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AMMONIA RELEASE ON HEATING OF MECHANICALLY TREATED VERMICULITE SATURATED SUBSEQUENTLY WITH AMMONIUM

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Abstract

The differences in thermal behaviour of vermiculite before and after mechanical treatment (sonication and grinding), saturated subsequently with ammonium, were studied by TG, DTA, EGA and IR techniques. Sonication produces only a small modification in the NH_4-vermiculite decomposition attributed to a small particle size. Grinding causes an important but different change in the thermal behaviour of NH_4-vermiculite. The temperature of ammonium loss is lowered stepwise showing that grinding modifies the bonding energy between NH_4^+ and the surface of vermiculite.

Keywords: ammonium intercalation, grinding, infrared spectroscopy, layer charge, sonication, thermal analysis, vermiculite

Introduction

Vermiculite is a clay mineral of great practical importance in technological treatment. Mg^{2+} as originally present in the interlayer space of natural vermiculite is usually exchanged by various cations to modify its properties. One of this cations may be NH_4^+, which also may be present in the interlayer space of mineral soils and sediments and is of special interest from the point of view of agriculture [1] and genesis of soils [2–4]. The study of the thermal decomposition of NH_4^+-saturated vermiculite shows that NH_3 escapes at a temperature which is variable. Barshad [5] and Scott *et al.* [6] found that between 255 and 500°C only a small amount of NH_3 was lost, whereas between 550 and 600°C all the exchangeable NH_4^+ decomposed. At a lower temperature only water was lost. The NH_4^+ mass loss was dependent on the type of exchange sites of this ion in the clay particle.

Grinding, either wet or dry, causes a reduction of particle size of clays and clay minerals and the physicochemical properties of the resulting powders depend on the character of this process [7]. It has been observed that grinding of vermiculite pro-

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duces progressive amorphization increasing with grinding time [8]. Particle size may be also reduced by sonication. Micron and submicron-size vermiculite flakes were prepared recently by sonication from a natural vermiculite [9, 10]. The resulting materials were crystalline, as shown by X-ray diffraction.

Mechanical treatment of vermiculite causes delamination, decrease in particle size, amorphization, agglomeration, etc. and also a change may be produced in the layer charge and in the bonding energy between the cation intercalated and the surface of vermiculite. The temperature of the NH_4^+ mass loss may be changed as compared to the untreated material and it may be measured by thermal analysis [11].

Change in position of the IR band at 1440 or 1400 cm^{-1} (KBr matrix) has been used for the evaluation of the layer charge of smectites [12]. The band at 1400 cm^{-1} is attributed to NH_4Br originated from the replacement of NH_4^+ in the clay by K^+ from KBr. For swelling clay minerals this band indicates that the layer has a permanent low charge density and/or a variable charge. For non-swelling clay minerals this band characterizes the presence of variable charges only. On the other hand, the band at 1440 cm^{-1} suggests that the NH_4^+ ions in the clay were not replaced by K^+ ions and they remain in the interlayer space of the clay minerals. This is due to NH_4^+ compensating only the interlayer permanent charge or a part of the interlayer charge in case of a high charge density. The presence of both bands suggests that the clays have a heterogeneous interlayer charge.

The mechanical treatment may change the bonding energy of NH_4^+ to the vermiculite surface, which may be evaluated by using the method proposed by Petit *et al.* [12]. The heating of the KBr pellets may also modify the intensity of the absorption bands at 1440 and 1400 cm^{-1} giving more information about the alteration of the layer charge produced by the mechanical treatment. The aim of this work is to study ammonium loss by heating of mechanically treated vermiculite, either by grinding or by sonication, to check the effects of this treatment on the layer-charge of this mineral.

Experimental

Material

A raw vermiculite from Santa Olalla (Huelva, Spain) of a half-unit cell $(Si_{2.64}Al_{1.36})(Mg_{2.48}Fe^{3+}_{0.324}Fe^{2+}_{0.036}Al_{0.14}Ti_{0.01})O_{10}(OH)_2Mg_{0.439}$ was used. NH_4^+ saturation of mechanical treated samples were prepared by repeated contact with 1 M ammonium acetate solution at pH=7 and room temperature. The samples were finally washed with distilled water until the solution was free of CH_3COO^-.

