

Physicochemical Characterization of Natural and Na⁺-, K⁺-, Ca²⁺- and Mg²⁺-modified Clinoptilolite from Gördes (Manisa, Turkey)

Tevfik Ünal^{1*}, Önder Orhun² and Selahattin Kadir³ (1) Department of Physics, Eskişehir Osmangazi University, TR-26480 Eskişehir, Turkey. (2) Department of Physics, Anadolu University, TR-26470 Eskişehir, Turkey. (3) Department of Geological Engineering, Eskişehir Osmangazi University, TR-26480 Eskişehir, Turkey.

(Received 21 July 2009; revised form accepted 15 November 2009)

ABSTRACT: Physicochemical characterization of the natural solid-phase Gördes clinoptilolite and of the Na⁺-, K⁺-, Ca²⁺- and Mg²⁺-modified forms of the mineral (as obtained through ion-exchange) by batch methods, X-ray diffractometry (XRD), X-ray fluorescence (XRF), infrared spectroscopy (IR) and scanning electron microscopy (SEM) is described. It was found that the Na⁺- and Ca²⁺-forms exhibit high ion-exchange rates relative to the Mg²⁺- and K⁺-forms. In addition, the high rate of ion selectivity towards Na⁺ and K⁺ ions, together with lower rates for Mg²⁺ and Ca²⁺ ions, indicate that the rate of ion selectivity is negatively correlated with the ionic potential of the ions. Such ion-exchange and ion selectivity result in a decrease in pore size and an increase in the surface area of the modified clinoptilolite relative to the natural form; this may possibly be related to the entrance of the ions into the mineral structure. It was concluded that clinoptilolite modified with exchangeable ions from aqueous solutions at two different normalities exhibits features which differ from those of natural clinoptilolite. Thus, modification of clinoptilolite by different cationic forms from aqueous solutions at different normalities might prove suitable for applications in other fields of study.

INTRODUCTION

The total reserves of the clinoptilolite deposits in Turkey amount to ca. 50 million tonnes, with 20 million tonnes occurring in the Gördes area, Manisa Province (Büyükakyol 1988). Clinoptilolite has the structural formula (Na,K)₆(Al₆Si₃₀O₇₂) • 24H₂O and consists of two rings, one eight-membered of dimensions 3.3 × 4.6 Å in the ab-plane and the other 10-membered of dimensions 3.0 × 7.6 Å in the channels, together with an eight-membered ring of dimensions 2.6 × 4.7 Å in the bc-plane (Gottardi and Galli 1985; Mumpton 1960; Breck 1974; Mozgawa and Bajda 2006). Clinoptilolite also contains exchangeable Na⁺, K⁺, Ca²⁺ and Mg²⁺ ions in its channels (Ackley *et al.* 1992; Howe 1993; Cooney *et al.* 1999) (see Figure 1).

Studies of clinoptilolite have been conducted with the purpose of characterizing its adsorption properties towards NH₄⁺, Cd²⁺, Cu²⁺, Pb²⁺, Cr³⁺ and the cations of other heavy metal elements (Langella *et al.* 2000; Inglezakis *et al.* 2003; Erdem *et al.* 2004; Mozgawa and Bajda 2006; Karadağ *et al.* 2006; Wang *et al.* 2007; Sprynskyy 2009), towards radioactive materials (Osmanlioglu 2006; Smiciklas *et al.* 2007), its use for the retention and separation of various gases, its use as an adsorbent and a molecular sieve (Ackley *et al.* 2003; Zhao *et al.* 2009), its production as a doping material for feeding plants and as an additive to soils for assisting the

*Author to whom all correspondence should be addressed. E-mail: tunaldi@ogu.edu.tr.

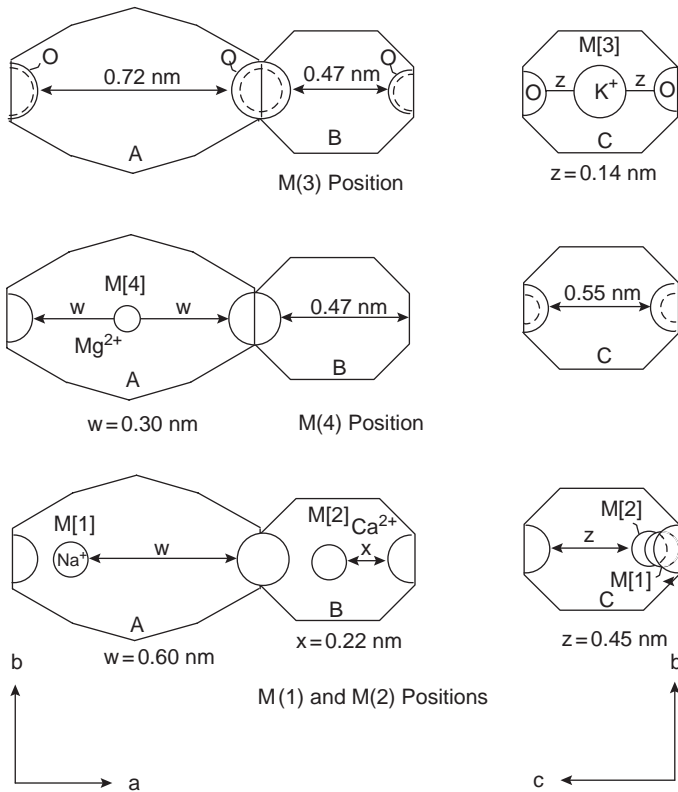


Figure 1. Ion positions in clinoptilolite (Ackley *et al.* 1992).

growth of various plants (Mumpton 1999; Rehakova *et al.* 2004). These studies have been mainly conducted on the solid/solution phases of modified zeolite. However, no information is at present available concerning the cation-exchange behaviour of the solid phases of clinoptilolite and the effect of modifying the ionic forms and normalities. Hence, the purpose of the present study was to characterize natural clinoptilolite and its related structural modifications by studying their rates of ion-exchange, their ion selectivity, their unit-cell volumes and surface areas using solid-phase physicochemical procedures without analyzing the solution phases involved in these processes.

