

Comparative study of the sonication effect on the thermal behaviour of 1:1 and 2:1 aluminium phyllosilicate clays

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Abstract

The aim of this work is to compare the effect of sonication on the thermal behaviour of kaolinite and pyrophyllite. The results show that sonication produces a significant particle size reduction of both clays. Besides, this treatment modifies the thermal behaviour of these samples. Nevertheless, the change in particle size and in the modification of the thermal behaviour is different for both clays. Sonication facilitates the dehydroxylation of both clays, although, the temperature shift of the dehydroxylation is more significant for pyrophyllite than for kaolinite. Additionally, the exothermic effect at 987 °C for kaolinite is not affected by sonication while that at 1210 °C for pyrophyllite is shifted to lower temperatures.

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1. Introduction

Kaolinite and pyrophyllite are both aluminium-phyllosilicates but with different crystalline structure. Thus, kaolinite has a 1:1 structure, while pyrophyllite has a 2:1 structure. Both kaolinite and pyrophyllite have many industrial applications in their natural form or as raw materials for the production of ceramics.¹ Thus, kaolinite is used as a coating and filler in the manufacturing of paper, as extender in inks and paints, as starting material for aluminosilicate-based ceramics, as cracking catalysts, as raw material in the production of fibreglass, as additive in the production of rubber and polymers, etc. On the other hand, pyrophyllite is mainly used as a ceramic raw material in refractory industry for applications such as insulating firebrick or foundry specialities and also in various white-ware bodies.

Grinding is a common procedure in the processing of these two phyllosilicates. Grinding of kaolinite and pyrophyllite results in particle size reduction (delamination and lateral size reduction), folding and gliding of layers, and aggregation of the newly formed particles into spherical particles.^{2–5} Additionally, grinding also produces rearrangement of the coordination polyhedra and diffusion within the structure of atoms (mainly protons, “prototropy”) yielding after progressive grinding amorphous materials.^{2,6–9} Finally, grinding also produces surface modification on the kaolinite surface.^{10–12}

In both pyrophyllite and kaolinite, the thermal behaviour is very much affected by grinding. Thus, for kaolinite, the thermal dehydroxylation, observed in the thermogravimetric curve as a mass loss and in the differential thermal analysis curve as an endothermic effect, is shifted to lower temperature as grinding time proceeds. After 120 min of grinding, this endothermic effect disappears. The sharp exothermic effect about 980 °C is also shifted to lower temperature for the ground samples.^{13,14} For pyrophyllite,

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grinding produces significant structural and microstructural modification in the original material that strongly influences its thermal behaviour. Thus, the mass loss on the TG curves and the endothermic DTA effects corresponding to the dehydroxylation shift to lower temperatures with grinding, until the mechanochemical limit is reached. Further grinding produces a disruption of the 2:1 aluminosilicate structure giving an exothermic DTA effect.^{13,15} Additionally, the contaminations produced by the mill components during grinding of kaolinite and pyrophyllite and their influence on their thermal behaviour and crystalline phase formed after thermal treatment have been studied in literature.^{16,17}

Very recently, it has been reported the use of sonication, as an alternative to grinding, for particle size reduction of clay minerals. Sonication produces significant delamination and lateral size reduction in phyllosilicates while the crystalline structure is retained. Thus, for example, crystalline nanometric and submicron-sized vermiculite and mica flakes have been prepared from natural macroscopic vermiculite and mica samples by a sonication procedure.^{18–20} The effects of sonication on the thermal behaviour of clays have not been extensively studied. The aim of this work is to compare the influence of sonication on the thermal behaviour of two different clays, a kaolinite (1:1 structure) and pyrophyllite (2:1 structure).

