Journal of Inclusion Phenomena and Molecular Recognition in Chemistry **24:** 263–272, 1996.

Intercalation Compounds between Nicotine and a High Surface Area Saponite

M. SUÁREZ BARRIOS,[1] M.A. VICENTE-RODRÍGUEZ[2,*] and
J.M. MARTÍN POZAS[1]
[1]*Area de Mineralogía y Cristalografía, Departamento de Geología, Facultad de Ciencias, Plaza de la Merced, s/n. 37008-Salamanca Spain.*
[2]*Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Plaza de la Merced, s/n. 37008-Salamanca Spain.*

(Received 24 November 1995; in final form: 5 March 1996)

Abstract. The retention of nicotine by a high surface area saponite has been studied using two methods: (1) in repose at room temperature, and (2) heating at 70 °C under reflux. Different contact times were considered for each method. The intercalation compounds obtained were studied by chemical analysis, X-ray diffraction, infrared spectroscopy and thermal analysis. Nicotine is retained both in the interlayer region and at the edge of clay particles. The amount of nicotine retained in the interlayer region has been calculated from thermal analysis and CHN measurements.

Key words: Nicotine, saponite, interlayer compounds, intercalate.

1. Introduction

Laminar silicates are able to form interlayer compounds with organic molecules by intercalation of these molecules in the interlayer region of the clay and expansion, if necessary, of this interlayer space. The size of the organic molecule, the presence on it of groups able to interact by H-bonding or by formation of a coordination compound with the compensating cations of the clay and the nature of the clay determine the formation of the interlayer compounds [1]. If the organic molecule is a pesticide, its elimination depends strongly on the interaction with the silicate clays in the soil.

Nicotine [3-(1-methyl-2-pyrrolidinyl) pyridine] is a polar compound in which the N atom of the pyrrolidine ring is the most active part, with the pyridine N also being active. Nicotine is toxic by inhalation or contact, acting on the central nervous system. In agriculture, a 40% solution of nicotine sulphate has been used as insecticide, combinations with bentonite being used for this application. In veterinary applications, nicotine has been used as an ectoparasiticide and antihelmintic [2]. Singhal *et al.* [3, 4] have studied the interaction of nicotine with dickite and montmorillonite, focusing their work on obtaining the adsorption isotherms and discussion of the possible mechanisms of the nicotine–clay interaction, both by

---

[*] Author for correspondence.

physical adsorption and chemisorption. They found that the adsorption is higher when H^+ or Al^{3+}-exchanged montmorillonites are used and lower when Ba^{2+}, Ca^{2+}, Na^+ and NH_4^+-exchanged samples are studied.

Saponite is a trioctahedral smectite, originating as a sedimentary rock and as a product of the hydrothermal alteration and weathering of basalts and ultramafic rocks. In some aspects, saponite is very similar to vermiculite. Thus, saponite has a negatively charged tetrahedral sheet, partially balanced by the positive charge in the octahedral sheet [5]. It has an excellent pillaring ability, the pillared compounds being used in catalysis and adsorption [6, 7]. New important deposits of saponite have recently been described in the literature [8–11].

Although montmorillonite has been widely used for preparing interlayer compounds with a large variety of organic substances, very little has been reported on the study of these compounds with saponite. Thus, the aim of the present work is to study the formation of interlayer compounds between nicotine and a high surface area saponite. The mechanism of the intercalation and the influence of the method used and of the interaction time in the formation of interlayer compounds are discussed.

2. Experimental

A saponite from Yunclillos (Toledo, Central Spain), supplied by TOLSA, S.A. was employed. The sample was very pure and only small amounts of quartz and traces of sepiolite were observed as impurities. The <2 μm fraction obtained after aqueous decantation of raw saponite was used for retention experiments.

(−) Nicotine (>99%, for synthesis), liquid at room temperature, was supplied by Dr. Th. Schuchardt & Co. (Hohenbrunn, Germany). It was used as supplied, without further purification.