EXPERIMENTAL

Clinoptilolite samples from a product called “NMF 9000, Agro-Clino” were obtained from the Enli Mining Corporation in Gördes, Manisa Province, Turkey. The physicochemical characteristics of the samples were determined by X-ray powder diffractometry (XRD) (Rigaku, Geigerflex), X-ray fluorescence spectrometry (Siemens SRS 3000) and scanning electron microscopy (SEM) (LEO 440). In addition, the specific surface areas of the samples were determined using a Nova 2200 High Speed Gas Sorption Analyzer, while their infrared spectra were measured using a PerkinElmer Spectrum 100 FT-IR spectrometer. Quantitative estimates of the contents of clinoptilolite and associated minerals in the samples were obtained using the intensities of the basal peaks of the various minerals (Gottardi and Galli 1985).

Chemical data for the bulk and representative treated samples of clinoptilolite were obtained using the rock standards of the MBH Reference Material (1998/99) and Breitländer (1988). The error for each element in these data was less than $\pm 2\%$. The loss on ignition (LOI) for each sample was also determined by drying the samples overnight at 105 °C and then determining their water content (and the contents of other volatiles) by heating the samples up to 1050 °C.

The cation-exchanged forms of the clinoptilolite obtained from the Gördes area were produced via a batch method, employing 0.1 N and 1 N solutions of the nitrate salts of Na⁺, K⁺, Ca²⁺ and Mg²⁺ ions as prepared in 50 ml de-ionized water. Thus, 5 g of a 300-mesh clinoptilolite sample was poured into each solution and stirred gently, and the resulting suspension stored for 72 h at room temperature. The clinoptilolite/solution suspension system was then filtered and the clinoptilolite residue washed eight times with de-ionized water at 98 °C and dried at 110 °C for 16 h (İnel *et al.* 1992; Hulbert 1987).

The a, b, c and β parameters of the clinoptilolite sample were obtained from the h, k and l dimensions in the crystal structure of monoclinic clinoptilolite, while the volume (V) of the monoclinic structure was calculated from the basal reflection peaks via the relationship:

$$V = abc \sin \beta$$

Similarly, the mineral contents of the samples were calculated from the equation:

$$W_i = (K_i I_i / \sum K_i I_i) \times 100$$

where W_i is the percentage mineral in the sample, K_i is the approximate area of a given peak to the total peak area and I_i is the intensity of the basal peak (Müller 1967; Gündoğdu 1982).

The crystallization extent of the minerals was calculated on the basis of the equation:

$$k = (\text{peak intensity of the modified form}) / (\text{peak intensity of the natural form})$$

while the chemical formula of clinoptilolite was calculated on the basis of a unit cell of 72 oxygen atoms using the following relationship:

$$X_{\text{form}} = [1 - (A_{\text{form}}/A_{\text{natural}})] \times 100$$

where X_{form} is the cation-exchange rate of the cation-exchanged form, A_{form} is the number of atoms in the unit cell of this cation-exchanged form and A_{natural} is the number of atoms in the unit cell of the natural form.

As termed by us, the “rate of ion selectivity” differs from the “ion selectivity” of an ion-exchanged form; this was calculated from the percentage of ions in the structure and is similar to the rate of cation-exchange. This rate of ion selectivity was calculated from:

$$\alpha_{\text{form}} = [(A_{\text{form}}/A_{\text{natural}}) - 1] \times 100$$

where α_{form} is the rate of ion selectivity of the ionic form, while A_{form} and A_{natural} have the same meanings as given above.

Specific surface areas were calculated on the basis of the Langmuir, Brunauer–Emmett–Teller (BET) and Dubinin–Radushkevitch (DR) methods (Sing 1985).

Representative natural and Na⁺-, K⁺-, Ca²⁺- and Mg²⁺-modified samples of clinoptilolite were prepared for SEM analysis by adhering the fresh, broken surface of each sample onto an aluminium sample holder with double-sided tape and thinly coating the sample with a film (350 Å) of gold using a Giko ion coater.

RESULTS AND DISCUSSION

XRD determinations

The mineralogical compositions of the natural and modified forms of clinoptilolite were determined using powder XRD methods (see Figure 2). The composition of natural clinoptilolite was determined on the basis of the basal reflections at 8.96, 3.99 and 2.97 Å. The intensities of these reflections remained unchanged in the K⁺- and Ca²⁺-modified forms, whereas those associated with the Na⁺- and Mg²⁺-modified forms exhibited a reduction in intensity.

