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THERMAL BEHAVIOR AND WATER ADSORPTION OF NATURAL AND MODIFIED SEPIOLITE HAVING DOLOMITE FROM TURKEY

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The water adsorption properties of sepiolite having dolomite supplied from Eskisehir region and their exchanged forms (K^+, Na^+, Mg^{2+} and Ca^{2+}) were investigated. The sepiolite samples were characterized using XRD, TG-DTA, DSC and nitrogen adsorption methods. The temperature ranges were determined for the dehydrations of hydroscopic and zeolitic water as 30–200°C, for the dehydration of the bound water as 250–750°C and for the dehydroxylation of hydroxyls as 810–850°C in the sample. It was observed that the value of percent mass loss for natural and modified samples varied in the range from 36.70 to 39.05%. Two mass loss steps for all samples were observed using a differential scanning calorimetry (DSC) in the range of 30–550°C. Adsorption isotherms for water on natural and modified forms were obtained at pressures up to 2.39 kPa. Uptake of water increased as K-SEP.<Na-SEP.<Mg-SEP.<Ca-SEP. for sepiolite samples at 293 K.

Keywords: *adsorption, dehydration, sepiolite, thermal analysis, water vapor, XRD*

Introduction

Sepiolite, of structural formula $Si_{12}O_{30}Mg_8(OH)_4(H_2O)_4\cdot 8H_2O$, is a fibrous, hydrated Mg–Al silicate clay mineral. This mineral contains in its crystal structure; zeolitic and adsorbed water, four H_2O molecules coordinated with bordering octahedral cations and hydroxyl groups at the 2:1 ribbons [1, 2]. The clays with the clay mineral sepiolite contain chiefly carbonates with dolomite ($MgCO_3\cdot CaCO_3$), magnesite ($MgCO_3$) and calcite ($CaCO_3$) as nonclay minerals. Sepiolite occurs as fibers and dolomite as subhedral or euhedral crystals [3]. Sepiolite has good adsorption properties due to its structural channels. It has molecular-sized channels (dimensions about 3.7·10.6 Å) distributed along the fiber axis [4]. Each structural block comprises two tetrahedral silica sheets and a central octahedral sheet containing Mg. Owing to the discontinuity of the external silicate sheets, an important number of silanol groups (Si–OH) take place at the surface of this mineral. The structure of sepiolite mineral includes active adsorption sites, oxygen atoms on the tetrahedral sheet, water molecules coordinated to the Mg ions at the edges of the structural ribbons and silanol groups formed as a result of broken Si–O–Si bonds. Isomorphic substitutions of Si^{4+} in the tetrahedral sheet of the mineral lattice with Al^{3+} constitute negatively charged adsorption sites. Exchangeable cations that compensate the electrical charge occupy these sites. Sepiolite has a high adsorptive capacity for many gases and vapors [5]. The adsorption of water vapor in porous materials is related with the hydrophobic-hydrophilic properties of solid surfaces [6]. The interaction of water with soil colloids plays an important role in soil science and numerous studies have shown that exchangeable cations significantly influence soil–water relations [7–12]. Many studies have been carried out on the water vapor adsorption behavior of clay in literature [13–22].

Abundant sedimentary deposits of sepiolite have been discovered in Turkey. There are, however limited studies on water vapor adsorption properties of cation exchanged forms of sepiolite from Turkey. The aim of this study is to evaluate the thermal behavior and water adsorption of sepiolite containing dolomite and those of modified forms from Turkey.

Experimental

Materials and methods

The sepiolite containing dolomite used in this study was obtained from Eskisehir region of Turkey. It was crushed, ground and then sieved to 63 μm<using ASTM standard sieves. These clay fractions were exchanged with K^+, Na^+, Mg^{2+} and Ca^{2+} to determine the influence of the exchangeable cation on their water sorption behavior. Inorganic chemicals such as HCl, NaCl, KCl, $MgCl_2$ and $CaCl_2$ were obtained from Merck (Darmstadt, Germany) and all solutions were prepared using de-ionized water.

