

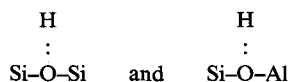
## INFRARED STUDIES OF SURFACE ACIDITY AND REVERSIBLE FOLDING IN PALYGORSKITE

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**Abstract**—The infrared absorption spectra of a palygorskite sample from Cáceres, Spain, showed two previously unreported bands in the OH-stretching region at 3420–3440 and 3220–3230  $\text{cm}^{-1}$  after evacuation at 90°–230°C. These bands, which reached maximum intensity after the sample was heated at 150°C, were assigned to OH in the



groups, respectively. To characterize the nature of these OH groups, pyridine was adsorbed on the sample. The resultant spectra suggest that at 150°C the palygorskite folded and OH groups protonated, resulting in the formation of a deformed pyridinium ion between 150° and 290°C. A high concentration of thermally stable Lewis-acid sites on the surface of the palygorskite was also noted.

**Key Words**—Infrared spectroscopy, Lewis-acid sites, Palygorskite, Protonation, Pyridine.

### INTRODUCTION

Several authors (e.g., Forni, 1973; Benesi and Winquist, 1978; Serratos, 1979; Adams *et al.*, 1983; Ballantine *et al.*, 1984) have described the use of clays as catalysts or catalyst supports for hydrocarbon conversion in both the petroleum industry and in the processing of organic compounds containing different functional groups, e.g., the catalytic transformation of glycolaldehyde and glyceraldehyde into sugars (Evole Martin and Aragón de la Cruz, 1986a, 1986b) and epoxides into carbonilic compounds (Ruiz-Hitzky and Casal, 1985). In most of these studies the surface acidity of the clays has been considered a determinant to their catalytic activity. Transformation by way of a carbonium ion anchored preferentially on Brønsted surface centers, or olefins conversion through  $\pi$ -complexes on surface Lewis-acid centers, have often been postulated. The high surface area, adsorption capacity, and distribution of potentially active anchorage sites suggest that palygorskite may be used as a catalyst or catalyst support (Serratos, 1979).

Infrared spectroscopy of a chemisorbed base is a powerful tool for the characterization of acidic groups in solids (Benesi and Winquist, 1978). Parry (1963) suggested the use of pyridine, and according to Knözinger (1976), the 19b and 8a vibrational modes of the pyridine ring are both affected by the nature of intermolecular interactions through the 2s electron pair of the nitrogen atom. These two modes appear at 1440–1447 and 1580–1600  $\text{cm}^{-1}$ , respectively, if pyridine

interacts with hydrogen bonds; at 1535–1550 and 1640  $\text{cm}^{-1}$  if pyridinium ions (Brønsted acidity) are formed; and at 1440–1464 and 1600–1634  $\text{cm}^{-1}$  if the molecule is coordinatively bound ( $\sigma$ -donation bonding) to Lewis-acid centers (Knözinger, 1976; Kung and Kung, 1985).

In general, the 1550 and 1450- $\text{cm}^{-1}$  bands are widely used to identify the pyridinium ion and Lewis-acid centers, respectively (Parry, 1963), although Farmer and Mortland (1966) reported the absence of the 1550- $\text{cm}^{-1}$  band if the pyridinium ion is involved in a strong hydrogen bond. Thus, the simultaneous observation of the changes produced in the OH-stretching region (Hughes and White, 1967) and the shifts in the pyridine vibrational modes can be used to illuminate the type of interaction and acidity of the surface of solids.

In the present work, pyridine adsorption has been used to identify the nature and character of the surface acidic groups of a palygorskite sample from Serradilla, Cáceres, Spain, and to provide information concerning the changes produced in the sample by thermal treatment.

### EXPERIMENTAL

#### Materials

The palygorskite sample used in this study was from the deposit at Serradilla, Cáceres, Spain, described by Galán (1981; Galán *et al.*, 1975). A <2- $\mu\text{m}$  fraction was provided by Tolsa, S.A.