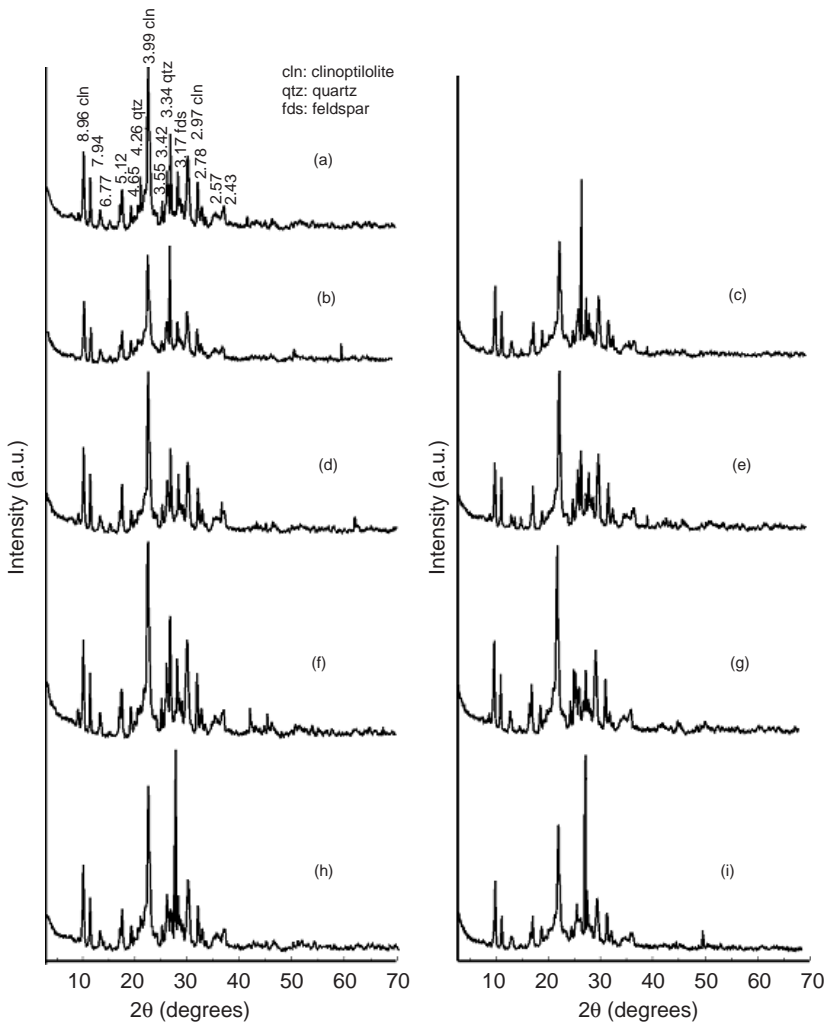


Figure 2. X-Ray diffractograms of (a) natural clinoptilolite, (b) Na⁺-modified clinoptilolite from 0.1 N solution, (c) Na⁺-modified clinoptilolite from 1.0 N solution, (d) K⁺-modified clinoptilolite from 0.1 N solution, (e) K⁺-modified clinoptilolite from 1.0 N solution, (f) Ca²⁺-modified clinoptilolite from 0.1 N solution, (g) Ca²⁺-modified clinoptilolite from 1.0 N solution, (h) Mg²⁺-modified clinoptilolite from 0.1 N solution, (i) Mg²⁺-modified clinoptilolite from 1.0 N solution.

Unit-cell volume

The unit-cell volume parameters of the clinoptilolite forms as prepared at two different normalities are presented in Table 1. These unit-cell volume parameters are similar to those reported by Ackley *et al.* (1992) where the samples studied were prepared at only one normality. Increasing the normality in the case of the Na⁺- and Ca²⁺-modified samples resulted in an increase in the unit-cell volume; in contrast, increasing the normality for the K⁺- and Mg²⁺-modified samples led to a decrease in the unit-cell volume (Table 1). Structurally, the ac-plane values are consistent with the unit-cell volume of clinoptilolite. Hence, the unit-cell volume values exhibit a positive correlation with the ac-plane values, which is not unexpected since changes in these values occur as a result of changes in the ionic radii and the positions of the ions in the clinoptilolite structure.

Relative mineral abundance

Comparison of the relative peak intensities for natural clinoptilolite with those for the Na⁺-, K⁺-, Ca²⁺- and Mg²⁺-modified forms generated by cation-exchange (Table 2) show that the overall abundance of quartz increased whereas that of feldspar diminished as a result of such treatment. However, the content of clinoptilolite in the cation-modified samples was not substantially different from that present in the natural form.

It should be noted that the peak intensities of the K⁺- and Ca²⁺-modified forms of clinoptilolite seemed to vary with storage time, in contrast to the corresponding behaviour of the Na⁺- and Mg²⁺-modified forms.

Degree of crystallinity, k (%)

The degrees of crystallinity of the modified forms of clinoptilolite are listed in Table 3. Increasing the normalities of the aqueous solutions from which the Na⁺-, K⁺- and Ca²⁺-forms were prepared led to an increase in crystallinity; in contrast, such an increase in normality led to a decrease in

TABLE 1. X-Ray Diffraction Data: Unit-cell Parameters of Natural and Na⁺-, K⁺-, Ca²⁺- and Mg²⁺-modified Forms of Clinoptilolite

Form	Parameter					
	a (Å)	b (Å)	c (Å)	β (°)	V (Å ³)	ac-plane (Å ²)
Natural	17.1272	17.9260	7.4022	115.6	2050	127
0.1 N Na ⁺ -modified	16.8084	17.6060	7.0787	110.7	1960	119
1 N Na ⁺ -modified	18.1301	17.8900	7.6508	119.2	2165	139
0.1 N K ⁺ -modified	18.1033	17.9260	7.6234	118.9	2165	138
1 N K ⁺ -modified	17.1957	17.9620	7.2138	112.2	2060	124
0.1 N Ca ²⁺ -modified	17.6598	17.9260	7.4224	116.1	2110	131
1 N Ca ²⁺ -modified	17.9365	17.9260	7.5139	117.9	2135	135
0.1 N Mg ²⁺ -modified	17.8103	17.9260	7.5465	117.1	2146	134
1 N Mg ²⁺ -modified	17.7822	17.8540	7.5057	117.4	2116	134

TABLE 2. X-Ray Diffraction Data: Relative Peak Intensities (%) of Natural and Na⁺-, K⁺-, Ca²⁺- and Mg²⁺-modified Forms of Clinoptilolite

Form	Clinoptilolite	Feldspar	Quartz
Natural	81	15	4
0.1 N Na ⁺ -modified	78	8	14
1 N Na ⁺ -modified	72	11	17
0.1 N K ⁺ -modified	82	3	15
1 N K ⁺ -modified	82	3	15
0.1 N Ca ²⁺ -modified	80	4	16
1 N Ca ²⁺ -modified	83	2	15
0.1 N Mg ²⁺ -modified	79	8	13
1 N Mg ²⁺ -modified	74	12	14

TABLE 3. Relative Crystallinity (k) of Natural and Na⁺-, K⁺-, Ca²⁺- and Mg²⁺-modified Forms of Clinoptilolite

Form	Crystallinity, k (%)
Natural	–
0.1 N Na ⁺ -modified	50
1 N Na ⁺ -modified	60
0.1 N K ⁺ -modified	85
1 N K ⁺ -modified	97
0.1 N Ca ²⁺ -modified	78
1 N Ca ²⁺ -modified	92
0.1 N Mg ²⁺ -modified	86
1 N Mg ²⁺ -modified	64

the crystallinity of the Mg²⁺-form. These changes were supported by SEM determinations. Tanaka *et al.* (2003) have also demonstrated that the sharpness of the basal reflections and the crystallinity of modified clinoptilolite are both increased by adding NaOH and KOH to the solutions from which such forms are precipitated and also by lengthening the modification period.

XRF determinations

Rate of ion-exchange

Chemical analyses of the natural and Na⁺-, K⁺-, Ca²⁺- and Mg²⁺-modified clinoptilolite samples are listed in Tables 4 and 5. The exchange rates of the cation forms in binary systems are discussed below.