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5 g of sepiolite were activated by washing with 100 mL of 0.1 M HCl solution followed by a washing in de-ionized water. Afterwards, these samples were added to 1 M chloride solutions and maintained at a temperature of 100°C treatment time of 8 h, with continuous stirring. The treated samples were subsequently washed with distilled water, dried at 110°C for 16 h and stored in a desiccator. The resulting modified samples were labeled K-SEP., Na-SEP., Ca-SEP. and Mg-SEP., respectively. The chemical composition of the sepiolite sample was determined by classical chemical analysis (Table 1). SiO_2, Al_2O_3, Fe_2O_3, TiO_2, Na_2O and K_2O are only due to sepiolite. The CaO is originated only from dolomite. 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.

Table 1 Chemical composition of the sepiolite having dolomite

Constituent	%
SiO_2	13.240
Al_2O_3	1.360
Fe_2O_3	0.510
Na_2O	0.090
K_2O	0.150
CaO	23.180
MgO	22.280
TiO_2	0.080
SO_3	0.030
P_2O_5	0.009
LOI	39.020

Instrumentation

Sepiolite having dolomite supplied from Eskisehir region and those of modified forms were characterized by using XRD, TG-DTA, DSC and nitrogen adsorption methods. X-ray diffraction (XRD) patterns were recorded on powdered samples with a Rigaku RINT-2200 diffractometer using CuK_α radiation and operated in the 2θ range between 3 and 40°, with a step size of 0.02°.

The thermal behavior of the samples was investigated in the temperature range 30–1000°C using a Setsys Evolution Setaram thermal analysis apparatus with a linear heating rate of 10°C min^{-1}. For all experiments the sample mass was about 40 mg. DSC analyses of samples were carried out by heating the samples from 30 to 550°C at 5°C min^{-1} rate using a Setaram DSC 151 analyser. Powdered samples were loaded into sealed aluminum pan. The empty aluminum pan was used as reference and the heat flow between the sample and the reference pan was recorded.

The BET surface areas of the samples were measured with volumetric sorption analyzer (NOVA 2200, Quantachrome Instruments, USA) using nitrogen gas adsorption at –196°C. Water vapor adsorption isotherms were measured using volumetric apparatus (Autosorb 1-Quantachrome Instruments, USA) by static technique at 293 K. Before each measurement the samples were outgassed for 3 h by heating 120°C under vacuum.

Results and discussion

X-ray analysis

Figure 1 shows the X-ray diffractograms of the natural and modified samples. In the XRD pattern of the natural rock, sharp and strong reflection at 0.289 nm is characterized dolomite (D) mineral. The weak reflections at 1.216 and 0.449 nm related to the sepiolite (S) peaks [23]. The other reflections in the same pattern belong to dolomite. Therefore, the natural rock contains sepiolite and dolomite as clay and non-clay minerals, respectively. There are no significant changes in the XRD patterns of the other samples. The modified samples display the characteristic sepiolite and dolomite peaks after treatment.

Thermal properties

DTA has been used widely in the study of thermal reactions of clay minerals. The DTA peak temperatures are characteristic for each mineral and DTA curves are applicable for identification and determination of many clays [24, 25]. There have been numerous studies regarding the thermal behavior of clay minerals [26–32]. The thermogravimetric and DTA analyses of all forms of sepiolite samples are shown in Fig. 2. The TG/DTA curves of the samples are similar. The results of TG/DTA analyses are given in Table 2. The removal of hydroscopic water from the external surface and zeolitic water from the voids of the structure was completed up to 200°C. This removal gave a high peak in the DTA curve. The bound water was found in magnesium coordination in the crystal structure. It is known that dehydration of water occurs in two steps, accompanied by structural changes. Literature studies have shown that the first part of the bound water left the structure between 250 and 450°C [33, 34]. In the present study, the first part of the bound water was evolved from the structure up to 400°C. The removal of bound water was completed before 750°C. The removal of structural water molecules (hydroxyl groups) was completed up to 850°C.

