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The influence of ultrasound on the thermal behaviour of clay minerals

J.L. Pérez-Rodríguez [a,*], J. Pascual [b], F. Franco [c], M.C. Jiménez de Haro [a], A. Duran [a], V. Ramírez del Valle [a], L.A. Pérez-Maqueda [a]

[a] Instituto de Ciencia de Materiales de Sevilla. CSIC-Universidad de Sevilla, C/Américo Vespucio s/n, 41092 Sevilla, Spain
[b] Departamento de Ingeniería Civil, Materiales y Fabricación, ETSII, Universidad de Málaga, 29013 Málaga, Spain
[c] Departamento de Química Inorgánica, Cristalografía y Mineralogía, Campus de Teatinos, Universidad de Málaga, 29071 Málaga, Spain

Abstract

The aim of this work is to compare the influence of sonication on the thermal behaviour of kaolinites (KGa-1, KGa-2), pyrophyllite, talc and muscovite. Sonication produces a significant increase of the specific surface area due to particle size reduction. As sonication time increases and the particle size decreases, the thermal behaviour of these clay minerals is strongly modified. Thus, there is a significant increase of the weight loss at low temperature which is related to the loss of some outer hydroxyl groups and protonated hydroxyls whose proportion in the minerals increase as the new surface generated increases. Additionally, the original endothermic dehydroxylation effects of all these minerals shift to lower temperatures. Disordered kaolinite shows the smallest shift (9 °C) while muscovite presents the largest (184 °C). A linear relation has been established between the temperature shift of the dehydroxylation and the percentage of increase in the specific surface area. The influence of sonication on the high temperature DTA effects of kaolinite, pyrophyllite, and muscovite is also studied.

Keywords: Clays; Thermal properties; Sonication

1. Introduction

Phyllosilicates are naturally occurring inorganic polymers with a layer structure formed by condensation of siloxane and gibbsite- or brucite-like sheets. The major types of phyllosilicates are designated 1:1 or 2:1, depending on the ratio of tetrahedral to octahedral sheets in one respective unit. The siloxane sheet is composed of SiO_4 tetrahedra linked in a hexagonal array. The bases of the tetrahedra are approximately coplanar and the apical oxygens are linked to a second sheet of aluminium or magnesium and hydroxyl groups, in phyllosilicates 1:1, or linked to a second sheet of aluminium or magnesium and to the apical oxygens of another siloxane sheet, in phyllosilicates 2:1. Both types of phyllosilicates, 1:1 and 2:1, have one hydroxyl group situated in each hexagonal cavity of siloxane sheets in the plane of the apical oxygens. Thus, kaolinite (aluminium phyllosilicates) belong to the 1:1 type, whereas pyrophyllite (aluminium phyllosilicate) and talc (magnesium phyllosilicates) to the type 2:1. In some phyllosilicates 2:1, as occurs in muscovite, isomorphic sustitutions in both thetrahedral and octahedral sheets (e.g. Si^{4+} by Al^{3+} or Mg^{2+}, or Al^{3+} by Al^{3+}, Mg^{2+}, Fe^{2+}, etc.) create a deficit of positive charge, compensated by interlayer cations.

All these phyllosilicates have widespread industrial applications.[1] The technological application of clay minerals demands their proper workability which may be improved by a decrease in particle size. Particle size distribution is a very sensitive issue in the thermal behaviour of materials and its importance has been recognized in the literature by several authors who observed changes in the profiles of the thermogravimetric curves.[2,3]

Particle size decrease has been usually obtained by grinding. Mechanical treatments are of great importance in the preparation and processing of raw materials. It is well known that grinding of clay minerals produces various effects on their structure and properties.[4,5] The significant processes involved in the preparation of ceramic raw materials have been extensively studied, especially those for kaolinite,[6–8] pyrophyllite,[9] talc,[10] micas[11] and vermiculite.[12] Grinding of phyllosilicates results in particle size reduc-

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[*] Corresponding author. Fax: +34 95 4460665.

