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INFRARED STUDY OF THE THERMAL TREATMENT OF SEPIOLITE AND PALYGORSKITE SATURATED WITH ORGANIC AMINES

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ABSTRACT

Butylamine (BA), pyridine (PY) and 2,4,6-trimethylpyridine (TMP) were adsorbed by sepiolite and palygorskite under reflux. The adsorption and the thermal stability of the organo-clay complexes were studied by IR thermospectrometry. In this technique KBr disks of the organo-clay complexes were heated to 100, 200, 300 and 400°C and IR spectra were recorded after each thermal treatment. The spectra proved that the adsorbed amines were located in the channels, replacing part of the zeolitic and bound water. The three amines were hydrogen bonded to the zeolitic water. Associations were also obtained between BA or PY and bound water in sepiolite but not in palygorskite and not with TMP. Small amounts of adsorbed BA and TMP were protonated. During the thermal treatment of the organo-clay, associations were formed between BA or PY and octahedral Mg exposed to the channel. From the thermal study it can be concluded that hydrophobicity of the clays increases and their thermal stability decreases as a result of the adsorption of the organic bases.

INTRODUCTION

Sepiolite and palygorskite are unique among the clay minerals due to their characteristic channel structure. In spite of their great potential as catalysts, very little work has been carried out to

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study their surface acidity. In the present study the adsorption of three amines and the effects of thermal treatments on this adsorption were investigated by infrared thermospectrometry analysis. The amines were butylamine (BA), which represents strong aliphatic bases, pyridine (PY), representing weak aromatic bases and 2,4,6-trimethylpyridine (TMP), representing amines with both, aliphatic and aromatic properties.

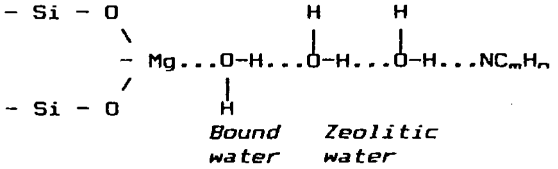
All three amines may react as Bronsted or Lewis bases. On the other hand, under certain conditions BA may serve as a proton donor (Bronsted acid). By analogy with previous studies on the adsorption of amines by clay minerals, and especially by montmorillonite, six types of association for amines sorbed by sepiolite or palygorskite may be postulated on the basis of interaction between organic species, water and Mg^{2+} (or Al^{3+}) located at the edges of the channels [1-6]. These are shown in Schemes I-VI.

IR spectroscopy was successfully applied to differentiate between ionic (protonated) and molecular butylamine adsorbed on montmorillonite [7], silica-alumina [8] and zeolites [9]. It was also used to differentiate between pyridinium cation and molecular pyridine in montmorillonite [10]. Moreover, the IR spectra can be applied to determine whether the molecular pyridine is bound to Lewis or Bronsted acid sites [11-14]. Blanco et. al. [15] studied the surface acidity of palygorskite by IR spectroscopy, after evacuating for 2 hours at 150°C. The thermally treated clay was than saturated with PY and IR spectra showed the formation of weak hydrogen bonds between PY and Bronsted acid sites which were developed as a result of the thermal treatment.

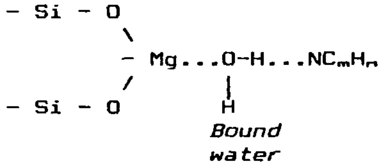
EXPERIMENTAL

Sepiolite from Vallecas, Spain and palygorskite from Quincy, Florida, were supplied by Ward's Natural Science Establishment. The clays were manually ground and the fraction <400 mesh was used in the present study. BA, PY and TMP were supplied by Aldrich. They were distilled before being used. Adsorption of the amines on the clays was carried out under reflux conditions for 24 hours, followed by drying under a pressure of 0.01 torr at 50°C for 6 hours.