Methods

Sonication

Sonication treatment was performed with a Misonix ultrasonic liquid processor of 600 W output with a 20 kHz converter and a tapped titanium disruptor horn of 12.7 mm diameter. The horn tip was dipped into a cylindrical cooling cell of the 5 cm internal diameter; 3 g of vermiculite flakes were mixed with 25 cm^3 of hydrogen peroxide solution (30%)

and 25 cm^3 of deionised water. The mixes were sonicated for time ranging between 10 and 100 h at 20°C const. due to a cooling circulator.

Grinding

Large flakes of the raw vermiculite were ground using a knife-mill (Retsch 25SM-1) and were sieved to get fraction <80 μm. It was ground in batches of 10 g in a vibratory mill (Herzog ZM-100), working by friction and impact at 1500 rpm.

Thermal study

Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were carried out simultaneously in static air with an automatic thermal analyser system (Seiko, TG/DTA 6300). Samples of about 50 mg were packed loosely into a platinum holder and were thermally treated at a heating rate of 10°C min^{-1}. Evolved gas analysis (EGA) experiments were performed under vacuum (10^{-5} torr) using a quadrupole mass spectrometer (Quadruvac Q100, LH) at the heating of 6 K min^{-1}.

Specific surface area

The specific surfaces area (*ssa*) was determined with an automatic system Micromeritics 2200 A Model, Norcross GA using the BET method and liquid-nitrogen. Nitrogen gas was used as an adsorbate.

Infrared study

Fourier transform infrared spectra were recorded in transmission mode in the 4000–400 cm^{-1} range with a resolution of 4 cm^{-1} by a Nicolet 510 FT-IR Spectrometer. Pressed pellets of 2 cm diameter were prepared after mixing the 4 mg samples with 300 mg KBr. The measurements of the integrated intensity of the absorption bands were done using a Lorentz–Gauss cross-product function with the minimum number of component bands used for the fitting process.

Results and discussion

TG and DTA study

TG and DTA curves of untreated vermiculite and that treated for 20 and 100 h with ultrasound saturated subsequently with ammonium are shown in Figs 1 and 2, respectively. TG and DTA curves indicate that the mass losses and thermal effects are very similar, although some differences are found. The small and the slight mass loss between 20 and 200°C and between 200 and 600°C, respectively, observed in the untreated sample increase with sonication time. The high mass loss between 600 and 900°C is similar in all samples studied. The intensity of the endothermic effect between 25 and 200°C observed in the untreated sample increases with sonication time, whereas the endothermic effect at 820°C remains unchanged. The exothermic effect at 850°C is more sharp and is lowered by 7°C in the sonicated samples.

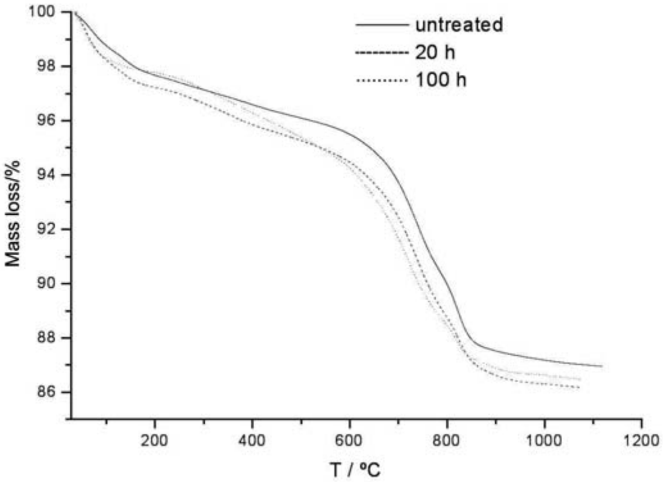

Fig. 1 TG curve of untreated vermiculite and treated for 20 and 100 h with ultrasound and saturated subsequently with ammonium