2. Experimental

2.1. Materials

The starting kaolinite used in this work is a well-ordered sample from Washington County, Georgia (KGa-1), supplied by Source Clays Repository (Missouri, USA, Clay Minerals Society). The raw pyrophyllite used is from Zalamea la Real (Huelva, Spain). This sample is a mixture of pyrophyllite, kaolinite, mixed layer smectite and illite, and a small content of rutile and quartz. The raw pyrophyllite was purified by a procedure described in literature.^{21,22} The purified sample has been previously characterized by X-ray diffraction, FTIR, and chemical analysis.²³ The purification procedure removes all the extraneous phases except for a small admixture of rutile. The pyrophyllite is the polytypic modification 1Tc.

2.2. Methods

Ultrasonic 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 of diameter that produces a double (peak-to-peak) amplitude of the radiating face of the tip of 120 μm . The horn tip was dipped into a cylindrical jacketed cooling cell of 5 cm internal diameter, where 3 g of samples were mixed with 50 ml of freshly deionised water.

Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were carried out simultaneously in an

automatic thermal analyser system (Seiko, TG/DTA 6300). Special attention was paid to the experimental conditions to ensure high accuracy. For all experiments, samples of about 40 mg were gently packed into a platinum holder, and heating was performed at a heating rate of 10 $^{\circ}\text{C min}^{-1}$ in Ar flow (400 $\text{cm}^3 \text{min}^{-1}$). Experiments were repeated three times to check reproducibility. The mass loss was estimated graphically and the temperature range was found as the intersection with the TG curve of the bisecants to its respective tangents.

The specific surface areas were determined with an automatic system (Micromeritics 2200 A Model Norcross GA) using the BET method, at liquid-nitrogen temperature. Nitrogen gas was used as adsorbent. Samples were studied by scanning electron microscopy (SEM) using a Jeol JSM-5400 model. Diffraction patterns were obtained using a diffractometer (Kristalloflex D-500 Siemens) at 36 kV and 26 mA with Ni-filtered $\text{CuK}\alpha$ radiation and a graphite monochromator.

3. Results

Fig. 1 includes the evolution of the specific surface area and equivalent spherical diameter as a function of the sonication time for both pyrophyllite and kaolinite samples. This graph indicates that, for kaolinite the specific surface area (SA) increases in the entire sonication range. Thus, the SA of the untreated sample rises from 8.5 to 45 $\text{m}^2 \text{g}^{-1}$ after 10 h of sonication, and to 67 $\text{m}^2 \text{g}^{-1}$ for 20 h of sonication. The situation is quite different for the pyrophyllite, the SA increases up to 20 h of treatment remaining unchanged for longer treatment times. Thus, the SA of the untreated sample (4.0 $\text{m}^2 \text{g}^{-1}$) increases to 52 and 70 $\text{m}^2 \text{g}^{-1}$ after 10 and 20 h of sonication, respectively, remaining at 70 $\text{m}^2 \text{g}^{-1}$ for longer treatment times.

The values of the equivalent spherical diameters (esd) are also included in Fig. 1 as a function of the treatment time. Although, these values are not pretended to give absolute val-

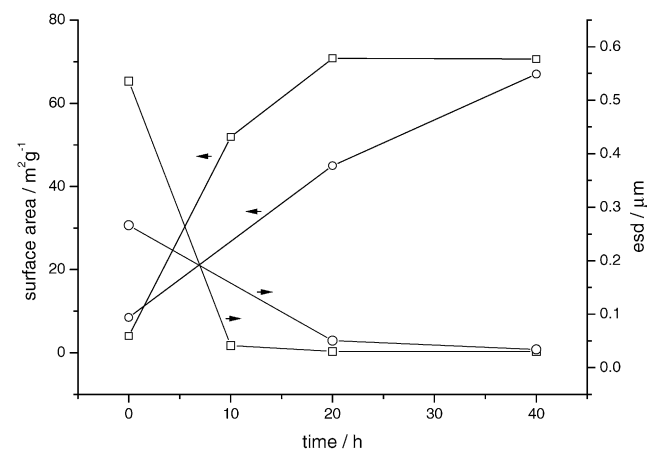


Fig. 1. Evolution of the surface area and equivalent spherical diameter (esd) for kaolinite (○) and pyrophyllite (□) as a function of the sonication time.