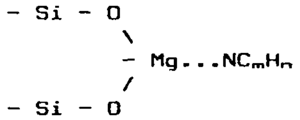
KBr Disks were pressed from 2 mg clay and 150 mg KBr. Each disk was heated at 100, 200, 300 and 400°C for 48 hours at each temperature. After each thermal treatment the disk was cooled to RT



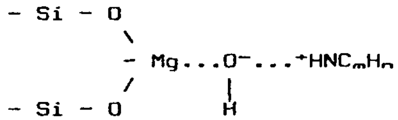
Scheme I – Possible association between amine (proton acceptor) and zeolitic water (proton donor) via hydrogen bond.



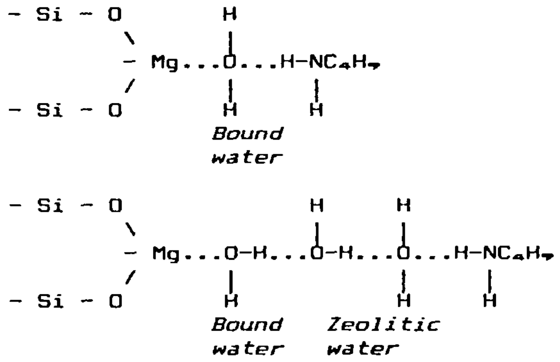
Scheme II – Possible association between amine (proton acceptor) and bound water (proton donor) via hydrogen bond.



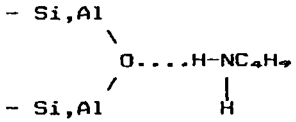
Scheme III – Possible association between amine (electron pair donor) and octahedral magnesium exposed to the channel (electron pair acceptor).



Scheme IV – Possible protonation of amine. Bound water serves as proton donor.



Scheme V – Possible association between butylamine (proton donor) and zeolitic or bound water (proton acceptor) via hydrogen bond.



Scheme VI – Possible association between butylamine (proton donor) and siloxane group at the surface of the channel (proton acceptor) via hydrogen bond.

in a desiccator and re-pressed taking precautions not to damage it during the process. IR spectra were recorded using a Nicolet 20dxb FTIR. It was previously shown that this technique gives reliable information about the thermal behavior of organic complexes of sepiolite and palygorskite [16].

RESULTS

IR spectra of the disks at room temperature

Figs. 1 and 2 show the IR spectra of sepiolite and palygorskite saturated with the three amines recorded prior to and after heating treatments of the disks to several temperatures. For comparison, the spectra of untreated sepiolite and palygorskite before and after identical thermal treatments are also shown.

Zeolitic water gives rise to broad absorption bands at 3420, 3250 and 1670 cm^{-1} in the spectrum of sepiolite and at 3400, 3290 and 1660 cm^{-1} in the spectrum of palygorskite [17-22]. The intensities of these peaks decreased as a result of the adsorption of the three amines by both minerals, indicating that zeolitic water is replaced by the adsorbed amine. The presence of amine inside the channels of both clays has an effect on the structure of their residual zeolitic water as can be inferred from the location of the HOH deformation vibrations. In the spectra of the PY and TMP treated sepiolite the principal absorption is located at 1653 cm^{-1}. In the spectrum of BA treated sepiolite this absorption is located at 1662 cm^{-1}. In the spectra of the organo derivatives of palygorskite this shift is small and the HOH deformation vibration is located at 1655 cm^{-1}. A posssible association is shown in Scheme I.

