Journal of Thermal Analysis and Calorimetry, Vol. 87 (2007) 2, 375–381

STRUCTURAL CHARACTERISTICS OF ORGANO-MODIFIED BENTONITES OF DIFFERENT ORIGIN

A. Tabak[1*], *B. Afsin*[2], *S. F. Aygun*[2] *and E. Koksal*[2]

[1]Department of Chemistry, Faculty of Arts and Sciences, Rize University, 53100 Rize, Turkey
[2]Department of Chemistry, Faculty of Arts and Sciences, Ondokuz Mayis University, 55139 Kurupelit, Samsun, Turkey

Organobentonites were synthesized by treating Na-bentonites (Wyoming and Reşadiye) with cetylpyridinium chloride (CPC) using ion exchange method. The difference in the basal spacing by 0.65 Å and a higher mass loss by 13.32% of organobentonite (Wyoming) in the temperature range 200–550°C comparing with that of organobentonite (Reşadiye) were in conformity with the CEC values of organobentonites. The HOH stretching and bending peaks of bentonites became sharper following the treatment with the organo-cation. The intensity decrease of the Al–OH band for organobentonite (Reşadiye) and in particular, the significantly higher amount of *m*-cresol retained by the organobentonite of lower CEC than that by the organobentonite (Wyoming) indicate the influence of the CP cation on the adsorption process.

Keywords: *cetylpyridinium, hydration state, ion exchange, organo-bentonite*

Introduction

Organo-clays produced by treatment of clay minerals such as bentonite and montmorillonite with organics have a lot of applications in many fields of industry due to their high surface area, specific active sites and attractive adsorptive properties [1–4]. Isomorphous substitutions of Si^{4+} cation by Al^{3+} cation in the tetrahedral layer and those of Al^{3+} cations by Mg^{2+}, Fe^{2+} etc. cations in the octahedral layer of the aluminosilicate structured clay minerals result in a negative charge which is balanced by the cations such as Na^{+}, K^{+}, Ca^{2+} etc. These substitutions and hydrated cations strongly give rise to hydrophilic nature of the clay surface.

The surface modification is necessary for making natural clays suitable for specific adsorption and catalysis [5] since they are not very effective by themselves in removal of hazardous compounds from water and soil environments [6–8]. One of these modification processes is to insert the organic compound into the interlayer space of the clay minerals as a cationic species or a neutral molecule under certain conditions [9–11]. These type organoclays can be ascribed referring to the changes in the d-basal spacing, thermal stability, surface area and the structural properties which are closely connected to the intercalation ratio, arrangement form and the type of the organic species as well as the cation exchange capacity (CEC) [12–14]. Penetration of cationic surfactant into the interlayer in particular results in an enhancement in the affinity towards the removal of organic pollutants in the environment and soil through the organo-clay interactions [15–17].

Although vast number of studies on the interactions mentioned above has been available in the literature [18–22], there seemed not much comparable studies on the structural characteristics of organoclay originating from both Reşadiye-bentonite and other type of organoclays. Therefore, X-ray diffraction (XRD), thermal analysis (DTA/TG), Fourier Transform Infrared (FTIR) and surface area measurement techniques were employed to enlighten the structures of organobentonites prepared by interacting Na-bentonites of different origin (Wyoming and Reşadiye) with cetylpyridinium cation (CP) in present study. The other aim of the research was to shed light on the surface structures of these organobentonites through *m*-cresol adsorption since *m*-cresol and its isomers are widespreadly released and used in every day life [23].

Experimental

Preparation of organobentonites

The bentonites (Wyoming, and Reşadiye, Turkey) with elemental compositions of $[Al_{1.50}Fe_{0.17}Mg_{0.33}][Si_4]O_{10}(OH)_2$ and