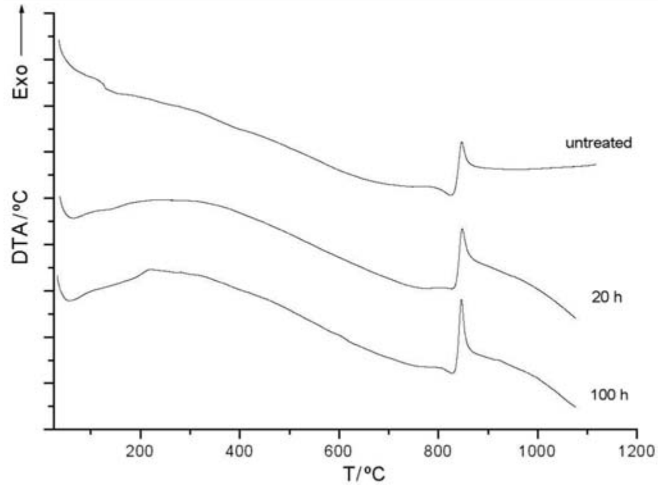

Fig. 2 DTA curve of untreated vermiculite and treated for 20 and 100 h with ultrasound and saturated subsequently with ammonium

The sonication produces a reduction in particle size. The *ssa* changes between about 0.5 $m^2 g^{-1}$ in the original sample to 34 $m^2 g^{-1}$ after 40 h ultrasound treatment. This effect may be responsible for the increase in mass loss at a lower temperature ascribed to sorbed water and to the weakly bonded OH groups placed on the particle borders, produced by the sonication treatment. Also a small loss of NH_4^+ ion from the borders may be partly responsible for that mass change. The narrowing and shift of the high temperature exothermic peak may be also attributed to the smaller particle size obtained by ultrasounds [13].

Table 1 Mass loss in % of ground samples in different temperature ranges

Time	a	b	c	d	e
	25–1000°C	25–200°C	200–1000°C	200–575°C	575–1000°C
30 s	15.30	5.18	10.12	3.65	6.47
1 min	17.60	7.60	10.00	5.07	4.93
2 min	19.00	9.05	9.95	6.95	3.00
3 min	20.80	10.50	10.30	7.30	2.80
4 min	21.00	11.00	10.00	7.35	2.65
6 min	21.00	11.00	10.00	7.35	2.65
8 min	21.00	11.00	10.00	7.35	2.65

TG and DTA curves of ground vermiculite, saturated subsequently with ammonium are shown in Figs 3 and 4, respectively. The total mass loss of the samples increases between 30 s and 4 min grinding (Table 1, column a). At a longer grinding time the mass loss remains constant. The increase of the mass loss occurs only between 25 and 200°C (Table 1, column b) whereas the values of mass loss between 200 and 1000°C are similar (Table 1, column c). The DTA curves show, in agreement with the TG curves, an increase in intensity of the endothermic effect between 25 and 200°C. These changes could be ascribed to sorbed water content, varying due to the delamination, particle size decrease, and amorphization produced during grinding. The mass loss between 200 and 575°C increases with grinding time until 4 min (Table 1, column d), whereas between 575 and 1000°C it decreases (Table 1, column e) showing that the loss of water and/or NH_4^+ ions between 200 and 1000°C is shifted towards lower temperature. An endothermic effect is shown between 350 and 575°C (DTA). The intensity of this effect increases till 2 min grinding being broader at lon-

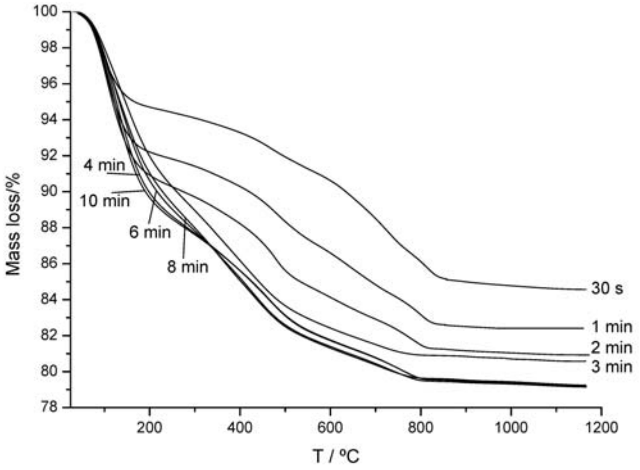

Fig. 3 TG curve of ground vermiculite for different times, saturated subsequently with ammonium