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tion (delamination and lateral size reduction), folding and gliding of layers, and aggregation of the newly formed particles into spherical aggregates.[13–15] Moreover, grinding also produces rearrangement of the coordination polyhedra and the diffusion within the structure of some ions (mainly protons, "prototropy") yielding after progressive grinding amorphous materials.[16–19] In addition, grinding also modifies strongly the particle surfaces of clay minerals.[20–22] The influence of dry grinding of the thermal behaviour of phyllosilicates has been previously studied by several workers.[23–25]

Recently, we have proposed the use of sonication as a method for particle size reduction of clays. Cavitational collapse leads to microjet and shock-wave impact on the surface, together with interparticle collisions.[26] Thus, we have observed that sonication on several clay minerals produces delamination and particle size reduction of the clay flakes. By this procedure, we have prepared submicronic and nanometric particles with a relatively narrow particle size distribution from different samples, such as kaolinites, talc, micas.[27–33] The aim of this work is to compare the influence of sonication on the thermal behaviour of well-crystallized kaolinite, poorly crystallized kaolinte, pyrophyllite, talc, and muscovite.

2. Experimental

2.1. Materials

The clay minerals used for this study were a low-defect and a high defect Georgia kaolinite (KGa-1 and KGa-2, previously referred to as "well-crystallized" and "poorly-crystallized", respectively), supplied by the Clay Minerals Society, Source Clays Minerals Repository, University of Missouri, Columbia, MO, USA[34,35]; a commercial sample of pyrophyllite from Hillsboro (North Carolina, USA), supplied by Ward's N.S. Establishment Inc., Rochester N.Y.[24,25] a talc from Puebla de Lillo (León, Spain)[10]; and muscovite from Fuente Obejuna (Córdoba, Spain).[30]

2.2. Methods

Ultrasonic treatments were performed with a Misonic ultrasonic liquid processor of 600 W output with a 20 kHz converter and tapped titanium disruptor horn of 12.7 mm in diameter that produce 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 in internal diameter, where 1.5 g of clay were mixed with 40 ml of freshly deionized water. The dispersions were sonicated for periods ranging from 5 to 100 h. The temperature reactor was kept constant at 20 °C during the entire treatment by means of a cooling recirculator. After treatment, samples were lyophilised to remove the water of the suspension.

Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were carried out simultaneously in an automatic thermal analyser system (Seiko, TG/DTA 6300). Samples of about 40 mg were packed loosely into a platinum holder and were thermally treated at a heating rate of 10 °C min^{-1} in Air flow (400 cc min^{-1}). 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.

3. Results

3.1. Kaolinite

The TG curve of untreated KGa-1 (Fig. 1Ia) shows that a continuous heating rate originates a slight mass loss below 140 °C, associated with the loss of the loosely bonded adsorbed water on the particle surface, which is accompanied with a weak endothermic effect in the DTA curve (Fig. 1IIIa). A small mass loss between 230 and 440 °C is followed by a change in the slope of the TG curve which leads to a faster mass loss from 440 to 580 °C. After this temperature, the mass loss rate decreases and stops at 835 °C. These three stages of mass loss are associated with the dehydroxylation process and originates an endothermic effect (between 400 and 650 °C) centred at 506 °C (Fig. 1II and III) and indicate that dehydroxylation of KGa-1 does not occurs according to a single elementary process. At higher temperatures, an intense exothermic effect is also observed (between 961 and 1004 °C) at 987 °C. The origin of this effect is controversial in literature and no crystalline phases are observed after this effect.[8]