The retention experiments were carried out under two different conditions: (1) in repose at room temperature; (2) heating at 70 °C with continuous stirring and under reflux. In both cases, samples were maintained under the described conditions for 2, 5 and 8 days. In all experiments, 1.5 grams of saponite and 5 mL of nicotine were used, the saponite always being covered by the nicotine. After treatment, the different samples were filtered and dried at 50 °C.

Elemental analysis of the silicate was carried out by plasma emission spectrometry using a Perkin-Elmer emission spectrometer, Plasma II model. The sample was previously digested with a hydrofluoric–nitric acid mixture, under pressure in a PTFE autoclave. The carbon, hydrogen and nitrogen content in the intercalated samples was measured using a Perkin-Elmer CHN 2400 analyzer.

The X-ray diffraction study employed a Siemens D–500 diffractometer with filtered Cu K_α radiation, working at 40 kV and 30 mA (1200 W). This apparatus is equipped with a DACO-MP data station and uses Diffract-AT software.

The IR spectra were obtained using a Perkin-Elmer M1700 2B FT-IR spectrophotometer, in the region between 4000 and 350 cm^{-1} and using the KBr pellet technique. Pellets were obtained by mixing the sample and dried KBr (1 : 300 by wt. aprox.), and applying a pressure, under vacuum, of 8 ton/cm^2. The spectrum of nicotine was obtained from a drop of this compound deposited between two pellets of KBr.

Thermal analyses were performed on Perkin–Elmer analyzers, models 1700 and TGS–2 for DTA and TGA, respectively, both equipped with a 3600 data station. In all cases the heating rate was 10 °/min and a 60 cm^3/min air flow was used.

3. Results and Discussion

3.1. RAW SAPONITE

As indicated, saponite from Yunclillos, supplied by TOLSA, S.A. was employed for the present study. The Yunclillos saponite deposit is located in Toledo Province, Central Spain, a zone very rich in Mg-silicates. This deposit has been recently discovered and not much work has been carried out on this clay. Only recently we have studied its physicochemical properties and the improvement of these properties by acid activation [12].

Raw saponite is very pure and only small amounts of quartz and sepiolite are observed as impurities. The <2 μm fraction obtained after aqueous decantation of this saponite was used for retention experiments. Some of the data on this <2 μm fraction are [12]:

Chemical composition: SiO_2: 49.45; Al_2O_3: 4.72; Fe_2O_3: 1.29; MgO; 24.34; TiO_2: 0.20; MnO: 0.03; CaO: 0.78; Na_2O: 0.07; K_2O: 0.44; H_2O: 18.31%.

Structural formula: $[Si_{3.71}\ Al_{0.29}]\ O_{10}\ (OH)_2\ [Al_{0.13}\ Mg_{2.58}\ Fe_{0.07}\ Ti_{0.009}\ Mn_{0.02}]\ [Ca_{0.062}\ Mg_{0.12}\ Na_{0.010}\ K_{0.042}]$.

Cation exchange capacity (CEC): 115 mEq/100 g.

BET surface area: 165 m^2/g.

3.2. INTERLAYER COMPOUNDS

Interlayer compounds between saponite and nicotine were prepared by two different methods and with different contact times. The interlayer compounds change in color depending on the time of contact, from yellow (repose, 2 days) to red-brown (reflux heating, 8 days). The differences in colour may be due to coordination between the nicotine and the Fe(III) cations in the octahedral sheet of saponite. These compounds were first studied by X-ray diffraction. The <2 μm saponite has a basal spacing of 14.53 Å. In the compounds obtained after saponite–nicotine interaction, the basal spacing increases to values of 15.51–16.51 Å (Table I). No significant differences were observed between the basal spacing of samples obtained by repose or reflux heating method. The time of contact for the series prepared for each of the methods considered does not have a great influence on the basal spacing. For the repose method, the sample obtained after 2 days of contact has the larger basal

Table I. Basal spacings of saponite and saponite-nicotine intercalation compounds.

