ACIDITY OF MONTMORILLONITE-(Ce OR Zr) PHOSPHATE CROSS-LINKED COMPOUNDS

F. del Rey-Bueno, A. García-Rodríguez, A. Mata-Arjona and F. J. del Rey-Pérez-Caballero

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada
Av. Fuentenueva s.n., 18071 Granada, Spain

Abstract—The nature and number of acid sites per unit weight on a series of materials obtained by interaction of a montmorillonite with zirconium or cerium hydrogenphosphates precipitated *in situ* by reaction between their precursors have been investigated.

The quantitative determination of the surface acidity has been carried out by three different methods: titration with triethanolamine in aqueous media; TG analysis of the samples after n-butylamine treatment and vacuum desorption; and chemisorption of NH_3 at 239.8 K. Additional information about the nature of the surface acid sites has been obtained from the IR spectra of the samples with bases adsorbed.

Results show that the acid site density on the montmorillonite-cerium or zirconium phosphate cross-linked compounds is greater than on the parent montmorillonite and increases as the content in tetravalent metal phosphate rises throughout the different series. Also the number of acid sites for the cerium phosphate-montmorillonite materials is lower than for zirconium ones and the characteristics obtained depend on the bases used for their evaluation.

The presence of two IR adsorption bands at 1400 and 3145 cm^{-1}, assigned to the NH_4^+ ion, and the absence of the 1170–1361 cm^{-1} bands, characteristic of the NH_3 adsorbed on a Lewis site, strongly suggest the Brönsted character of the acidity of these compounds.

Key Words—Layered phosphates, Montmorillonite, Surface acidity.

INTRODUCTION

In the 1950's, Tamele (1950) postulated that the principal factors determining the activity of the silica-alumina catalysts are acid strength and the number of acid sites on its surface. Since then, much research has focused on the evaluation of surface acidity Benesi (1957) used n-butylamine to evaluate the surface acidity of a catalyst and Mapes and Eischens (1954) chemisorbed NH_3 on a silica-alumina catalyst and studied the infrared spectrum of the ammonia-catalyst surface complex. These researchers established the existence of two kinds of acid sites: one in which NH_3 is chemisorbed by formation of a coordinated bond between the Lewis base (NH_3) and the corresponding Lewis surface acid site, and another in which there is a proton transfer from a Brönsted site to the base to form NH_4^+.

On the other hand, considering the existence of $\equiv P-OH$ acid groups in the layers of tetravalent metal phosphates with layered structure, and the affinity of such groups for ammonia and amines, intercalation of both has been used to study the structural and surface characteristics of those materials (Clearfield *et al* 1976, Alberti *et al* 1982, Liansheng Li *et al* 1991). These works enable one to reach the conclusion that each $\equiv P-OH$ group retains one ammonia or amino molecule, yielding the diammonium salt form as the product, following the reaction (Alberti *et al* 1982)

$$[M(PO_4)_2]H_2 \cdot H_2O + 2NH_3$$
$$\rightarrow [M(PO_4)_2](NH_4)_2 \cdot H_2O$$
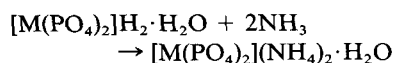
The surface acidity of these materials has also been studied by the intercalation of NH_3 and amines of different basicity (Hattori *et al* 1978) using for instance, pyridine and n-butylamine. In this work the surface acidity of the Ce or Zr phosphate-montmorillonite cross-linked compounds synthesized by us are quantitatively evaluated. Three different methods are used: 1) titration with a triethanolamine aqueous solution (Primo-Yufera *et al* 1981); 2) TG analysis of the previously n-butylamine saturated samples (Forni 1973); and 3) study of the NH_3 adsorption isotherms at 239.8 K. The first method (1) is normally applied to the measurement of the surface acidity of clays and soils. The latter two methods (2 and 3) are usually used for the determination of surface acid centres in adsorbent solids. The corresponding IR spectra have been used to determine how the different bases are retained on the surface of the studied adsorbents. The effect of temperature on the retention of NH_3 by the samples has also been studied.

