The effect of pre-heating on the evolution of the acidity of pillared clays

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(Received 15 September 1992)

Abstract

Thermal studies under vacuum show that the minimum in the DTG curves ascribed to the dehydroxylation of the pillars of Al-PILC and Al-Ga-PILC samples occurs at 335 and 415°C respectively. This process produces an increase in the concentration of acid centres. This phenomenon has been related to the results obtained for pyridine desorption by IR spectroscopy. The IR spectrum of an Al-PILC sample without thermal treatment prior to pyridine sorption showed a decrease in the intensities of the typical bands of Lewis-acid centres when pyridine desorption was performed from 200 to 250°C. However, the intensities of these bands increased when pyridine desorption was performed at 300°C. In contrast, for the Al-Ga-PILC sample, there was always a decrease in the intensities of the bands. Nevertheless, when the two samples were treated at 400 or 600°C prior to pyridine sorption, they both showed a continuous decrease in the intensity of the bands of the acid centres in the pyridine desorption process over the whole temperature range tested.

INTRODUCTION

The intercalation of inorganic polyoxycations between layers of clays is an essential process in the preparation of pillared clays with thermally stable porosity. The inorganic polyoxycations are converted to the corresponding oxides to function as props between the silicate layers thus generating a microporous material with potential interest for use as adsorbents and catalysts [1, 2]. So far the predominant polymeric species employed as pillars has been the $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ polyoxycation [3–5]. The thermal stabilities of the resulting PILC vary widely but, unfortunately, none has proved adequate enough to survive the high temperature treatment required to regenerate poisoned catalysts [6–10]. This has led to a recent search for new pillaring agents with Ga as the stabilizing cation in the pillars of Al polyoxycations [11–13].

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The TG–DSC technique provides information on the dehydration and dehydroxylation of the polymeric cations when they are calcined to obtain oxides. The acidity of the samples can be modified by this process. This acidity makes the samples suitable for use in cracking as Brönsted-acid catalysts [14, 15].

The IR spectral patterns as a function of temperature of a solid on which pyridine is desorbed give information on the surface acidity of catalysts [16, 17]. Indeed, some IR bands are known to be characteristic of pyridine adsorbed on Brönsted sites (1545 cm^{-1}) and of pyridine adsorbed on Lewis sites (1465–1440 cm^{-1}) [18]. In the literature [19–21], it is reported that Lewis acidity in these materials appears to be almost temperature independent in the 100–300°C range. As a result, the intensity of the bands assigned to pyridine on Lewis-acid sites decreases slightly. However, above 300°C in vacuo, the intensities of these bands are reduced significantly.

Thermal analysis together with IR spectroscopy has provided us with information concerning the evolution of the acidity of pillared clays. The aim of this research was to study the effect of the pre-heating temperature on the evolution of the acidity of clays pillared with Al polyoxycations and with a combination of Al and Ga polyoxycations, in order to deduce the thermal pre-treatment conditions for generation of the optimal acidity in the material.

EXPERIMENTAL

Materials

A Spanish montmorillonite from Serrata de Níjar (Almería, Spain) supplied by Minas de Gador S.A. was used as the raw material. Its structural formula, previously determined in ref. 22, is

$$(Si_{8.00})_T(Al_{2.69}Fe_{0.32}Mg_{0.97})_O(Ca_{0.13}Mg_{0.26}Na_{0.23}K_{0.02})_{EC}O_{20}(OH)_4$$
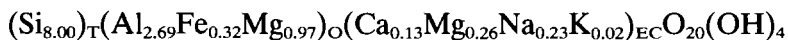
The montmorillonite was purified by means of conventional sedimentation, collecting the <2 μm fraction. It was then exchanged with a 1 M solution of NaCl to obtain Na-homoionic montmorillonite. The exchanged clay was washed with distilled water until chloride-free. The sample obtained in this way will be denoted S–Na. Its exchange capacity was 59 mequiv per 100 g of clay and it had a surface area of 87 m^2 g^{-1}.

Preparation of pillaring agent

An aluminium hydroxy oligomeric solution was prepared according to a previously reported method [23] to obtain an OH/Al ratio of 2.0. The method of preparation of the pillaring agent with Al and Ga was the same as that described by González et al. [13]. Appropriate volumes of NaOH

were gradually added to stirred $AlCl_3 \cdot 6H_2O + GaCl_3$ solutions with a Ga/Al proportion of 25/75 in order to obtain an OH/(Al + Ga) ratio of 2.0. The resulting solutions were then aged at 60°C for 2 h before being used in the pillaring process.