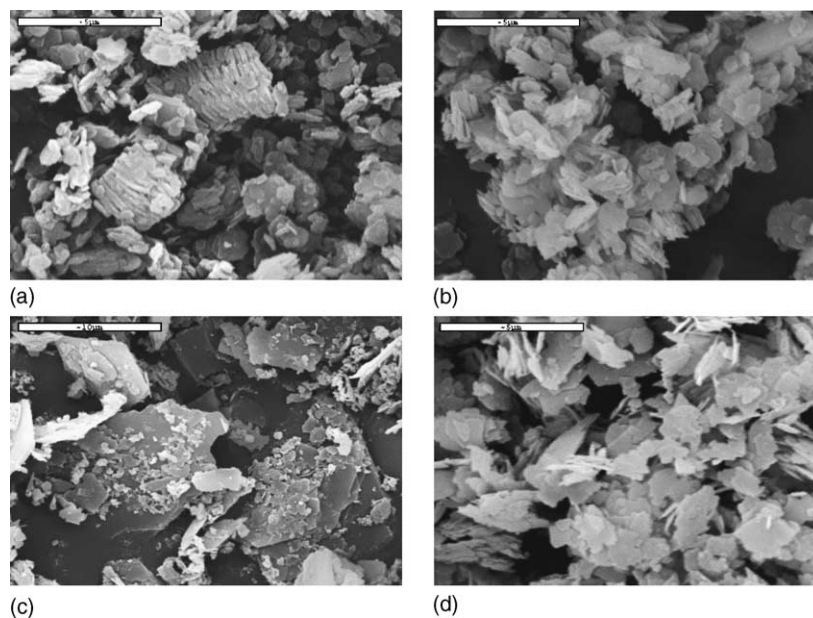


Fig. 2. SEM micrograph of the kaolinite sample before (a) and after sonication for 40 h (b), and of pyrophyllite before (c) and after sonication for 40 h (d).

ues of particle size due to the anisotropic shape of the clays, they give information about the evolution of the particle size with the treatment. This graph indicates that there is a sharp decrease in the particle size for the sonicated samples. For kaolinite, the esd of the untreated material ($0.266\ \mu\text{m}$) drops to 0.050 and $0.034\ \mu\text{m}$ when the sample is sonicated for 20 and 40 h, respectively. For the pyrophyllite, 10 h of sonication decrease the esd from 0.535 to $0.041\ \mu\text{m}$, while 20 h of sonication decrease this value to $0.030\ \mu\text{m}$, remaining unchanged for longer treatment times. The resulting particles after sonication for 40 h are of similar size for both clays. Nevertheless, sonication is more efficient in particle size reduction of pyrophyllite than of kaolinite; because under identical experimental conditions, it is necessary to use double sonication time to obtain similar values of particle size for kaolinite than for pyrophyllite.

The SEM electron micrographs of the untreated kaolinite and pyrophyllite samples are included in Fig. 2a and c. These samples are quite heterogeneous in terms of particle size distribution and consist of both small submicron particles and stacks of flakes of several tens of microns. After sonication for 40 h the situation changes drastically (Fig. 2b and d). Thus, although both samples retain the characteristic plate-like morphology of the clays, the particle size is drastically reduced in all directions by delamination and breaking of the plates. Additionally, both sonicated materials are more homogeneous in terms of particle size distribution. For the sonicated samples, the length of the plates, as directly estimated from SEM micrographs, is $0.81\ \mu\text{m}$ with a standard deviation of $0.37\ \mu\text{m}$ for the kaolinite, and $0.98\ \mu\text{m}$ with a standard deviation of $0.54\ \mu\text{m}$ for the pyrophyllite. These results indicate that the resulting plate length of both samples after sonication for 40 h are quite similar, being slightly smaller for kaolinite. The esd data obtained from SA mea-

surements also indicates that both samples have similar dimensions when sonicated for 40 h. Nevertheless, the absolute values obtained from SEM and SA measurements are quite different. These differences can be explained by the anisotropy of the particles. Thus, the esd data are obtained by assuming that the particles are spherical and only gives the trend of the evolution with the treatment, while by data obtained by SEM directly give the plate length.