---

[*] Author for correspondence: ahmtabak@hotmail.com

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

$[Al_{1.47}Fe_{0.29}Mg_{0.23}][Al_{0.076}Si_{3.29}]O_{10}(OH)_2$, respectively were transformed into Na-bentonites by treating with 1.0 M NaCl solution repeatedly which was followed by washing with distilled water until freed from chloride ion, centrifugation, drying, and grinding to 200 μm. The cation exchange capacity (CEC) values of Wyoming and Reşadiye-bentonites, which consisted of primarily Ca-montmorillonite and Na-montmorillonite, respectively, were determined as 92 and 76 meq/100 g clay, respectively by methylene blue adsorption [24]. Organobentonites were prepared by applying the procedure similar to that of Pospisil *et al.* [25]. Organic cation used for surface modification was cetylpyridinium chloride (CPC) (Sigma, 99%). The suspensions with 3.0 mass% of Na-bentonites in distilled water were treated with the CPC solution in a water/isopropyl alcohol (1:1) mixture. These organo-bentonites were separated from water/isopropyl alcohol mixture by centrifugation and washed with doubly distilled water thoroughly and then freeze-dried and ground to size 200 μm.

Methods

FTIR and thermal analyses

FTIR spectra of the original and organobentonite samples were recorded in the region 4000–200 cm^{-1} on a Mattson-1000 FTIR spectrometer at 4 cm^{-1} resolution. XRD patterns of the products were taken on a Rigaku 2000 automated diffractometer using Ni filtered CuK_{α} radiation. Thermal analyses were performed simultaneously on a Rigaku TG 8110 thermal analyzer combined with TAS (Thermal Analysis System) 100 (range 25–1000°C) under static air atmosphere at a heating rate of 10°C min^{-1}. Calcinated α-alumina was taken as the reference. Moisture and gases on the solid surface or penetrated into the pore openings were removed by heating at 120°C for 2 h prior to the surface area measurements by nitrogen adsorption at 77 K using Quantachromosorb.

Adsorption procedure

m-cresol used for adsorption study was of analytical grade (Merck). 50 mg of adsorbent and 50 mL of an aqueous solution of *m*-cresol in the concentration range (0.015–0.050) mmol were put into plastic tubes and shaken rigorously at constant temperature (25±1ºC) for 24 h to ensure the equilibrium. The pH of each mixture was fixed to 6.0. The suspensions were centrifuged at 15.000 rpm and the concentrations of supernatants were determined by a Perkin-Elmer Series 4 UV-1000 Spectra System liquid chromatograph equipped with SN 4000 detector. The amount of *m*-cresol retained by the organobentonites was calculated by the equation $q=\Delta n/W$ where Δn is the difference between the initial and final mmoles of adsorbates in the solutions and W is the mass of the adsorbent (g).

Results and discussion

Physicochemical properties of organobentonites

The d_{001} basal spacing values of cetylpyridinium (CP)-modified Wyoming- and Reşadiye-bentonites were 22.30 and 21.65 Å at 3.960 and 4.08 (2θ) respectively, while that of untreated bentonites (Wyoming and Reşadiye) were 14.24 Å at 6.20 (2θ) and 12.54 Å at 7.040 (2θ) which correspond to the major montmorillonite (M) component (Figs 1a–d). The (001) basal peak was expanded by 14.60 Å for Wyoming bentonite and 14.15 Å for Reşadiye bentonite after treatment with water. The higher expansion of the d_{001} basal distance of Reşadiye bentonite comparing to Wyoming bentonite represents the Na-montmorillonite which is expanded more than Ca-montmorillonite as a result of the layer charge and the size and charge of the exchangeable cation. In the case of NaCl-saturated

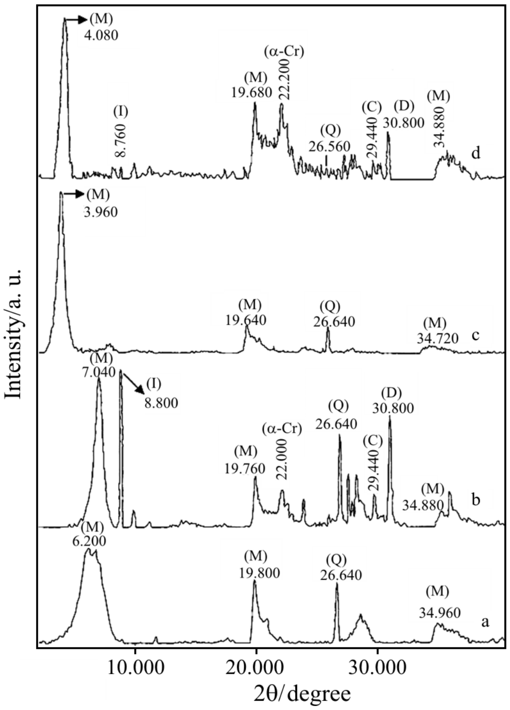

Fig. 1 XRD spectra of a – Wyoming-bentonite, b – Reşadiye-bentonite, c – CP-bentonite (Wyoming), and d – CP-bentonite (Reşadiye)