TABLE 5. Ion-exchange Rates, X_{form} , for Na^+ -, K^+ -, Ca^{2+} - and Mg^{2+} -modified Clinoptilolite Forms Relative to Natural Clinoptilolite

Form	Clinoptilolite modification							
	0.1 N Na^+	1.0 N Na^+	0.1 N K^+	1.0 N K^+	0.1 N Ca^{2+}	1.0 N Ca^{2+}	0.1 N Mg^{2+}	1.0 N Mg^{2+}
	X_{form}	X_{form}	X_{form}	X_{form}	X_{form}	X_{form}	X_{form}	X_{form}
Na^+	–	–	21.11	63.15	12.70	28.62	8.94	9.12
K^+	2.71	10.06	–	–	2.86	4.54	0.82	1.38
Ca^{2+}	14.90	51.03	22.71	59.44	–	–	0.30	4.43
Mg^{2+}	10.57	6.76	6.24	11.61	3.64	13.52	–	–

(a) Exchange of Na^+ – K^+ and K^+ – Na^+ ions

In the K^+ -form, the Na^+ ions leave the structure at a higher rate than the K^+ ions. Although the ionization potential of the K^+ ion is smaller than that of the Na^+ ion, the binding of the Na^+ ions to the structure is weaker than that of the K^+ ion.

(b) Exchange of Ca^{2+} – Mg^{2+} and Mg^{2+} – Ca^{2+} ions

Since Mg^{2+} ions leave the structure at a higher rate than Ca^{2+} ions, this shows that the Ca^{2+} ions are more readily removed than the Mg^{2+} ions despite the ionization potential of the Ca^{2+} ion being lower than that of the Mg^{2+} ion. The ready removal of Ca^{2+} ions relative to Mg^{2+} ions may possibly be due to their location in the 10-membered and eight-membered rings, respectively (see Figure 1).

(c) Exchange of Na^+ – Ca^{2+} and Ca^{2+} – Na^+ ions

Although the ionization potential of the Na^+ ion is lower than that of the Ca^{2+} ion, Ca^{2+} ions leave the structure at a higher rate than Na^+ ions, possibly due to the location of the Na^+ ion in the loop of two eight-membered chains in the bc-plane.

(d) Exchange of Na^+ – Mg^{2+} and Mg^{2+} – Na^+ ions

The ion-exchange of these two ionic states is similar insofar as both Mg^{2+} and Na^+ ions exist in the 10-membered rings.

(e) Exchange of K^+ – Ca^{2+} and Ca^{2+} – K^+ ions

In the K^+ -form, the high rate of removal of Ca^{2+} ions from the structure compared to the low rate of removal of K^+ ions from the Ca^{2+} -form is possibly related to the position of the K^+ ion between the 10-membered and 8-membered chains and the Ca^{2+} ion in the 8-membered ring.

(f) Exchange of K^+ – Mg^{2+} and Mg^{2+} – K^+ ions

In the K^+ -form, the Mg^{2+} ions leave the structure in a manner comparable to the K^+ ions in the Mg^{2+} -form. The K^+ ions are tightly bound to the structure, and thus the Mg^{2+} ions which are only loosely bound to the 10-membered ring leave the structure more readily.

The general order of the exchange rate of cation-modified Gördes clinoptilolite is as follows (Table 5): $\text{Na}^+ > \text{Ca}^{2+} \gg \text{Mg}^{2+} > \text{K}^+$. Cations with lower ionization potentials are characterized by higher rates of ion-exchange, other than the K^+ ion. The latter has a low ionization potential and exhibits a low cation-exchange capacity, possibly due to K^+ ions binding tightly to the structure. This is verified by the order reported in Table 6. The solid-phase modification undertaken in the present study is comparable with the solid-solution-modified phase reported by Ackley *et al.*

The order of the rates of the ion selectivity of the various ions is: $\text{Na}^+ > \text{K}^+ \gg \text{Ca}^{2+} > \text{Mg}^{2+}$. The rate order of the selectivity for the univalent ions Na^+ and K^+ entering the structure was 25–236%, while the corresponding rate order for the divalent ions Ca^{2+} and Mg^{2+} was 7–25%. Thus, the ionization potentials follow the order: $\text{K}^+ < \text{Na}^+ < \text{Ca}^{2+} < \text{Mg}^{2+}$. Ions with high ionization potentials enter the structure with difficulty relative to those with lower ionization potentials. In contrast, the Na^+ ion enters the 10-membered structure more readily than does the K^+ ion. The selectivity order for Na^+ , Ca^{2+} and Mg^{2+} ions is consistent with that reported by Ames (1960, 1964a,b), except for the K^+ ion whose selectivity relative to that of the Na^+ ion was less than that reported by Ames, viz. $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{NH}_4^+ > \text{Ba}^{2+} > \text{Sr}^{2+} > \text{Na}^+ > \text{Ca}^{2+} > \text{Fe}^{3+} > \text{Al}^{3+} > \text{Mg}^{2+} > \text{Li}^+$.

Although the normalities employed for the K^+ ion in solution were similar to those for the other ions, the low selectivity of K^+ may be due to the fact that its ionic radius (1.33 Å) is larger than those of Na^+ , Ca^{2+} and Mg^{2+} ions. Thus, the data for the K^+ ion are not suitable in ordering the rate of ion selectivity for Gördes clinoptilolite. In fact, clinoptilolites from various regions of the world exhibit different ion-selectivity orders, as listed below:

Rehakova *et al.* (2004): $\text{Cs}^+ > \text{NH}_4^+ > \text{Pb}^{2+} > \text{K}^+ > \text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Ba}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$

Chelischev *et al.* (1974): $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Sn}^+ > \text{Li}^+$

Ackley and Yang (1991): $\text{K}^+ > \text{NH}_4^+ > \text{Ca}^{2+} \approx \text{Na}^+ > \text{Mg}^{2+}$

Falamakia *et al.* (2004): $\text{Ca}^{2+} > \text{Na}^+ > \text{K}^+ \gg \text{Mg}^{2+}$

Specific surface areas

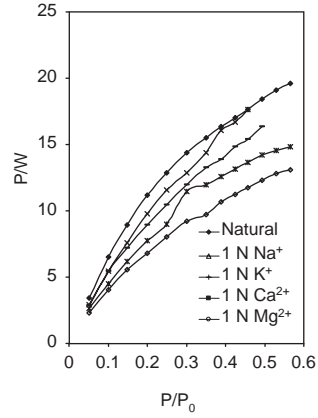
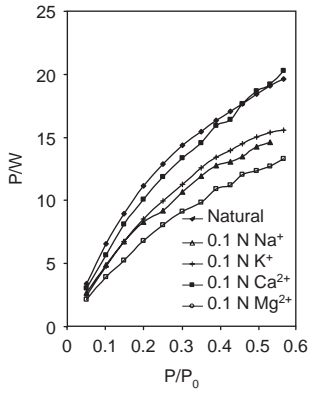
Measurements of the specific surface areas of the natural, Na^+ -, K^+ -, Ca^{2+} - and Mg^{2+} -forms of Gördes clinoptilolite were undertaken, with the results obtained being listed in Table 8 and depicted in Figure 3.