The X-ray diffraction patterns of the untreated and sonicated samples (figure not shown) indicate that sonication does not produce significant change in the structure of the clays. Thus, only broadening of the diffraction lines was recorded due to the particle size reduction produced by the treatment. For the kaolinite, it has been observed an increase of the structural disorder due to translations between layers.²⁴

Fig. 3 includes the TG of the untreated and sonicated kaolinite samples. The TG traces (Fig. 3a) show two mass losses for the untreated material (one below $120\ ^\circ\text{C}$ and another above $400\ ^\circ\text{C}$), while for the sonicated samples (Fig. 3b and c) three mass losses (below $130\ ^\circ\text{C}$, between 130 and $390\ ^\circ\text{C}$, and above $390\ ^\circ\text{C}$) are discriminated. The amount of the mass loss of the first step (below $130\ ^\circ\text{C}$) increases with the sonication time reaching a value of about 2.6% for the sample sonicated for 20 h and of about 3.5% for the sample sonicated for 40 h. This small mass loss could be attributed to the release of loosely bound water due to the increase in the SA for sonicated samples. The second mass loss (between about 130 and $390\ ^\circ\text{C}$) also increases with the sonication procedure, reaching values of 2.9 and 3.8% for the samples sonicated for 20 and 40 h, respectively. The main mass loss in the range from about 390 to $800\ ^\circ\text{C}$ decreases with the sonication treatment from 13.7% for the untreated material to 10.7 and 9.2% for the samples sonicated for 20 and 40 h, respectively. Nevertheless, for the sonicated samples, considering the two latter

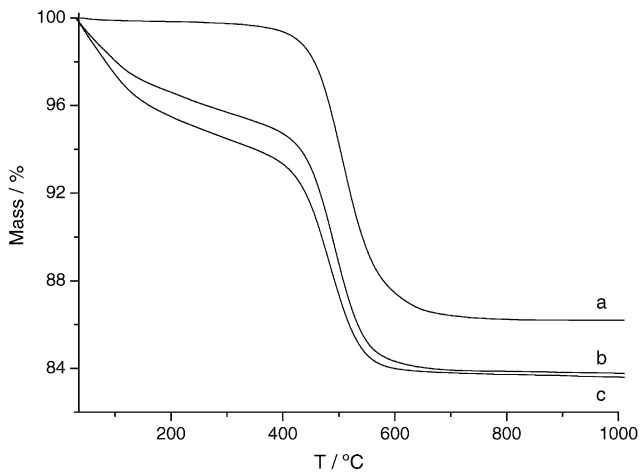


Fig. 3. TG traces for kaolinite: (a) untreated and sonicated for (b) 20 h and (c) 40 h.

mass losses (in the range from about 130 and 800 °C) and subtracting the sorbed water released below 130 °C, one obtains a total mass loss of about 13.7% that correspond to the mass loss of the untreated sample due to dehydroxylation.

Sonication produces a decrease in the mean temperature of the dehydroxylation. Thus, the temperature of the DTG (Fig. 4) maximum associated with the dehydroxylation decreases as sonication time increases, reaching a minimum value of 482 °C after 40 h of sonication.

The DTA (Fig. 5b and c) of the sonicated kaolinite samples show two endothermic effects corresponding to the mass losses in the TG, and a narrow exothermic effect at 987 °C. The temperature of the most intense endothermic effect is shifted with the sonication time in a similar way to the DTG trace. The exothermic effect at 987 °C remains unchanged and it is not affected by sonication.