EXPERIMENTAL METHODS

Series of montmorillonite-(Ce or Zr) phosphate crosslinked compounds were synthesized by reacting a cerium or zirconium cation exchanged montmorillonite with phosphoric acid under appropriate conditions of concentration, addition rate and temperature (García-Rodríguez *et al* 1995). The samples obtained are labelled M, 2M, 4M, 5M and 10M, according to the concentration of tetravalent metal ion solution (M is used in state of C for cerium samples and Z for zir-
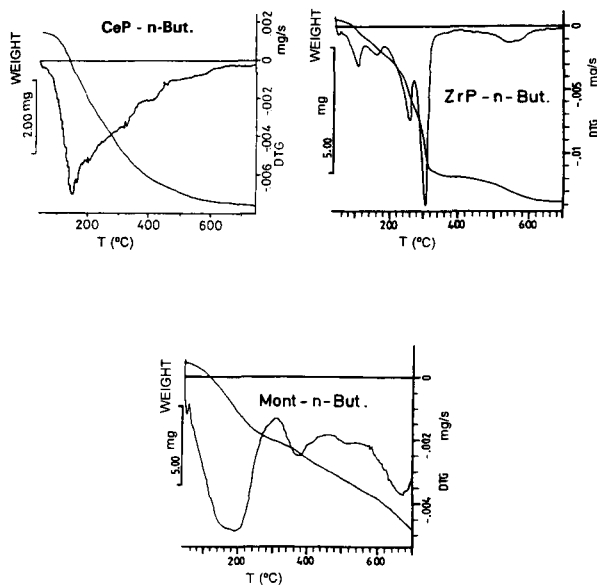
Figure 1. ATG-DTG curves of previously n-butylamine saturated CeP, ZrP and montmorillonite.

conium ones). The samples labelled with a prime, M', (C' or Z') correspond to addition of a double quantity of phosphoric acid compared to M, C or Z, which are the theoretical quantities needed for all the ions added to form $M(HPO_4)_2 \cdot xH_2O$.
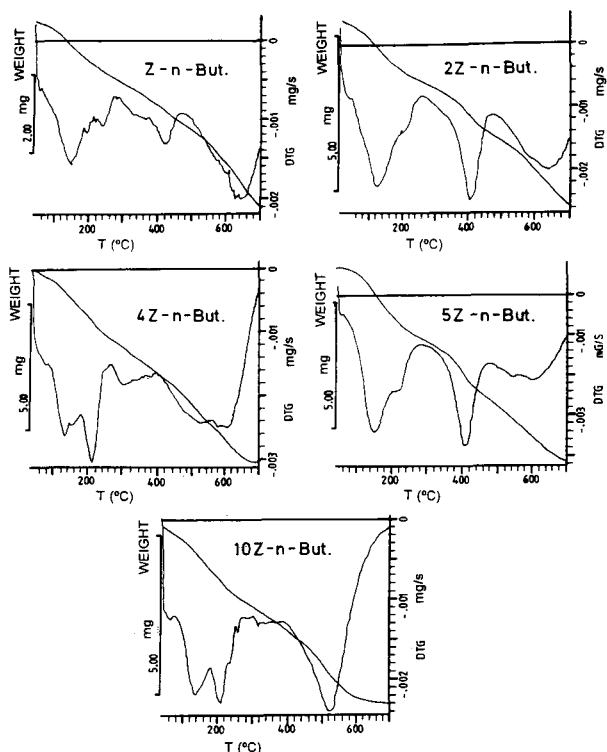

Figure 2. ATG-DTG curves of previously n-butylamine saturated samples of Z series.

Table 1. Surface acidity of the studied compounds.

	Surface acid sites/10^{20} (a.s.g^{-1})		
Sample	Trietha-nolamine	n-butyl-amine	Ammonia
Mont.	1.7	0.4	17.1
CeP	—	10.2	7.0
C	6.5	0.5	18.1
2C	6.3	1.3	17.4
4C	6.4	1.0	19.6
5C	6.7	2.0	16.9
10C	9.0	2.4	16.7
4CR	8.8	1.2	17.5
5CR	9.0	2.9	16.8
10CR	10.1	4.3	19.0
C'	6.8	0.9	17.1
2C'	7.3	0.9	18.0
4C'	8.6	1.9	19.3
5C'	9.2	4.0	19.4
10C'	11.5	3.8	18.5
4C'R	10.8	3.9	18.9
5C'R	9.8	5.0	18.2
10C'R	8.8	4.3	18.5
ZrP	—	27.7	—
Z	5.8	4.8	17.8
2Z	7.0	4.5	18.1
4Z	10.7	9.1	20.4
5Z	12.3	7.3	20.8
10Z	16.6	12.2	22.9
4ZR	12.4	9.9	23.1
5ZR	13.3	11.4	21.8
10ZR	13.8	12.8	22.2
Z'	8.6	6.3	18.4
2Z'	10.7	7.8	19.9
4Z'	13.5	11.8	21.8
5Z'	14.8	12.2	21.7
10Z'	14.5	15.0	23.0
4Z'R	14.9	10.9	19.6
5Z'R	13.8	11.9	21.2
10Z'R	13.4	12.1	23.6