The TG, DTG and DTA curves of the sonicated KGa-1 samples (Fig. 1) show greater mass losses below 440 °C compared to that observed in the TG curve of untreated kaolinite. When sonication time increases, the weight loss in this first stage increases as the mass loss in the dehydroxylation process decreases. The endothermic centred at 110 °C is complex and appears formed, at the least, by two effects centred at 110 and 219 °C, which can be attributed to the loss of adsorbed water and the loss of protonated hydroxyls formed during the sonication treatment due to prototropy and to the hydroxyl groups located on the external surface of the particle, respectively. At higher temperatures, the DTG and DTA curves of sonicated KGa-1 samples shows that the dehydroxylation process shifts to lower temperatures (from 506 to 482 °C after 40 h of sonication) and decreases in intensity as the endothermic effect centred at 219 °C increases. According to Franco et al.[34] and Dion et al.[35], this shift may be explained in terms of particle size reduction along the *c*-axis and increasing of structural disorder induced by the sonication treatment. In the dehydroxylation, the mass continues decreasing up to 717 and 655 °C in the KGa-1 samples sonicated 20 and 40 h, respectively. Thus, the particle-size reduction progressively reduces the temperature of the end of the dehydroxylation process.

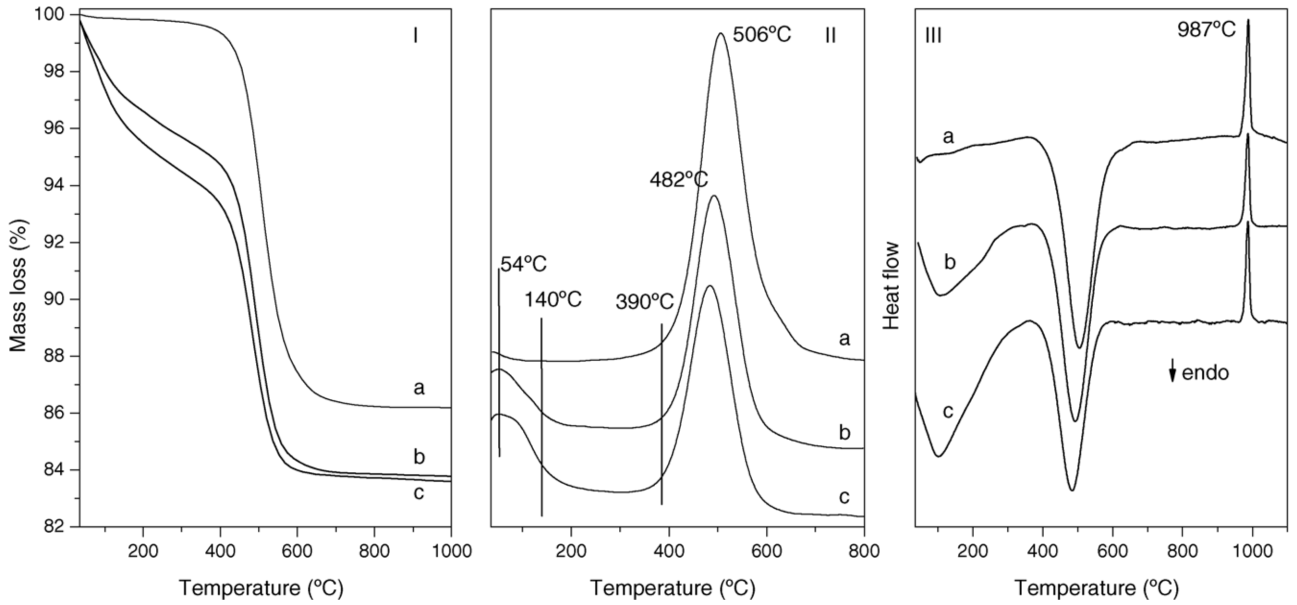

Fig. 1. TG (I), DTG (II) and DTA (III) curves of untreated KGa-1 (a) and sonicated KGa-1 samples (b = 20 h, c = 40 h).

The DTG-DTA curves of untreated KGa-2 (Fig. 2) present some differences in the temperature of the effects as compared with those of the KGa-1 (Fig. 1), which can be attributed to the smaller particle size and the higher structural disorder of the KGa-2 sample.[8,33]

The TG-DTG-DTA curves of sonicated KGa-2 samples (Fig. 2) also show an increase of the mass loss between 140 and 440 °C and the shift of the dehydroxylation process to lower temperatures as sonication time increases, as occurred with the KGa-1 sample. Nevertheless, the smaller modifications, compared with those obtained with KGa-1, can be explained in terms of lower effectiveness in the particle size reduction process. The comparative study of the effect of sonication on different ordered kaolinites showed that the intensity of the induced modifications by ultrasound treatment are influenced by the characteristic features of starting kaolinites, mainly the fraction of kaolinite with particle-size higher than 1 μm, which are the most sensitive for the particle size reduction process.