Pillaring process

The Al-PILC and Al-Ga-PILC were synthesized by adding solutions of the pillaring agent to specific volumes of the clay slurry so as to adjust the (Al + Ga) content to a desired value. The resulting system used in the two experiments had 20 mequiv (Al + Ga) per g of clay.

Methods

TG and DTG measurements were carried out using a Setaram TG-DSC 111 apparatus with an air flow of 20 cc min^{-1} and a heating rate of 5°C min^{-1} or in a dynamic vacuum of 10^{-3} Torr. Thermal treatment of the samples was carried out at 400 and 600°C for 2 h in a fixed bed reactor. A current of 100 cc min^{-1} of dry air was used. IR spectra were recorded in a single-beam Perkin-Elmer Model 1605 FT-IR spectrophotometer with a sensitivity of ± 4 cm^{-1} in the 1700–1400 cm^{-1} range and $\pm 1\%$ in transmittance. Self-supporting wafers were prepared by pressing approx. 25 mg of a sample on a 18 mm diameter die. The wafer was degassed by heating at 200°C in vacuo before performing pyridine adsorption on the sample for 30 min. Infrared spectra were recorded after evacuation at room temperature and also after evacuation for 2 h at various temperature from 100 to 400°C.

RESULTS AND DISCUSSION

Figure 1 shows the thermogram of the S–Na sample in the range from room temperature to 825°C. The thermogram clearly shows two steps. The first, between 25 and 204°C, is generally interpreted as being caused by loss from the external free surface of molecular water condensed in the mesopores and weakly bonded between the structural sheets of the material (7.02%). The second is said to be due to the dehydroxylation of the silicate structure (5.86%) at higher temperatures (331–825°C). A shoulder can also be seen in this sample between 204 and 331°C and can be ascribed to the molecular water in the hydration shells of Na$^+$ (1.36%).

Figure 2(A) shows the TG–DTG trace of the Al-PILC sample, which shows three steps. The first, between 25 and 260°C, presents a weight loss of 16.38%. This value corresponds to the adsorbed water on the external surface and indicates the higher surface area of this sample (353 m^2 g^{-1}) [13] than that of the S–Na sample (87 m^2 g^{-1}). This is corroborated by measuring N$_2$ adsorption at 77 K and applying the BET equation to the first points of the isotherms [24]. Between 260 and 520°C, there is a mass loss
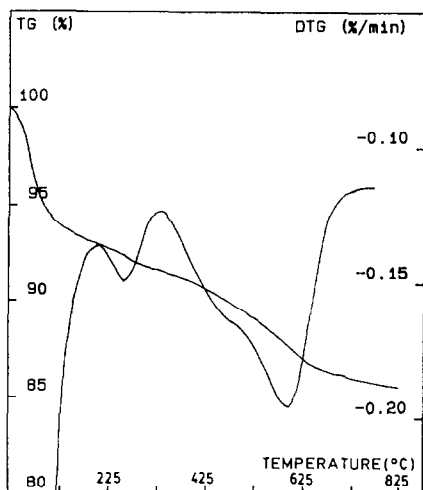
Fig. 1. Thermogram of S–Na sample.

