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A COMPARATIVE STUDY OF THE DEHYDROXYLATION PROCESS IN UNTREATED AND HYDRAZINE-DEINTERCALATED DICKITE

F. Franco[*] *and M. D. Ruiz Cruz*

Departamento de Química Inorgánica, Cristalografía y Mineralogía, Facultad de Ciencias, Campus de Teatinos
Universidad de Málaga, 29071 Málaga, Spain

A dickite from Tarifa (Spain) was used to study the influence of the intercalation and the later deintercalation of hydrazine on the dehydroxylation process.

The dehydroxylation of the untreated dickite occurs through three overlapping endothermic stages whose DTA peaks are centred at 586, 657 and 676ºC. These endothermic effects correspond, respectively, to the loss of the inner-surface, the inner hydroxyl groups, and the loss of the water molecules, product of dehydroxylation process, which has been trapped in the framework of the dehydroxylated dickite.

The intercalation of hydrazine in the interlayer space of dickite and the later deintercalation affect the dehydroxylation process. It occurs through only two endothermic stages which DTA peaks are centred at 575 and 650ºC. The first corresponds to the simultaneous loss of both the inner and the inner-surface hydroxyl groups, whereas the second one is analogous to that at 676ºC observed in the DTA curve of untreated dickite. These effects appear shifted to lower temperatures compared to those observed in the untreated dickite.

Keywords: *dehydroxylation, dickite, differential thermal analysis, hydrazine, infrared spectroscopy, intercalation complex*

Introduction

The study of dehydroxylation of clay minerals is important in industry, particularly in the ceramic industry [1, 2]. The dehydroxylation of kaolinite has been extensively studied using several techniques [3–9]. It takes place through a homogeneous process which results from the interaction of two adjacent hydroxyl groups in a two steps process [3]. The reaction may be shown chemically as follows [3]:

$$OH^{-}\leftrightarrow H^{+}+O^{2-} \text{ and } H^{+}+OH^{-}\leftrightarrow H_2O$$

Frost and Vassallo [3] indicated that both the inner and inner-surface hydroxyl groups are progressively removed simultaneously. Thus, this process appears, in the DTA curves, as a single endothermic effect at about 500ºC. Various authors [4, 10, 11] showed that the interval of temperatures in which this process takes place depends on the particle-size and the structural disorder of kaolinite.

On the contrary, the dehydroxylation of dickite has received less attention. Several authors have pointed out that the dehydroxylation of dickite takes place in two different stages [3, 12]. They indicated that in the first stage, the inner-surface hydroxyl groups are lost through a homogeneous mechanism, similar to that described for kaolinite, whereas, in the second one, the inner hydroxyl groups are lost through a heterogeneous mechanism that requires the diffusion of protons through the structure [3]. However, there are many aspects of this process that have not been properly explained [13]. For this reason, the objective of this work it is to carry out the study of the dehydroxylation of dickite, using differential thermal analysis (DTA) and Fourier transform infrared spectroscopy (FTIR), and evaluate the effect, on this process, of the increase of the structural disorder and the decrease of particle-size originated by the intercalation and the subsequent deintercalation of hydrazine.

Experimental

The specimen used for this study was a low-defect dickite from Tarifa (Spain). This consists of dickite alone and no other impurities were detected by X-ray diffraction (XRD) (Fig. 1a) [14]. The reagent used was 98% pure hydrazine monohydrate (Hz) (Prolabo Company, Fontenay, France). The dickite-hydrazine intercalation complex was obtained by immersing of 1 g of dickite in 20 cm^3 of Hz. Two days of reaction were necessary to obtain the complete intercalation of dickite. Intercalation of Hz molecules in the interlayer space of dickite caused the expansion of the basal spacing from 7.15 to 10.24 Å [15]. After this treatment, the intercalation complex was heated from room tempera-

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[*] Author for correspondence: ffranco@uma.es

