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EFFECT OF SONICATION ON THE THERMAL DECOMPOSITION OF AMMONIUM VERMICULITE AS STUDIED BY TG-MS HYPHENATED TECHNIQUE

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Abstract

The thermal decomposition of the ammonium exchanged vermiculite takes place in three steps. A strong correlation exists between the mass loss of ammonia and water suggesting a simultaneous release. It is proposed that proton transfer from the ammonium ion to the hydroxyl units results in this simultaneous release. This behaviour could be explained by a mechanism where a resulting proton, produced by the release of ammonia out of ammonium cation, combines with a structural hydroxyl to form water. Sonication produces a substantial reduction in the particle size of the vermiculite sample. Thus, the macroscopic particle size of the untreated material is drastically reduced to the micrometers range while the structure as assayed by XRD remains unchanged. The particle size reduction produced by the sonication treatment modifies the thermal decomposition profile, mainly the mass percentages of the different steps.

Keywords: ammonia release, ammonium vermiculite, sonication, TG-MS, water release

Introduction

Vermiculite is a laminar clay mineral with many important industrial applications, mainly when its particle thickness and length are reduced [1, 2]. Sonication have been recently proposed as an alternative to grinding for reducing the particle size of clays [3–6] because, unlike grinding, sonication does not modify the crystal structure and prevents amorphization [7, 8].

Every layer of vermiculite is composed of a central magnesium octahedral sheet in-between two silica tetrahedral sheets. Different cationic substitutions in the octahedral and tetrahedral sheets determine the negative charge of the mineral. This layer charge is neutralized by the presence of cations in the interlaminar space. The nature of the cations in the interlayer determines the properties of the clays. Recently, special attention is being paid to ammonium exchanged laminar clays because of their possible relevance in plant nutrition [9, 10] and their application as catalyst [11].

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In the study of the thermal degradation of minerals, hyphenated techniques such as TG-MS or TG-IR are very useful because both the mass loss or gain and the partial pressure of the gases released or consumed during the process are simultaneously recorded, yielding very valuable information about such transformations. Recently, the above mentioned techniques have been used in several publications for the study of thermal transformation of different inorganic solids [12–16]. These methods have been also applied to the study of kinetics of thermal decomposition of very stable solids that have a very low equilibrium pressure in the temperature range at which the reaction takes place [17]. The aim of this paper is the study of the thermal decomposition of ammonium vermiculite by means of the TG-MS hyphenated technique. In this study both the partial pressure of water and of ammonia are simultaneously recorded. Additionally, the effect of the sonication on the thermal behaviour of the material is analyzed.

Experimental

Materials

A vermiculite sample from Santa Olalla (Huelva, Spain) with a half-unit cell composition of $[(Si_{2.64}\ Al_{1.36})(Mg_{2.48}Fe^{3+}_{0.324}Fe^{2+}_{0.036}Al_{0.14}Ti_{0.01}Mn_{0.01})O_{10}(OH)_2]Mg_{0.439}$ was used for this study. The flakes of the natural vermiculite where cut to about 2 cm maximum size. The ammonium form was obtained by stirring with a 1 M NH_4-acetate solution at room temperature. The excess of $CH_3CO_2NH_4$ was washed out with distilled water. Sonicated samples were firstly sonicated and secondly saturated in ammonium.

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 in diameter that produces a double (peak-to-peak) amplitude of the radiation of 120 μm. Four different samples were prepared by sonication for 10, 20, 40 and 60 h, respectively. Each sonication treatment was performed at 20ºC with 3 g of vermiculite mixed with 25 mL of hydrogen peroxide (30%) solution and 25 mL deionized water.

Characterization

Particle size distribution was determined by the low angle laser light scattering (LALLS) method with a Mastersizer instrument manufactured by Malvern. Specific surface area was determined with nitrogen using the BET method at liquid nitrogen temperature with a Micromeritics 2200. X-ray diffraction patterns were determined with Ni-filtered CuK_α radiation with a Siemens Kristalloflex D-500.