Samples labelled with R (MR and M'R) were treated so as to achieve complete saturation of the exchange ion in the clay.

Acidity study

The "exchange acidity" is determined by titration of the H_3O^+ extracted from samples by means of a $BaCl_2$ and triethanolamine solution (Primo-Yufera *et al* 1981).

Following the method proposed by Forni (1973), samples of every prepared compound were immersed for ten days in recently distilled n-butylamine; the supernatant n-butylamine and the n-butylamine soaking the sample were evaporated under 10^{-3} torr vacuum for 24 hours. After that, thermogravimetric analysis of the samples was performed by a TA 3000-TG 50 Mettler thermobalance at a heating rate of 10^{-3} K min^{-1} in the temperature range 300 to 973 K.

The NH_3 adsorption was performed at ammonia boiling point (Rey Bueno *et al* 1989) in a gravimetric gas adsorption apparatus equipped with Heraeus fused
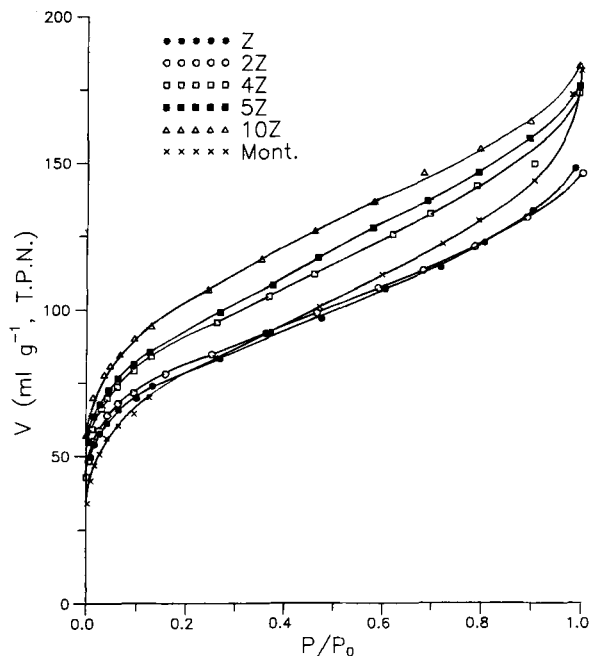
Figure 3. NH_3 (239.8 K) adsorption isotherms of montmorillonite and of the samples of Z series.

Table 2. Monolayer volume and surface area accessible to NH_3 at 239.8 K.

Sample	V_m (ml·g^{-1}, T.P.N.)	a_s (m²·g^{-1})	Sample	V_m (ml·g^{-1}, T.P.N.)	a_s (m²·g^{-1})
Mont.	63.50	202			
C	67.45	214	Z	66.26	211
2C	64.81	206	2Z	67.20	214
4C	72.84	232	4Z	75.81	241
5C	62.72	200	5Z	77.35	246
10C	62.24	198	10Z	85.23	271
4CR	65.13	207	4ZR	85.78	273
5CR	62.61	199	5ZR	81.08	258
10CR	70.75	225	10ZR	82.73	263
C'	63.75	203	Z'	68.60	218
2C'	67.10	213	2Z'	74.15	236
4C'	71.89	229	4Z'	80.94	257
5C'	72.11	229	5Z'	80.66	257
10C'	68.98	219	10Z'	85.71	273
4C'R	70.47	224	4Z'R	73.04	232
5C'R	67.73	215	5Z'R	78.78	251
10C'R	68.65	218	10Z'R	87.67	279

silica helical springs and three Balzers vacuum gauges allowing the precise measurement of pressure in the range $3.75 \cdot 10^{-9}$ to 750 torr.