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

ture to 300ºC, until the complete deintercalation of Hz molecules. The total evolution of the Hz molecules caused the restoring of the original basal spacing of the dickite (7.15 Å) [16]. Moreover, to differentiate the effect of the deintercalation and the effect of the heating to 300ºC, the untreated dickite was also heated from room temperature to 300ºC, in the same conditions used to deintercalate the Hz molecules. The three samples, untreated, deintercalated dickite and thermally treated dickite were previously characterized by XRD, DTA and FTIR. Nevertheless, since were not differences in the XRD, FTIR DTA curves of the untreated dickite and the dickite heated to 300ºC, the analyses of this later were not included in the work. In order to obtain more information about the modifications on the dehydroxylation process, aliquots of untreated dickite and deintercalated sample heated in the DTA analyser to 567, 600, 663 and 750ºC were taken for their respective FTIR analyses. This methodology has allowed to reproduce the conditions of DTA-curve measurement.

XRD patterns were obtained using a Siemens D-5000 diffractometer. The XRD patterns were obtained using CuK$_\alpha$ radiation, at 40 kV and 35 mA, and a step size of 0.02º 2θ at a counting time of 3 s. Measurements were performed on randomly oriented powder preparations. The apparent coherent scattering thickness of the dickite crystals along the c^*-axis was calculated using the 002 reflection (CS$_{002}$) according to the Scherrer formula [17].

DTA was performed in a Setaram thermal analyser equipped with a CS32 controller. Al_2O_3 was used as reference material. 20 mg of sample was used in the analysis of both untreated and deintercalated dickites. DTA curves were recorded in dry air flow at a heating rate of 10ºC min^{-1}.

FTIR spectra were recorded using KBr pellets (2 mass% sample) in a Nicolet spectrometer (20SXB) in the range 4000–400 cm^{-1}. Resolution was of 2 cm^{-1}. 300 scans were accumulated to improve the signal to noise ratio in the spectra. To avoid grinding effects in the preparation of the disk, samples and KBr were gently mixed manually.

Baseline adjustment and band component analysis of FTIR spectra and DTA curves were carried out using the peakfit software from Jandel Scientific. Peak fitting was carried out until correlation coefficients with r^2>0.997 were obtained.

Results and discussion

Figure 1 shows the XRD pattern of the untreated dickite and the deintercalated sample. The reflections 11*l* and 02*l* (between 17 and 27º 2θ) of untreated sample are narrow and intense, indicating that this dickite is well crystallized [18, 19]. Comparisons of the diffraction peak profiles of the deintercalated sample with that of the untreated dickite shows that the intercalation of Hz and its posterior deintercalation caused:

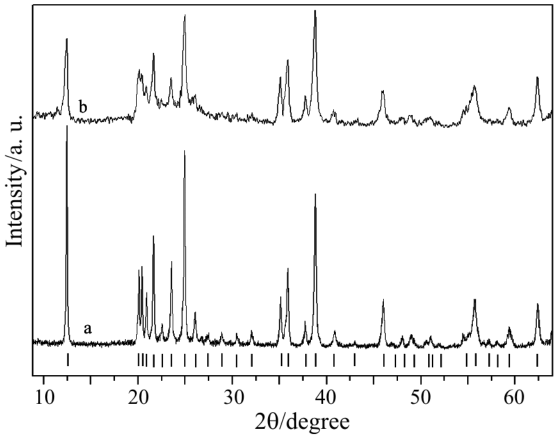

Fig. 1 X-ray diffraction pattern of a – untreated dickite and b – hydrazine-deintercalated sample

- A broadening of the basal reflections, which indicates that the thickness of the dickite crystallite decreased with treatment. The apparent coherent scattering thickness of dickite particles along the *c*-axis decreased from 521 to 264 Å [17]. Thus, the number of layers within an individual crystallite decreases from 37 to 19.
- Important modifications of the 11*l* and 02*l* reflections. These reflections were broadened causing the overlapping among them and the increase of the signal between peaks. According to Brindley and Porter [18], this suggests an increase of the structural disorder.

The modifications induced by the intercalation and deintercalation processes in the dickite structure was also studied by FTIR spectroscopy. Figure 2a shows the OH stretching region of the FTIR spectrum of the untreated dickite. This spectrum shows three bands in the ν_{OH} region at 3708, 3653 and 3621 cm^{-1}. Intercalation and deuteration studies [20] have established that the bands at 3708 and 3653 cm^{-1} arise from the inner-surface hydroxyls, whereas the 3621 cm^{-1} band is due to inner OH group. The curve-fitted infrared spectrum displays five bands at 3717, 3709, 3654, 3621 and 3428 cm^{-1}, corresponding to the stretching modes of the OH groups and labelled, following Shoval *et al.* [21, 22], as A_A, A_Z, C, D_Z and D_A respectively. Position, area and width of these bands are shown in Table 1.