TG-MS measurements were performed with a Cahn electrobalance connected to a high vacuum system equipped with a quadrupole mass spectrometer (masstorr FX, VG). For water and ammonia were recorded 18 and 16 mass/charge signals, respectively. For ammonia, the corresponding value of 17 could not used because of the interference with the water signal.

Results and discussion

Figure 1 shows the evolution with the sonication time of the median diameter, coherently diffracting domain in the [001] direction (D_{001}) and surface area. It is clear from this figure that sonication produces a significant decrease of the particle size. Thus, the macroscopic size of the original vermiculite is reduced to 15±12, 10±7, 2±2 and 3±2 μm after 10, 20, 40 and 60 h of sonication, respectively. 40 h of sonication seem to be an optimum limit for sonication, because longer treatments produce a small increase of the median diameters. This increase of the diameter for sonication treatment longer than 40 h can be understood in terms of aggregation of the smaller particles during the sonication treatment. The decrease in the median diameter produced by sonication is also accompanied by a significant delamination of the clay following a similar evolution to that of the median diameter (Fig. 1). The sample sonicated for 10 h have a D_{001} of 102 nm that decreases to 73 and 39 nm after 20 and 40 h of sonication, respectively, remaining unchanged at this latter value for longer treatments. On the other hand, the decrease in particle size produces an increase in the surface area. Thus, the sample sonicated for 10 h has a surface area of 22 $m^2\ g^{-1}$ that increase to 31, 33 and 34 $m^2\ g^{-1}$ after sonication for 20, 40 and 60 h, respectively. The small increase observed for the sample sonicated for 60 h, as compared with that sonicated for 40 h, can not be directly attributed to a decrease in surface area but to some penetration of the nitrogen between individual layers of the vermiculite, and not to a decrease of the particle size.

Figure 2 includes the TG-DTG curves of the untreated NH_4^+-vermiculite in the range of temperatures from 100 to 1000ºC. In this range of temperatures, three mass-loss steps are observed, the first one in the range from 150ºC to about 475ºC, the second one from 475 to 740ºC and the last one from 740 to 920ºC. The mass

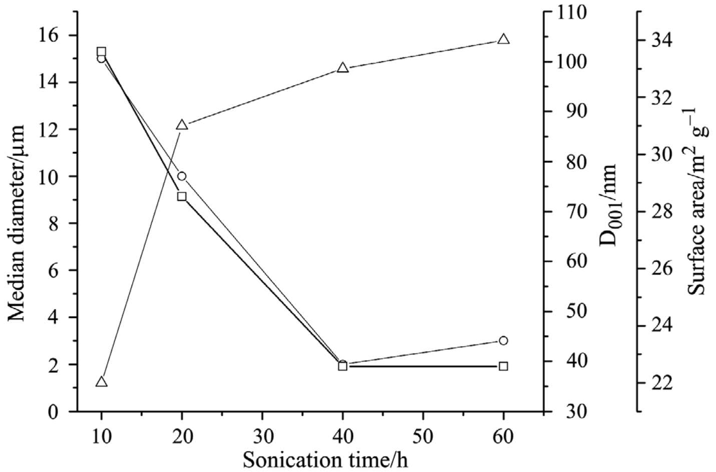

Fig. 1 Evolution of the median diameter (○), coherently diffracting domain in the [001] direction (D_{001}) (□), and surface area (△)with the sonication time

losses corresponding to these three steps are ~1.75, ~4.7 and ~3.5%, respectively, being the total mass loss about 10%. This total mass-loss value is larger than those reported in literature for the same vermiculite but with different cations in the interlayer space. Thus, for the Mg^{2+} and Na^+ forms of vermiculite, a mass loss of about 4.7% have been reported for the dehydroxylation [18–20]. Additionally, the layer distance of 10.54 Å obtained by X-ray diffraction for the NH_4^+-vermiculite indicates that the ammonium ions are strongly bound to the silicate layer and nearly no water is present in the interlayer space. Therefore, the excess of mass loss for the NH_4^+-vermiculite as compared with the Mg^{2+} - and Na^+ - vermiculite corresponds to the ammonium in the interlayer space that is released during the decomposition.