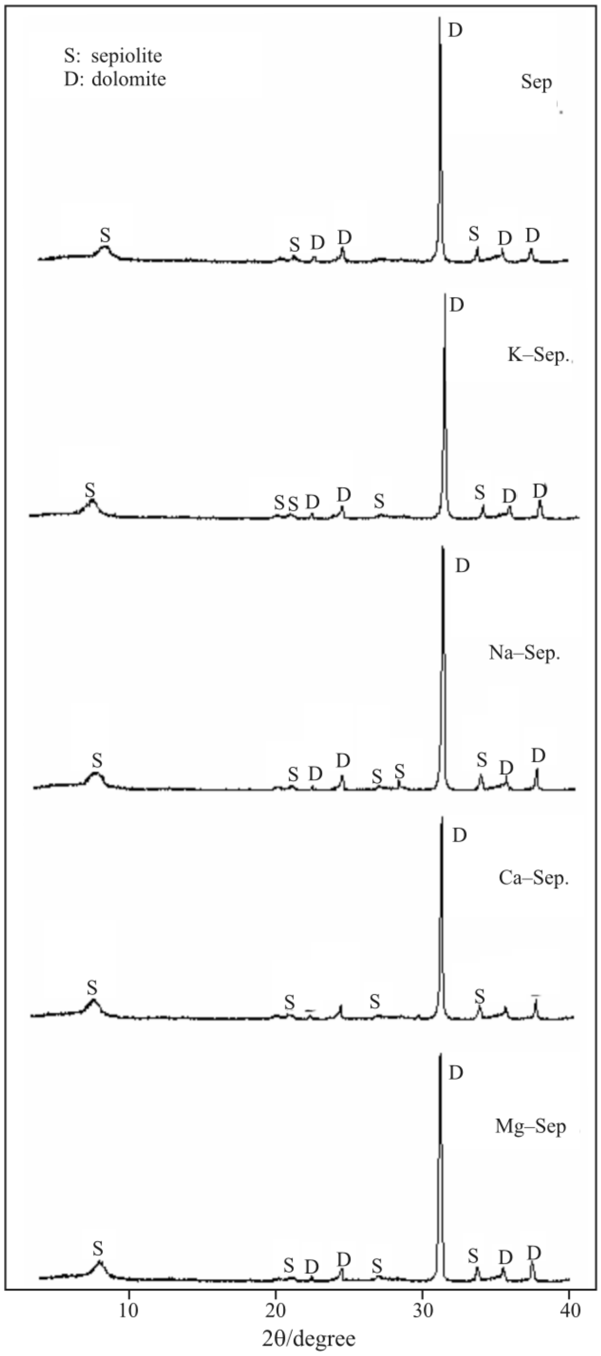

Fig. 1 XRD patterns of the natural and modified samples

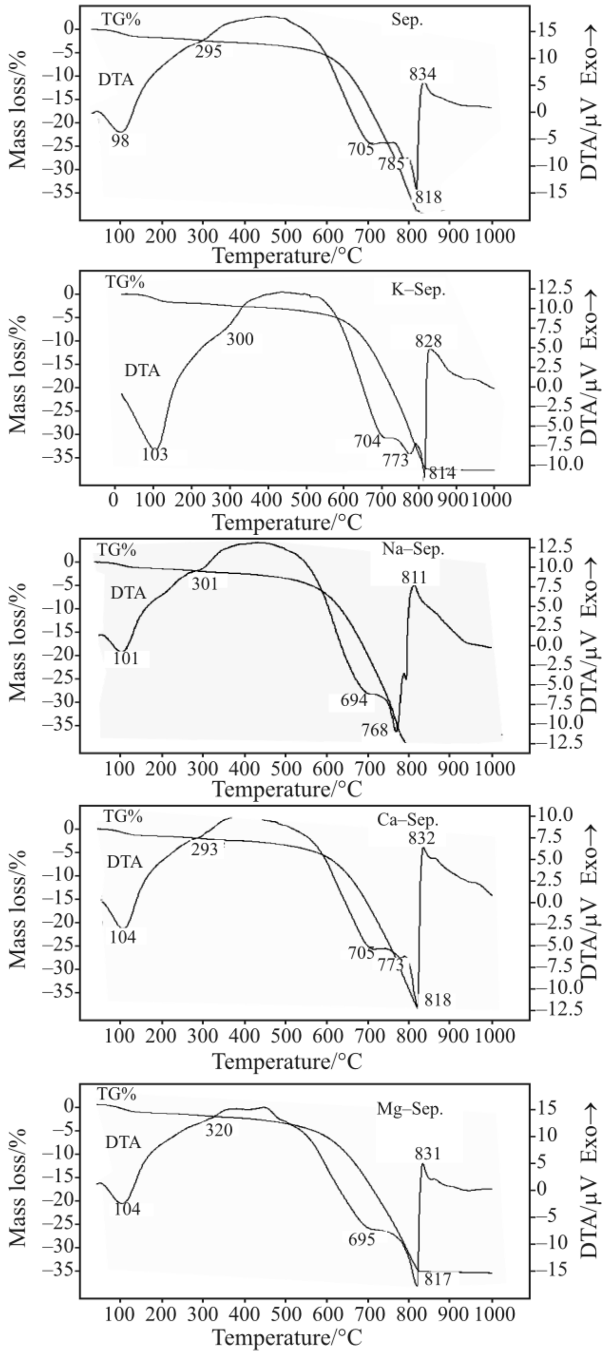

Fig. 2 TG-DTA curves for natural and modified samples

Table 2 DTA-TG analyses data of natural and modified sepiolite samples

Sample	Step 1/ °C	Mass loss/%	Step 2/ °C	Step 3/ °C	Mass loss/%	Step 4/ °C	Mass loss/%	Step 5/ °C	Mass loss/%	Total mass loss/%
SEP.	98	1.77	295	705	20.10	785		818	16.79	38.66
Na-SEP.	101	1.28	301	694	25.41	768	11.57			38.26
K-SEP.	103	1.86	300	704	23.45	773		814	11.39	36.70
Mg-SEP.	104	2.13	320	695	25.48	817	11.44			39.05
Ca-SEP.	104	1.57	293	705	21.61	773		818	15.30	38.48