(6.14%) associated with the dehydration and dehydroxylation of the Al polyoxycation incorporated between the sheets of clay. The DTG of this sample shows the minimum of this peak at 365°C. Finally, between 520 and 825°C, there is a mass loss of 3.10%, which is less than that of the S–Na
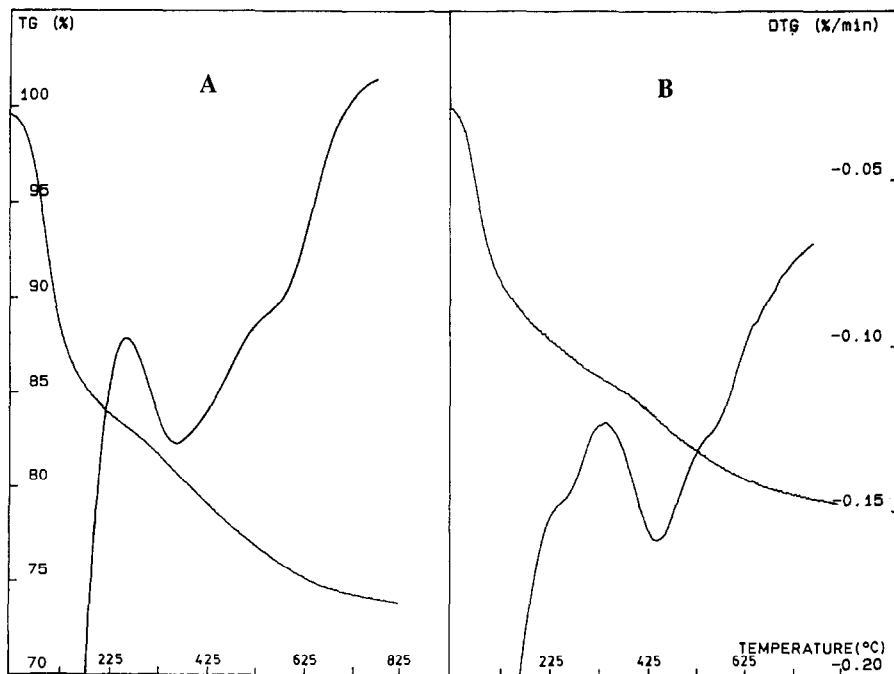

Fig. 2. Thermograms of (A) Al-PILC, and (B) Al-Ga-PILC under air.

sample and is attributable to the dehydroxylation of the hydroxyl groups of the silicate structure.

Figure 2(B) shows the TG–DTG curve of the Al-Ga-PILC sample. The first step, 25–337°C, again shows a mass loss, 14.18%, which is higher than that of the S–Na sample (7.02%) but less than that of the Al-PILC sample (16.38%). This step is ascribed to the adsorbed water on the external surface and its value is due to the smaller surface area (287 m^2 g^{-1}) of this sample in relation to the Al-PILC sample [13]. A shoulder can also be observed between 225 and 276°C, probably due to the hydration water of the remaining Na$^+$ cations and Ga^{3+} oligomers, which are positioned on the surface of the material rather than as pillars [13]. This is confirmed by the X-ray diffractograms, where there is a second broad peak between 10.6 and 11.5 Å indicating the fraction of clay that remains unpillared [13]. The second step, between 337 and 515°C, indicates a mass loss of 1.56% associated with the dehydration and dehydroxylation of the mixed Al-Ga polyoxycations between the sheets of the clay. This process is more extensive in the Al-PILC than in the Al-Ga-PILC sample, because the pillaring process was incomplete in the latter. The DTG shows the minimum of this peak to be at 444°C. Finally, between 515 and 825°C, the mass loss (3.09%) is due to the dehydroxylation of the hydroxyl groups of the raw material.
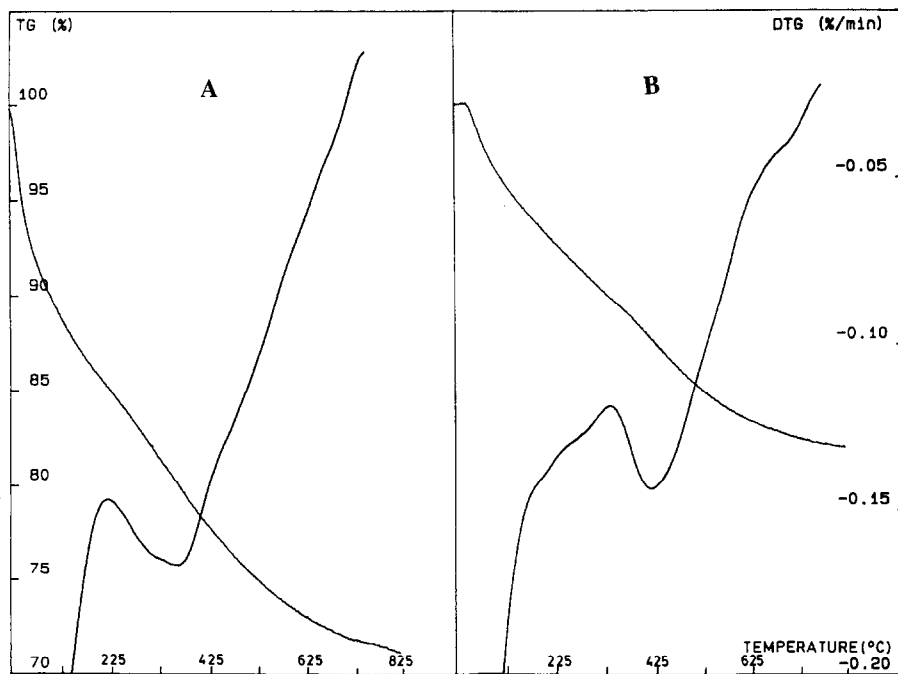