González (1988) reported the following composition

and structural and textural properties for this material:  $\text{SiO}_2$ , 53.41%;  $\text{Al}_2\text{O}_3$ , 10.9%;  $\text{MgO}$ , 7.4%;  $\text{CaO}$ , 0.12%;  $\text{Fe}_2\text{O}_3$ , 3.9%;  $\text{K}_2\text{O}$ , 0.9%;  $\text{Na}_2\text{O}$ , 0.8%; L.O.I. 21.95%. The cation exchange capacity (CEC), reported by González (1988), was 42.5 meq/100 g, with 0.7 meq Ca, 19.8 meq Mg, 1.4 meq K, and 19.1 meq Na, and was determined by the following method: 10 g of solid was vigorously stirred with 250 ml of 1 M ammonium acetate for 16 hr at room temperature. The suspension was then filtered, and the exchanged cations in the liquid were analyzed. Transmission electron micrographs show a predominance of needle packets about 0.7–0.15  $\mu\text{m}$  long and 0.03  $\mu\text{m}$  thick. From X-ray powder diffraction analysis, the sample was found to contain predominantly palygorskite, with some quartz and dolomite mineral impurities. The surface area,  $S_{\text{BET}}$ , after evacuation at room temperature was 153  $\text{m}^2/\text{g}$ , and decreased to 71  $\text{m}^2/\text{g}$  after degassing under standard conditions (140°C,  $10^{-4}$  torr, 16 hr). The total ideal surface calculated from crystallographic data is about 700  $\text{m}^2/\text{g}$ ; differences between these values are probably due to the fact that  $\text{N}_2$  molecules did not diffuse into the palygorskite channels (González, 1988; Barrer and Mackenzie, 1954). The pore volume was 2.08  $\text{cm}^3/\text{g}$ . The pyridine used was Uvasol quality from Merck.

### Methods

Self-supporting films (2  $\text{mg}/\text{cm}^2$ ) were prepared following Russell (1974), from 0.6 w/v suspensions of the solid in deionized water. They were mounted in a quartz sample holder, placed in an evacuable Pyrex infrared cell having  $\text{CaF}_2$  windows, and coupled to a  $10^{-6}$ -torr vacuum system. The film was degassed for at least 2 hr either at room temperature or at 150°C before pyridine adsorption. Afterwards, the sample was exposed to pyridine vapor (12 torr) at room temperature, and its infrared spectrum was recorded after 30-min exposure and subsequent evacuation at room temperature. Finally, new spectra were run after 2 hr of evacuation at various temperatures from 50° to 500°C. Infrared spectra in the 4000–1100- $\text{cm}^{-1}$  range were always taken at about 35°C, using a Perkin-Elmer spectrophotometer equipped with a wedge attenuator in the reference beam.

## RESULTS AND DISCUSSION

### Effect of temperature

Infrared spectra of films evacuated at various temperatures between room temperature and 300°C are given in Figure 1. The principal bands are the same as those described by Van Scoyoc *et al.* (1979). In addition, two previously unreported broad bands at 3430–3440 and 3220–3230  $\text{cm}^{-1}$  were noted for palygorskite heated between 90° and 230°C. Both bands (actually the one at 3420  $\text{cm}^{-1}$  was only a shoulder if the evac-

uation was carried out at 90°C) reached their maximum intensity for the palygorskite degassed at 150°C.

Bands in this stretching region have previously been reported in the literature. Although they used a different thermal treatment, Hayashi *et al.* (1969) found for palygorskite a band at 3200  $\text{cm}^{-1}$  which they ascribed to zeolitic water. Farmer and Russell (1971) described for adsorbed water on saponite and vermiculite two bands which were attributed to hydrogen bound to oxygen in Si–O–Si and Si–O–Al groups, respectively, at 3480–3495  $\text{cm}^{-1}$  and 3220–3230  $\text{cm}^{-1}$ .

On the basis of this last work, the two new bands found in palygorskite, were probably due to OH on



Si–O–Si and Si–O–Al linkages. In addition, taking into account (1) the asymmetry of the coordinated water (Serna *et al.*, 1976) and (2) the temperature, 150°C in vacuum, at which these bands reached their maximum intensity (i.e., the same temperature at which folding in palygorskite occurs), this H probably came from water coordinated to edge Mg of the octahedral sheet (Figure 2). The new bands can also be attributed to the bond between hydrogen of coordinated water to the exchangeable cations and oxygen of the tetrahedral layer, as was described by Farmer and Russell (1971) for smectites and reviewed by Yariv and Cross (1979).

### Pyridine adsorption



Knowing that Si–O–Al presents Brönsted acidity against most bases (Corma and Wojciechowski, 1985), the behavior of these bonds was studied by adsorbing pyridine on palygorskite. In Figure 3, the infrared spectra corresponding to palygorskite degassed at room temperature can be seen before (3a) and after (3b) reversible adsorption of pyridine at room temperature. The most relevant differences of the 3b spectra with respect to the 3a spectra are: (1) a strong decrease in intensity of the 3510- $\text{cm}^{-1}$  band due to OH groups coming from Mg-coordinated water (Van Scoyoc *et al.*, 1979), along with a parallel decrease in the accompanying 1620- $\text{cm}^{-1}$  band from water; (2) the presence of bands at 1610, 1490, 1450, and 1227  $\text{cm}^{-1}$ , which denote Lewis acidity, although the 1490- $\text{cm}^{-1}$  band has also been assigned to Brönsted centers; (3) a shoulder at 1640  $\text{cm}^{-1}$  and a band at 1200  $\text{cm}^{-1}$ , both attributed to pyridinium ion. An accompanying band at 1550  $\text{cm}^{-1}$  was not found.