bentonites, these values were determined as 12.70 and 12.20 Å for Wyoming and Reşadiye bentonites, respectively (not shown here). When Na-bentonites were exposed to water, the d_{001} value of Reşadiye reached 14.52 Å but that of Wyoming bentonite varied slightly because of not completely conversion from Ca-montmorillonite to Na-montmorillonite as well as generation of the gel. However, the peaks due to the quartz (Q) except of clay component for bentonite (Wyoming) and the illite (I), α-cristobalite (α-Cr), quartz, calcite (C) and dolomite (D) for bentonite (Reşadiye) were still observed in the XRD patterns of bentonites and organobentonites [26]. The replacement of interlayer metallic cations of bentonite by large organic cations caused the increases in the basal spacing with respect to that of bentonites here. The thickness of a SiO_2–Al_2O_3–SiO_2 sheet is estimated to be about 9.0 Å and, this value was substracted from the d_{001} values of CP-modified bentonites. It may be suggested referring to the d_{001} values of CP-modified bentonites that the CP cations might be oriented as pseudotrimolecular for Reşadiye (Fig. 2 for Reşadiye) and as paraffin complex for Wyoming in the interlamellar spacing [18]. If the organic cation had lied flat, i.e., parallel to the clay platelets or perpendicular to the layers of clay without any interaction with the clay and/or the organic cations themselves, the expansion would have been more different than the value observed considering the C–C, C–H and C–N bond lengths [27].

Thermal analysis data for CP-bentonite (Wyoming) demonstrated mass losses by 2.17 and 33.41% in the temperature ranges 20–190 and 200–700°C, respectively, which correspond to the decomposition of water and CP cation and removal of structural OH of the clay respectively, while that of the bentonite exhibited mass losses by 5.15% at 20–193°C and 3.25% at 566–739°C due to the thermal evolution of moisture and interlayer water, and structural OH groups, respectively (Figs 3a, b) (Table 1). The exothermic DTA peaks in the region 200–700°C were attributed to the stepwise removal of interlayer CP cation of Wyoming-bentonite through oxidation (Figs 3c, d).

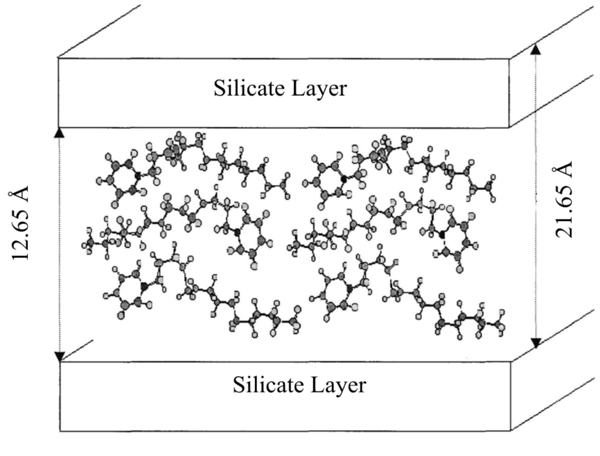

Fig. 2 3-D representation of CP cation in the interlayer space of Resadiye-bentonite