Sample	Basal spacing (Å)
Raw saponite	14.53
Repose 2 days	16.51
Repose 5 days	16.17
Repose 8 days	15.45
Reflux heating 2 days	15.51
Reflux heating 5 days	16.03
Reflux heating 8 days	15.94
Repose 2 days washed with water	15.83
Repose 2 days washed with ethanol	14.52
Repose 2 days washed with benzene	15.47
Repose 2 days washed with cyclohexane	15.33

Rep.=Repose method; R. heating=Reflux heating method.

spacing, which decreases for samples in which the time of contact is longer. When the reflux heating method is considered, the sample obtained after 5 days of contact has the larger spacing, samples obtained after 2 or 8 days having smaller spacings.

If the basal spacing of totally dehydrated saponite (9.77 Å) is considered, the molecules in the interlayer occupy 5.73–6.73 Å. This thickness does not permit the formation of multilayer compounds, but only a monolayer. The different basal spacings indicate that α-type complexes are formed; that is, that nicotine molecules are situated coplanar to the clay layers, parallel to them. The differences in the thickness of the interlayer region in the different samples must be due to the different orientation of nicotine molecules in this region, depending on the treatment conditions and, perhaps, on the different elimination of water molecules in each sample. Singhal and Singh [3] have reported maximum basal spacings of 15.22 Å when preparing interlayer compounds between nicotine and montmorillonite, explaining the differences in basal spacing by the reorientation of nicotine molecules in the interlayer space so as to facilitate a closer packing on the surface. In saponite, the increase in basal spacing is higher than that reported for montmorillonite but cannot be explained by formation of bilayer compounds; the different orientation and packing of the nicotine molecules are responsible for the different basal spacings observed.

The FT-IR spectra of raw saponite, nicotine and the intercalated compound are given in Figure 2. The assignment of the different bands is given in Table II. As observed, the bands of saponite are the most intense in the intercalation compound and only some small bands of nicotine are clearly observed. Bands

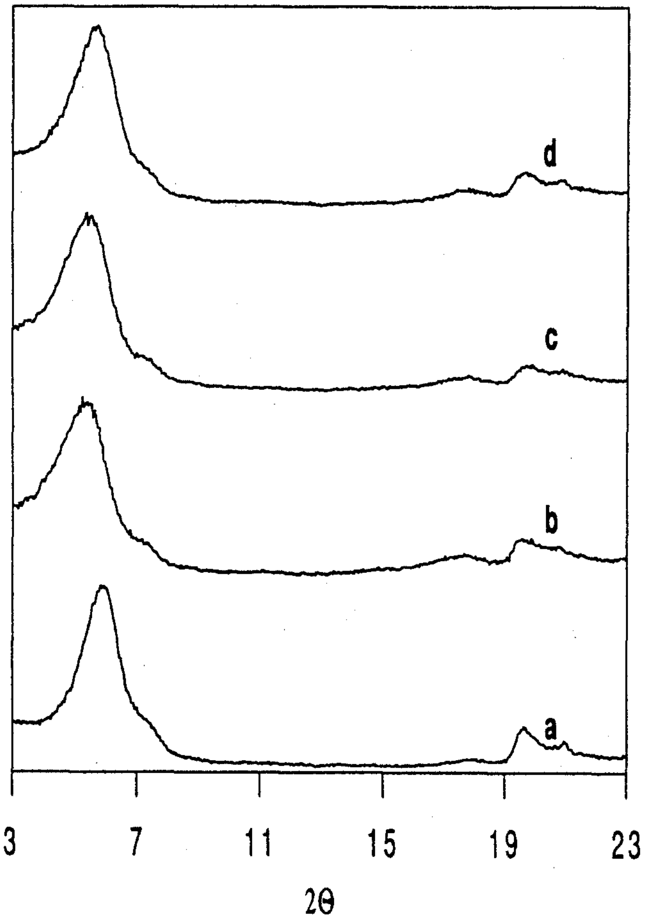

Figure 1. X-ray diffractograms of natural saponite (a) and saponite–nicotine intercalation compounds obtained after repose for 2(b), 5(c) and 8(d) days.