Bound water gives rise to two stretching absorptions located at 3625 and 3568 cm^{-1} for sepiolite and at 3585 and 3550 cm^{-1} for palygorskite. Deformation bands appear at 1622 and 1638 in the spectra of sepiolite and palygorskite, respectively [17-22]. In the case of BA and PY treated sepiolite the relatively sharp band of 3568 cm^{-1} shifts to 3590 and 3576 cm^{-1}, respectively, and is relatively weak. The shift in the absorption bands may indicate the formation of new hydrogen bonds between bound water and BA or PY (Scheme II) whereas the weakening in the inensity of the bands is an indication that part of the bound water is replaced by the amines. In the case of sepiolite the bound water is affected by the adsorption of PY in that the 3625 cm^{-1} band disappears. Prost

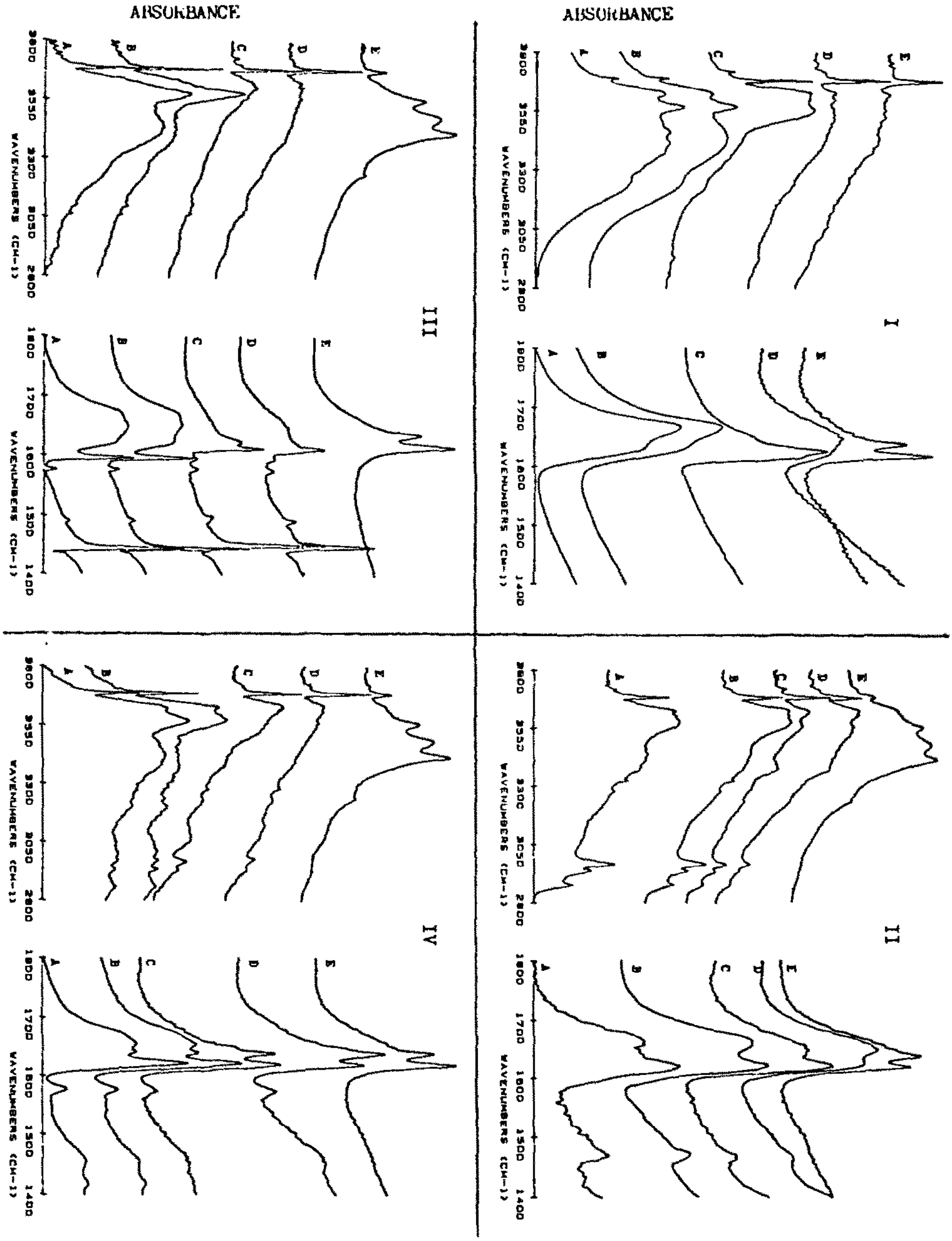


Fig. 1: Infrared spectra of KBr disks of untreated sepiolite (I) and of sepiolite saturated with BA (II), PY (III) and TMP (IV). Disks were recorded before thermal treatment (A) and after heating at 100° (B), 200° (C), 300° (D) and 400°C (E).