Figure 2b shows the OH stretching region of the FTIR spectrum of the deintercalated dickite. A comparison between the infrared spectra of the untreated dickite (Fig. 2a) and the deintercalated dickite shows that the intercalation followed by the evolution of Hz molecules caused: 1) The increase of the signal noise in this region of the spectra (this is not detectable in

Table 1 Band positions, full width at half-maximum (FWHM) and band areas calculated from the hydroxyl stretching region of the FTIR spectra of untreated dickite and deintercalated sample after heating to 300ºC

Sample	Band	Center/ cm^{-1}	Area	FWHM/ cm^{-1}
dickite	D_A	3614	6	45
	D_Z	3621	9	12
	C	3654	10	25
	A_Z	3708	4	21
	A_A	3717	11	67
deintercalated dickite	D_A	3608	3	47
	D_Z	3622	7	14
	C	3653	5	20
	B	3673	2	25
	A_Z	3706	3	22
	A_A	3721	15	336

the figure because the spectra were smoothed to facilitate the band component analysis), 2) The shift to higher wavenumbers of the A_A band (from 3717 to 3721 cm^{-1}), 3) The appearance of a new band at 3671 cm^{-1}, and 4) a general decrease in intensity of the OH stretching bands. The increase of the signal noise can be explained in terms of increasing of random displacements between adjacent layers, which modify the homogeneity of the orientation of the hydroxyl groups. These displacements would increase the distance between the OH_3 group and the oxygen atoms of the adjacent layer causing the shift to higher wavenumbers of the A_A band. Moreover, the appearance of a new band at 3671 cm^{-1}, which is present in the infrared spectrum of kaolinite [23], suggests that some inner-surface hydroxyl groups acquire an orientation, respect the (001) plane, similar to that of kaolinite. Finally, the decrease in intensity of the OH stretching bands, relative to the intensity of the ν_{SiO} bands, can be related with the loss of some OH groups through a prototropic mechanism, which occurs in the new external surface generated with the particle-size reduction [24–26].

Figure 2c shows the 1200–850 cm^{-1} region of the FTIR spectrum of untreated dickite. This spectrum shows six bands at 884, 901, 914, 935, 957, 970 cm^{-1} (bands δ_1, δ_2, δ_3, δ_4, δ_5 and δ_6) which correspond to the deformation modes of the OH groups. The bands δ_4, δ_5 and δ_6 were previously identified with the inner-surface OH groups, whereas the bands δ_2 and δ_3 were identified with the inner OH groups [27]. On the other hand, band δ_1 was assigned to non-hydrogen bonding OH groups [27]. The spectrum also shows well defined bands at 1000, 1032 and 1119 which correspond to the vibrational modes of the Si–O groups [28].

In this range (1200–850 cm^{-1}) we have observed a decrease in intensity of the δ bands (Table 2, Figs 2c and d) in the spectrum of deintercalated dickite, which is in agreement with the decreasing of the OH stretching bands (Table 1, Figs 2a and b) and suggests that prototropy occurs, possibly, at the new surface generated. On the other hand, Si–O bands remain almost unaffected after the treatment (Table 2, Figs 2c and d). Therefore we can conclude that the tetrahedral sheets are not affected by the intercalation and deintercalation processes.