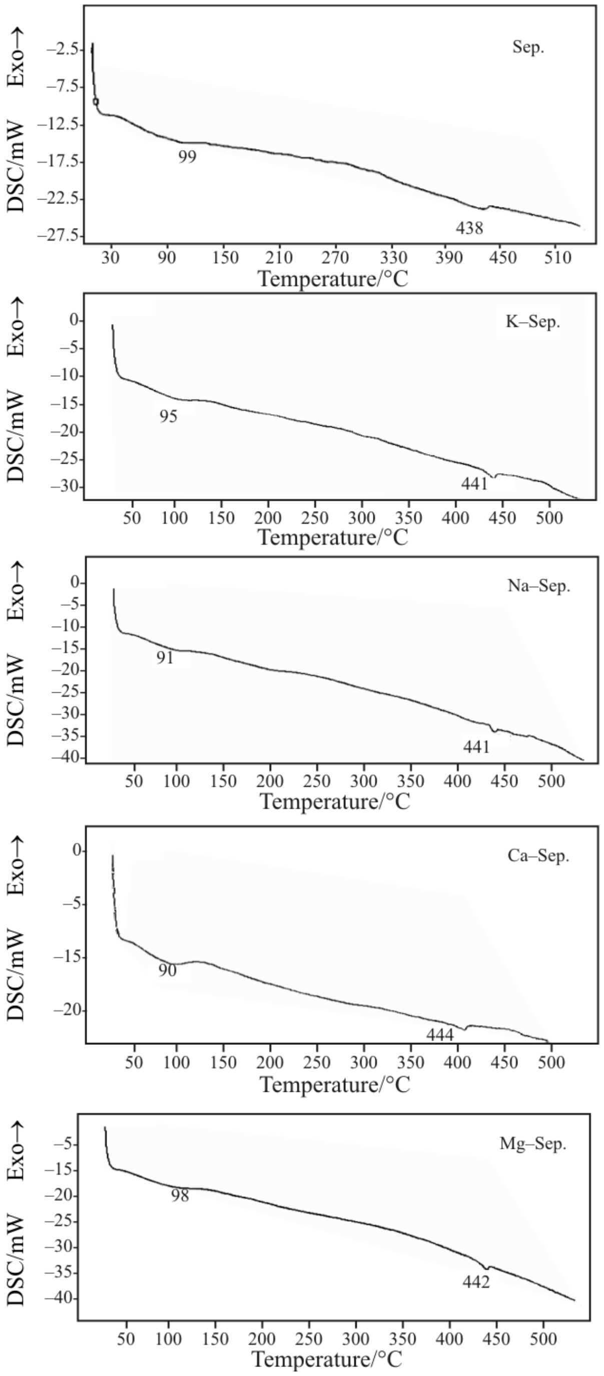

Fig. 3 DSC curves for natural and modified samples

Table 3 DSC thermal analysis data of natural and modified sepiolite samples

Sample	Step1/°C	Step 2/°C
SEP.	99	438
Na-SEP.	91	441
K-SEP.	95	441
Mg-SEP.	98	442
Ca-SEP.	97	444

The combined endo/exothermic reaction observed in the 811–834°C represents dehydroxylation, destruction of sepiolite, calcination of dolomite and crystallization of high temperature phases. It was observed that the percent mass loss for natural and modified sepiolite samples varied in the range from 36.70 to 39.05%. For natural sample, the mass loss during thermal decomposition is 20.1% at 700°C and 38.66% at 1000°C.

DSC curves for clay samples are shown in Fig. 3. DSC experiment is temperature limited and any higher endotherms are not observed using this technique. The results of the DSC analyses for all samples are reported in Table 3. There are two endotherms observed for sepiolites in the 30–550°C regions. One endotherm is attributed to adsorbed and zeolitic or ‘channel’ water. The temperatures of the endotherms are lower than those of observed for the thermogravimetric analysis. The first mass loss step is observed in the 91–99°C region. This difference may be attributed to the rates of heating of the two experiments. The second endotherm is observed in the 438–444°C region. This endotherm is assigned to the heat required to remove chemically bound water and hydroxyls from the octahedral cation.

Specific surface area

The results of N_2 adsorption experiments which were carried out between the relative equilibrium pressure range of $0.05<P/P_0<0.30$ were interpreted using BET methods [35]. BET surface area values of the samples dehydrated at 180°C for 4 h under vacuum are summarized in Table 4. The BET surface area of natural mineral was found 80 $m^2\ g^{-1}$.

Adsorption

Adsorption isotherms for water on natural and modified forms were obtained at pressures up to 2.39 kPa. As shown in Fig. 4, clay samples exhibit a hydrophilic behavior. Sorption isotherms were Type II (S-shaped), as commonly found for the sorption of water by clay (Fig. 4) [36]. At the end of the water vapor experiments, it was determined that

Table 4 Calculated surface areas of the natural and modified samples

Sample	BET surface area/$m^2\ g^{-1}$
SEP.	80
Na-SEP.	93
K-SEP.	94
Mg-SEP.	90
Ca-SEP.	71