Fig. 3. Thermograms of (A) Al-PILC, and (B) Al-Ga-PILC under dynamic vacuum.

These results were obtained when the samples were heated under air flow. When, however, the experiments were performed in a dynamic vacuum, the dehydroxylation of the samples was seen to shift to lower temperatures (Fig. 3). Thus, for the Al-PILC sample, the minimum of the second peak corresponding to the dehydroxylation of the cation occurs at 335 instead of 365°C, and for the Al-Ga-PILC sample this minimum is at 415 instead of 444°C.

The dehydroxylation process of the pillars started at 215 and 337°C for the Al-PILC and the Al-Ga-PILC samples respectively, suggesting that the latter has a higher thermal stability than the former. This clearly shows that the incorporation of a larger radius cation (Ga^{3+}) into the Al pillars results in a structure with a significantly greater stability and, at the same time, the basal spacing and the S_{BET} of the sample remain constant at higher temperatures [13].

Figure 4 shows the IR spectra of pyridine adsorbed on Al-PILC without thermal treatment. After evacuation at 200°C, the sample shows the bands assigned to Lewis-acid sites at 1619, 1490 and 1453 cm^{-1}, together with a shoulder at 1549 and the band at 1637 cm^{-1} assigned to the pyridinium ion. As can be seen, there is a clear decrease in the intensity of the band typically associated with Brönsted-acid sites ($\approx 1550 cm^{-1}$) and a slight decrease in the bands ascribed to Lewis-acid centres ($\approx 1454 cm^{-1}$) when the pyridine is desorbed from 200 to 250°C. The latter increase again when desorption takes place at 300°C. After evacuation at 400°C for 2 h, the Lewis-acid sites clearly decrease.

However, when the sample has previously undergone treatment for 2 h in air at 400 or 600°C (Fig. 5), a continuous decrease in the intensity of the acid centres is observed when the desorption temperature of pyridine is increased to 400°C.

The IR spectra of the Al-Ga-PILC sample without thermal treatment (Fig. 6) show the same behaviour as the Al-PILC sample when pyridine desorption is performed from 200 to 250°C, i.e. there is a decrease. However, when the temperature is increased up to 400°C, a decrease in the intensity of the bands is observed. When this sample has been treated at 400 or 600°C for 2 h in air prior to pyridine sorption, its behaviour is seen to be similar to that of the Al-PILC sample with the same thermal treatment (Fig. 7).