TG diagrams of untreated and sonicated pyrophyllite samples are shown in Fig. 6. The untreated sample (Fig. 6a)

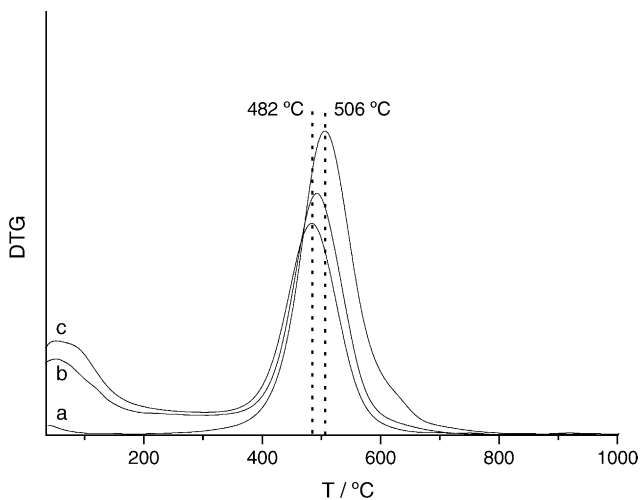


Fig. 4. DTG traces for kaolinite: (a) untreated and sonicated for (b) 20 h and (c) 40 h.

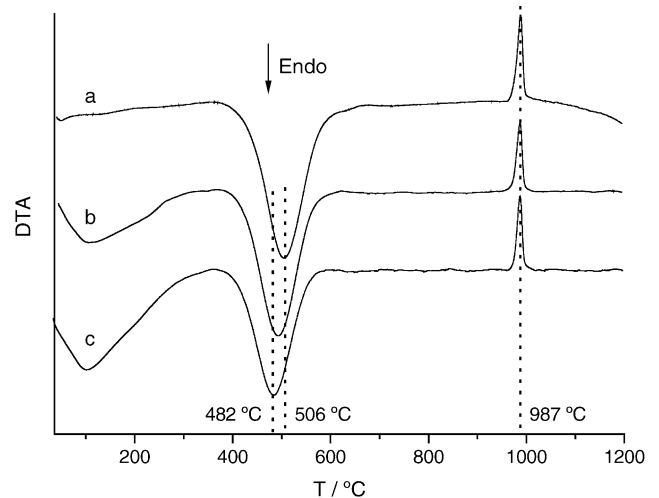


Fig. 5. DTA traces for kaolinite: (a) untreated and sonicated for (b) 20 h and (c) 40 h.

shows a single mass loss that begins about 450 °C and is over at 900 °C. The found mass loss percentage (4.95%) is that expected from the release of structural OH for an ideal pyrophyllite. For the sonicated material, three mass losses are discriminated in the TG traces (Fig 6b and c). The first one takes place below 120 °C and corresponds to 0.2 and 0.4% for the samples sonicated for 10 and 20 h, respectively. This first mass loss, as in kaolinite, could be attributed to sorbed water. The second mass loss is observed in the range from about 120 to 400 °C and increases with the sonication time reaching a value of 0.2 and 0.3% for the samples sonicated for 10 and 20 h, respectively. Finally, the last mass loss (above 400 °C) decreases with the sonication time to 4.8 and 4.6% for the samples sonicated for 10 and 20 h, respectively. If the water released below 120 °C is subtracted, the total mass loss from 120 to 800 °C is identical to the mass loss of the original pyrophyllite. The sample sonicated for 40 h (not shown in the figure) present a very similar profile to that of the sample son-

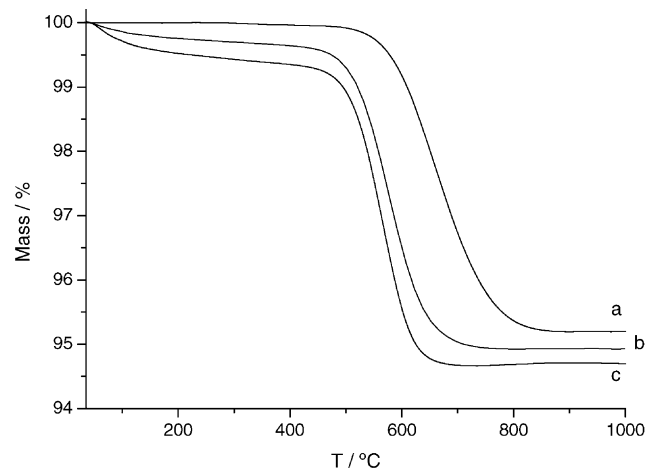


Fig. 6. TG traces for pyrophyllite: (a) untreated and sonicated for (b) 10 h and (c) 20 h.