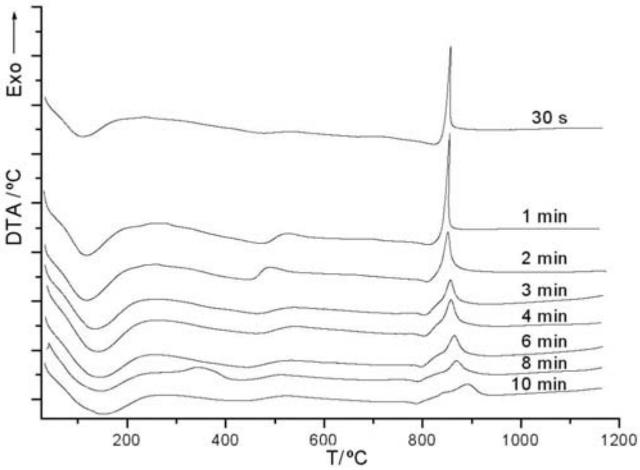

Fig. 4 DTA curve of ground vermiculite for different times, saturated subsequently with ammonium

ger grinding time. This increase corresponds with the increase of the mass loss at a similar temperature. In untreated sample an endothermic effect appears followed by an exothermic one at 834 and 852°C, respectively. The peak of the exothermic effect is sharp at a short grinding time, but after 1 min grinding the form of the peak changes again and it becomes broader. After a grinding time exceeding 3 min, the exothermic peak shifts to a higher temperature reaching 892°C after 10 min grinding and simultaneously a shoulder appear at 832°C. The phases formed at the temperature of the exothermic effect are the same in the untreated and in all the ground samples, i.e. enstatite and spinel, (XRD not shown). More studies are necessary to be carried out to determine the causes of the shift of the exothermic effect.

EGA study

The TG-DTA study of sonicated samples shows a thermal behaviour similar to the untreated ones suggesting that sonication treatment does not modify the ammonium loss by heating. Thus the interaction between NH_4^+ and the vermiculite lamellae is similar as in samples not sonicated. On the other hand, grinding treatment produces important changes in TG-DTA curves in comparison with untreated ones. The shift of the mass loss suggests that NH_4^+ and structural OH are decomposed at a lower temperature after grinding. Anyway, these techniques do not provide information on the temperatures of NH_4^+ loss during heating that can be obtained using the EGA technique.

EGA profiles of untreated samples and those sonicated during 20 and 60 h are shown in Fig. 5. The profile of untreated sample (Fig. 5a) shows no NH_3 loss up to 200°C. Between 200 and 400°C a small quantity of NH_3 is detected and between 500 and 800°C almost all the NH_3 is lost, showing in the profile a wide peak with a maximum at 650°C. Finally, at a higher temperature (825–925°C) there appears a small peak of NH_3 loss. The profiles of sonicated samples (Figs 5b and c) are very similar to

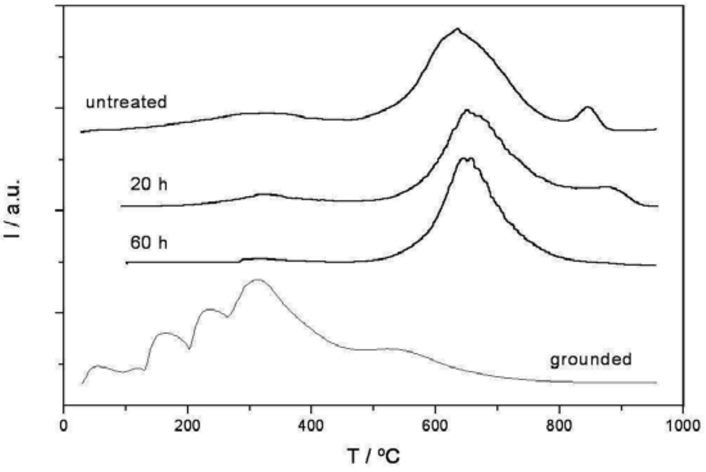

Fig. 5 Evolution ofNH_3 from vermiculite: a – untreated, b – sonicated for 20h and c – 60 h and gruond for 2 min and all of therm subsequently saturated with ammonium

the untreated ones showing less broad and lower intense peaks within the range 500–800 and 825–925°C, respectively. These small differences may be attributed to the decrease of the particle size produced by sonication. Similar behaviour has been found in sonicated micas [13]. These data show that the highest part of NH_4^+ ions, present in untreated and sonicated samples are lost at high temperatures and that sonication practically does not modify the NH_3 emanation during heating.