If pyridine was adsorbed on palygorskite heated in vacuum at 150°C (Figure 4b), i.e., the temperature at which the 3420–3440- $\text{cm}^{-1}$  and 3220–3230- $\text{cm}^{-1}$  bands were most intense, bands at 1610, 1490, 1450, 1227 and 1220  $\text{cm}^{-1}$ , as well as a small shoulder at 1635–1640  $\text{cm}^{-1}$  (Figure 4a) were present. Two bands at 3620 and 3510  $\text{cm}^{-1}$  were also present, and, in con-

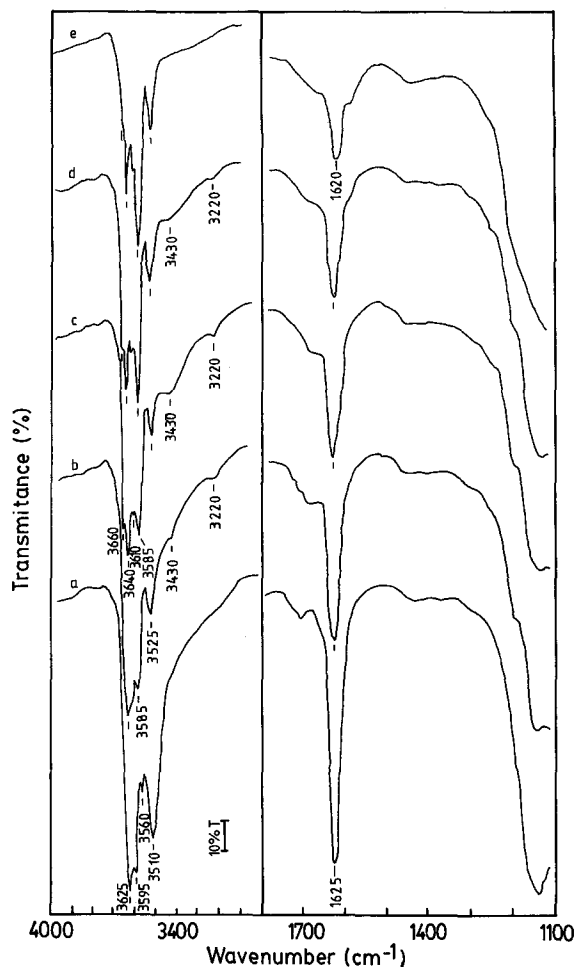


Figure 1. Infrared spectra of a palygorskite film ( $2 \text{ mg/cm}^2$ ): (a) degassed at room temperature; (b) degassed at  $90^\circ\text{C}$ ; (c) degassed at  $150^\circ\text{C}$ ; (d) degassed at  $230^\circ\text{C}$ ; (e) degassed at  $300^\circ\text{C}$ .

trast, the bands at  $3420\text{--}3440$  and  $3220\text{--}3230 \text{ cm}^{-1}$  were absent. Significantly, the bands corresponding to folded palygorskite at  $3640$  and  $3660 \text{ cm}^{-1}$  (Van Scoyoc *et al.*, 1979) were absent. This last observation can be related to the unfolding of palygorskite due to pyridine entering its channels.

After degassing at  $150^\circ\text{C}$  (Figure 4d), two sharp bands at  $1640$  and  $1610 \text{ cm}^{-1}$  were present, but the bands at  $3525$  and  $3585 \text{ cm}^{-1}$  due to water coordinated with different environments (Van Scoyoc *et al.*, 1979) were absent. Instead, only a weak band at  $3525 \text{ cm}^{-1}$  from incompletely diffused pyridine, could be found. Here also, the bands at  $3660$  and  $3640 \text{ cm}^{-1}$ , due to the folded material, reappeared and those at  $3430$  and  $3220 \text{ cm}^{-1}$  become much more intense than in the original spectrum. Finally, these last bands disappeared if the sample was heated in vacuum at  $290^\circ\text{C}$  (Figure 4e), but then, those at  $3585$  and  $3525 \text{ cm}^{-1}$  reappeared. The sharp band at  $1640 \text{ cm}^{-1}$  was not found; instead,