corresponding to nicotine are observed in the regions 3000–2700, 1600–1300, 810 and 715 cm^{-1}. At high wavenumbers, bands corresponding to OH, NH and CH bonds are found. The position of these bands does not vary significantly from nicotine to the interlayer complexes, very small differences being observed when comparing the spectra of free nicotine and saponite with those of the interlayer compounds. The most significant variation in this region is the great increase in the intensity of the Mg_3OH mode at 3682 cm^{-1}, which may be due to the exclusion of water molecules from the interlayer during intercalation, preventing H-bonding of the Mg_3O—H hydroxyl and making this mode more intense.

Between 1650–1300 cm^{-1}, a large number of bands are observed, the first corresponding to the water deformation mode and all the other corresponding to nicotine molecules. The presence of water bands indicates that interlayer water is

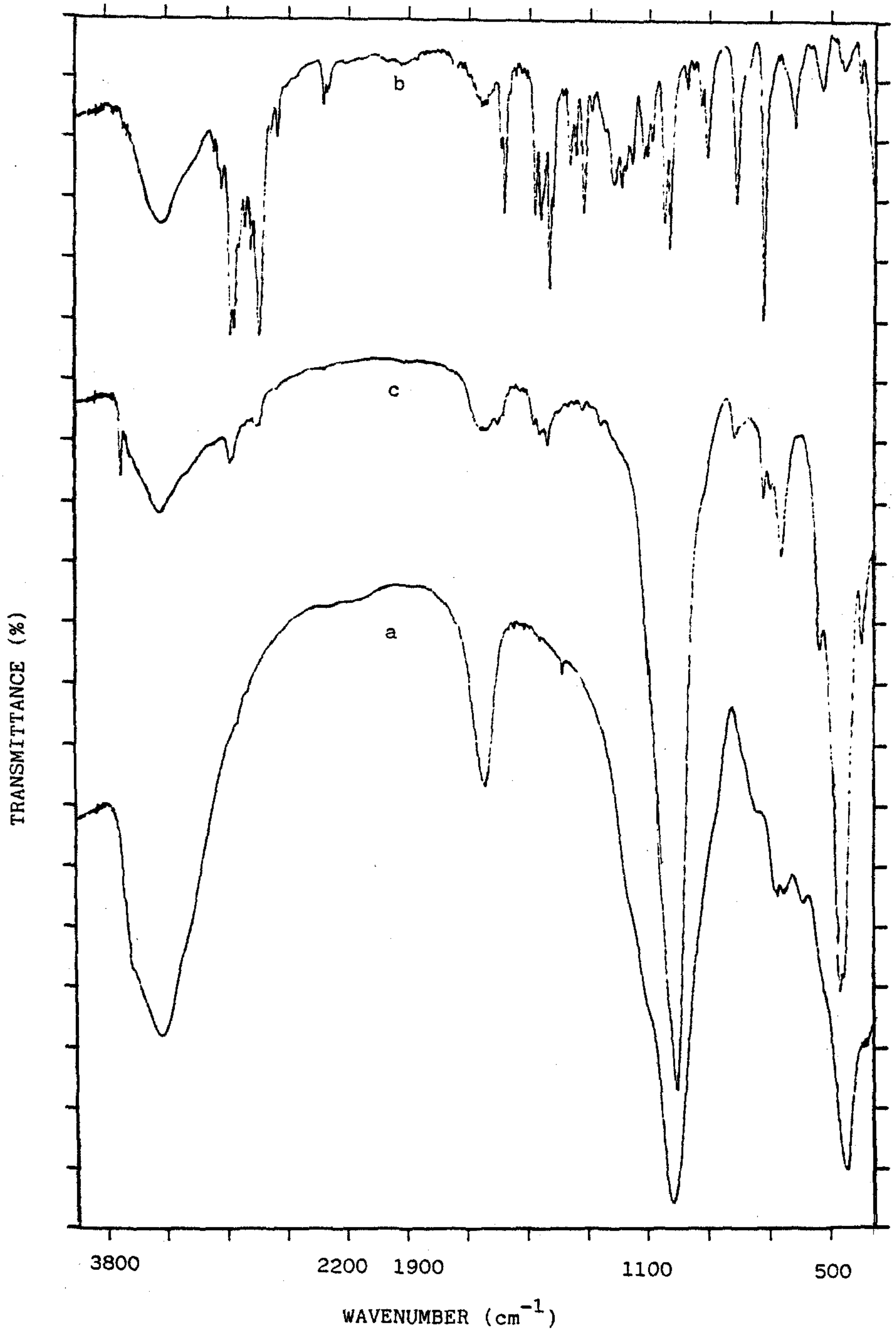

Figure 2. FT-IR spectra of natural saponite (a), pure nicotine (b) and the saponite–nicotine intercalation compound obtained after reflux heating for 2 days (c).

Table II. Assignment of the FT-IR absorption bands of saponite and saponite-nicotine intercalation compounds.

	Wavenumber (cm^{-1})		
Assignment	Saponite	Nicotine	Interlayer compd.*
ν (O—H)	3678(sh), 3426	–	3682, 3426
ν (N—H)	–	3422	3426
ν (C—H)	–	2968, 2779	2968, 2782
ν (ring)	–	1577	1580
ν (C—H) + δ (C—H)	–	1478, 1458, 1428	1479, 1461, 1432
δ (H_2O)	1637	–	1640
Overtone	–	1316	1318
δ (ring) + δ (C—H)		1045, 1024	–
Si—O—Si	1011	–	1002
δ (ring) + γ (C—H)		807, 717, 617	808, 716
Si—O—Si	658	–	657
Si—O—Mg	448	–	461, 449

*Similar in all the interlayer compounds. Data on the solid obtained after 2 days under reflux is given as example.