These results agree with the thermograms of the samples. As seen above, the minimum of the DTG step ascribed to the dehydroxylation process of the Al pillars occurs at 335°C under dynamic vacuum. This means that, when the wafer is heated at 300°C under vacuum for pyridine desorption, the dehydroxylation process is taking place. This produces a higher concentration of Lewis centres generated by the dehydroxylation of the pillars, which is not compensated for by their destruction due to the thermal effect.
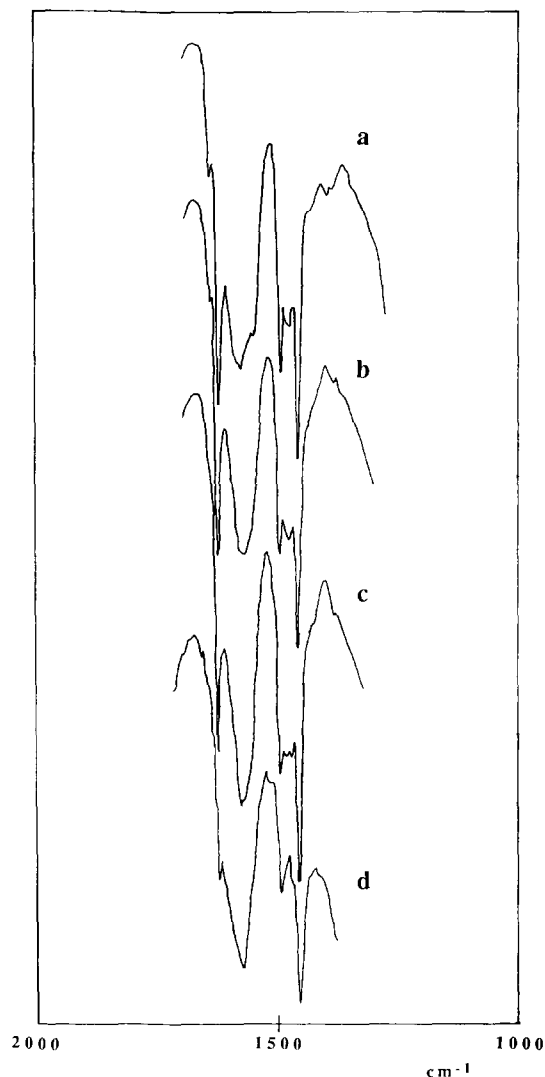
Fig. 4. The effect of evacuation temperature on the IR spectra of pyridine adsorbed on Al-PILC sample previously degassed at 200°C for 2 h under dynamic vacuum and evacuated for 2 h in vacuo at (curve a) 200, (curve b) 250, (curve c) 300, and (curve d) 400°C.

However, when the sample has been pre-heated at 400 or 600°C for 2 h in air, the dehydroxylation process has already finished and only a decrease in the intensities of the bands is observed as the temperature rises.

In the Al-Ga-PILC sample, the minimum of the DTG step of the dehydroxylation process of the Al-Ga polyoxycations incorporated between the sheets of the clay occurs at 415°C under a dynamic vacuum. Therefore, when pyridine desorption is performed between 200 and 400°C, there is no increase in the intensity of the bands due to dehydroxylation. In
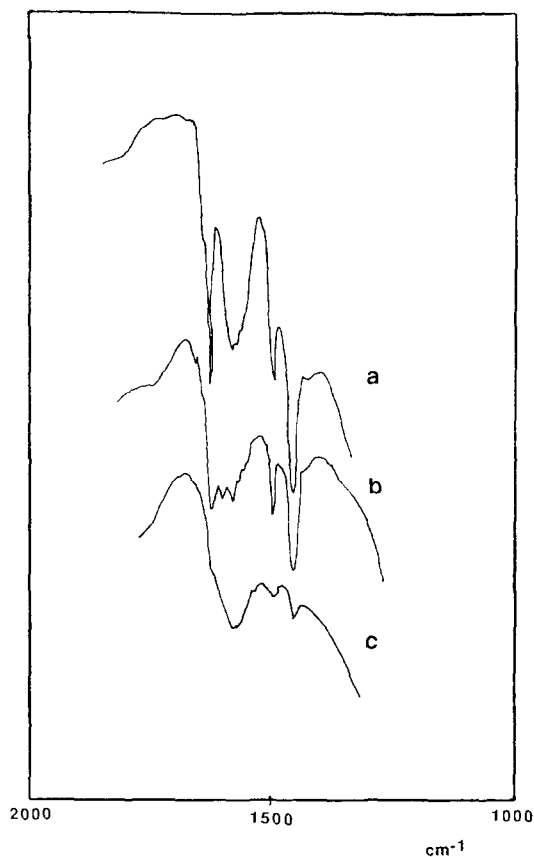
Fig. 5. IR spectra of pyridine adsorbed on Al-PILC pre-treated for 2 h in air at 400°C and evacuated for 2 h in vacuo at (curve a) 200, (curve b) 300, and (curve c) 400°C.

this case, the generation of Lewis-acid centres due to the dehydroxylation of the pillars occurs at such a high temperature that it is compensated for by the destruction of Lewis centres by the thermal effect. The samples pre-treated at 400 or 600°C for 2 h in air behave in a similar way as the Al-PILC samples undergoing the same treatment.