3.2. Pyrophyllite

TG, DTG and DTA curves of untreated and sonicated pyrophyllite are shown in Fig. 3. The TG of untreated sample

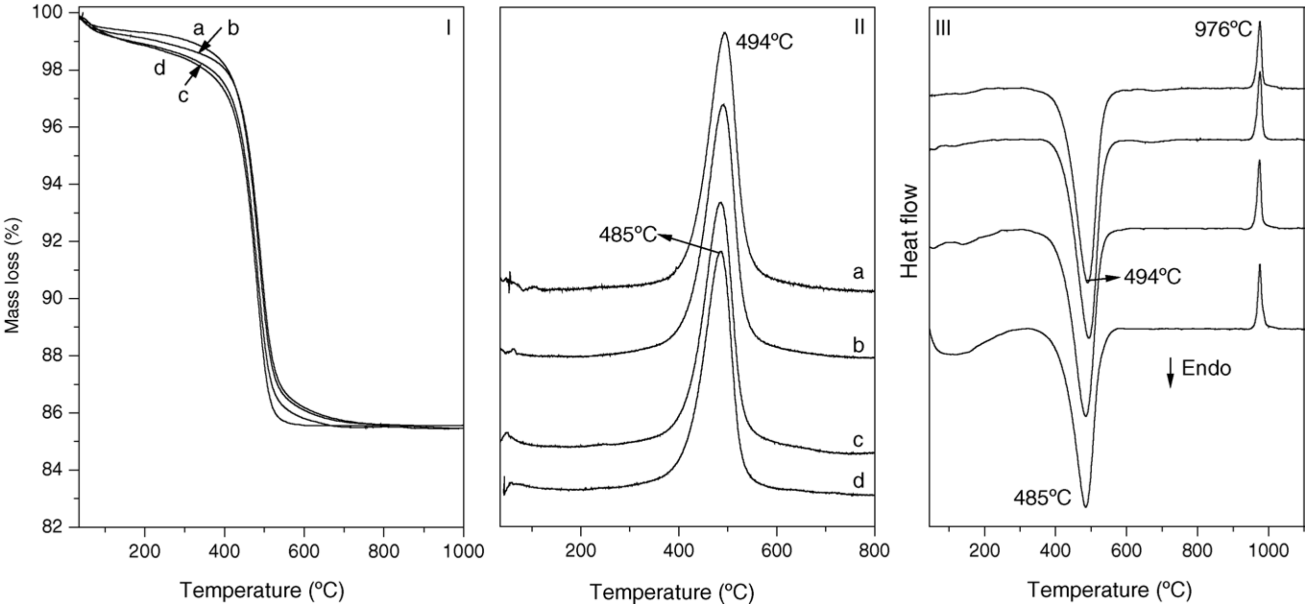

Fig. 2. TG (I), DTG (II) and DTA (III) curves of untreated KGa-2 (a) and sonicated KGa-2 samples (b = 20 h, c = 40 h and d = 60 h).

