nadiye-Tabbiruku, Clays Clay Miner., 23 (1975) 428.

23 A. J. Dandy and M. S. Nadiye-Tabbiruku, Clays Clay Miner., 30 (1982) 347.

24 Y. Sarıkaya, A. Yücel, Ö. Eğilmez, G. Makul, R. Almac, I. Harman and İ. Bozdoğan, Doğa Bil. Der., B9 (1985) 277 (in Turkish).

25 Y. Sarıkaya, H. Ceylan, İ. Bozdoğan and A. Müfit, Turk. J. Chem., 17 (1993) 119.

26 A. Corma and J. Perez-Pariante, Clay Miner., 22 (1987) 423.

27 Y. Grillet, J. M. Cases, M. François, J. Rouquerol and J. E. Poirier, Clays Clay Miner., 36 (1988) 233.

28 H. Ceylan and Y. Sarıkaya, Doğa Türk Kim. Der., 13 (1989) 130 (in Turkish).

29 Q. K. Wang, T. Matsuura, C. Y. Feng, M. R. Weir and C. Detellier, J. Membrane Sci., 184 (2001) 153.

30 M. R. Weir, E. Rutinduka, C. Detellier, C. Y. Feng, Q. K. Wang, T. Matsuura and R. Le Van Mao, J. Membrane Sci., 182 (2001) 41.

31 J. L. Post, Clays Clay Miner., 26 (1978) 58.

32 E. Galán and A. Ferrero, Clays Clay Miner., 30 (1982) 191.

33 T. İrkeç, Acta Miner.-Petrogr., Szeged XXIX, (1988) 95.

34 M. Yeniyol, Clays Clay Miner., 34 (1986) 353.

35 Ö. I. Ece and F. Çoban, Clays Clay Miner., 42 (1994) 81.

36 Ö. I Ece, Clays Clay Miner., 46 (1988) 436.

37 S. Kadir, H. Baş and Z. Karakaş, Can. Miner., 40 (2002) 1091.

38 K. Inukai, R. Miyawaki, S. Tomura, K. Shimosaka and T. İrkeç, Appl. Clay Sci., 9 (1994) 11.

39 H. Arık, S. Kadir and S. Sarıtaş, Turk. J. Eng. Environ. Sci., 20 (1996) 233.

40 S. Balcı, J. Chem. Technol. Biotechnol., 66 (1996) 72.

41 M. Özdemir and İ. Kıpçak, Clays Clay Miner., 52 (2004) 714.

42 Y. Sarıkaya and S. Aybar, Commun. Fac. Sci. Uni. Ank., 24B (1978) 33.

43 H. Hayashi, R. Otsuka and N. Imaii, Am. Mineral., 53 (1969) 1613.

44 J. L. M. Vivaldi and P. H. Hach-Ali, Palygorskites and sepiolites, Chapter 20, In: R. C. Mackenzie, Differential Thermal Analysis, Vol. 1, 1970, p. 553.

45 A. Corma, A. Mifsud and E. Sanz, Clay Miner., 22 (1987) 225.

46 M. Gal, J. Thermal Anal., 37 (1991) 1621.

47 A. Acosta, I. Iglesias, M. Aineto, M. Romero and J. Ma. Rincün, J. Therm. Anal. Cal., 67 (2002) 249.

48 H. Zou, M. Li, J. Shen and A. Auroux, J. Therm. Anal. Cal., 72 (2003) 209.

49 A. Fodor, L. Chizdavu, A. Suteu and A. Caraban, J. Therm. Anal. Cal., 75 (2004) 153.

50 J. Ma. Rincün, M. Romero, A. Hidalgo and Ma. J. Liso, J. Therm. Anal. Cal., 76 (2004) 903.

51 S. Brunauer, P. H. Emmett and E. Teller, J. Am. Chem. Soc., 60 (1938) 308.

52 S. Gregg and K. S. W. Sing, Adsorption Surface Area and Porosity, Academic Press, London 1982.

53 Y. Sarıkaya, M. Önal, B. Baran and T. Alemdaroğlu, Clays Clay Miner., 48 (2000) 557.