EGA profile of sample ground for two minutes is shown in Fig. 5d and it is different from that of untreated sample. The highest quantities of NH_3 are detected below 400°C, small quantity only is lost between 400 and 700°C. The profile shows also that the NH_3 is emanated in six different steps. The decrease in temperature of NH_3 escape and the increase in the mass loss of ground samples in comparison with the untreated and sonicated ones suggests a decrease in bonding energy and increase in number of the interactions sites, respectively.

IR study

The charge evaluation by IR spectroscopy [14] may give information on the interaction of NH_4^+ ion with vermiculite. Figure 6 shows a comparable set of spectra obtained for the original NH_4-vermiculite and that after heating at 110, 200, 300 and 400°C. The spectra of the original sample shows bands at 3250, 3040, 2830 and 1430 cm^{-1} assigned to the modes of NH_4^+ combination band $\nu_d/\delta_d(E)+\delta_d(F_2)NH_4^+$, overtone of $\delta_d(F_2)NH_4^+$ and $\delta_d(F_2)NH_4^+$, respectively [14]. There appear also bands of the OH-stretching within the lattice at 3650 and 3700 cm^{-1} and of the hydration water at 3450 cm^{-1}. The spectra of the KBr pellets heated up to 400°C do not show any appreciable change of the intensity or shift of these bands. An exception is the 3450 cm^{-1} band assigned to the OH-stretching vibration of hydration water which dissappears and the bands at 3700, 3650, 3250, 3040 and 2830 cm^{-1} are more clearly

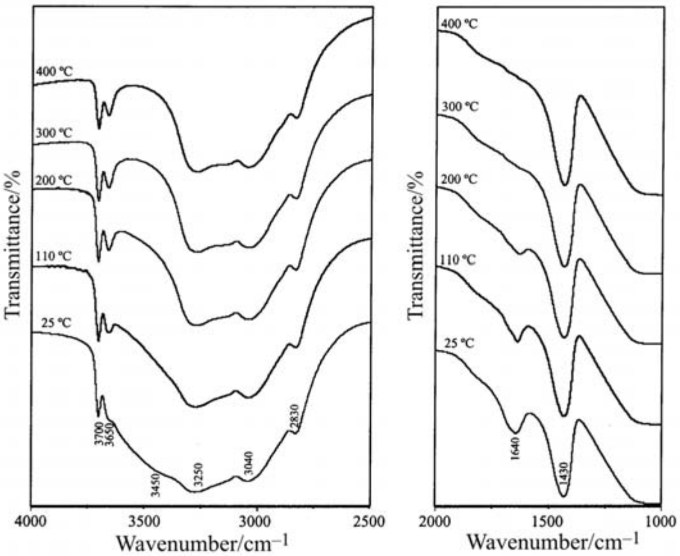

Fig. 6 IR spectra of the original NH_4-vermiculite and after heating at 110, 200, 300 and 400°C

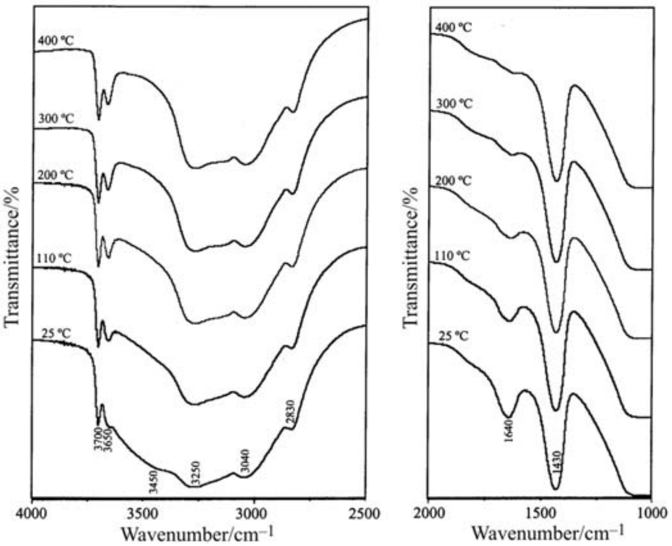

Fig. 7 IR spectra of sonicated vermiculite during 100 h followed by NH_4^+ saturation

observed. The spectra of the original NH_4-vermiculite show a band at 1640 cm^{-1} that may be assigned to HOH bending or to distorted ammonium tetrahedron. The heating shows that this band disappears as well as the band at 3450 cm^{-1} whereas the NH_4^+ absorption bands do not show any changes, so they should be assigned to HOH bending.