not completely substituted by nicotine molecules. Bands due to nicotine appear in the interlayer compounds almost at the same wavenumber as in free nicotine, only small shifts to higher wavenumbers of 3–4 cm^{-1} being observed. The breathing mode of the pyridine ring is observed at 1026 cm^{-1} in nicotine and cannot be observed in the interlayer compounds because of the very intense vibration in this region of clay Si—O—Si bonds. The absorption maximum of Si—O—Si bonds in saponite is centered at 1011 cm^{-1}, while in the intercalation complexes the maximum is at 1006 cm^{-1}, perhaps due to the influence of nicotine. The breathing mode has been observed to be very sensitive to coordination by σ donation [13]; this can be confirmed by Raman spectroscopy but, unfortunately, this technique was not available for the present work. The band at 658 cm^{-1}, due to Si—O—Si bonds, appears at the same wavenumber in the interlayer compound, encompassing the band of nicotine in this region, observed at 615 cm^{-1} in the free molecule. Also the band of the silicate at 460–450 cm^{-1}, due to Si—O—Mg bonds, clearly appears in the intercalated solids.

The TGA and DTA curves of saponite and the intercalated compounds are given in Figure 3. Saponite shows the usual behaviour of this clay, with weight losses from 30 to 200 °C, due to the loss of adsorbed water, a very gentle slope from 200 to 800 °C and, above this temperature, the loss of constitution hydroxyl groups, these losses adding up to 18% of the weight of the clay. In the DTA curve, the corresponding endothermal effects due to the loss of water molecules and hydroxyl groups are observed, giving a final exothermic effect at 845 °C due to the final phase change from saponite to enstatite [14].