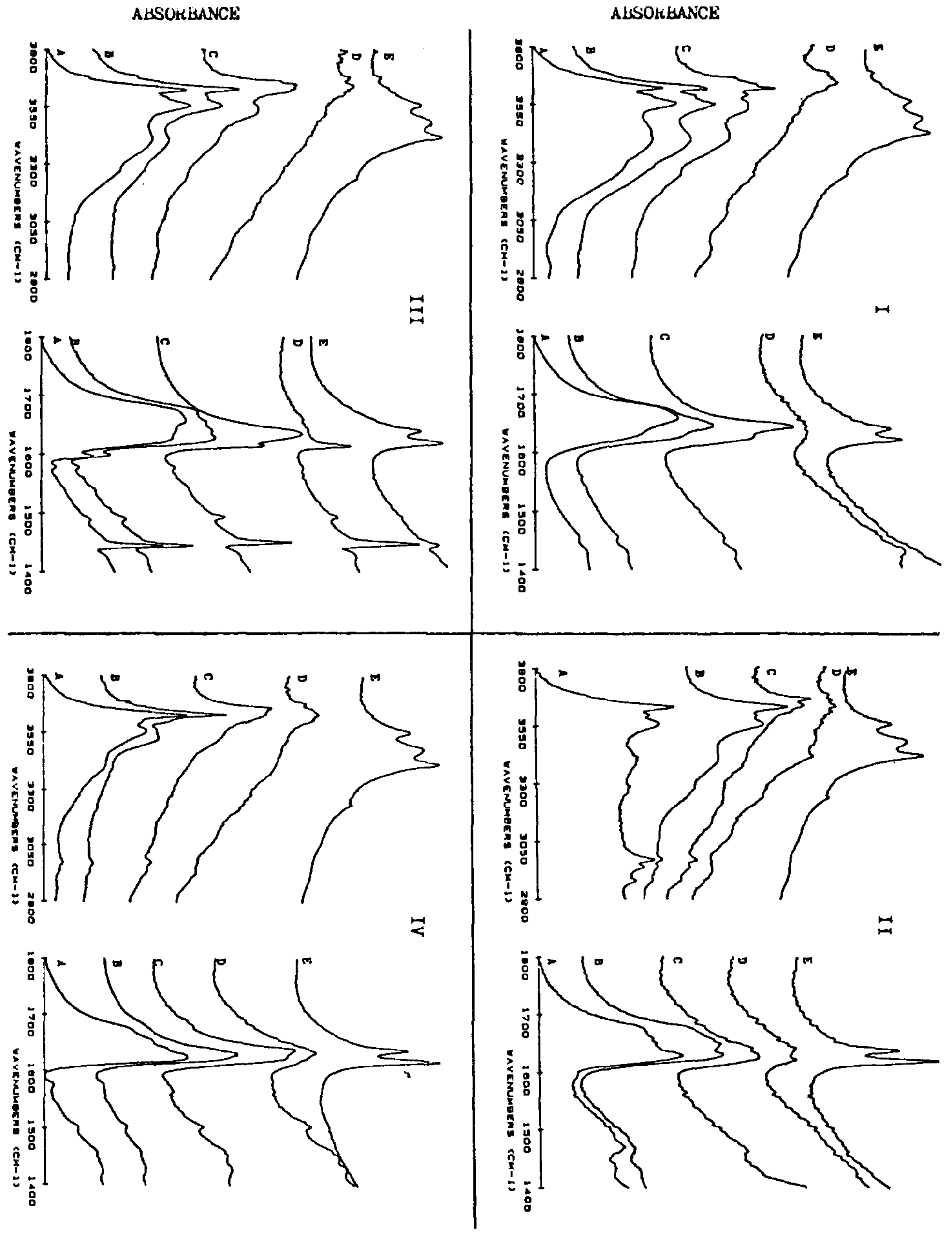


Fig. 2: Infrared spectra of KBr disks of untreated palygorskite (I) and of palygorskite saturated with BA (II), PY (III) and TMP (IV). Disks were recorded before thermal treatment (A) and after heating at 100° (B), 200° (C), 300° (D) and 400°C (E).

[20] and Serna et al. [22] argued that the appearance of two stretching bands is due to the fact that the two water molecules coordinated to each of the octahedral cations exposed to the channels are not identical. The drastic change that we observed in the spectrum of PY treated sepiolite should be an indication that some of the bound water is replaced by this amine (Scheme III).

TMP treated sepiolite and the three amine treated palygorskites did not show shifts in the locations of the absorption bands of the bound water, indicating that in these organo-clays, the association shown in Scheme II was not formed. However, the three bands which characterize bound water became weaker as compared with the peaks of the untreated samples, indicating replacement of bound water by the amines. In the case of BA or PY treated palygorskite they became only slightly weaker, however, with TMP treated palygorskite the bands became extremely weak. This is due to the reflux temperature employed for the preparation of this sample which was higher than the reflux temperatures of BA or PY. It is possible that the escape of bound water is the result of the high refluxing temperature. The larger TMP molecules block the narrow pores of palygorskite and prevent the readsorption of water from the atmosphere.