It will be seen from the data that the surface areas of the Mg^{2+} - and Na^+ -forms of clinoptilolite increased relative to that of natural clinoptilolite as the normality of the solution from which they were prepared increased while those of the Ca^{2+} - and K^+ -forms decreased. This suggests that the

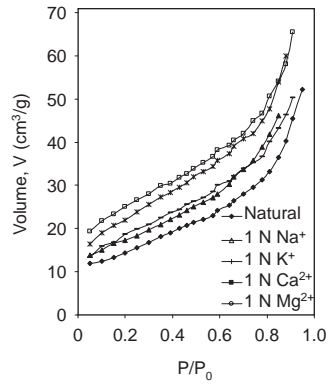
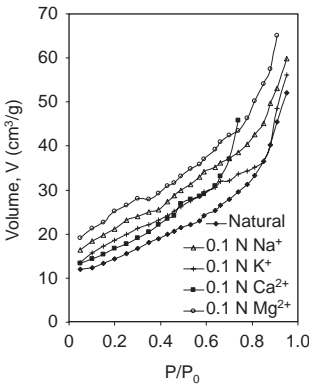
TABLE 8. Surface Characteristics of Natural and Na^+ -, K^+ -, Ca^{2+} - and Mg^{2+} -modified Clinoptilolite Forms

Form	Adsorption equation					
	Langmuir	BET	DR method			
	Surface area (m ² /g)	Surface area (m ² /g)	Average pore width (nm)	Adsorption energy (kJ/mol)	Micropore volume (cm ³ /g)	Micropore surface area (m ² /g)
Natural	118	51	9.66	2.69	0.044	125
0.1 N Na^+ -modified	154	68	9.34	2.78	0.057	164
1.0 N Na^+ -modified	177	71	9.46	2.74	0.061	175
0.1 N K^+ -modified	146	63	8.67	2.99	0.050	143
1.0 N K^+ -modified	131	61	9.35	2.77	0.052	148
0.1 N Ca^{2+} -modified	151	56	9.15	2.83	0.047	135
1.0 N Ca^{2+} -modified	116	57	9.07	2.86	0.048	138
0.1 N Mg^{2+} -modified	180	80	9.05	2.87	0.066	189
1.0 N Mg^{2+} -modified	209	83	9.28	2.80	0.067	192

(a) Langmuir isotherms



(b) BET plots



(c) DR plots

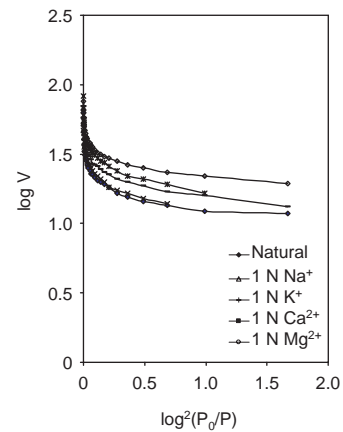
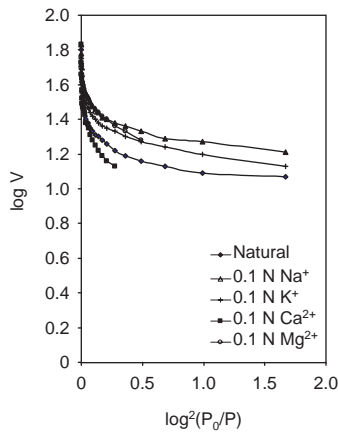


Figure 3. (a) Langmuir isotherms, (b) BET plots and (c) DR plots for various clinoptililite forms.

specific surface areas are related to the characters of the incorporated ions (i.e. the ionic radii and the location of the ions in the structure). The order of the specific surface areas was as follows: $Mg^{2+} > Na^{+} > Ca^{2+} > K^{+} >$ natural clinoptilolite.

This order is inversely related to the ionic radii of the ions. These results are consistent with the specific surface areas of the natural and Na^{+} -, K^{+} - and Ca^{2+} -modified forms of clinoptilolite as