Figure 3 shows the DTA curves of untreated and deintercalated dickite. In the untreated dickite (Fig. 3a), dehydroxylation yields three overlapping endothermic effects whose ATD peaks are centred at 587, 657 and 676ºC. According to Frost and Vassallo [3] and Stoch [12], the endothermic peak centred at 587ºC can be assigned to the loss of inner-surface hydroxyl groups, whereas the endothermic peak centred at 657ºC can be assigned to the loss of the inner hydroxyl ones. The effect at 676ºC has no been previously assigned. These effects appear notably modified

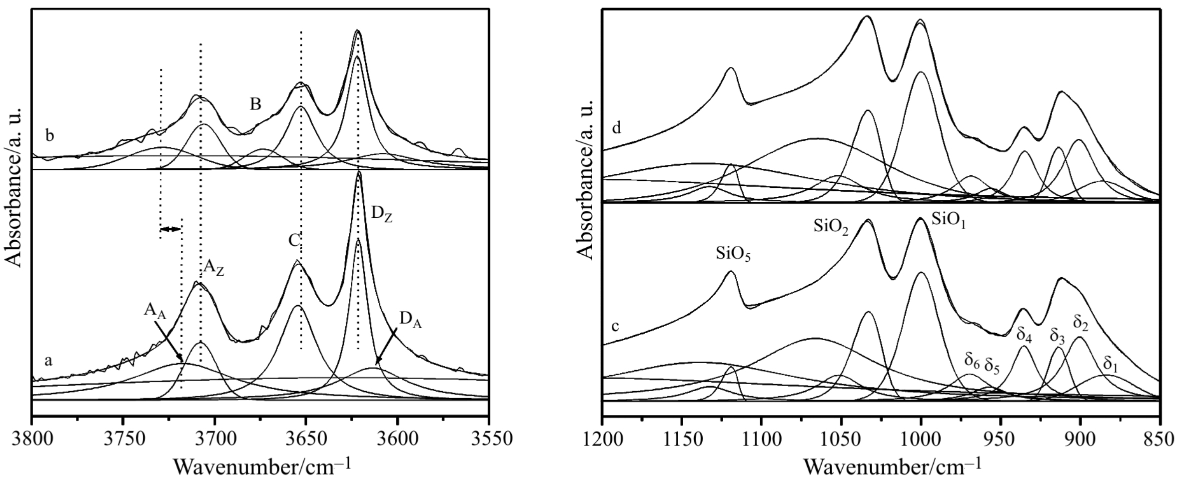

Fig. 2 Band component analysis of the OH stretching region of FTIR spectra of a – untreated dickite, b – hydrazine-deintercalated sample, c – Si–O stretching region of untreated dickite and d – hydrazine-deintercalated sample

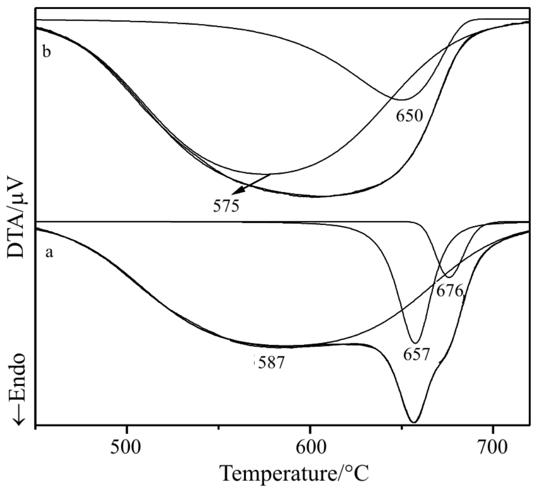

Fig. 3 Band component analysis of DTA curves at 400–730ºC region of a –untreated dickite and b – hydrazine-deintercalated sample

in the DTA curve of deintercalated dickite (Fig. 3b). The band component analysis of the dehydroxylation effect of deintercalated dickite shows that it appears to be formed by only two broad endothermic peaks at 575 and 650ºC. These effects occur at lower temperatures and in a narrower range of temperatures than those observed in the untreated dickite.

To ensure the correct interpretation of the endothermic effects observed in the DTA curve of dickite and the modifications observed after the intercalation and deintercalation of Hz, samples of untreated and deintercalated dickite, previously heated in the TG-DTA analyser to 567, 660, 663 and 750ºC, were taken for their respective FTIR analysis. To study the evolution of the area of the hydroxyl group bands with the temperature, the OH stretching bands were discarded because the high noise in this region of the spectra difficults the accurate measurement of its respective areas. For this purpose, the OH deformation bands were selected.