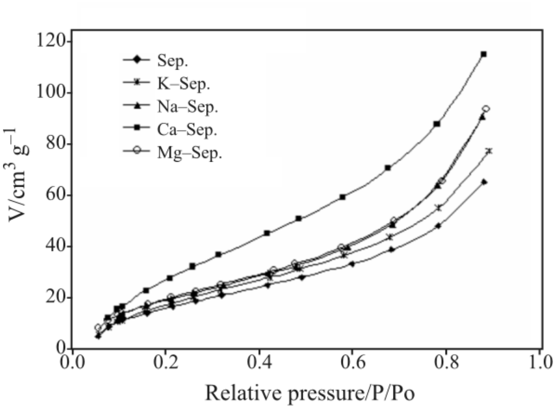

Fig. 4 Water adsorption isotherms of natural and modified samples

the amount of adsorbed water increased in the following order: K-SEP.<Na-SEP.<Mg-SEP.< Ca-SEP. The nature of exchangeable cation influences both the shape of the isotherm and the amount of water sorbed. The sepiolite samples exchanged with monovalent cations showed less water sorption compared to those of exchanged with divalent cations. The amount of water sorbed by the samples was strongly correlated to the hydration energy of the cations. These results indicate that hydration of exchangeable cations has an important effect on water sorption and approve that water, which is a polar molecule, has a significant affinity for cations on the clay samples. Our data agree with other studies regarding the relative effect of exchangeable cations on water sorption by different clays [7].

Conclusions

In this study, characterization of natural and modified clay samples (XRD, TG-DTA, DSC and N_2 adsorption methods) and water vapor adsorption characteristics of those samples have been investigated. The thermal behavior is similar in shape for all samples. The temperature ranges were determined for the dehydrations of hydroscopic and zeolitic water as 30–200°C, for the dehydration of the bound water as 250–750°C and for the dehydroxylation of hydroxyls as 810–850°C in the sepiolite. It was observed that the value of percent mass loss for natural and modified sepiolite samples varied in the range from 36.70 to 39.05%. It was found that DSC results supported the DTA results. In the DSC curves, two mass loss steps are observed and are structure and composition dependent. The first mass loss step was observed in the 91–99°C region. The second mass loss step was observed in the 438–444°C region.

Water adsorption isotherms on sepiolite having dolomite have been conducted at ambient temperature (293 K) up to 2.39 kPa. The water uptake of sepiolite containing dolomite samples can be substantially improved when it is modified with calcium, potassium, magnesium and sodium chloride. The amount of adsorbed water was influenced by the exchangeable cation increased in the order K-SEP.< Na-SEP.<Mg-SEP.<Ca-SEP. It was found that exchangeable cations, as a treatment, had a highly significant effect on the amount of water adsorbed by sepiolite samples. In clay samples, amount of water adsorbed by clays exchanged with monovalent cations was less than those of exchanged with divalent cations. In conclusion, the amount of sorbed water increased as the hydration energy of the exchangeable cation increased. Thus, the hydration characteristics of the clay mineral strongly depend on the exchangeable cation.

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References

1 B. F. Jones and E. Galan, Hydrous Phyllosilicates (Exclusive of Micas) (S.W. Bailey, Ed.), Reviews in Mineralogy, 19, Mineralogical Society of America, Washington, D.C. 1988, p. 631.
2 E. Galan and I. Carretero, Clays Clay Miner., 47 (1999) 399.
3 N. Karakaya, M. C. Karakaya, A. Temel, Ş. Küpeli and C. Tunoğlu, Clays Clay Miner., 52 (2004) 495.
4 K. Brauner and A. Preisinger, Tschermaks Miner. Petr. Mitt., 6 (1956) 120.
5 E. Galan, Clay Miner., 31 (1996) 443.
6 R. K. Collier, R. S. Barlow and F. H. Arnold, J. Solar Energy Eng., 104 (1982) 28.
7 K. M. Dontsova, L. Darrell Norton, C. T. Johnston and J. M. Bigham, Soil Sci. Soc. Am. J., 68 (2004) 1218.
8 W. Xu, C. T. Johnston, P. Parker and S. F. Agnew, Clays Clay Miner., 48 (2000) 120.
9 J. M. Cases, I. Berend, M. Francois, J. P. Uriot, L. J. Michot and F. Thomas, Clays Clay Miner., 45 (1997) 8.
10 I. Berend, J. M. Cases, M. François, J. P. Uriot, L. Michot, A. Masion and F. Thomas, Clays Clay Miner., 43 (1995) 324.
11 P. L. Hall and D. M. Astill, Clays Clay Miner., 37 (1989) 355.
12 R. Keren and I. Shainberg, Clays Clay Miner., 27 (1979) 145.
13 I. Fujiwara and M. Sato, J. Chem. Eng. Jpn., 25 (1992) 609.