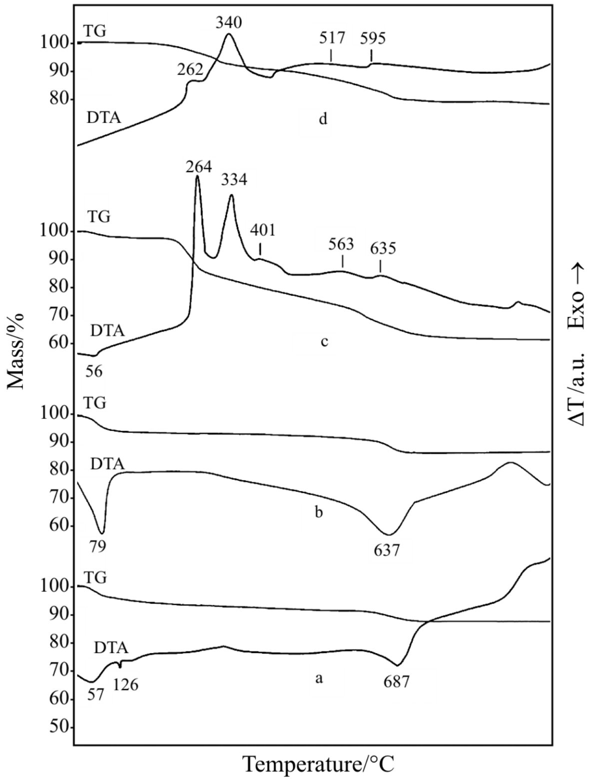

Fig. 3 Thermal analysis curves of a – Wyoming-bentonite, b – Reşadiye-bentonite, c – CP-bentonite (Wyoming) and d – CP-bentonite (Reşadiye)

Table 1 Thermal analysis data of untreated- and CP-exchanged-bentonites (Wyoming and Reşadiye)

Sample	Temperature range/°C	Mass loss/%
Wyoming-bentonite	20–193 566–739	5.15 3.25
Reşadiye-bentonite	20–134 210–566 566–732	5.80 2.30 5.50
CP-bentonite (Wyoming)	20–190 200–700	2.17 33.41
CP-bentonite (Reşadiye)	20–190 200–700	1.06 21.20

The two endothermic peaks in the DTA curve of Wyoming-bentonite in the range 20–193ºC denote the release of different water species coordinated to the interlayer cations and surface humidity. Especially, the second peak at 126ºC accompanied by the decomposition up to 193ºC represents stronger hydrogen bonding between water molecules and exchangeable Ca^{2+} cation which has a higher polarizing power than the Na^{+} cation of Resadiye bentonite. However, the thermal analysis curves of Na-bentonites (Wyoming and Reşadiye) are almost equal except for external clay components (not shown here). The differences (at 200–700ºC) in the thermal analysis curves of CP- and Reşadiye-bentonite and those of Wyoming bentonite result from the existence of the impurities such as dolomite, α-cristobalite, quartz, calcite next to the main component of Na-montmorillonite within the Reşadiye-bentonite. The lower mass losses ascribed to the decomposition of all organic cations together with structural OH and clay components in the range 200–700°C for CP-bentonite (Reşadiye) with respect to the CP-bentonite (Wyoming) may be related to the CEC value (Table 1). This difference seems parallel

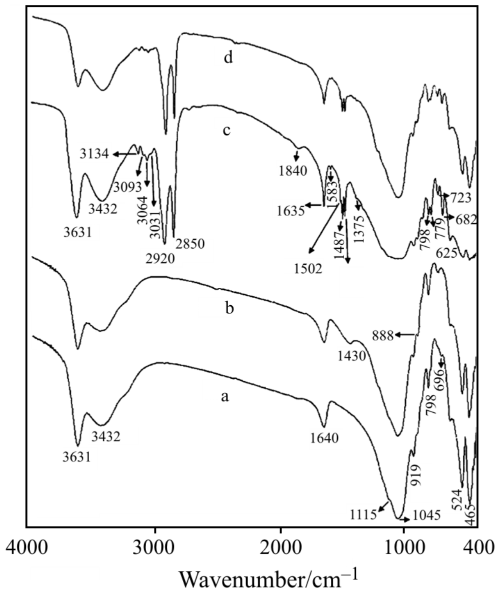

Fig. 4 FTIR spectra of a – Na-bentonite (Wyoming), b – Na-bentonite (Reşadiye), c – CP-bentonite (Wyoming) and d – CP-bentonite (Reşadiye)

Table 2 IR spectral data of Na- and CP-exchanged-bentonites (Wyoming and Reşadiye)