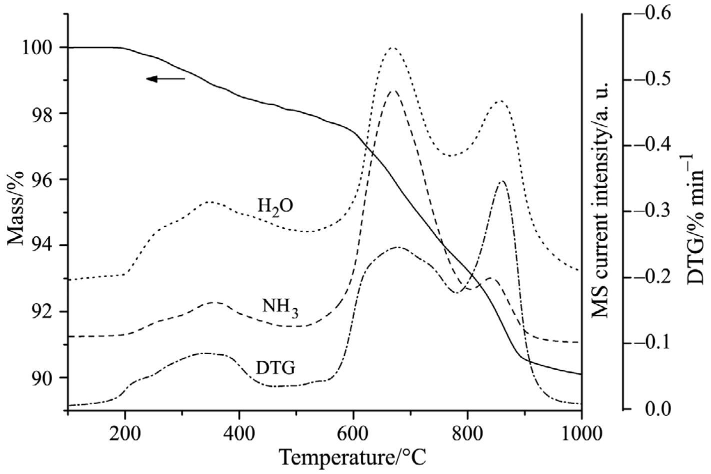

Fig. 2 TG-DTG curves for the thermal decomposition of the untreated ammonium vermiculite. Evolution of ammonia and water as registered simultaneously by MS are also included

Figure 2 also includes the evolution of the recorded gases released during the decomposition of the NH_4^+-vermiculite corroborating the release of both H_2O and NH_3. Both gases are released simultaneously in the three steps in which the thermal decomposition takes place. The release of water and ammonia in three steps accompanies the three steps observed in the TG-DTG trace and could be related to three different degrees of interaction of the NH_4^+ groups with the vermiculite layer. Thus, the first step at low temperature (150 to 475ºC) could be related to groups attached to the borders or very closed to the borders that are loosely bond and could be released at relatively low temperature. In a previous study by thermodiffractometry [20], it has been observed that there is no change in the interlayer space in this temperature range, indicating that the structure remains unchanged and there is no collapse of the vermiculite layers. The release of gases in this temperature range has also been detected in literature with emanation thermal analysis by an increase in the rate of radon emanation [18–20]. The two more severe mass losses at higher temperatures, i.e. 450–920ºC, should correspond to groups more strongly attached to the vermiculite layer. In these temperature ranges, a change in the thermodiffraction pattern has been reported [19]. Thus, an additional and very broad diffraction peak corresponding to lower values of *d*-spacing has been observed, both diffractions disappear at 950ºC. Additionally, we have previously observed in an IR study of different vermiculite samples with different cations in the interlayer space that the hydroxyl groups bonded to certain cations are more strongly attached than those bounded to other cations [21]. Thus, the cations and their distribution in the layer determine the energy of such bonding. For ammonium vermiculite, the OH^- groups bonded to trivalent ions are more strongly attached than those bound to Mg^{2+}. Thus, in the present case, the cationic substitutions in the Santa Olalla vermiculite layer may be responsible of the presence of two different bonding sites with different bonding energies that determine the two steps decomposition in the temperature range 450–920ºC.

It has been mentioned above that the release of ammonia and water takes place simultaneously during the three decomposition steps observed in the studied temperature range. This finding indicates that the dehydroxylation of the NH_4^+-vermiculite seem to be triggered by the ammonia release. Thus, during the NH_3 release, the remaining proton of the NH_4^+ cation may recombine with an NH_4^+ group of the vermiculite to produce water that is released simultaneously with the NH_3 according to the following reaction:

$$NH_4^+ + OH^- \rightarrow NH_3\uparrow + H_2O\uparrow$$

This statement is in agreement with previous results that have indicated that the amount of water released from ammonium vermiculite is larger than that expected from the stoichiometric combination of two hydroxyl groups to produce a single water molecule [21].