The temperature was kept at 239.8 K. Elongation changes suffered by the spring were measured with an Ealing cathetometer sensitive to 0.01 mm. The samples were outgassed at 353 K to 10^{-6} torr. After the corresponding adsorption isotherms were obtained, the samples were outgassed again, at 353 K to 10^{-3} torr. Subsequently, they were taken out of the adsorption apparatus and the respective IR spectra were determined using KBr pellets, in a Perkin Elmer 983-G IR spectrophotometer, over a range of 4000–300 cm^{-1}. IR spectra of the samples treated with triethanolamine or n-butylamine were also determined under the above mentioned experimental conditions. The ammonia gas used in these experiments was 99.999% pure.

RESULTS

Figures 1 and 2 show the TGA-DTG curves recorded for samples of Ce and Zr phosphates, the parent montmorillonite, and by way of example, montmorillonite-zirconium phosphate (Z series) cross-linked compounds, after being saturated with n-butylamine and vacuum dried. Table 1 shows the number of surface acid sites calculated from the recorded curves.

Figure 3 shows the NH_3 adsorption isotherms at 239.8 K for the samples of the Z series. Isotherms of the remaining samples are qualitatively similar and may be classified as BDDT type II (Sing *et al* 1985).

V_m values, assuming the BET model (Sing *et al* 1985)

and the surface accessible to NH_3 molecules, taking 0.12 nm² as the cross-sectional area of NH_3 molecule (McClellan *et al* 1967), are shown in Table 2. From the values of V_m obtained from BET representation, the number of molecules of NH_3 attached to the surface acid sites was evaluated (Table 1). Table 1 also includes the number of acid sites calculated by triethanolamine back titration.

DISCUSSION

Surface acidity

It was not possible to evaluate by triethanolamine the acidity of the referential ZrP synthesized following the method proposed by Clearfield *et al* (1964), because of difficulties posed by this compound's hydrolysis. NH_3 adsorption was also unhelpful because of difficulties in the outgassing of the adsorbent. Table 1 shows the data for cerium hydrogen phosphate (CeP) obtained using n-butylamine and ammonia (Rey-Bueno *et al* 1989).

From the data shown in Table 1, we can infer that ammonia neutralizes a greater number of acid sites than triethanolamine, and the latter neutralizes more than n-butylamine. At first sight, taking into account the pK$_b$ values (3.38 for n-butylamine, 4.75 for ammonia and 7.24 for triethanolamine) (Weast 1978, Christensen *et al* 1976), this order would seem contradictory. We would expect n-butylamine to neutralize the highest number of acid sites, followed by ammonia and finally triethanolamine. However, the following must be taken into account: the sequence obtained for the number of acid sites cannot be justified using the pK$_b$ values because of (1) the different nature of the experimental methods used (2) the fact that
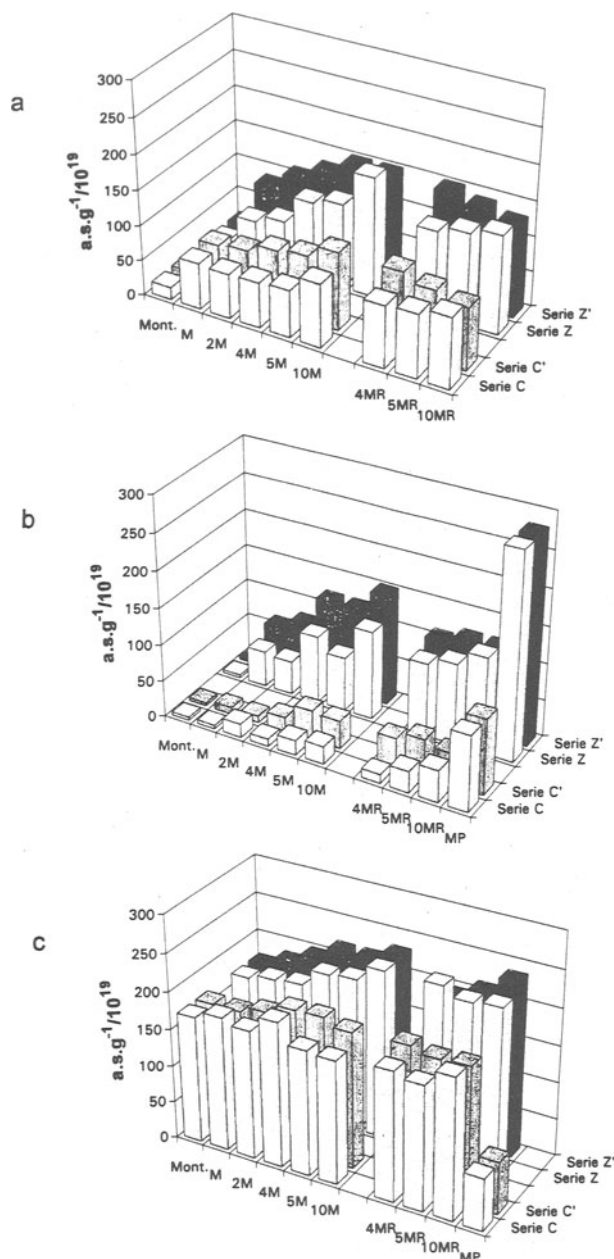
Figure 4. Influence of the preparation method on the number of surface acid sites. a) triethanolamine evaluated, b) n-butylamine evaluated, c) ammonia evaluated.