Assignment	Na-bentonite/cm^{-1}		CP-bentonite/cm^{-1}	
	Wyoming	Reşadiye	Wyoming	Reşadiye
Al(Mg)–O–H stretching	3631	3631	3631	3631
H–O–H stretching (for H_2O)	3432	3432	3432	3432
H-O-H bending	1640	1640	1635	1635
CO_3 stretching of calcite and dolomite	–	1430–1382	–	1430–1382
Si–O stretching	1115	1115	1115	1115
Si–O–Si stretching	1090, 1045	1090, 1045	1045	1045
OH bending bounded 2 Al^{3+}	919	919	919	919
OH bending bounded Fe^{3+} and Al^{3+}	888	888	888	888
OH bending bounded Mg^{2+} and Al^{3+}	843	843	847	847
Si–O stretching of silica and quartz	798	798	798	798
Si–O stretching + in-plane bending of calcite and dolomite	–	710–715	–	710–715
Al–Si–O bending	524	524	524	524
Si–O–Si bending	465	465	465	465
Aromatic C–H stretching	–	–	3134, 3093, 3064, 3031	3134, 3093, 3064, 3031
Overtone of C–H out-plane bending (for ring)	–	–	2000–1600	2000–1600
C=C stretching (for ring)	–	–	1583	1583
C=C skeleton stretching (for ring)	–	–	1502	1502
C–H out-plane bending (for ring)	–	–	779	779
C–H stretching (for alkyl groups)	–	–	2920, 2850	2920, 2850
C–H in-plane bending (for alkyl groups)	–	–	1487, 1469, 1375	1487, 1468, 1375
C–H out-plane bending (for CH_2)	–	–	723	723

with the thermal stability and the d_{001} value of each organo-bentonite proving the greater amount of organic cation in the gallery space of Wyoming bentonite. Furthermore, the exothermic DTA peaks of all CP-modified bentonites in the temperature range above illustrate the gradual decomposition of the organic cation which gives rise to the desorption of high amount of organic H_2O and CO_2 species resulting from high-temperature oxidation of black residue [28]. Moreover, the thermal stability of the organic cation in the interlamellar space up to 700ºC point out the presence of π interactions between the oxygen planes of the clay sheets and the aromatic ring of the cation, and shielding effect of alumino-silicate layers [29, 30]. The extrathermal stability of the CP-bentonite (Wyoming) proves the high stability of the first decomposition product (black residue) which may be acquired to the high CEC of this organo-clay relative to that of Resadiye bentonite.

Figures 4a–d shows the FTIR spectra of Na- and CP-cation exchanged-bentonites (Wyoming and Reşadiye). In the spectra of Na-bentonites, the OH stretches in the 3600–3400 cm^{-1} region, and the Si–O stretching bands between 1100 and 900 cm^{-1}, the bending peaks within the range 750–450 cm^{-1} are clearly seen. FTIR spectral data of CP cation-exchanged-bentonites (Wyoming and Reşadiye) together with those of Na-bentonites are summarized in Table 2. It was concluded from the vibrations of aromatic ring and alkyl groups that organic compound could penetrate into the interlayer space of bentonite as organic cation, displacing inorganic cations. The CP cation can interact with the bentonite samples through *i*) long-range electrostatic interactions due to attraction between negatively charged clay platelets and cations, *ii*) π interactions resulting from overlapping nonbonding sp^2 orbitals of oxygen in the silicate layer and antibonding π orbitals of aromatic ring of organic cation [31], and *iii*) van der Waals forces between the oxygen planes and organic cation, and organic cations themselves. The surface properties of the bentonite samples would be changed to hydrophilic character which is associated with the strong hydration of inorganic cations as a result of the replacement of inorganic cations with organic cations. The decrease in the intensities of the OH stretching and bending vibrations, and also the shift to lower frequency by 5 cm^{-1} and the sharpness of the bending peak of organobentonite comparing to untreated bentonite confirm this phenomenon. However, the decrease in the intensity of Al–OH stretching peak of organobentonite (Reşadiye) may be interpreted in terms of electrostatic interactions between the OH group and the organic cation substitution of Na^+ cation. The differences in cationic radius, the charge and the hydration energies of the exchangeable cations influence the hydroxyl group vibrations in the octahedral layer which may be taken as another proof to this result [32]. The contribution of the external clay components of the organobentonite (Reşadiye) to the latter interaction can not be ruled out.