The spectra of BA treated sepiolite and palygorskite show the presence of the NH_2 group. Asymmetric and symmetric stretching vibrations appear at 3325 and 3278 cm^{-1} and 3286 and 3261 cm^{-1} in the spectra of sepiolite and palygorskite, respectively. The location of these bands in the spectrum of liquid BA is at 3370 and 3292 cm^{-1}. The shift which is observed in the present study is due to hydrogen bonds which are formed between the amine and water molecules in which the amine is proton acceptor and the water molecule is proton donor (Schemes I and II). Deformation bands appear at 1617 and 1626 cm^{-1} in the spectra of sepiolite and palygorskite, respectively. These bands are very intense probably due to the fact that they overlap the HOH vibrations. It would be expected that a protonated species (BAH^+) would give an absorption band at 1500-1520 cm^{-1}. A very small absorption is detected in this region in the spectra of both minerals indicating that hydrolysis of BA in sepiolite or palygorskite takes place to a small extent (Scheme IV).

Adsorbed PY shows absorption maxima at 1593, 1576, 1489 and 1443 cm^{-1} in the spectrum of sepiolite and at 1598, 1578, 1490 and 1443 cm^{-1} in palygorskite. There are only small shifts of these bands from their locations in the spectrum of pyridine in chloroform (1600, 1583, 1520, 1480 and 1440 cm^{-1}) or of liquid pyridine (1598, 1581, 1574, 1482 and 1437 cm^{-1}) characteristic for weak hydrogen bonds which are formed between the pyridine and water molecules (Schemes I and II). Bands which characterize pyridinium cation do not appear and it is obvious that the pyridine which was adsorbed either by sepiolite or by palygorskite was not protonated.