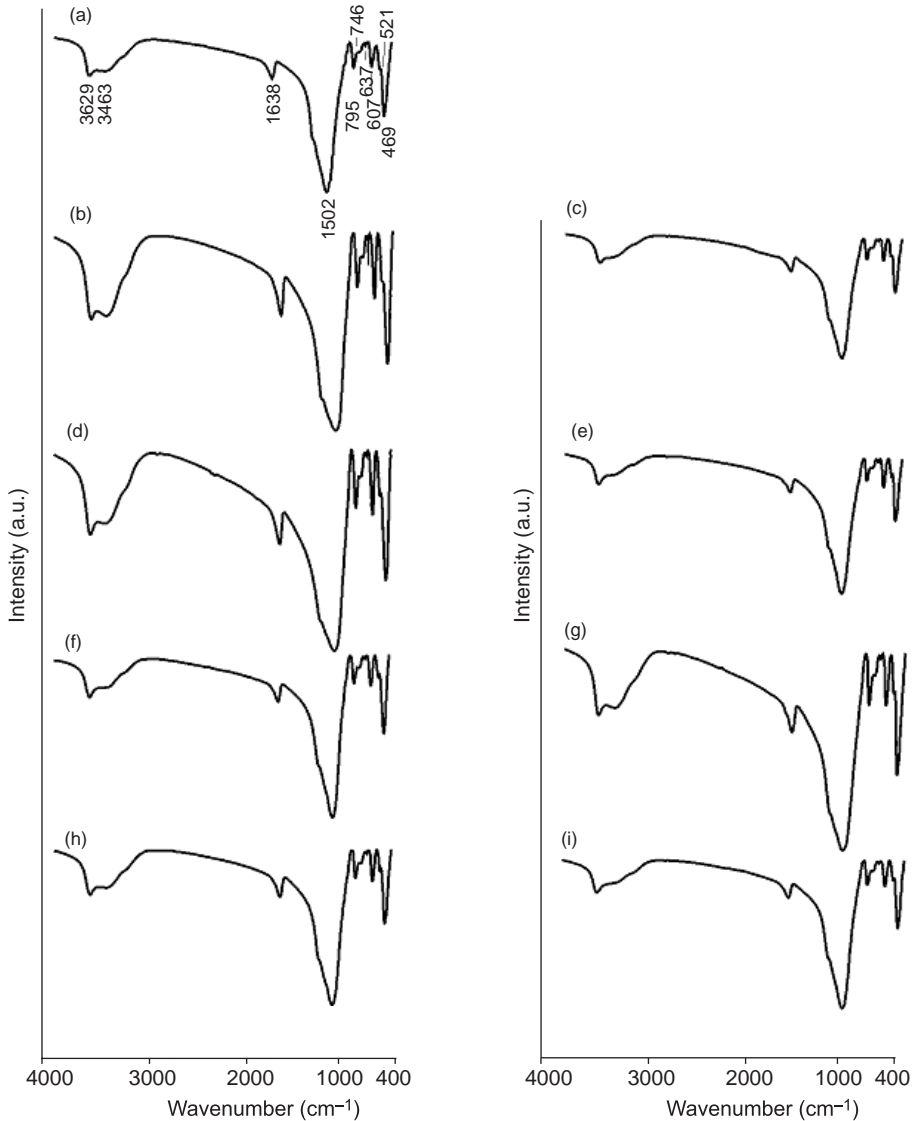


Figure 4. IR spectra of (a) natural clinoptilolite, (b) Na^{+} -modified clinoptilolite from 0.1 N solution, (c) Na^{+} -modified clinoptilolite from 1.0 N solution, (d) K^{+} -modified clinoptilolite from 0.1 N solution, (e) K^{+} -modified clinoptilolite from 1.0 N solution, (f) Ca^{2+} -modified clinoptilolite from 0.1 N solution, (g) Ca^{2+} -modified clinoptilolite from 1.0 N solution, (h) Mg^{2+} -modified clinoptilolite from 0.1 N solution, (i) Mg^{2+} -modified clinoptilolite from 1.0 N solution.

obtained from various regions of the world and analyzed by the BET method (Armenta *et al.* 2001; Kowalczyk *et al.* 2006; Erdoğan *et al.* 2008; Faghiehian *et al.* 2008).

Infrared spectra

The IR spectra for the representative samples of natural clinoptilolite and the Na⁺-, K⁺-, Ca²⁺- and Mg²⁺-modified forms are depicted in Figure 4. Clinoptilolite is characterized by bands at 3630,

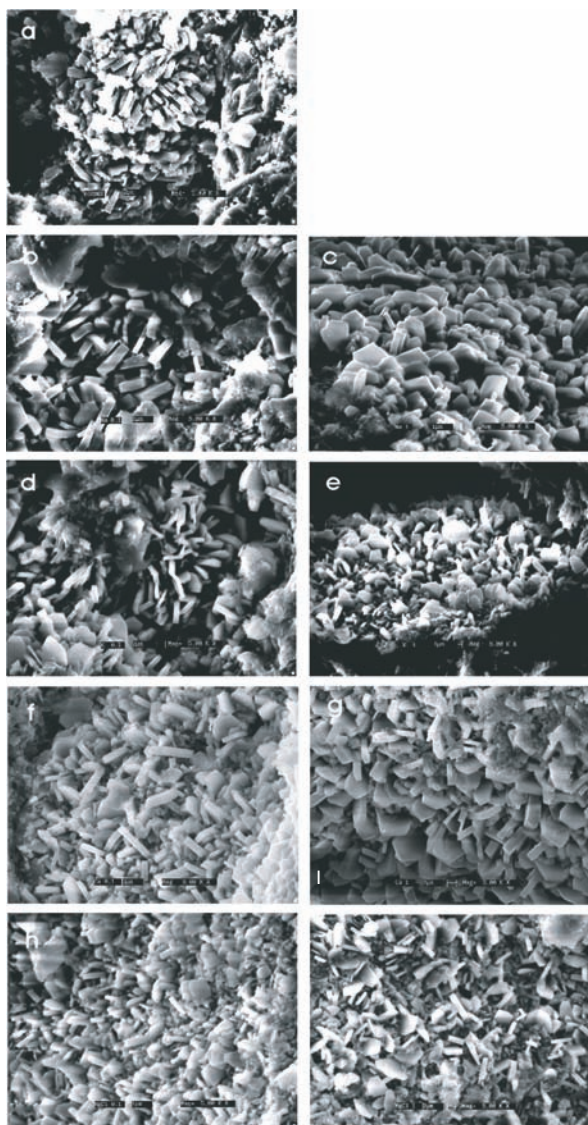


Figure 5. SEM images of (a) natural clinoptilolite, (b) Na⁺-modified clinoptilolite from 0.1 N solution, (c) Na⁺-modified clinoptilolite from 1.0 N solution, (d) K⁺-modified clinoptilolite from 0.1 N solution, (e) K⁺-modified clinoptilolite from 1.0 N solution, (f) Ca²⁺-modified clinoptilolite from 0.1 N solution, (g) Ca²⁺-modified clinoptilolite from 1.0 N solution, (h) Mg²⁺-modified clinoptilolite from 0.1 N solution, (i) Mg²⁺-modified clinoptilolite from 1.0 N solution.

1630, 1200, 1055, 673 and 607 cm^{-1} , respectively. The band at ca. 3630 cm^{-1} occurs in the frequency range normally associated with the OH-stretching vibration of the hydroxyl group in Al–OH–Si, and those of the hydrogen atoms positioned on different oxygen atoms in the structure (Doula 2007). The OH-stretching band in the 3600–3400 cm^{-1} region and the band at 1620 cm^{-1} have also been attributed to the free water of hydration (i.e. zeolitic water) and intermolecular hydrogen bonding of the monomeric structure (Serratosa 1962; Doula *et al.* 2002). In turn, the bands in the 1200–400 cm^{-1} range have been attributed to Si–O–Si and Si–O–Al vibrations in tetrahedral coordination and alumina- and silica-oxygen bridges (Farmer and Russell 1964; Moenka 1974; Mozgawa and Pichór 2006; Mozgawa and Bajda 2006).