Figure 3 includes the mass loss and the evolution of ammonia and water for the vermiculite sample sonicated for 20 h. Sonication slightly modifies the temperature ranges of the thermal decomposition; thus, the first stage takes place in the range from 150 to 460ºC, the second from 460 to 720ºC and the third one from 720 to 920ºC. Additionally, sonication modifies the mass loss percentages of the two last mass losses. Thus, the mass loss of the second step increases from ~4.7%, for the untreated sample, to ~5.4%, for the sample sonicated for 20 h, while the mass loss of the third step decreases from ~3.5%, for the untreated sample, to ~2.8%, for the sample sonicated for 20 h. Nevertheless, the total mass loss remains unchanged. It is also significant that as for the untreated sample, the release of water and ammonia takes place simultaneously in the three stages.

After 40 h of sonication (Fig. 4), the mass loss percentage of the last step decreases even more than for the sample sonicated for 20 h accounting only for ~0.9%, while the second step accounts for 7.3%. Additionally, the second step seems to split into two (a shoulder can be observed in the DTG trace about 750ºC). The release of water and ammonia takes place simultaneously, as in all the previous cases, except for the last step where the release of ammonia is almost insignificant. Finally, for the

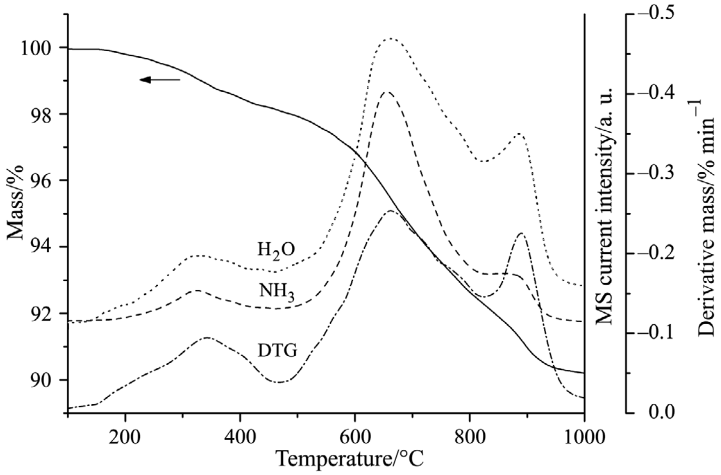

Fig. 3 TG-DTG curves for the thermal decomposition of the ammonium vermiculite sonicated for 20 h. Evolution of ammonia and water as registered simultaneously by MS are also included

sample sonicated for 60 h, the thermal decomposition profile (Fig. 5) is identical to that of the sample sonicated for 40 h (Fig. 4). These results seem to indicate that there is a correlation between the particle size effect produced by the sonication and the modification in the thermal behaviour, because sonication produces significant particle size reduction while the structure does not suffer any modification. Additionally, it was observed that 40 h of sonication is a practical limit because sonication treatments longer that 40 h do not produce particle size reduction. Thus, up to 40 h of sonication, the vermiculite particle size is reduced and this particle size reduction has an effect on the modification of the thermal profile by decreasing the mass loss percentage of the last step. Further sonication (up to 60 h) does not produce any reduction in the particle size and, therefore, it does not have any significant effect on the thermal behaviour. This particle size reduction modifies the release of the NH_4^+ groups due to a modification either of the interaction of the groups with the layer or to the diffusion of the species during the thermal treatments. Modifications in the thermal behaviour of sonicated clay minerals have been reported for other clays. Thus, it has been established a relation between the modification in the thermal behaviour due to sonication and the particle size reduction produced by the sonication treatment. For muscovite and pyrophyllite [22, 23], it has been observed that as particle size decreases, produced by sonication, there is a shift of the dehydroxylation towards lower temperatures. These shifts could be of more than 100ºC in the average temperature of the process for very significant modifications in the particle size. Additionally, for biotite [22], it has been observed that particle size reduction produces a change in the two steps profile of the dehydroxylation. Thus, as sonication proceeds and the particle size decreases, the mass loss percentage of the lower temperature step increases at the expense of the mass loss percentage of the higher temperature