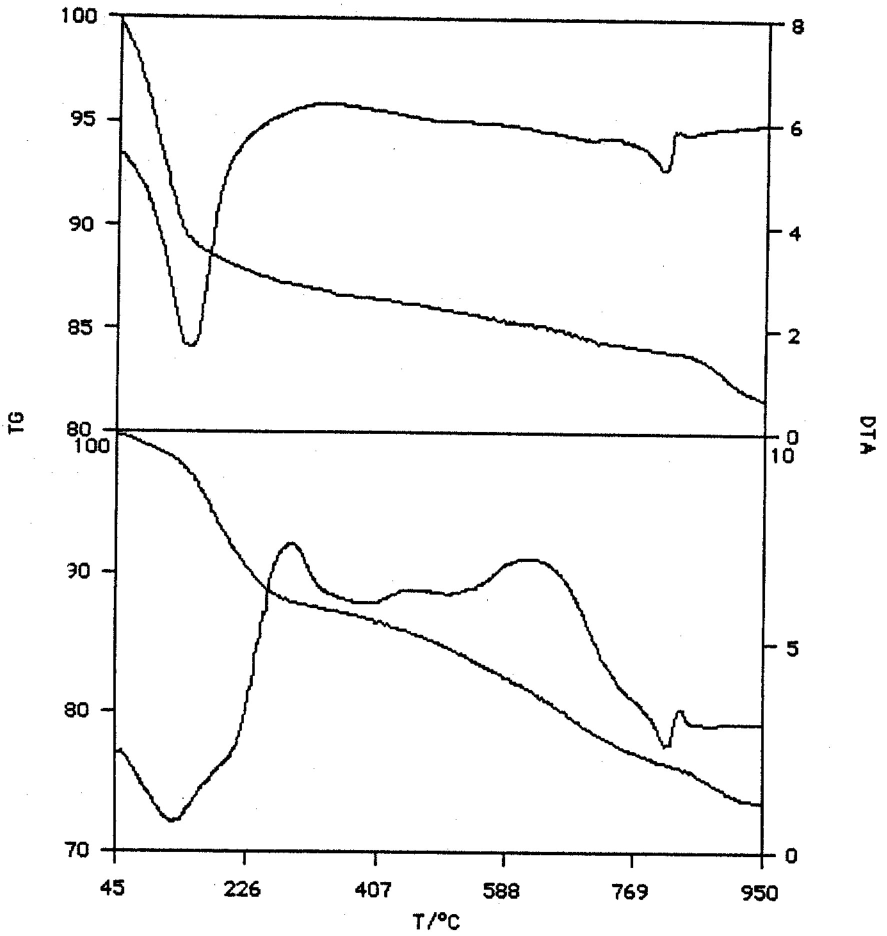

Figure 3. TGA and DTA curves of natural saponite (upper traces) and saponite–nicotine intercalation compound obtained after repose for 8 days (lower traces).

In the interlayer compounds, a very different behaviour is observed. The first weight loss appears between 30 and 300 °C, with a very broad associated endothermal effect. Most of the nicotine will be eliminated in this step, together with the small amounts of water that can remain in the solids. The boiling point of free nicotine, with partial decomposition, is 247 °C. In the region between 300 and 600 °C, two endothermal effects are observed, centered at 425 and 540 °C, which must correspond to the loss of the last fragments of nicotine and/or to the loss of more intensely retained nicotine, perhaps strongly chemisorbed. At higher temperature, the thermal behaviour of intercalated solids is very similar to that of saponite, with the final phase change to enstatite.

In order to see if all the nicotine is eliminated in the first thermal process, a portion of the sample intercalated in repose for 5 days was heated at 250°C for 2 h. The X-ray diffractogram of the sample thus obtained shows a peak at 13.40 Å, while its CHN analysis confirms the presence of a small amount of organic compounds, thus confirming that nicotine has not been completely eliminated at this temperature. When heated at 550 °C for 2 h, a very small amount of nicotine degradation organic product remains in the solid, and a wide peak between 10–12 Å is obtained in its X-ray pattern.