Liquid TMP absorbs at 1612 (principal band), 1571, 1536, 1461 and 1412 cm^{-1}. A CCl_4 solution of TMP absorbs at 1612 (principal band), 1574, 1518-1515, 1459, 1446 (shoulder) and 1407 cm^{-1}. When TMP is adsorbed by sepiolite these bands are shifted to 1621, 1577, 1456 and 1417 cm^{-1}. Here again the small shifts observed after adsorption are due to weak hydrogen bonds formed between the amine and water molecules (Scheme I). In the spectrum of TMP treated palygorskite recorded before any thermal treatment, TMP bands appear at 1626, 1575, 1501, and very small peaks at 1457, 1445, 1437, 1429, 1421 and 1402 cm^{-1}. The band at 1626 cm^{-1} seems to be superimposed by the deformation vibration of the bound water and the ring vibration of TMP.

The most intense absorption band of the hydrochloride salt of TMP appears at 1635 cm^{-1}. It is therefore to be expected that a similar band in the spectra of TMP treated sepiolite or palygorskite will characterize the presence of $TMPH^+$. A band at 1640 cm^{-1} in the spectrum of TMP treated sepiolite, which persists at 300°C, indicates that protonation of this molecule takes place to a small extent. The relative intensity of this band increases with the thermal treatment of the disk. In the spectrum of TMP treated palygorskite this band is observed only after heating the disk at 200°C, indicating that the protonation of TMP on this mineral occurs only after the evolution of the zeolitic water. At this stage the TMP molecules are able to reach bound water molecules which serve as an acid (proton donors).

IR spectra of the disks after thermal treatment

When KBr disks of natural sepiolite or palygorskite were heated to 100°C, they lost considerable amounts of the zeolitic water. However, most zeolitic water was lost only at 200°C. With both minerals the loss of bound water starts already at 200°C but with sepiolite this loss is very small at this stage. The loss of bound water is not complete until 300°C.

The amine treated sepiolites and palygorskites showed a higher hydrophobicity compared to the natural clays. In the case of PY treated sepiolite and palygorskite, they both lost their zeolitic water as well as most of their bound water already when the disks were heated at 200 and 150°C, respectively. At 200°C the locations of ring vibrations of PY shifted to 1613, 1578, 1492 and 1447 cm^{-1} in the spectrum of sepiolite and to 1613, 1577, 1493 and 1449 cm^{-1} in the spectrum of palygorskite. This change in the spectrum indicates that after the removal of most zeolitic water as well as part of the bound water, the pyridine molecules coordinate directly to the partial dehydrated octahedral cations exposed to the channel (Scheme III). A small peak at 1595 cm^{-1} in the spectrum of PY treated sepiolite indicates that a very small fraction of PY remained associated to zeolitic water molecules (Scheme I).

With both BA treated clays the two NH_2 stretching bands which initially appeared at 3325 and 3278 cm^{-1} in sepiolite and at 3286 and 3261 cm^{-1} in palygorskite, were replaced at 200°C by a single broad absorption at 3372 cm^{-1}. As well, the NH_2 bending bands shifted to 1630 cm^{-1} at 150°C in palygorskite and to 1627 cm^{-1} at 300°C in sepiolite. This change in the spectrum indicates that at this stage, after the removal of most zeolitic water as well as part of the bound water, the BA molecules coordinate directly to the partial dehydrated octahedral cations exposed to the channel (Scheme III).

TMP treated sepiolite and palygorskite did not show such changes. It is possible that TMP does not give the association which is described in Scheme III due to steric hindrance.

The Si-O stretching bands at 1080, 1019 and 980 cm^{-1} in the spectrum of sepiolite and at 1029 and 984 cm^{-1} in the spectrum of palygorskite persist up to 300 and 200°C, respectively. At these temperatures the initial sharp peaks are replaced by a single broad absorption at about 1015 cm^{-1} in the spectra of both clays indicating that at these temperatures the symmetry of the tetrahedral sheets is distorted. In the presence of the amines this perturbation was already observed after a thermal treatment of the disks at 200°C in the spectra of sepiolite and palygorskite. This distortion is associated with the evolution of the bound water which occurs in the presence of the organic compounds at a lower temperature than in the natural clay.