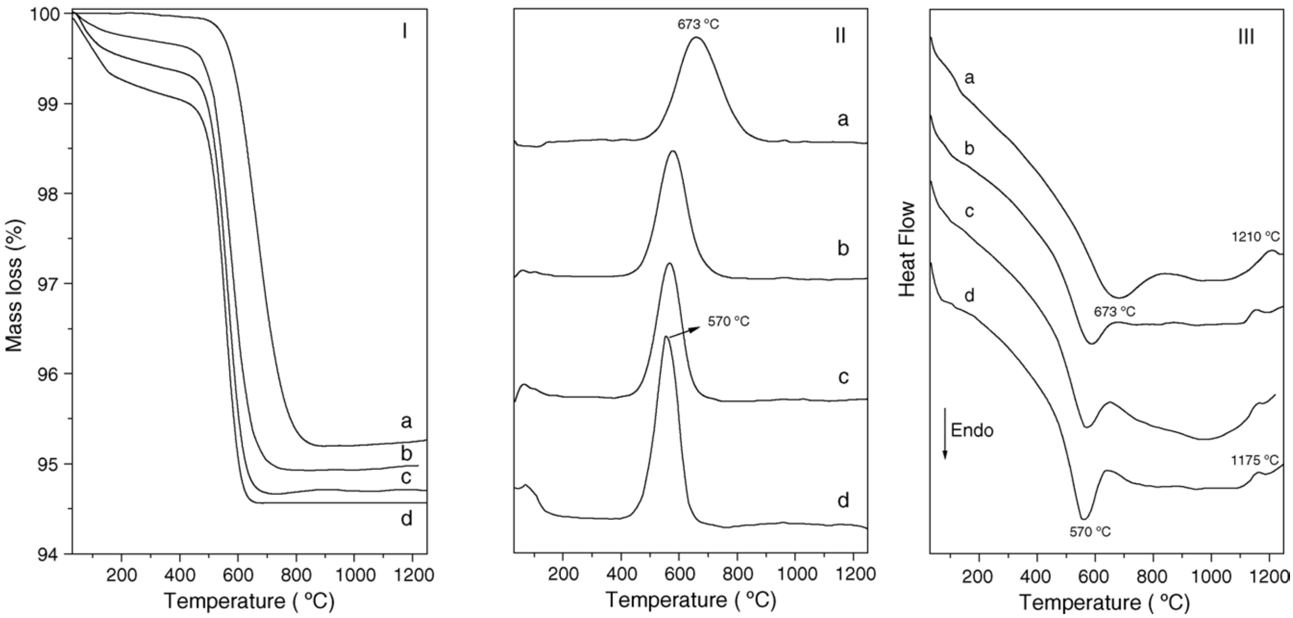

Fig. 3. TG (I), DTG (II) and DTA (III) curves of untreated pyrophyllite (a) and sonicated pyrophyllite samples (b = 10 h, c = 20 h and d = 40 h).

shows that weight loss begins about 500 °C and it is over at 825 °C. This weight loss, which is observed in the DTG curve as a broad band centred at 673 °C and is accompanied, in the DTA curve, with an endothermic effect centred at the same temperature, corresponds to the expected loss (4.95%) from the total dehydroxylation of an ideal pyrophyllite. The DTA curve shows a small exothermic effect centred at 1210 °C which corresponds to mullite formation.[24]

The TG curves of the sonicated samples show an increasing weight loss below 150 °C. Nevertheless, contrary to that observed in the sonication of kaolinites, the weight loss percentage for the dehydroxylation of sonicated samples (400–825 °C) is identical to that of the untreated sample. Thus, the increase of the weight loss below 150 °C can be only related to the increase of adsorbed water due to the increase of surface area. As sonication time increases, the broad band at 673 °C observed in the DTG and DTA curves of the untreated sample shifts to lower temperatures (from 673 to 570 °C) and progressively becomes narrower. These modifications can be related with the decreasing and the homogenisation of the particle size of pyrophyllite. Finally, the exothermic effect, corresponding to mullite formation, shifts from 1210 to 1175 °C after 40 h of sonication treatment. This data shows that sonication reduces the temperature of formation of high temperature phases.

3.3. Talc

Fig. 4 shows the TG, DTG and DTA curves of the original and sonicated talc samples. The dehydroxylation of untreated talc occurs at temperatures notably higher than those observed for the other clays studied in this work. Thus, the TG curve of untreated talc shows that the weight loss in this process begins at 800 °C and is over at 1100 °C. This weight loss appears as a peak centred at 952 °C in the DTG curve and it is accompanied, in the DTA curve, by an endothermic effect centred at the same temperature.