cerium and zirconium phosphates are in some way covering and shielding the clay particles and hence, (3) the predominant acid sites are the deprotonizable HPO_4^{2-} groups, the strength of which should be homogeneous compared with the strength due to the clay's Brönsted and Lewis acid sites which would not be easily accessible in these cross-linked compounds. A steric factor must therefore be considered. This would explain easier access for ammonia molecules than for the

other two larger molecules resulting in the neutralization of a higher number of acid sites.

A more detailed study of Table 1, shows that the number of acid sites for the cerium phosphate-montmorillonite cross-linked compounds is lower than for the zirconium ones. The greatest difference for the number of acid sites among the samples is found by n-butylamine evaluation, and the smallest by ammonia adsorption. One factor that could account for these differences is that cerium phosphate precipitated under the already reported conditions (Alberti *et al* 1968), exhibits mainly a fibrous-like texture, instead of the micro-crystalline structure characteristic of zirconium phosphate, and so, a fraction of the cerium phosphate could be inaccessible to the bases used to determine the surface acidity, because of a more extensive penetration of the CeP in the interlayer voids of the montmorillonite particles.

Figure 4 shows the graphical representation of the surface acidity values assigned to the metal phosphate-montmorillonite cross-linked compounds as a function of their Ce or Zr phosphate content and the data corresponding to the parent clay mineral and Ce or Zr phosphates as a reference (Table 1). Figure 4a shows an increase in the acidity of the samples compared with the acidity of the montmorillonite. This rise is more significant for the Z and Z' series than for the C and C' series. For the CR, C'R, ZR and Z'R series, the small compositional differences of their members do not seem to justify the tendency shown by the number of acid sites. Similarly, Figure 4b clearly shows that the acidity exhibited by these mixed compounds is, in general, greater than that assigned to the parent montmorillonite and significantly smaller than that of Ce or Zr phosphates. It can also be seen that the number of acid sites increases as the tetravalent metal phosphate content of the samples increases.

With respect to the values obtained by ammonia adsorption, Figure 4c shows great similarity in the number of surface acid sites of the samples in the different series studied. Due to the size and properties of the ammonia molecules and to the experimental method used (adsorption in the vapor phase in the absence of solvent or intermolecular association), it seems that these molecules penetrate all samples almost to the same extent. Because of this, we can take an average surface acidity for cerium $(1.8 \cdot 10^{21}$ a.s.g$^{-1})$ and for zirconium samples $(2.1 \cdot 10^{21}$ a.s.g$^{-1})$.

Also, unlike n-butylamine or triethanolamine evaluation, for ammonia, the acidity values of the different samples are similar to that of montmorillonite, and much higher than that of CeP. This could be explained assuming a higher contribution of montmorillonite to the total acidity, shown more clearly in the evaluation with ammonia. The use of n-butylamine and triethanolamine results in a measure of the phosphate anions located at the surface rather than evaluation of the total

acidity. This is probably due to the fact that, unlike ammonia molecules, these two molecules cannot reach the inner centers because of their size. It should be mentioned that during synthesis, montmorillonite particles ($\varnothing \leq 2$ μm) are acid activated by the 0.1 M HCl or the 0.1 M H_2SO_4 solution in which Zr(IV) or Ce(IV) cations are diluted during saturation or by the H_3PO_4 added in the *in situ* synthesis of the corresponding metal phosphate (García-Rodríguez *et al* 1995).