Figure 4a shows the FTIR spectra of untreated dickite obtained at room temperature and after heating to 567, 600 and 663ºC, and Fig. 4b shows the evolution of the intensity of δ bands with the temperature. These figures clearly show two different trends in the evolution of the hydroxyl groups in a continuous heating rate. A group of bands, which correspond to the non-bonded (δ_1) and the inner-surface hydroxyl groups (δ_4, δ_5 and δ_6) have strong losses of intensity (60–90% of its initial values) between the beginning of dehydroxylation (~ 400ºC) and 567ºC (Figs 4a and b). On the contrary, the bands corresponding to the deformation modes of the inner hydroxyl groups (δ_2 and δ_3) show lower decreases in intensity (10–25%) in this interval of temperatures. Nevertheless, from 567ºC, the decrease in intensity of this later group of bands is notably higher. At 663ºC, all the hydroxyl deformation bands have disappeared. These results indicate that the different types of hydroxyls groups in the dickite structure are lost through two main stages at about 550 and 600ºC, whose occur simultaneously in a wide range of temperatures.

The FTIR results, described above, confirm the assignment of Frost and Vassallo [3], which indicate that the endothermic effect at 587ºC is due to the dehydroxylation of the inner-surface and non-bonded OH group, and the endothermic effect at 657ºC to the dehydroxylation of the inner OH groups. Nevertheless, the nature of the endothermic peak centred at 667ºC has not been previously studied. The FTIR spectrum of the dickite obtained after heating to 663ºC do not show any hydroxyl band (Figs 4a, 5b), for this reason the endothermic peak at 676ºC can not be assigned to the loss of OH groups. This spectrum (Fig. 5b) shows a group of bands near 1600 cm^{-1}, which already appeared, but much less intense, in the spectrum a of the starting dickite (Fig. 5a). This group of bands can be related with the bending vibration of the water molecules (δH_2O bands) [28] which appear as a product of the dehydroxylation process. This suggests that the endothermic peak centred at 676ºC must

Table 2 Band positions, full width at half-maximum (FWHM) and band areas calculated from the 1250–850 cm^{-1} region of the FTIR spectra of untreated dickite and deintercalated sample after heating to 300ºC

Sample	Bands	Center/ cm^{-1}	Area	FWHM/ cm^{-1}
dickite	δ_1	884	2	41
	δ_2	901	8	25
	δ_3	914	3	15
	δ_4	935	5	19
	δ_5	957	2	27
	δ_6	970	4	30
	SiO_1	1000	13	27
	SiO_2	1033	7	22
	–	1051	4	34
	–	1066	29	96
	SiO_3	1119	2	12
	–	1132	3	35
	–	1139	28	155
	–	1220	38	396
deintercalated dickite	δ_1	887	1	36
	δ_2	901	6	24
	δ_3	914	3	15
	δ_4	935	4	19
	δ_5	956	2	23
	δ_6	969	3	27
	SiO_1	1000	13	27
	SiO_2	1033	17	22
	–	1052	5	38
	–	1065	24	102
	SiO_3	1119	2	13
	–	1113	3	31
	–	1136	25	167
	–	1213	31	336