TG, DTG and DTA curves of sonicated samples show a weight loss at low temperatures, not observed in the untreated sample, which increases as sonication time increases. This loss is attributed to the release of adsorbed water which increases with the increasing of surface area caused by the particle size reduction. Sonication also influences the temperature of dehydroxylation process of talc. Thus, the maximum of the peak centred at 952 °C in the DTG and DTA curves of untreated talc shifts to 930 °C, after 10 h of sonication, to 925 °C after 40 h of sonication, and to 905 °C, after 100 h of treatment, while the weight loss of the sonicated samples is identical to that of the untreated one.

3.4. Muscovite

TG, DTG and DTA curves of untreated and sonicated muscovite are shown in Fig. 5. This figure shows that untreated sample has an unique weight loss that begins at 650 °C and is over at 920 °C. This weight loss agrees with the total dehydroxylation for an ideal muscovite (4.70%). The DTG curve shows a relatively sharp weight loss centred at 824 °C which is accompanied with an endothermic effect centred at the same temperature. Sonication modifies strongly the thermoanalitical curves. Thus, the TG curve shows a new mass loss in the range from 300 to 450 °C that appears as a shoulder in the DTG curve and increases with sonication time. At higher temperatures the band centred at 824 °C in the DTG and DTA curves of untreated muscovite shifts to 700 °C, after 10 h of sonication, and reaches a limit for 40 h sonication time (maximum at 640 °C). In addition, the dehydroxylation of the weakly bonded OH groups situated in the new borders cre-

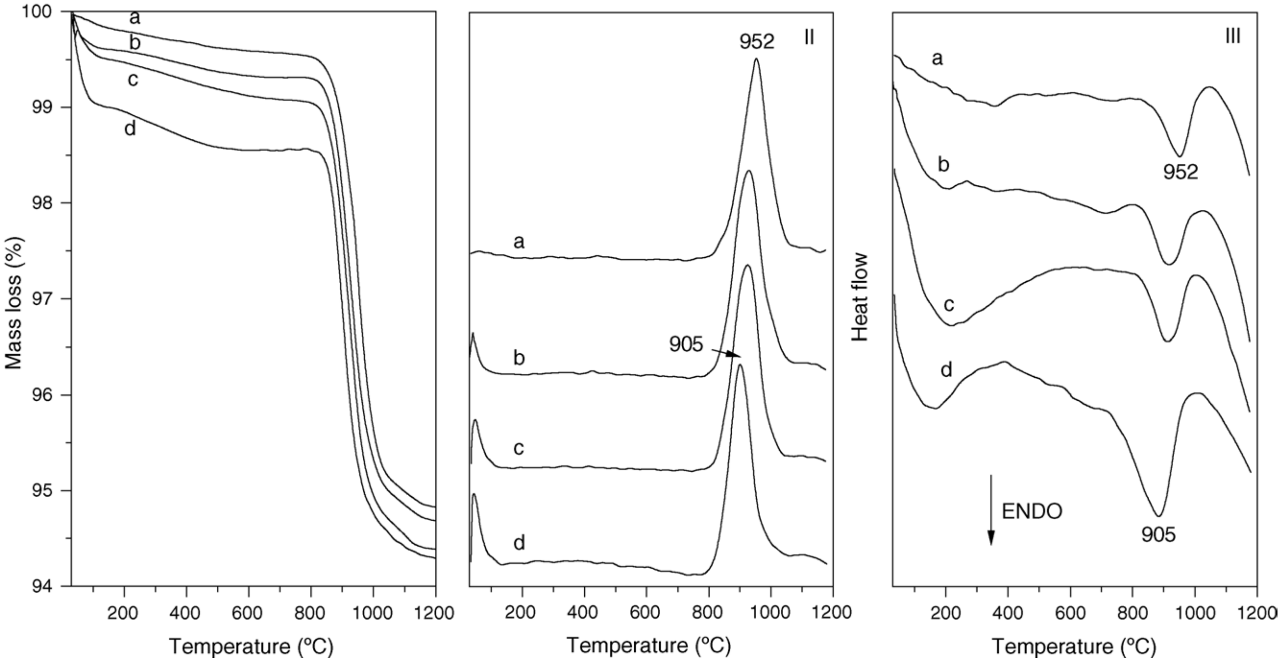

Fig. 4. TG (I), DTG (II) and DTA (III) curves of untreated talc (a) and sonicated talc samples (b = 10 h, c = 40 h, d = 100 h).