IR spectra

IR spectroscopy is successfully used for determining the number and type of acid sites on a surface by the adsorption of bases of different strength on it. The possibility that ammonia or other organic bases have to coordinate to Lewis sites, or to form conjugate acids with the deprotonizable hydrogens of Brönsted sites, leads to the existence of characteristic bands due to different vibration modes, showing the symmetry loss of the adsorbed molecules that enables us to differentiate between the two kinds of acid sites. Therefore, for ammonia adsorption on different metal oxides, a symmetric bending band around 1170 cm^{-1}–1361 cm^{-1} shows the existence of NH_3 coordinated to Lewis sites. On the other hand, asymmetric stretching modes around 3145 cm^{-1} and especially the existence of a symmetric bending band around 1400 cm^{-1} show the existence of NH_4^+ ions in the Brönsted acid sites (Davidov 1990).

IR spectra of the triethanolamine saturated samples do not show any characteristic band that could point to the way in which that base is bonded to the solid surface. This could be due to the experimental method used and to the natural characteristics of the triethanolamine molecule, that is, that vibrational modes of the -OH and -CH$_2$ groups would be masking the bands due to R$_3$-NH groups, if they were present. On the contrary, IR spectra of the n-butylamine or ammonia saturated samples show characteristic bands of N-H vibration modes.

Figure 5 shows the IR spectra of the four more representative samples, saturated with n-butylamine. The different -OH stretching modes can be seen in the range between 3400 cm^{-1} and 3700 cm^{-1}. Also, the NH$_3$ asymmetric stretching vibration bands in the 3250–3280 cm^{-1} range are present (Wright *et al* 1972, Liansheng Li *et al* 1991, Mortland *et al* 1963). Bands in the range 2900 cm^{-1} to 2970 cm^{-1} may be due to stretching CH$_2$ modes (Liansheng Li *et al* 1991), or to shifting the -OH stretching vibration band, due to H-bonding between n-butylamine and the -OH of the montmorillonite's structural framework (Morimoto *et al* 1974, Van Cauwelaert *et al* 1971). Bands in the range 1390–1470 cm^{-1} are observed and are due to deformation modes of the n-butylamine^{-1}-CH groups (Liansheng Li *et al* 1991, Morimoto *et al* 1974), and another composite band in the range 1489–1520 cm due to symmetric bending of the NH$_3$ group (Morimoto
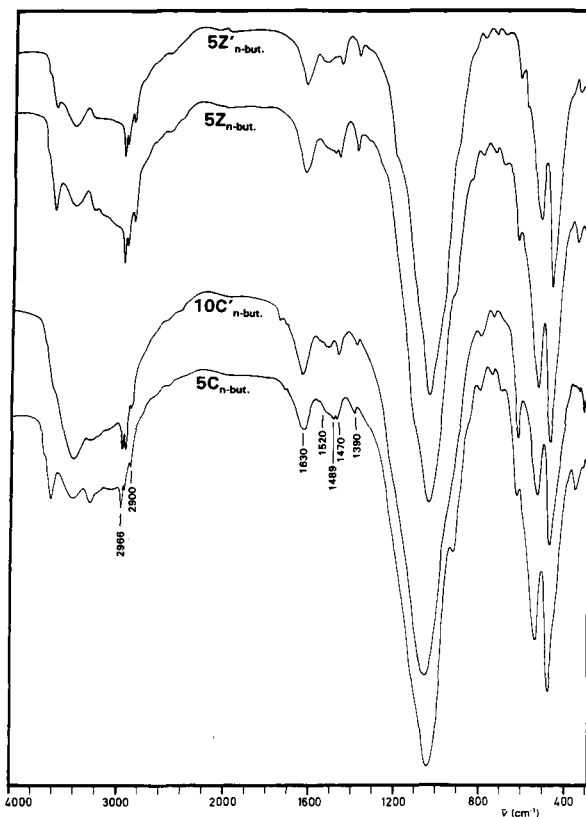

Figure 5. IR spectra of the previously n-butylamine saturated 5C, 10C', 5Z and 5Z' samples.

et al 1974, Little 1966). However, the NH$_3$ asymmetric bending band cannot be found, because it would be masked by the H O bending band, both being at 1630 cm (Liansheng Li *et al* 1991, Little 1966).