Table 3 Surface area values of Na- and CP-exchanged-bentonites (Wyoming and Reşadiye)

Sample	Surface area/m^2 g^{-1}
CP-bentonite (Wyoming)	2.15±0.02
CP-bentonite (Reşadiye)	2.90±0.02
Na-bentonite (Wyoming)	34.80±0.02
Na-bentonite (Reşadiye)	33.80±0.02

The surface area decrease of organobentonite (Wyoming) in comparison with untreated bentonites (Wyoming and Reşadiye) was relatively higher than that of organobentonite (Reşadiye) (Table 3) which may be connected to the amount of organic cation inserted into interlayer space. The differences in the surface areas of organobentonites support the other spectrophotometric data and the CEC values. The surface area decreases of all organobentonites may be explained in terms of the micropore openings blocked by the organic cation species embedded in the interlayer space which form a macroporous structure [33].

Adsorption of the m-cresols on the organobentonites

The amounts of *m*-cresol retained by the organobentonites (Wyoming and Reşadiye) are illustrated in Fig. 5. *m*-cresols, being weak acids (pKa~10.09) and having environmental relevant pH

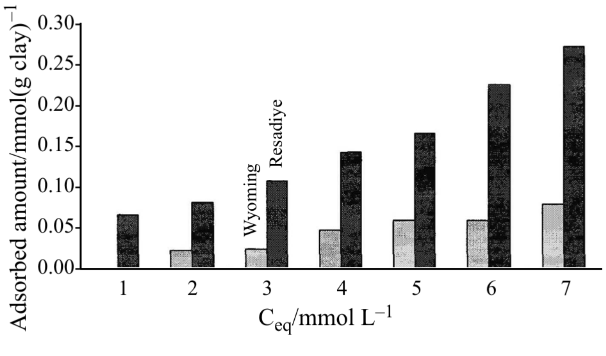

Fig. 5 A comparison of adsorption of *m*-cresol on the organobentonites (Wyoming and Reşadiye)

values in the range (5–9), exist largely in non-dissociated forms in aqueous solution. The interaction between *m*-cresol and organobentonite surfaces is mainly hydrophobic nature since the *m*-cresol forms molecular aggregates in the aqueous medium in the concentration and pH ranges employed here [34]. The amount of *m*-cresol adsorbed on the organobentonite (Reşadiye) was higher than that of organobentonite (Wyoming) in parallel with the CEC values of organobentonites which favours the lower surfactant amount in the interlayer space of this organo- bentonite. A higher affinity of organobentonite (Reşadiye) towards *m*-cresol than that exhibited by organobentonite (Wyoming) was noticed in parallel with the concentration increase. This difference may also reflect the effect of clay impurities other than the main component as well as the interaction between the adsorbent and the adsorbate. The internal hydrocarbon cores and external hydrophilic surfaces lead to a surface orientation of the hydrocarbon tails of the adsorbed surfactant onto the organo-montmorillonite, thus, diminish the influence of the effective organic carbon shown by the toxic organics in a similar work [35]. This process would be more effective in case of flocculation among the organo-montmorillonite intra-particles in line with the surfactant amount in the interlayer.

Conclusions

Organobentonites were prepared by ion exchange process between inorganic cations and cationic surfactant in the interlayer space. It was concluded from the XRD, thermal analysis, FTIR and surface area measurements data that the amount of organic cation penetrated into the interlamellar space of Na-bentonite (Wyoming) was higher than that of Na-bentonite (Reşadiye). In all concentration ranges, the amount of *m*-cresol adsorbed by organobentonite (Wyoming) was lower than that of organobentonite (Reşadiye) due to the decrease of the hydrophobic interactions between the cationic adsorbate in the interlayer and the organics. The lower selectivity of the organobentonite (Wyoming) which retains more organic cation than the Reşadiye organobentonite towards *m*-cresol may be explained by means of the decreased amount of active adsorbent in contact with the organics in solution that promotes flocculation of organoclay particles.

Acknowledgements

The authors are grateful to the Research Foundation of Ondokuz Mayis University for the financial support under the Project number F338.