ated by the particle size reduction should be responsible of the weight loss between 300 and 450 °C. Thus, the thermal behaviour changes while the particle size is reduced, that is up to 40 h of treatment time, remaining unchanged for longer treatment times.

The DTA endothermic peak that appears at 1145 °C in the untreated material that corresponds to the recrystallization into leucite, corundum and mullite shifts to lower temperature as sonication proceeds.

4. Discussion

Table 1 collects the temperature of the dehydroxylation effects of the original and 40 h sonicated samples presented above and their specific surface area (ssa). These data and the results described above reveal that sonication significantly modifies the thermal behaviour of clay minerals. Table 1 shows that the ssa increases with the sonication time as consequence of the particle size reductions. Moreover, it is

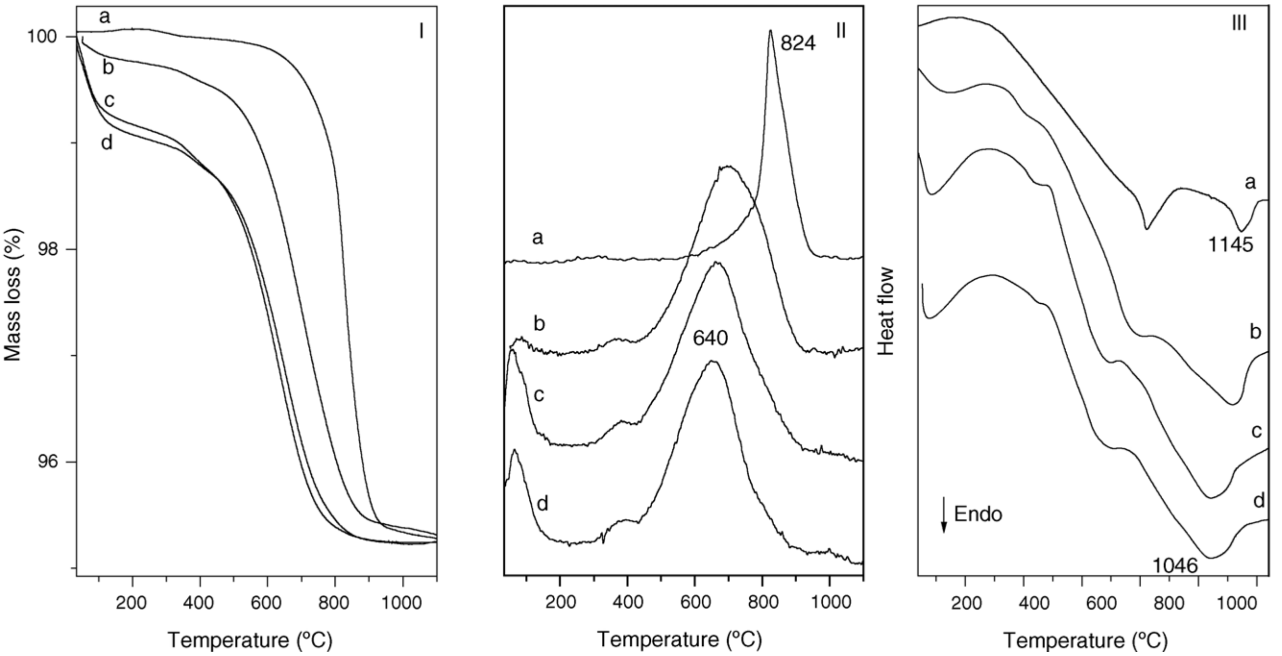

Fig. 5. TG (I), DTG (II) and DTA (III) curves of untreated muscovite (a) and sonicated muscovite samples (b = 10 h, c = 40 h, d = 100 h).