The IR spectra of the NH$_3$ saturated samples (Figure 6), show bands which are easier to assign (since they are more clear). All of them show the bands in the range 3440–3650 cm^{-1}, characteristic of an-OH stretching vibration in silica-alumina (Wright *et al* 1972). Nevertheless, the band at 3440 cm^{-1} could be assigned to the NH$_3$ asymmetric stretching vibration (Tsyganenko *et al* 1975, Mortland *et al* 1963, Pimentel *et al* 1962). The band around 3410 cm^{-1} in the IR spectra of the samples without NH$_3$ seems to indicate that a shift occurs due to a perturbation in the-OH stretching vibration owing to an interaction between the NH$_3$ molecule and the structural -OH of the substrate (Tsyganenko *et al* 1975). Finally, the P-NH symmetric stretching vibration around 3440 cm^{-1} (Peri 1971), could also contribute to the intensity of the above mentioned band.

A band is observed around 3200 cm^{-1}, which sharpens and increases in intensity as the phosphate to clay ratio rises along the entire series of mixed compounds, from a small shoulder in the NH$_3$-montmorillonite

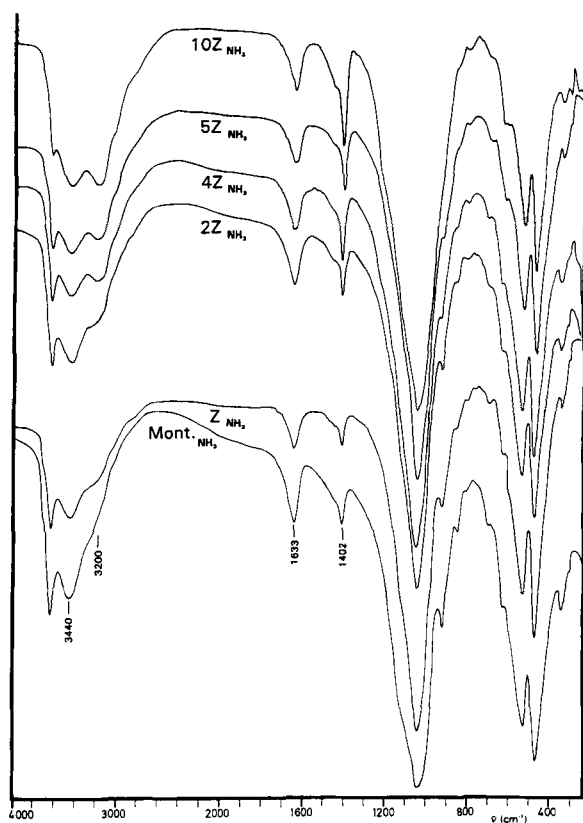Figure 6.   IR spectra of the montmorillonite and the series of Z samples after NH$_3$ adsorption.

Figure 7.   Influence of temperature on retention of NH$_3$ by the 5Z sample.

used as reference. This band is due to the NH$_4^+$ stretching vibration (Nakamoto 1978) and together with the one at 1400 cm^{-1}, assigned to NH$_4^+$ bending vibration (Nakamoto 1978), confirms the presence of NH$_4^+$ ions in the samples, originating from Brönsted acid sites (Davidov 1990).

It should also be mentioned that the NH$_4^+$ bending vibration band is at 1402 cm^{-1}, the characteristic vibration frequency for NH$_4^+$ in ionic compounds such as NH$_4$ Cl^{-1} (Waddington 1958), and that there is no symmetric stretching vibration band at 3040 cm^{-1} nor any symmetric bending at 1680 cm^{-1} nor its component around 1700 cm^{-1}, all of which are indicative of bending of the H bonds between the NH$_4^+$ group and the sample's surface (Davidov 1990). This could be explained by a proton capture from the HPO$_4^{2-}$ Brönsted acid group by the NH$_3$ molecule, followed by formation of NH$_4^+$ ions which would remain linked to the surface of the solid by ionic bonding.

No other band can be assigned to any other NH$_3$-Lewis site coordinated vibration in the spectra shown in Figure 6 or in any other spectra of the studied samples.