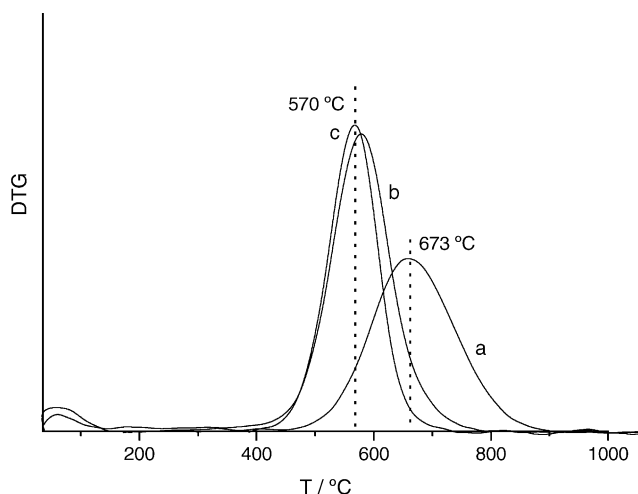


Fig. 7. DTG traces for pyrophyllite: (a) untreated and sonicated for (b) 10 h and (c) 20 h.

icated for 20 h. Sonication also produces a shift of the mass loss to lower temperatures and the DTG peak becomes narrower (Fig. 7). Thus, the broad DTG peak centred at 673 °C for the untreated samples (Fig. 7a) is shifted 103 °C to lower temperatures (to 570 °C) for the sample sonicated for 20 h (Fig. 7c).

The DTA curve of the untreated pyrophyllite (Fig. 8a) shows a very broad endothermic peak centred at 673 °C, and a small exothermic at 1210 °C, in agreement with previous results.²⁵ The temperature of the endothermic peak matches that of the mass loss in the DTG curve (Fig. 7a) and corresponds to dehydroxylation. The exothermic effect corresponds to the mullite formation. Sonication modifies the DTA profiles. Thus, the broad endothermic effect for dehydroxylation is converted into a narrower peak shifted to lower temperatures (570 °C), the width of the peak decreases with sonication time, and the exothermic effect that appears at 1210 °C

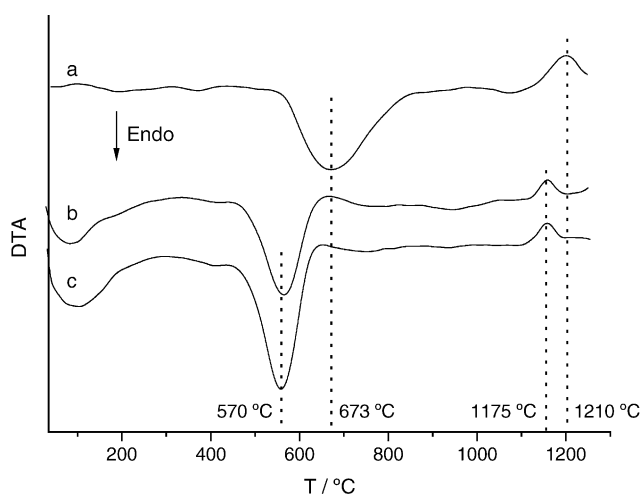


Fig. 8. DTA traces for pyrophyllite: (a) untreated and sonicated for (b) 10 h and (c) 20 h.

in the untreated sample also shifts to lower temperature, i.e., 1175 °C (Fig 8c).