Comparison of the spectra of the modified clinoptilolites with that of natural clinoptilolite revealed some differences. Thus, the peak heights in the spectra for 0.1 N modified forms of clinoptilolite increased relative to those for the natural material (other than the Ca^{2+} - and Mg^{2+} -forms). Furthermore, the sharpness of the peaks at 795, 607, 521 and 469 cm^{-1} were significantly greater in the spectra of the 0.1 N Na^{+} - and 0.1 N K^{+} -forms. In contrast, the spectra of the 1 N Na^{+} -, K^{+} - and Mg^{2+} -forms of clinoptilolite showed little significant change, except that the 1 N Ca^{2+} -form exhibited sharper peaks. Hence, the replacement of one Al^{3+} ion per unit cell by Na^{+} and K^{+} ions, and of two Al^{3+} ions per unit cell by Ca^{2+} and Mg^{2+} ions, resulted in frequency changes in the corresponding spectra (Fuentes *et al.* 1998).

SEM determinations

Natural and modified Gördes clinoptilolite crystals occur as euhedral to subhedral plates and in tabular forms, having lengths of $\pm 10 \mu\text{m}$ and thicknesses in the range 0.5–2.0 μm (see Figure 5). These crystals are coated with an irregular material which develops as a partial cement in the pores between the clinoptilolite crystals, possibly reflecting the substitution of Na^{+} , K^{+} , Ca^{2+} and Mg^{2+} ions into the crystal structure. The amount of this irregular material increased as the normality of the solution employed for modification increased.

CONCLUSIONS

The results of the studies reported may be summarized as follows:

1. The basal reflections in the XRD spectra of natural clinoptilolite which occur at 8.96, 3.99 and 2.97 Å remained unchanged following modification of the mineral to the K^{+} - and Ca^{2+} -forms. In contrast, the intensities of these peaks were reduced in the Na^{+} - and Mg^{2+} -forms. These results are consistent with the unit-cell volumes generated following modification by K^{+} and Ca^{2+} ions in the 10-membered ring relative to the value for natural clinoptilolite. However, these volumes remained unchanged when the eight-membered ring of the structure was modified by the introduction of Na^{+} and Mg^{2+} ions.
2. Both Na^{+} and Ca^{2+} ions exhibited high ion-exchange rates relative to Mg^{2+} and K^{+} ions. These changes were due to the fact that both Na^{+} and Ca^{2+} ions are bound symmetrically to the clinoptilolite structure relative to Mg^{2+} and K^{+} ions which are asymmetrically coordinated.
3. The high selectivity rates observed for univalent Na^{+} and K^{+} ions and the lower rates for divalent Mg^{2+} and Ca^{2+} ions demonstrated that the ion selectivity rates are negatively correlated with the ionic potentials of the ions.

4. The adsorption energy as determined by the Dubinin–Radushkevich relationship was in the range of 2–3 kJ/mol, suggesting physical adsorption which was supported by the applicability of the Langmuir adsorption isotherm.
5. The increase in the specific surface areas of the modified forms of clinoptilolite relative to that of natural clinoptilolite is possibly related to the entrances available to ions in the structure. Thus, the adsorption of ions occurs mainly in the various-sized pores in the zeolite. These results are consistent with the presence of irregular cement coatings in the pores between the clinoptilolite crystals as demonstrated by SEM, which possibly reflects substitution by Na^+ , K^+ , Ca^{2+} and Mg^{2+} ions.
6. The pore sizes in the modified clinoptilolite forms were smaller than those in the natural material. This decrease in pore size could be due to the positions of the ions in the structure, which result in channel blockage.
7. The magnitude of the specific surface areas could be negatively correlated with the ionic radii of the Na^+ , K^+ , Ca^{2+} and Mg^{2+} ions. Thus, the presence of ions with large ionic radii (e.g. Na^+ and K^+) led to the development of lower specific surface areas.
8. Other than the Ca^{2+} - and Mg^{2+} -forms, those prepared in solutions of lower normality (0.1 N) generally exhibited sharper IR spectra; in contrast, Ca^{2+} -forms prepared from 1 N solutions were characterized by sharper spectra while Mg^{2+} -forms exhibited less sharp spectra. This indicates that univalent Na^+ and K^+ ions are capable of substituting in clinoptilolites prepared at lower normality. On the other hand, these ions were only capable of substituting divalent Ca^{2+} and Mg^{2+} ions when preparation was conducted at higher normalities. These results are consistent with the results of ion-exchange and ion selectivity measurements.
9. The results obtained from the solid-phase analyses of the modified forms of clinoptilolite in this study are consistent with those obtained by other workers employing samples from various regions of the world.
10. Solid-phase analyses were preferred to solid/solution phase analyses in correlating binary systems of the various substituted forms of clinoptilolite. The binary ion-exchange rates of ions entering into and departing from the structure were not proportional to each other (e.g. with Na^+ -forms generated in 1 N solutions, 10% of the K^+ ions leave; in contrast, with K^+ -forms generated in 1 N solutions, 63% of the Na^+ ions leave). A similar observation was made on other binary systems with exchangeable ion forms.
11. The rates of ion exchange and the molecular-sieve character of clinoptilolite vary in response to the different solution normalities employed and the different type of ions. Hence, such factors could be important in any projected industrial application arising from this study.

ACKNOWLEDGMENTS

This study was supported financially by Eskişehir Osmangazi University within the framework of Project No. 199819018. The authors extend their thanks to Dr. Güneş Kürkçüoğlu for conducting the IR analyses.

REFERENCES

- Ackley, M.W. and Yang, R.T. (1991) *Ind. Eng. Chem., Res.* **30**, 2523.
Ackley, M.W., Giese, R.F. and Yang, R.T. (1992) *Zeolites* **12**, 780.