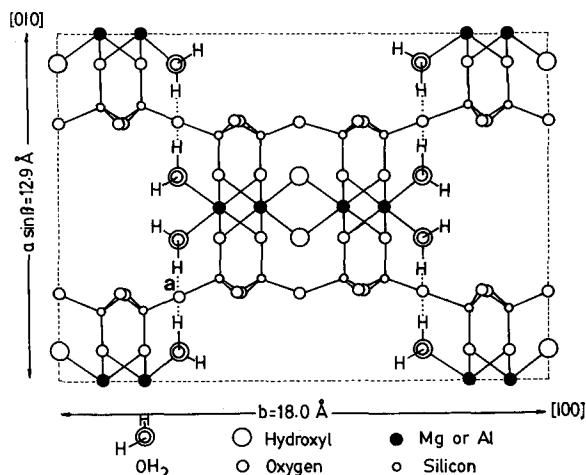


Figure 2. Palygorskite model from Bradley (1940) modified by Serna *et al.* (1977). Bond a gives a band at  $3420\text{--}3440 \text{ cm}^{-1}$  on Si-O-Si; and at  $3220\text{--}3230 \text{ cm}^{-1}$  on Si-O-Al.

a  $1620\text{-cm}^{-1}$  deformation band of coordinated water was noted.

On the basis of these spectral data, after pyridine was adsorbed on the palygorskite no water appeared to be coordinated to octahedral magnesium in the  $100^\circ\text{--}290^\circ\text{C}$  temperature range under vacuum; however pyridinium ions bound to the oxygen of the Si-O-Si or Si-O-Al groups were present. Two processes may account for these results:

- (1) Pyridine substituted for octahedral Mg-bound water; it then protonated under the influence of  $\text{H}^+$  produced by the polarization of water bound to exchangeable cations and bound to oxygen in the Si-O-Si or Si-O-Al, forming a deformed pyridinium ion.
- (2) Inasmuch as folding and unfolding appeared to be involved in the process, a hydrogen from Mg-coordinated water was displaced towards the oxygen of the Si-O-Si or Si-O-Al groups (see Figure 2) and protonated forming a deformed pyridinium ion.

Both processes are in accord with the results of Farmer and Mortland (1966) who reported existence of a deformed pyridinium ion despite the suppression of the  $1550\text{-cm}^{-1}$  band. The first process is in accord with the substitution of coordinated water by ammonia, as described by Van Scoyoc *et al.* (1979) for palygorskite, and agrees with the results of Yariv and Cross (1979) for smectites. The second process is based on the asymmetry of water molecules coordinated to octahedral Mg in palygorskite, as reported by Serna *et al.* (1976) and on the results of Farmer and Mortland (1966). Farmer and Mortland (1966) found that coordinated water could not be removed from a  $\text{Mg}^{2+}(\text{HOH}, \text{NC}_5\text{H}_5)_6$  complex, whereas residual water ionized to give pyridinium ions on heating under vacuum. Co-

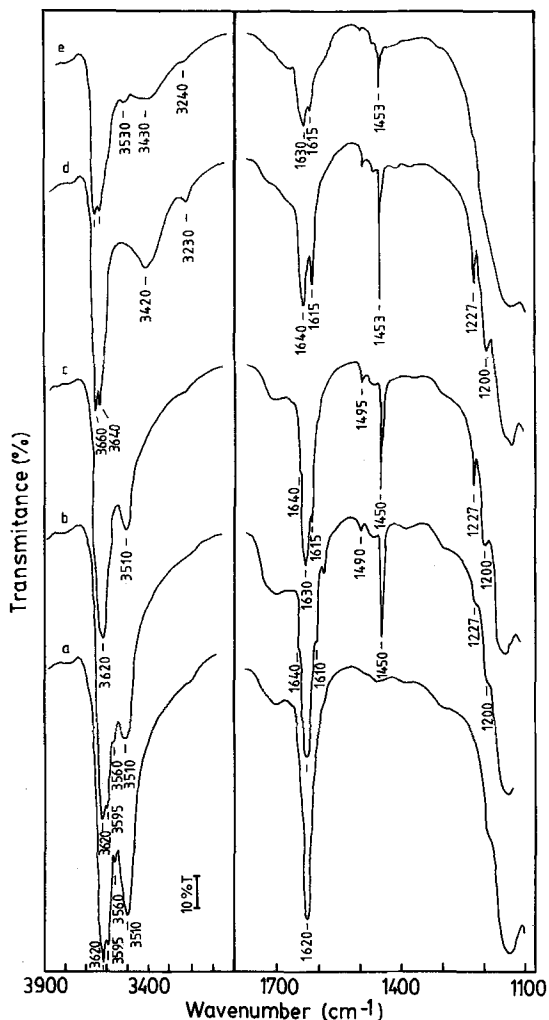


Figure 3. Infrared spectra of pyridine adsorbed on a palygorskite film: (a) palygorskite degassed at room temperature; (b) pyridine adsorbed and evacuated at room temperature; (c) after 2-hr evacuation at 100°C; (d) after 2-hr evacuation at 150°C; (e) after 2-hr evacuation at 230°C.