The results of TG analyses were used to discover the amount of nicotine retained in the different intercalation compounds. This amount varies irregularly. The weight losses deduced from the TG curves of the intercalated compounds vary from sample to sample, reaching values between 26 and 37% of the weight of the solids. The different amount retained by each solid indicates that nicotine is retained not only in the interlayer space, where the nicotine molecules may have different stackings, but variable amounts are also retained at the edges of the clay particles.

In order to obtain interlayer compounds without nicotine retained at the edges of saponite particles, careful washings of the solid were carried out. The sample obtained after repose for 2 days was chosen for investigating the effect of washing with water, ethanol, cyclohexane and benzene. The basal spacings of samples thus obtained are given in Table I. When water or ethanol is used for washing the solid, nicotine is completely removed and substituted by the solvents. In contrast, when cyclohexane or benzene is used, nicotine remains in the interlayer, as confirmed by CHN analyses. These analyses permit us to calculate the amount of nicotine retained in the interlayer, giving values of 178 and 189 mg of nicotine per gram of saponite for the solids washed with cyclohexane and benzene, respectively; values that agree with those obtained from TG analyses.

4. Conclusions

Intercalation compounds are obtained by treatment of saponite with nicotine, under conditions of repose at room temperature or heating at 70 °C and different times of treatment. Under the conditions employed, monolayer compounds are obtained, although with different basal spacings, attributable to different packing of nicotine molecules. Basal spacings that would permit the formation of bilayer compounds are not reached even under the more drastic conditions used.

Nicotine is retained both in the interlayer region and at the edges of saponite particles, reaching almost 40% of the weight of the solids. When the nicotine bonded at the edge of the particles is washed, the amount of nicotine retained in the interlayer region was found to be 185 mg/gram of saponite.

Acknowledgements

The authors thank Dr. Benigno Macías (Departamento de Química Inorgánica, Universidad de Salamanca) for CHN measurements. Finnancial support of Junta de Castilla y León (J090 Project) is also acknowledged.

References

1. B. K. G. Theng: *The Chemistry of Clay-Organic Reactions*, Adam Hilger, London (1974).
2. The Merck Index. Eleventh edition. Merck & Co., Inc. Rahway, N.J., USA. Susan Budavani, Editor. p. 6431, (1989).
3. J. P. Singhal and R. P. Singh: *Indian J. Chem.* **10**, 1100 (1972).
4. J. P. Singhal and G. K. Gupta: *Agrochimica,* **21**, 153 (1977).
5. De la Calle, C. and Suquet, H.: 'Vermiculites', in S. W. Bailey (ed.), *Hydrous Phyllosilicates*, Mineralogical Society of America, Washington. *Rev. Mineralogy* **19**, 455–496 (1988).
6. S. Chevalier, R. Franck, J. F. Lambert, D. Barthomeuf and H. Suquet: *Appl. Catal. A: General*, **110**, 153 (1994).
7. L. Bergaoui, J. F. Lambert, H. Suquet and M. Che: *J. Phys. Chem.* **99**, 2155 (1995).
8. E. Galán, A. Alvarez and M. A. Esteban: *Appl. Clay Sci.* **1**, 295 (1986).
9. H. Kodama, C. R. de Kimpe and Dejou: *Clays Clay Miner.* **36**, 102 (1988).
10. R. H. April and D. M. Keller: *Clays Clay Miner.* **40**, 22 (1992).
11. D. Beaufort and A. Meunier: *Clay Miner.* **29**, 47 (1994).
12. M. A. Vicente, M. Suárez, M. A. Bañares Muñoz and J. D. López González: *Langmuir*, **12**, 566 (1996).
13. S. Akyüz, T. Akyüz and J. E. D. Davies: *J. Incl. Phenom.* **18**, 123 (1994).
14. R. C. Mackenzie: Simple phyllosilicates based on Gibbsite- and Brucite-like sheets. in R. C. Mackenzie (ed.), *Differential Thermal Analysis*, Academic Press, London. **I**, 497–537, (1970).