4. Discussion

The above results show that sonication produces significant particle size reduction of both pyrophyllite and kaolinite. Besides, this particle size reduction modifies the thermal behaviour of these two clays. Nevertheless, the change in particle size and in the modification of the thermal behaviour is different for both clays.

The first difference observed in the behaviour of these two clays could be found in the evolution of the surface area with the sonication time. Thus, although, both clays yield similar maximum SA ($70 \text{ m}^2 \text{ g}^{-1}$) with sonication, pyrophyllite reaches this SA in about half of the time (20 h) than kaolinite (40 h) under identical experimental conditions. This result indicates that pyrophyllite is more sensitive to sonication than kaolinite in terms of rate of particle size reduction.

It is worth noting that the values of SA for these two samples treated with ultrasounds are higher than the maximum values reported for identical samples treated by grinding. Thus, for the kaolinite KGa-1 sample from Georgia, a maximum value of $18.3 \text{ m}^2 \text{ g}^{-1}$ is reported after 15 min of grinding.¹⁴ Longer grinding treatments produce aggregation of the particles into larger units with smaller surface areas. For other kaolinite samples ground under different experimental conditions, it has been reported a similar behaviour but different absolute values with maximum surfaces in the range from 10 to $64 \text{ m}^2 \text{ g}^{-1}$.^{14,26–28} For the pyrophyllite from Zalamea, the largest value of SA ($51.6 \text{ m}^2 \text{ g}^{-1}$) was obtained after 30 h of grinding.²⁹ As for kaolinite, longer grinding treatments produce a decrease in SA due to aggregation. This behaviour is also general for other pyrophyllite samples, but as in the case of kaolinite, the maximum values depend on the sample itself and on the experimental conditions used in the grinding experiment. Thus, for a commercial pyrophyllite of Japan, Temuujin et al.³⁰ have obtained a maximum SA of $73 \text{ m}^2 \text{ g}^{-1}$. Nevertheless, the sample used by these authors is different to our pyrophyllite and contains quartz as impurity. The importance of impurities of quartz as accelerator of the mechanochemical activation of other clays has been recognized in literature.³¹

By SEM it has been observed that the characteristic plate-like sample of the material remains even after sonication for 40 h while the particle size is drastically reduced both by delamination and flake breaking. The sonicated materials have a relatively narrow particle size distribution in the range of the submicrometers. These results contrast with those reported in literature for ground materials. Thus, it has been reported that grinding of both pyrophyllite and kaolinite produces deformation of the particle shape and severe aggregation.^{2–5,14}

The thermal behaviour of these two aluminosilicates is affected by the sonication treatment. For both clays, there is an increasing mass loss at temperatures below about 130 °C