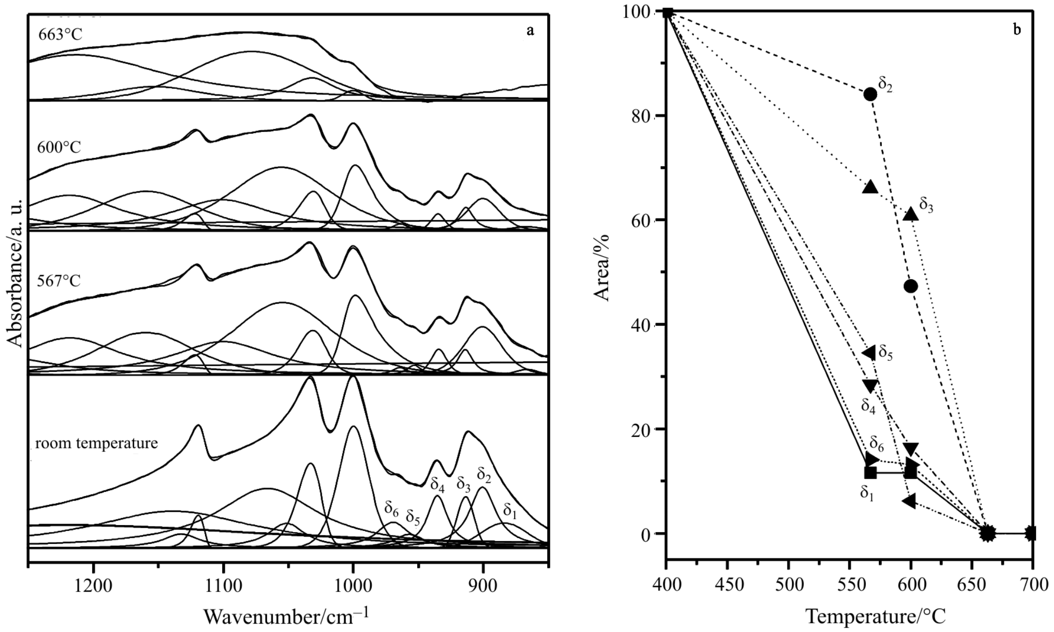

Fig. 4 a – Band component analysis of the Si–O stretching region of the FTIR spectra and the deformation modes of the OH groups of the untreated dickite at increasing temperatures, b –variation of the intensity of the ■ – δ_1, ● – δ_2, ▲ – δ_3, ▼ – δ_4, ◀ – δ_5 and ▶ – δ_6 bands

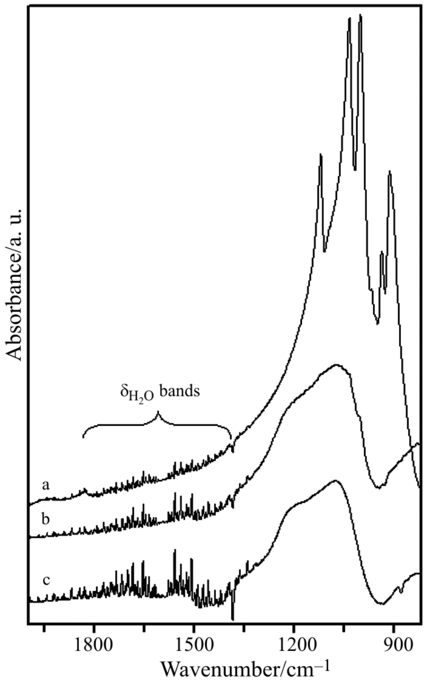

Fig. 5 Region between 1700 and 900 cm^{-1} of the FTIR spectra of a – untreated dickite at room temperature, b – untreated dickite after heating to 663ºC and c – hydrazine-deintercalated dickite after heating to 663ºC

to be related to the loss of some of this water molecules which has been trapped in the framework of the dehydroxylated dickite and are evolved after the end of dehydroxylation process.

On the other hand, the FTIR spectra of the deintercalated dickite obtained at increasing temperatures (Fig. 6a) show differences relative to those observed for the untreated dickite. The evolution of the area of the deformation bands (Fig. 6b) shows that both inner and inner-surface hydroxyl groups are lost simultaneously during the entire dehydroxylation processes. Between 400 and 567ºC, the δ_1 band disappears completely, and $\delta_{2,}$ $\delta_{4,}$ $\delta_{5,}$ δ_6 bands decrease about 80% of its original values. These results suggest that, in the deintercalated dickite, the hydroxyl groups are being lost simultaneously and at lower temperatures as occurs in the dehydroxylation of kaolinite [3]. These results agree with the appearance of a single endothermic effect in the DTA curve centred at 575ºC, which corresponds to the loss of the inner and the inner-surface hydroxyl groups (Fig. 3). The absence of hydroxyl bands in the FTIR spectrum obtained after heating at 663ºC (Fig. 5c) shows that the dehydroxylation process finished below this temperature. This result suggests that the endothermic effect observed at 650ºC in the DTA curve of deintercalated dickite, which is extended above 663ºC, by analogy to the 676ºC band observed in the DTA curve of untreated dickite, could be assigned to the loss of water molecules trapped in the framework of the dehydroxylated dickite. According with Franco *et al.* [4], the shift to lower temperatures of this later endothermic effect must be attributed to the size reduction of the dickite particles along the *c*-axis improving the diffusion of the evolved water molecules compared to their diffusion in the larger untreated dickite particles.