ordinated water on octahedral Mg probably reacts similarly. In the present work, the 3585- and 3525-cm<sup>-1</sup> bands reappeared at 290°C, consistent with a return of the coordinated water to its initial position. These phenomena are illustrated schematically below:

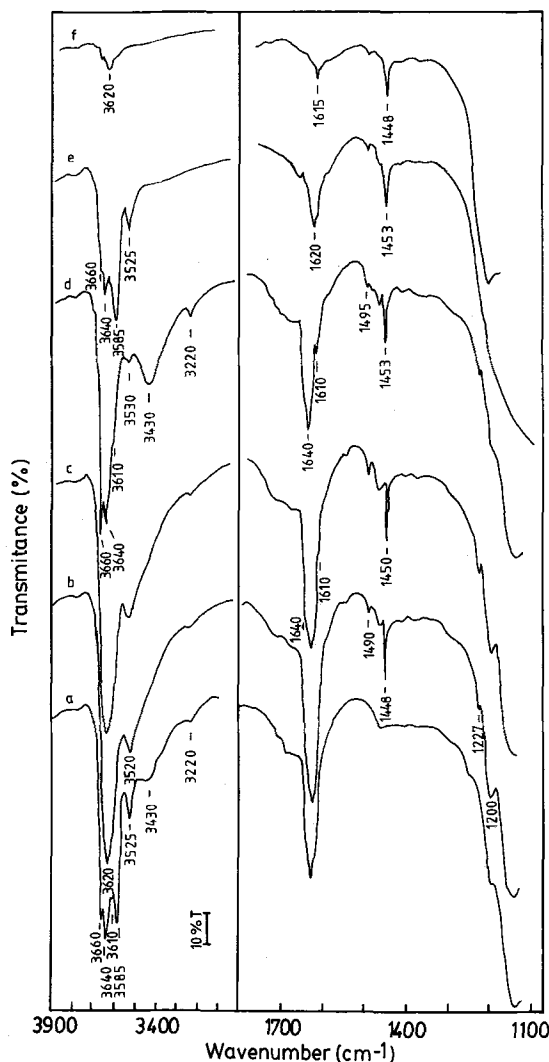
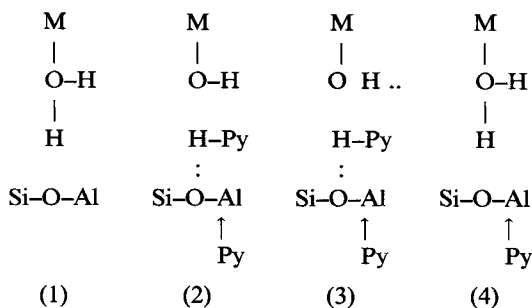


Figure 4. Infrared spectra of pyridine adsorbed on palygorskite degassed at 150°C: (a) palygorskite evacuated at 150°C; (b) pyridine retained after 2-hr evacuation at room temperature; (c) after degassing at 50°C; (d) after degassing at 150°C; (e) after degassing at 290°C; (f) after degassing at 500°C.

Here, state (1) is for palygorskite at room temperature, state (2) for palygorskite after pyridine adsorption, state (3) for palygorskite in the 150°–290°C temperature interval (under vacuum), and state (4) for palygorskite after evacuation at 290°C. M is an exchangeable cation or an octahedral magnesium ion.

Lewis-acid centers were present in a reasonable density at <500°C, as the spectral lines in Figures 2 and 4 suggest. The frequency of the most characteristic band, 1450 cm<sup>-1</sup>, shifted slightly to 1448 cm<sup>-1</sup> if pyridine was adsorbed at room temperature, and to 1453 cm<sup>-1</sup> if the sample was heated at 150°–250°C. At higher temperatures the frequency decreased to its initial value. Primet (1970) explained this same phenomenon for

the adsorption of pyridine on  $\text{TiO}_2$  by the creation of new (stronger) Lewis-acid centers. The results of the present work suggest that the environment of the centers varied with degassing temperature, the change in structure determining the change in acid strength.

In addition, the Brønsted acidity was increased with Lewis-acid centers to which the pyridine was coordinated, i.e., the partial negative charge in the oxygen of the Si–O–Si or Si–O–Al linkages was greater if the pyridine was coordinated to Al.

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