that could be related to sorbed and loosely bound water due to the significant increase in the surface area produced by the sonication. The dehydroxylation is also affected by the sonication. Thus, for both untreated clays, the dehydroxylation takes place in a single step, while for the sonicated samples the process takes place in two stages, being the total mass loss of both stages identical to that of the untreated materials. This finding seem to indicate that for the sonicated samples there are some OH groups with a lower energy of bonding that are released at lower temperatures (in kaolinite from 130 to 390 °C and in pyrophyllite from 120 to 400 °C). The temperature ranges of release of these latter OH groups are quite similar for both clays, suggesting that the nature of these OH groups might be similar for both samples. The percentage of these OH groups released at lower temperatures, as compared with the total OH groups, is much larger in kaolinite than in pyrophyllite, being the maximum values 29.2 and 6.1% for kaolinite and pyrophyllite, respectively. Another important difference between the effects of sonication on these two samples is in the shift of the maximum of the DTG and DTA peaks of the main dehydroxylation. Thus, for kaolinite, the maximum of the DTG or DTA peaks is shifted a maximum of only 24 °C, while for the pyrophyllite, it is shifted 103 °C. Additionally, the DTG or DTA peaks become narrower for the sonicated pyrophyllite as compared with the untreated material, while for kaolinite no modification of the peak shape is observed with the treatment. In recent studies on the thermal dehydroxylation of phyllosilicates, such as kaolinite, it has been proposed that the dehydroxylation is a kinetically controlled process where diffusion plays a substantial role.^{32–34} Therefore, the change in the diffusion length by the decrease in the particle size produced by sonication could explain the decrease in the temperature of dehydroxylation.³⁵ Another parameter that might play a role in the modification of the thermal behaviour of these two clays is the structural modifications induced by the sonication.³⁵ We have previously observed for kaolinite and pyrophyllite that sonication, unlike grinding, does not produce amorphization but some small translation disorder.³⁶ These disorders may play a role together with particle size reduction in the dehydroxylation of these two clays. The decrease in the width of the DTG and DTA peaks for the sonicated pyrophyllite could be attributed to a decrease of the range of particle size distribution, such it has been described in literature, both theoretically³⁷ and experimentally^{36,38} for kinetically controlled reactions. The differences in thermal behaviour for both minerals should be probably understood in terms of the different structure of these two clays, i.e., kaolinite has a 1:1 structure while pyrophyllite has a 2:1 structure.³⁹ During the dehydroxylation process, the hydroxyl groups are combined and water is released. For kaolinite, 3 out of 4 OH groups are on the layer, while the other one is inside the structure. On the other hand, in pyrophyllite all the OH groups are placed into the structure. This fact could be responsible of the lower temperature of release of structural OH of kaolinite as compared with pyrophyllite. Besides, these structural differences could ex-

plain that after sonication, for kaolinite the percentage of OH less energetically bound and released at lower temperatures is much higher than in pyrophyllite because the number of OH in borders should be larger for kaolinite than for pyrophyllite.

Significant differences were observed for these two samples in the influence of sonication on the exothermic effects in the DTA traces. Thus, for the kaolinite, the 987 °C peak is not affected at all by the sonication process. The origin of this peak is controversial in the literature.^{13,40–44} It has been attributed to the formation of either mullite nuclei or spinel or both. More recently, it has been related to the release of energy associated with the Al ions transforming to a more stable six-fold coordination that facilitates the formation of mullite.⁴⁴ On the other hand, for pyrophyllite, it has been observed that the exothermic effect at 1210 °C, attributed to the formation of mullite,²⁵ is shifted to 1175 °C. These results indicate that the particle size reduction and/or translation disorder produced by sonication facilitates the formation of mullite in pyrophyllite but it does not modify the exothermic effect at 987 °C of kaolinite.

5. Conclusions

For both kaolinite and pyrophyllite samples studied here, sonication produces a significant particle size reduction by delamination and lateral breaking of the layers, yielding plate-like particles that resemble the shape of the original clays. The resulting sonicated materials also have a much narrower particle size distribution than the original ones. This decrease in the particle size produces a significant increase in the specific surface areas. Additionally, the crystalline structure of the clays is retained after sonication. This results contrast with those previously reported for ground kaolinite and pyrophyllite samples, because grinding produces particle shape change, aggregation and amorphization. Besides, the surface areas obtained for sonicated kaolinite and pyrophyllite are higher than those reported in literature for these materials after dry grinding.

The particle size reduction induced by sonication produces a modification in the thermal behaviour of both samples. Firstly, for sonicated samples there is an increasing mass loss at low temperatures that has been attributed to sorbed or loosely bond water due to the increase in surface area. Additionally, the dehydroxylation is modified and shifted to lower temperatures. This can be directly related to the decrease in particle size, as previously reported for other samples. This shift is more significant for pyrophyllite than for kaolinite. The difference has been analyzed in terms of the different structures, and therefore different positions of the OH groups, for both samples. Finally, for the high temperature exothermic effects in the DTA, it has been also observed a different behaviour for both samples. For kaolinite the effect at 987 °C is not affected while for pyrophyllite the effect at 1210 °C, attributed to the formation of mullite, is shifted to lower temperature with the sonication.

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