References

1 C. G. Olson, M. L. Thompson and M. A. Wilson, in: Phyllosilicates, M. E. Sumner (Eds.), Handbook of Soil Science, CRC Press, New York, 1993, F80–124.
2 T. J. Pinnavia, Science, 220 (1983) 365.
3 G. Rytwo, R.Huterer-Harari, S. Dultz and Y. Gonen, J. Therm. Anal. Cal., 84 (2006) 225.
4 W. N. Delgass, G. L. Haller, R. Kellerman and J. H. Lunsford, Spectroscopy in Heterogeneous Catalysis, Academic Press, New York, 1979, p. 1.
5 F. Bergaya and G. Lagaly, Appl. Clay Sci., 19 (2001) 1.
6 O. R. Pal and A. K. Vanjara, Sep. Purif. Technol., 24 (2001) 167.
7 L. Yuncong and G. Gupta, Chemosphere, 28 (1994) 627.
8 J. Barrault, C. Bouchoule, K. Echachoui, N. Frini-Srasra, M. Trabelsi and F. Bergaya, Appl. Catal. B: Environ., 15 (1998) 269.
9 G. Sheng and S. A. Boyd, Clays Clay Miner., 46 (1998) 10.
10 A. V. Faridi and S. Guggenheim, Clays Clay Miner., 47 (1999) 338.
11 A. Gultek, M. G. Icduygu and T. Seckin, Mater. Sci. Eng., 107 (2004) 166.
12 Y. Sugahara, S. Satokawa, K. Yoshioka and C. Kato, Clays Clay Miner., 37 (1989) 143.
13 H. Favre and G. Lagaly, Clay Miner., 26 (1991) 19.
14 S. Gitipour, M. T. Bowers and A. Bodocsi, J. Colloid Interface Sci., 196 (1997) 191.
15 B. S. Krishna, D. S. R. Murty and B. S. J. Prakash, J. Colloid Interface Sci., 229 (2000) 230.
16 R. S. Juang, S. H. Lin and K. H. Tsao, J. Colloid Interface Sci., 254 (2002) 234.
17 S. Y. Lee, W. J. Cho, K. J. Kim, J. H. Ahn and M. Lee, J. Colloid Interface Sci., 284 (2005) 667.
18 G. Chen, B. Han and H. Yan, J. Colloid Interface Sci., 201 (1998) 158.
19 A. Alemdar, O. Atıcı and N. Gungor, Mater. Lett., 43 (2000) 57.
20 S. G. Starodoubtsev, A. A. Ryabova, A. R. Khokhlov, G. Allegra, A. Famulari and S. V. Meille, Langmuir, 19 (2003) 10739.
21 Y. Imai, S. Nishimura, Y. Inukai and H. Tateyama, Clays Clay Miner., 51 (2003) 162.
22 H. Hongping, D. Zhe, Z. Jianxi, Y. Pen, X. Yunfei, Y. Dan and F. L.Ray, Clays Clay Miner., 53 (2005) 287.
23 SIDS Initial Assessment Report for SIAM16, Paris, France, 2003, 2-377.
24 R. K. Taylor, J. Chem.Technol. Biotechnol., 35 A (1985) 195.

25 M. Pospisil, P. Capkova, D. Merinska, Z. Malac and J. Simonik, J. Colloid Interface Sci., 236 (2001) 127.
26 R. W. Grimshaw, The Chemistry and Physics of Clays and Allied Ceramic Materials, Ernest Benn Limited, London, 1971, Chapter XIV.
27 A. R. Mermut and G. Lagaly, Clays Clay Miner., 49 (2001) 393.
28 S. Yariv, Appl. Clay Sci., 24 (2004) 225.
29 M. Bora, J. N. Ganguli and D. K. Dutta, Thermochim. Acta., 346 (2000) 169.
30 Z. Yermiyahu, A. Landau, A. Zaban, I. Labides and S. Yariv, J. Therm. Anal. Cal., 72 (2003) 431.
31 A. Tabak and B. Afsin, Adsorp. Sci. Technol., 19 (2001) 673.
32 J. Madejova, Vib. Spectrosc., 31 (2003) 1.
33 A. Tabak, B. Afsin, S. F. Aygun and H. Icbudak, J. Therm. Anal. Cal., 81 (2005) 311.
34 T. Yamagishi, R. Takahashi, D. Nagatani, G. Konishi and Y. Nakamoto, Soc. Polym. Sci. Jpn., 60 (2003) 192.
35 K. R. Srinivasan and H. S. Fogler, Clays Clay Miner., 38 (1990) 287.

Received: July 20, 2006
Accepted: September 20, 2006
OnlineFirst: December 18, 2006

DOI: 10.1007/s10973-006-7886-6