- Ackley, M.W., Rege, S.U. and Saxena, H. (2003) *Microporous Mesoporous Mater.* **61**, 25.
- Ames, L.L. (1960) *Am. Miner.* **45**, 689.
- Ames, L.L. (1964a) *Am. Miner.* **49**, 127.
- Ames, L.L. (1964b) *Am. Miner.* **49**, 1099.
- Armenta, G.A., Ramirez, G.H., Loyola, E.F., Castaneda, A.U., Gonzalez, R.S., Munoz, C.T., Lopez, A.J. and Castellon, E.R. (2001) *J. Phys. Chem. B* **105**, 1313.
- Breck, D.W. (1974) *Zeolite Molecular Sieves*, Wiley, New York.
- Breitländer, H. (1988) *Pulverproben, Festproben Mineralische, Metallurgische Werkstoffe, -Eichproben und Labormaterial GmbH, Hans-Sachs-Strasse 12, D-59077 Hamm, Germany.*
- Büyükkayol, M. (1988) *Etibank Bülteni* **32**, 108.
- Chelishchev, N.F., Marynova, N.S., Fakina, L.K. and Berenhshtein, B.G. (1974) *Dokl. Akad. Nauk SSSR* **217**, 1140.
- Cooney, E.L., Cooker, N.A., Shallcross, D.C. and Stevens, G.W. (1999) *Sep. Sci. Technol.* **34**, 2307.
- Doula, M., Ioannou, A. and Dimirkou, A. (2002) *J. Colloid Interface Sci.* **245**, 237.
- Doula, M.K. (2007) *Chemosphere* **67**, 731.
- Dyer, A. and White, K.J. (1999) *Thermochim. Acta* **340**, 341.
- Erdem, E., Karapınar, N. and Donat, R. (2004) *J. Colloid Interface Sci.* **280**, 309.
- Erdoğan, B., Sakızci, M. and Yörükoğulları, E. (2008) *Appl. Surf. Sci.* **254**, 2450.
- Faghihian, H., Talebi, M. and Pirouzi, M. (2008) *J. Iranian Chem. Soc.* **5**, 394.
- Falamakia, C., Mohammadi, A. and Sohrabib, M. (2004) *Colloids Surf. A* **246**, 31.
- Farmer, V.C. and Russell, J.D. (1964) *Spectrochim. Acta* **20**, 1149.
- Fuentes, F.A., Santo Domingo, J.W. and Hazen, T.C. (1998) *Water Res.* **32**, 2154.
- Gündoğdu, M.N. (1982) *Doctoral Thesis*, Hacettepe Üniversitesi, pp. 386.
- Gottardi, G. and Galli, E. (1985) *Natural Zeolites, Minerals and Rocks*, Springer Verlag, Berlin, Germany.
- Howe, R.F. (1993) *Application of Zeolites for Environmental Solutions Conf.*, University of New South Wales, Sydney, Australia, Feb. 16–17.
- Hulbert, M.H. (1987) *Clays Clay Miner.* **35**, 458.
- İnel, O., Yörükoğulları, E., Orhun, Ö. and Albayrak, F. (1992) *Chem. Acta Turcica* **19**, 77.
- Inglezakis, V.J., Loizidou, M.D. and Grigoropoulou, H.P. (2003) *J. Colloid Interface Sci.* **261**, 49.
- Karadag, D., Koc, Y., Turan, M. and Armagan, B. (2006) *J. Hazard. Mater. B* **136**, 604.
- Kowalczyk, P., Sprynskyy, M., Terzyk, A.P., Lebedynets, M., Namiesnik, J. and Buszewski, B. (2006) *J. Colloid Interface Sci.* **297**, 77.
- Langella, A., Pansini, M., Cappelletti, P., de Gennaro, B., de Gennaro, M. and Colella, C. (2000) *Microporous Mesoporous Mater.* **37**, 337.
- MBH Reference Materials (1998/99) MBH Analytical Ltd., Barnet EN5 4DJ, U.K., ISO 9002 Accredited Company Cert. No. 0524, 99pp.
- Moenka, S.H. (1974) "The Three-dimensional Silicates, Borosilicates and Beryllium Silicates", in Farmer, V., Ed, *The Infrared Spectra of Minerals*, Mineral. Soc. Monograph No. 4, Mineralogical Society, Twickenham, Middlesex, U.K.
- Mozgawa, W. and Bajda, T. (2006) *J. Mol. Struct.* **792**, 170.
- Mozgawa, W. and Pichór, W. (2006) "Properties of Clinoptilolite-based Autoclaved Composites", *Proc. Int. Symp. "Brittle Matrix Composites 8"*, Brant, A.M., Li, V.C., Marshall, H., Eds, Woodhead Publishing Ltd., Cambridge, U.K./Zturek RSI, Warsaw, Poland, p. 477.
- Mumpton, F.A. (1960) *Am. Miner.* **45**, 351.
- Mumpton, F.A. (1999) *Proc. Nat. Acad. Sci. U.S.A.* **96**, 3463.
- Müller, G. (1967) *Methods in Sedimentary Petrology*, E. Schweizerbart'sche Verlagsbuchhandlung, Stuttgart, Germany.
- Osmanlioglu, A.E. (2006) *J. Hazard. Mater. B* **137**, 332.
- Rehakova, M., Cuvanová, S., Dzivak, M., Rimar, J. and Gavalova, Z. (2004) *Curr. Opin. Solid State Mater. Sci.* **8**, 397.

- Serratos, J.M. (1962) "Dehydration and Rehydration Studies of Clay Minerals by Infrared Absorption Spectra", *Proc. 9th Nat. Clays Conf.*, Pergamon Press, New York, p. 412.
- Sing, K.S.W. (1985) *Pure Appl. Chem.* **57**, 603.
- Smiciklas, I., Dimovic, S. and Plecas, I. (2007) *Appl. Clay Sci.* **35**, 139.
- Sprynsky, M. (2009) *J. Hazard. Mater.* **161**, 1377.
- Taffarel, S.R. and Rubio, J. (2009) *Miner. Eng.* **22**, 4.
- Tanaka, H., Yamasaki, N., Muratani, M. and Hino, R. (2003) *Mater. Res. Bull.* **38**, 713.
- Vainstein, B.K. (1981) *Modern Crystallography I*, Springer Verlag, Berlin, Germany.
- Wang, Y.F., Lina, F. and Pang, W.Q. (2007) *J. Hazard. Mater.* **142**, 160.
- Zhao, H., Vance, G.F., Urynowicz, M.A. and Gregory, R.W. (2009) *Appl. Clay Sci.* **42**, 379.