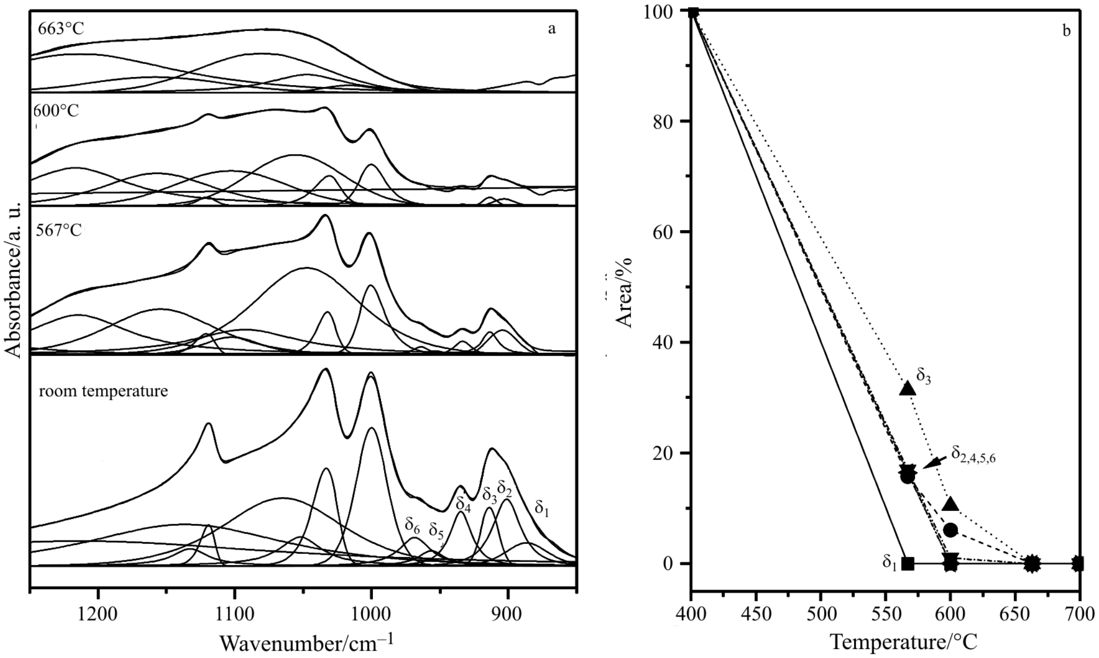

Fig. 6 a – Band component analysis of the Si–O stretching region of the FTIR spectra of the hydrazine-deintercalated dickite at increasing temperatures, b – variation of the intensity of the ■ – δ_1, ● – δ_2, ▲ – δ_3, ▼ – δ_4, ◀ – δ_5 and ▶ – δ_6 bands

Conclusions

The XRD results showed that the intercalation of Hz in the interlayer space of dickite and its posterior deintercalation caused the decrease of the particle thickness of dickite and a notable increase of the structural disorder as indicated by the broadening of the 11*l* and 02*l* reflections.

The FTIR and DTA studies have shown that the dehydroxylation of the untreated dickite occurs through three overlapping endothermic process. The inner-surface and the inner hydroxyl groups are lost through two endothermic processes whose DTA peaks appears centred at 587 and 657ºC, respectively. On the other hand, at 676ºC occurs the evolution of some water molecules, products of the dehydroxylation reaction, which has been trapped in the framework of the dehydroxylated dickite.

On the contrary, the dehydroxylation of the deintercalated dickite occurs through only two endothermic processes with DTA peaks centred at 575 and 650ºC. In the main process, at 575ºC, both the inner and the inner-surface hydroxyl groups are released simultaneously, at similar rates, as occurs in the dehydroxylation of kaolinite. The endothermic peak centred at 650ºC can be assigned, as in the case of the untreated dickite, to the loss of water molecules trapped in the framework of the dehydroxylated dickite. These effects appear shifted to lower temperatures because the thinner particles favour the evolution of these molecules.

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