Table 1
Specific surface area (ssa) and temperature of the maximum for the dehydroxylation for the untreated and 40 h sonicated samples

Sample	ssa ($m^2\ g^{-1}$)			Maximum of the dehydroxylation peak (°C)		
	Untreated	Sonicated	Δssa	Untreated	Sonicated	Δt
Kaolinite, KGa-2	16	31	15	494	485	9
Kaolinite, KGa-1	8	67	59	506	482	24
Talc	16	55	39	952	925	27
Pyrophyllite	4	70	66	673	570	103
Muscovite	~1	27	26	824	640	184

observed that the temperature of the dehydroxylation effect shifts to lower temperatures as the reduction of particle size takes place. Nevertheless, the clay minerals studied in this work show different shifts of the dehydroxylation temperature. In kaolinites and talc the shift of the endothermic effect, after 40 h of sonication, is smaller than 25 °C, whereas for pyrophyllite and muscovite the shift is higher than 100 °C. Fig. 6 represents the temperature shift of the dehydroxylation versus the percentage of increase of ssa. This figure shows a clear linear correlation between these two parameters. It is intriguing that despite the different structures of the laminar silicates studied here, the shifts of the dehydroxylation effects are linearly related to the relative increase of the ssa. The structure (1:1 or 2:1) or the composition of the silicate play a role in the temperature of the dehydroxylation, but the shifts of this dehydroxylation due to the sonication treatment are only related to the increase of the ssa (and, therefore, to the decrease of particle size). This result can be understood in terms of previous studies that have shown that the thermal dehydroxylations of laminar silicates, such as kaolinite, are diffusion controlled processes.[35,36] Thus, the increase of the specific surface area due to particle size reduction should enhance the diffusion controlled dehydroxylation. For minerals such as muscovite, that suffers the most severe relative particle size reduction, and, therefore, the largest increase in ssa, the diffusion controlled dehydroxylation is more significantly enhanced and the shift in the dehydroxylation is quite large. On the other hand, for the KGa-2 sample that suffers the smallest increase in ssa, the shift in the dehydroxylation is much smaller.

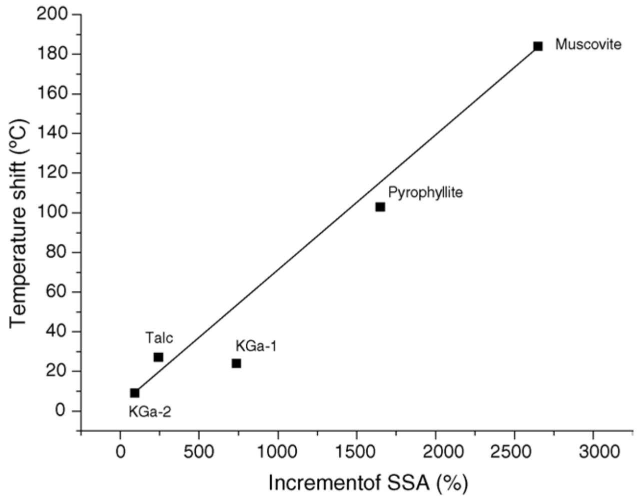

Fig. 6. Evolution of the temperature shift of the dehydroxylation maxima vs. percentage of increase of the specific surface area due to sonication for 40 h.

For pyrophyllite and muscovite, the high temperature effects that correspond to the crystallization into new phases are affected by the particle size reduction produced by the sonication treatment and they show a decrease in the average temperature of the process, indicating that a decrease in particle size enhances the crystallization. On the other hand, for kaolinite, the exothermic effect at high temperature, whose origin does not seem to be directly correlated to a crystallization process but to a release of energy due to a change in the coordination of Al,[37] is not affected by changes in particle size of the material.

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