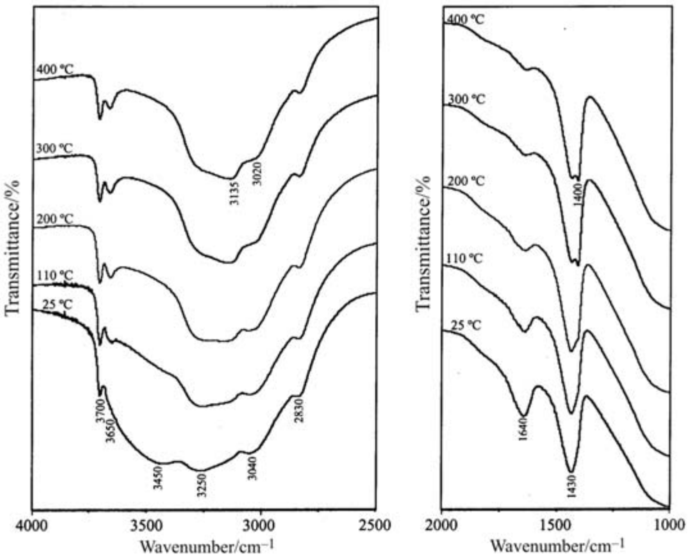

Fig. 8 IR spectra of vermiculite ground for 30 s followed by NH_4^+ saturation

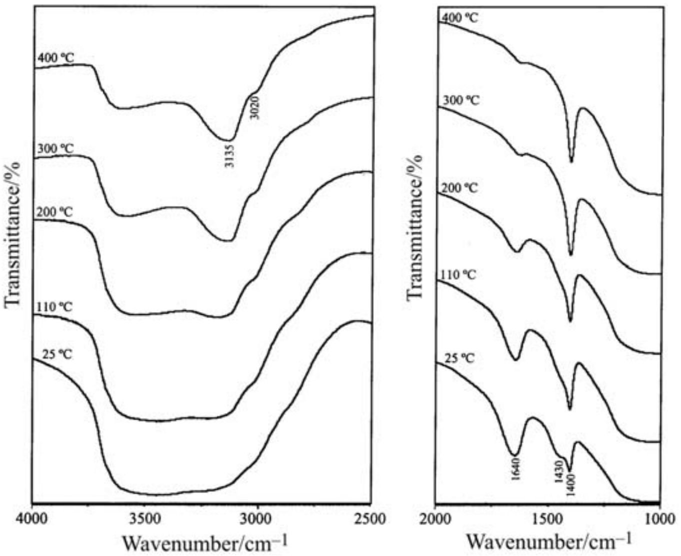

Fig. 9 IR spectra of vermiculite ground for 10 min followed by NH_4^+ saturation

Figure 7 shows a comparable set of spectra obtained for vermiculite after sonication during 100 h followed by NH_4^+ saturation. The peak frequencies and intensities of the spectra of the sonicated samples and heated between 25 and 400°C do not show any change in comparison with the original NH_4-vermiculite. These data show that the sonication of Santa Olalla vermiculite for 100 h and heating up to 400°C do not produce any change in the interaction of NH_4^+ with the surface of vermiculite.

Figures 8 and 9 show a comparable set of spectra obtained for vermiculite ground for 30 s and for 10 min followed by NH_4^+ saturation. These spectra indicate differences as compared to the sonicated vermiculite. The spectra of the sample ground for 30 s do not show appreciable changes with respect to the original vermiculite. However, after heating between 110 and 400°C other bands start to appear at 3135 and 1400 cm^{-1} together with the absorption bands at 3250, 2830 and 1430 cm^{-1} and the band at 3040 is shifted to 3020 cm^{-1}. The intensities of the new bands increase with temperature and grinding time. After 10 min grinding the sample is almost amorphous to the XRD (figure not shown) but some ammonium still remains as the exchangeable cation, which is especially apparent in the absorption bands at 1430 and 1400 cm^{-1}. The absorption bands at 1430 cm^{-1} disappear in the sample ground for 10 min, after heating at 200°C.