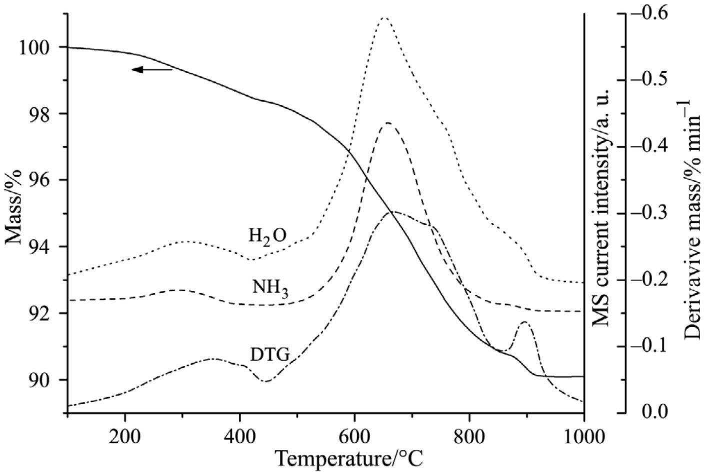

Fig. 4 TG-DTG curves for the thermal decomposition of the ammonium vermiculite sonicated for 40 h. Evolution of ammonia and water as registered simultaneously by MS are also included

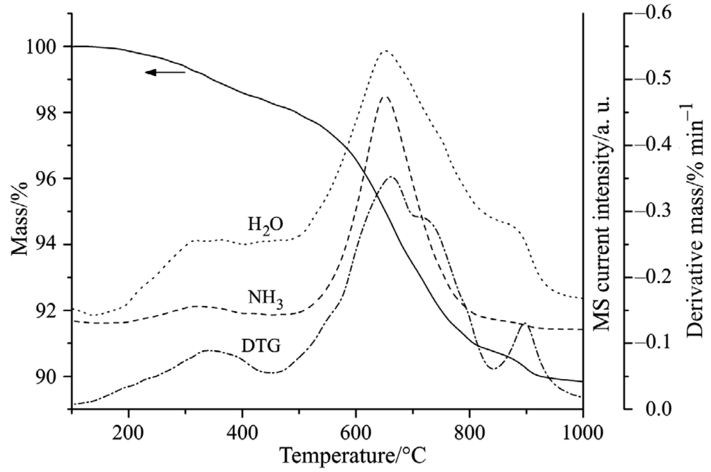

Fig. 5 TG-DTG curves for the thermal decomposition of the ammonium vermiculite sonicated for 60 h. Evolution of ammonia and water as registered simultaneously by MS are also included

step. In the present case, sonication of vermiculite produces a small decrease of the temperature of the process, this decrease is much smaller than those reported for other clays, but the TG profile is affected by a change in the mass% of the first and second steps, in a similar way to that reported for biotite [22]. It is also worth to note that the release of ammonia during the last step is very small.

Conclusions

The thermal decomposition of the NH_4^+-vermiculite takes place in three different steps: the first one in the range from 150 to about 475ºC, the second one from 475 to 740ºC and the last one from 740 to 920ºC. The first mass loss has been attributed to hydroxyl and ammonium groups loosely bond (i.e. in the borders or close to the borders). The two last mass losses might be explained by the different bonding sites in the interlayer of the vermiculite. These two bonding sites can be related to the different cationic substitutions in the vermiculite layer. The use of hyphenated TG-MS has allowed to record both the mass loss and the release of ammonia and water. Thus, it has been observed that the release of these two species takes place simultaneously, suggesting that the release of ammonia may trigger the release of water by means of the recombination of the remaining proton from the ammonium group with a structural hydroxyl group to form a water molecule.

Sonication up to 40 h of treatment yields substantial particle size reduction and delamination of the vermiculite flakes. Longer treatment times do not produce any additional particle size reduction. The particle size reduction modifies the thermal decomposition profile of the NH_4^+-vermiculite. Thus, the average temperature of the decomposition decreases while the mass loss percentage of the lower temperature step increases at the expense of the mass loss percentage of the higher temperature step. A similar behaviour has been previously observed for sonicated biotite samples. It has been shown that the hyphenated TG-MS is a very suitable technique for studying the thermal decomposition of these ammonium clay samples because not only the TG curve is recorded but both the release of water and ammonia can be registered simultaneously yielding interesting information about the thermal decomposition.

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