CONCLUSIONS

The results suggest that the Al-Ga-PILC sample has a higher thermal stability than the Al-PILC sample. Dehydroxylation starts at 215°C and 337°C for Al-PILC and Al-Ga-PILC respectively. The process is more extensive in the former because pillaring is complete in contrast to the Al-Ga-PILC sample, in which not all the Al-Ga cations occur as pillars. This is shown by the shoulder appearing between 225 and 276°C in the DTG curve of this sample.
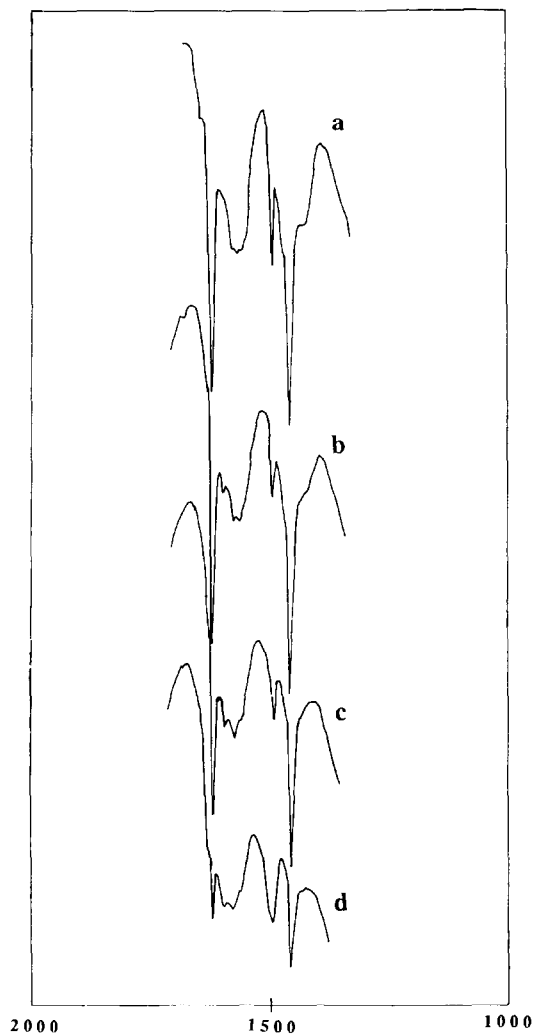
Fig. 6. IR spectra of pyridine adsorbed on Al-Ga-PILC degassed at 200°C and evacuated for 2 h in vacuo at (curve a) 200, (curve b) 250, (curve c) 300, and (curve d) 400°C.

Spectroscopy studies show that the pre-heating of samples has a great influence on the relative number and evolution of acid centres. The dehydroxylation of the pillars produces an increase in Lewis-acid sites. The temperature interval over which this process occurs should, therefore, be taken into account when samples are thermally treated prior to pyridine sorption.
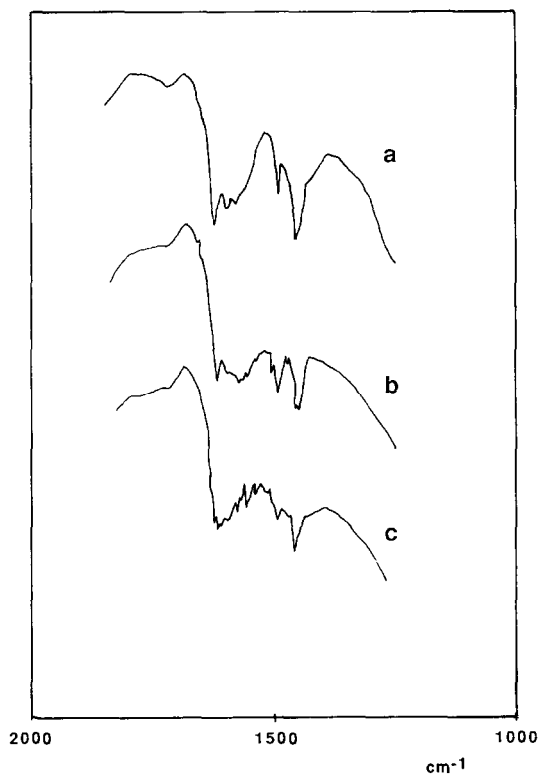
ACKNOWLEDGEMENTS

Fig. 7. IR spectra of pyridine adsorbed on Al-Ga-PILC pre-treated for 2 h in air at 400°C and evacuated for 2 h in vacuo at (curve a) 200, (curve b) 300, and (curve c) 400°C.

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