It is noticeable that sonication does not produce any change of the intensity and frequency of the absorption bands of NH_4^+. The heating up to 400°C of the original and sonicated samples saturated with NH_4^+ does not modify the intensity and frequency of the absorption bands of NH_4^+. Chourabi and Fripiat [15] showed decrease of the intensity of these bands after heating, but the experiments were carried out on the sample in form of film and heating was done in vacuum (10^{-4} torr) thus under more drastic conditions than those used in this work.

IR study of samples ground in a vibratory mill followed by NH_4^+ saturation shows an important modification of the absorption bands in comparison with the original NH_4-vermiculite.

The intensity of the absorption bands decreases with grinding time specially after 2 min grinding. The intensity of the 1430–1400 cm^{-1} band is correlated with the nitrogen content of the samples [16]. The decrease of the absorption band intensity of the ground sample shows that the NH_4^+ ion content decreases with grinding time.

After the grinding treatment the absorption bands occur of the NH_4^+ ion compensating permanent charge in the interlayer space of a high charge density. Also other bands appear at 3150, 3020 and 1400 cm^{-1} corresponding to NH_4Br, which shows the replacement of a part of NH_4^+ in the clay by K^+ from KBr. According to Petit *et al.* [12] these data show that grinding transforms the vermiculite with high charge density into a mineral with a heterogeneous interlayer charge. Figure 10 shows the ratio of the intensity of 1430 and 1400 cm^{-1} bands heated between 25 and 400°C, *vs.* grinding time. The increase of grinding time and the temperature both cause a lowering of this ratio. The sample ground for 30 s and heated at room temperature shows the highest ratio. However, the heating of this sample produces the highest decrease of the ratio. Between 30 and 120 s at room temperature and heating at 110°C appears the highest variation in this ratio, which is practically constant at 300 and 400°C. The variation of this ratio is less drastic at grinding time higher than 2 min, than at a shorter grinding time.

The method of evaluation of the layer charge proposed by Petit *et al.* [12] shows that grinding treatment produces a change of the layer charge of Santa Olalla vermiculite. The ground material shows heterogeneity in the layer charge compensated by NH_4^+ ion. The integrated intensities of the bands at 1430 and 1400 cm^{-1} used to measure quantitatively

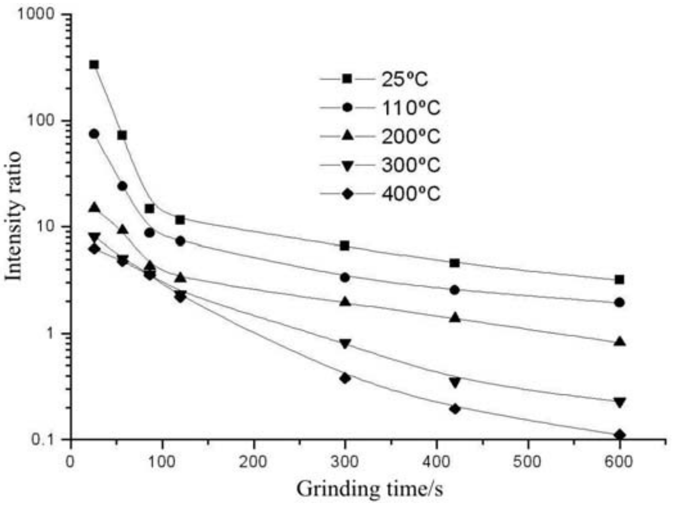

Fig. 10 Intensity ratio of 1430 and 1400 cm^{-1} IR bands heated between 25 and 400°C, *vs.* grinding time

the proportions of different types of charge show that the heterogeneity of the charge depends of the grinding time. The heating between 25 and 400°C of ground samples also shows a decrease in the ratio of the intensities of the bands at 1430 and 1400 cm^{-1} suggesting that the layer charge of vermiculite is more heterogeneous.

Conclusions

Thermal study of vermiculite sonicated and saturated with NH_4^+ ion shows a similar behaviour as the untreated one. Small differences are attributed to decrease of particle size obtained by ultrasound treatment.

Grinding has an important but different influence on the thermal behaviour of ground vermiculite saturated with NH_4^+. Ammonia is lost at a much lower temperature in different steps showing that grinding modifies the layer charge of vermiculite.

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