14 M. Molina-Sabio, F. Caturla, F. Rodríguez-Reinoso and G. V. Kharitonova, Microporous Mesoporous Mater., 47 (2001) 389.
15 F. Caturla, M. Molina-Sabio and F. Rodriguez-Reinoso, Appl. Clay Sci., 15 (1999) 367.
16 J. C. González, M. Molina-Sabio and F. Rodríguez-Reinoso, Appl. Clay Sci., 20 (2001) 111.
17 D. Balköse, F. Özkan, S. Ulutan and S. Ülkü, J. Therm. Anal. Cal., 71 (2003) 89.
18 R. T. Johansen and H. N. Dunning, E. Ingerson (Ed.), Clays and Clay Miner., U. S. Geol. Surv. Earth Sci. Ser. Monogr. 2. Pergamon Press, N.Y. 1959.
19 M. S. Gruszkiewicz, J. M. Simonson, T. D. Burchell and D. R. Cole, J. Therm. Anal. Cal., 81 (2005) 609.
20 W. J. Likos, W. J. Likos and N. Lu, Clays Clay Miner., 50 (2002) 553.
21 J. Pires and M. B. De Carvalho, J. Mater. Chem., 7 (1997) 1901.
22 J. Pires, M. Pinto, A. Carvalho and M. Brotas de Carvalho, Adsorption, 9 (2003) 303.
23 D. M. Moore and R. C. Reynolds, X-ray diffraction and the identification and analysis of clay minerals, Oxford University Press, Oxford 1997.
24 R. C. Mackenzie, Ed., The Differential Thermal Investigation of Clays, Mineralogical Society (Clay Minerals Group), London 1957.
25 R. C. Mackenzie, Differential Thermal Analysis 1, R. C. Mackenzie, Ed., Academic Press, London 1970.
26 Th. Perraki and A. Orfanoudaki, J. Therm. Anal. Cal., 91 (2008) 589.
27 R. L. Frost and Z. Ding, Thermochim. Acta, 397 (2003) 119.
28 N. Yener, M. Önal, G. Üstünışık and Y. Sarıkaya, J. Therm. Anal. Cal., 88 (2007) 813.
29 A. Tabak, B. Afsin, B. Caglar and E. Koksal, J. Colloid Interface Sci., 313 (2007) 5.
30 M. Önal and Y. Sarıkaya, J. Therm. Anal. Cal., 90 (2007) 167.
31 H. Bayram, M. Önal, G. Üstünışık and Y. Sarıkaya, J. Therm. Anal. Cal., 89 (2007) 169.
32 M. V. Kök, Energy Sources, 24 (2002) 907.
33 J. L. Martin Vivaldi and P. Fenoll Hach-Ali, Palygorskites and Sepiolites, Differential Thermal Analysis, R.C. Mackenzie, Ed., Academic Press, London 1969.
34 M. Yeniyol, Clays Clay Miner., 34 (1986) 353.
35 S. J. Gregg and K. S. W. Sing, Adsorption, Surface Area and Porosity, Academic Press, London 1982.
36 A. C. D. Newman, Chemistry of Clays and Clay Minerals, A. C. D. Newman, Ed., Longman, Birmingham, AL 1987.

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