This thermal distortion also occurs in the octahedral sheet of palygorskite, as can be concluded from the appearance of very small OH peaks at wavenumbers greater than that of the initial OH absorption band after heating the disks at 200 and 300°C. Initially the OH band is located at 3620 cm^{-1}. The new bands which appear after the thermal treatment at 200°C are located at 3630 and 3660 cm^{-1}. In the presence of the amines the new absorption bands are more intense, indicating that this distortion occurs to a higher extent. In natural or amine treated sepiolite, on the other hand, the thermal treatments at 200 or 300°C have only very small effects on the appearnce of new OH bands due to the higher thermal stability of this mineral.

After heating the disks of the amine treated sepiolite or palygorskite at 400°C the clays were decomposed and the organic matter was completely burned. Identical spectra are obtained from natural and amine treated palygorskite. At this stage the mineral has already been decomposed and the spectra are in fact those of meta palygorskite, an amorphous hydrated phase. On the other hand, spectra obtained from natural and amine treated sepiolites after heating the disks at 400°C are different. This is due to the fact that at this temperature only part of the untreated sepiolite is dehydroxylated whereas amine treated sepiolite is almost completely dehydroxylated, as can be seen from the diminishing of the OH stretching band.

Thermal stability of the ammonium cations

The spectra of BA treated clays show that BAH^+ cation did not persist after heating the disks at 200°C, whereas the spectra of TMP treated clays showed that the $TMPH^+$ cation persisted above this temperature. According to Ghosh et al. [23] BAH^+ adsorbed on zeolites decomposes at 175°C forming among other compounds butene and ammonia by the Hofmann degradation mechanism, whereas BAH^+ adsorbed on silica-alumina degradates only at much higher temperatures. It is possible that the thermal behavior of BAH^+ located inside the channels of sepiolite and palygorskite is similar to that of BAH^+ adsorbed by zeolites and it decomposes below 200°C. This subject is now under investigation in our laboratory.

CONCLUSIONS

During the adsorption of BA, PY and TMP by sepiolite or palygorskite, the amine penetrates into the channels replacing part of the zeolitic water. The adsorbed amines form hydrogen bonds with the zeolitic water (Scheme I).

Hydrogen bonds are also formed between BA or PY and bound water in sepiolite (Scheme II). This association was not detected in palygorskite with any of these amines or in sepiolite with TMP.

When PY is adsorbed by sepiolite it replaces some of the bound water (Scheme III). This replacement occurs to a smaller extent with palygorskite or when BA or TMP are adsorbed by any of the clays.

When BA or PY treated sepiolite and palygorskite are heated at 200°C, water is lost and hydrated amines are dehydrated forming associations with the octahedral cation exposed to the channel (Scheme III). TMP does not form this type of association, probably due to steric hindrance.

Bronsted surface acid strength of either sepiolite or palygorskite is weak and no ammonium cations (Scheme IV) of PY were detected under the conditions employed in the present study. Small amounts of BAH^+ were identified from the weak absorption at 1500 cm^{-1} in the spectra of BA treated clays. This cation disappeared at 200°C. Small amounts of $TMPH^+$ were identified in the spectrum of TMP treated sepiolite at room temperature, giving an absorption band at 1640 cm^{-1}. A similar band was detected in the spectrum of TMP treated palygorskite only after heating this sample to 200°C. This cation persisted at 300°C.

Basic surface sites (Schemes V and VI), either according to Bronsted or to Lewis, were not detected in the present study.

As one would expect, hydrophobicity of the clays increases as a result of the adsorption of the amines.

The present study shows that thermal stability of both clays decreases as a result of the adsorption of the organic bases and their dehydroxylation occurs at a lower temperature compared to that of natural clays. This result differs from our observation in DTA (paper in preparation). One should take into consideration the fact that in the present study each step of the thermal treatment is isothermic and is entirely different from the treatment which is applied in the DTA system. Also, the presence of KBr as the matrix of the disk, should be taken into consideration.

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