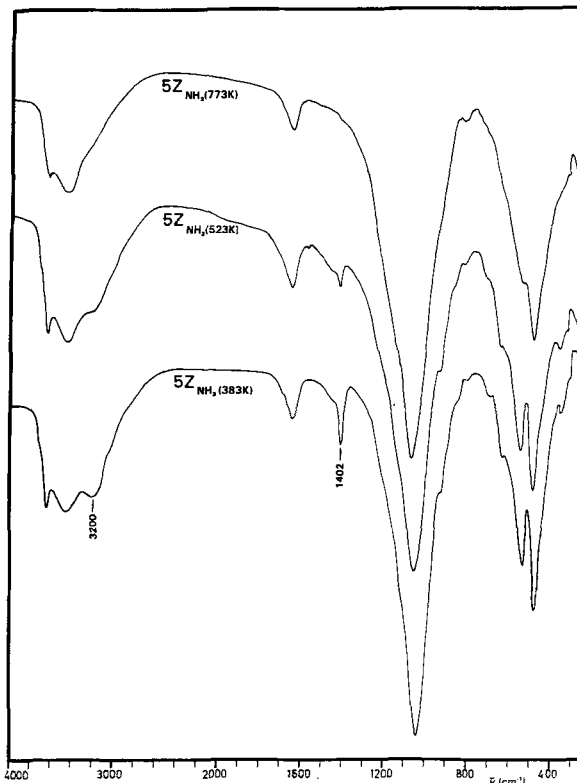Figure 7 shows IR spectra of the NH$_3$ saturated 5Z sample after heating at 383 K, 523 K and 773 K to test the influence of temperature on the way in which ammonia is bonded to the phosphate-montmorillonite sample surface. The higher the treatment temperature the lower the intensity of the bands around 3200 cm^{-1} and 1400 cm^{-1}, which disappear for the sample heated to 773 K.

It should be stressed that even though Wright *et al* (1972) reported the appearance of a band centered at 3470 cm^{-1}, indicative of the presence of protons in the tetrahedral vacancies of the octahedral layer as a consequence of the thermal deamination of layered silicates when ammonia has been adsorbed, we did not observe this band. Thus, the samples treated at 773 K show the same bands as the samples before ammonia adsorption.

Ammonia accessible surface area

Table 2 shows that the surface area calculated by ammonia adsorption at 239.8 K is greater for phosphate-montmorillonite compounds than for the parent montmorillonite (it should be noted that the corresponding surfaces occupied by either n-butylamine or triethanolamine are not reported because of the uncertainty of the individual areas covered by these molecules). These values are substantially greater than N$_2$ adsorption values at 77 K, which ranged from 128 to

266 m^2g^{-1}. These differences are logical considering that NH molecules are smaller than N ones (0.12 nm^{-2} vs. 0.16 nm^{-2}) (McClellan *et al* 1967) and that they have a high dipole moment ($\mu = 1.47$ D). All this enables the NH molecules access to a higher number of smaller pores than the nitrogen.

There is no clear correlation between the tetravalent metal phosphate to clay ratio and the quantity of ammonia retained, and hence, to the corresponding specific surface area. For Z and Z' series, the parameters studied increase as the zirconium hydrogen phosphate (ZrP) to clay ratio increases. On the contrary, for C and C' series the situation is not so clear, because of a noticeable decrease in the surface area at the end of each series.

CONCLUSIONS

IR spectra of the n-butylamine or ammonia saturated samples show evidence of the Brönsted nature of the acid sites detected, which could be identified with monohydrogen phosphate groups. However, the possible presence of Lewis acid sites on the montmorillonite framework should not be ruled out. One reason that they have remained undetected may be their small number with respect to the deprotonizable phosphate ions or, as suggested by Wright (1972), because the main part of these Lewis acid sites, due to trigonally coordinated aluminium atoms, are transformed into Brönsted sites by water molecule attachment during sample synthesis or manipulation. This would explain the absence in the IR spectra of any band assigned to the symmetric bending vibration of an ammonia molecule coordinated on a Lewis acid site. We cannot forget either the protective effect of the ZrP microcrystals or CeP fibers on the clay particles, which could make it difficult for the molecules of the bases used to reach the inside of the montmorillonite layers.

ACKNOWLEDGMENTS

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