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A study by thermal analysis of the reversible folding in palygorskite under vacuum thermal treatment [1]

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Abstract

The structural changes of a Spanish palygorskite, and their reversibility, have been examined by thermal analysis under vacuum. These changes have been related to the textural values obtained under similar conditions by N_2 adsorption–desorption. The folding of this material under vacuum starts at 125°C, where its microporosity disappears. This folding is reversible up to 300°C. From 125°C, the specific surface area remains stable, corresponding to the external surface of the mineral. Thermal treatment above 300°C generates irreversible folding in the structure.

INTRODUCTION

Palygorskite is a fibrous silicate with a relatively high surface area and acid properties, which make it useful as an adsorbent and catalyst. Its structure is composed of two bands of silica tetrahedrons linked by magnesium ions in octahedral coordination. Due to the alternating position of the apical oxygens which are not shared in the tetrahedrons, there are capillary channels 3.7 Å × 6.4 Å in size between the bands, oriented longitudinally with the fibers. In the unit cell, eight water molecules are bound to the octahedral cations, and others are present as zeolitic water bound to the exchange cations [1]. Palygorskite undergoes structural changes when heated; three steps can be distinguished in the dehydration process:

(1) The surface-adsorbed water and the zeolitic water are lost.
(2) With increased heat, structure folding takes place due to the loss of the first two water molecules coordinated to the octahedral sheet.
(3) At temperatures of 300°C and above, the rest of the coordinated water is lost, accompanied by dehydroxylation of the tetrahedral sheet.

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In this heating process, when a certain temperature is reached, the structure of the palygorskite undergoes permanent folding.

Folding in palygorskite has been identified and studied by a number of authors using various techniques: IR [2–4]; N_2 adsorption [5, 6]; and, recently, by N_2 and Ar microcalorimetry, and by immersion microcalorimetry in water [7].

The present work uses TG–DSC (thermal analysis) to identify the structural changes outlined above. Prior to the TG–DSC, samples were heated and cooled under different conditions in order to yield data for two sample sets. One set allows us to determine which step the samples have reached after exposure to a determined temperature in a vacuum. In addition, using samples from this set heated at different temperatures, we can compare their mass losses and thus note the correlation between determined temperatures and measurable losses of water. Data from the other set of samples allow us to determine whether the structural change is reversible, or irreversible.

In yet another approach, we can use these same sample sets to measure variance in surface area and texture at different temperatures.

EXPERIMENTAL

Starting material

The work was performed on a sample of Spanish palygorskite from a deposit in Serradilla (Cáceres), described by Galán et al. [8] as one of the most important in the world and whose reserves are estimated to be higher than 15 million tons. This sample was obtained from Tolsa S.A., the company that exploits the deposit.

A previous characterization of the sample by González [9, 10] gave the following results: fiber dimensions, 1500–7000 Å and 260–400 Å; surface area S_{BET}, 71 $m^2 g^{-1}$; cation exchange, 42.5 mequiv. per 100 g; mineralogical composition, 95% palygorskite, 5% mica and traces of quartz. The structural formula is reported to be $(Si_{7.91}Al_{0.09})_{tetr}(Mg_{1.69}Al_{1.62}Fe_{0.48})_{oct}$-$(Mg_{0.10}Ca_{0.003}K_{0.01}Na_{0.18})_{cc}O_{20}(OH)_2(OH_2)_4 \cdot nH_2O$.

Apparatus and methods

The thermal analyses were performed on a Setaram G-111 apparatus. The heating rate was 5°C min^{-1} under a dynamic flow of dry helium of 100 ml min^{-1}.

Using the same palygorskite, two sets of samples were prepared for thermal analysis. One set first underwent thermal treatment in a vacuum of 10^{-3} Torr for 16 h at different temperatures (75, 100, 125, 150, 200, 300, 400

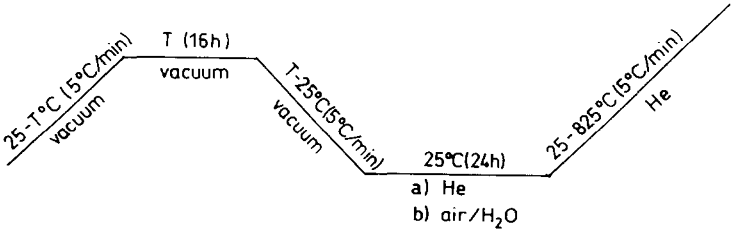

Fig. 1. The different steps to which samples were submitted.

and 500°C) using the apparatus which allows the experiments to be carried out in a dynamic vacuum. Subsequently, these samples were left to cool in the vacuum, and then exposed for 24 h to flowing He at 25°C. Thereafter they were submitted to thermal analysis performed in situ in an inert atmosphere of He. Samples from this set will be denoted Paly-75, Paly-100... etc, where 75, 100 refer to the treatment temperature in °C. For the second set, the samples received the same thermal treatment in a vacuum, but the subsequent step differs in that they were allowed to rehydrate under atmospheric conditions before the thermal analysis. These samples from the second set are denoted Paly-75-rehydrated, Paly-100-rehydrated, etc. (Fig. 1).

RESULTS AND DISCUSSION

Thermal analysis

During the thermal analysis temperatures reach such a point (825°C) that a sample of natural silicate passes through all the above-mentioned steps, as shown in Fig. 2 for natural palygorskite. In step one, as the temperature rises up to 100°C we note the presence of surface-adsorbed and zeolitic water bound to the exchange cations. In step two, up to 200°C, the first two water molecules coordinated to the octahedral sheet are lost. In step three (up to 600°C) the rest of the coordinated water is lost, a phenomenon which overlaps with the dehydroxylation of the tetrahedral sheet. This occurs when the sample is heated under He flow, whereas when the thermal analysis is performed in a dynamic vacuum, we can see a shift for the first and second steps to lower temperatures.

These losses of water are related to the changes produced in the structure of the clay (Fig. 3). The loss of the first two coordinated water molecules in step two is accompanied by a reversible structural folding; whereas in the next step, as the remaining coordinated water is lost, there is an irreversible, permanent folding.

The data from the two specially prepared sample sets show that for Paly-100 (Fig. 4) there is no part of the graph which corresponds to step

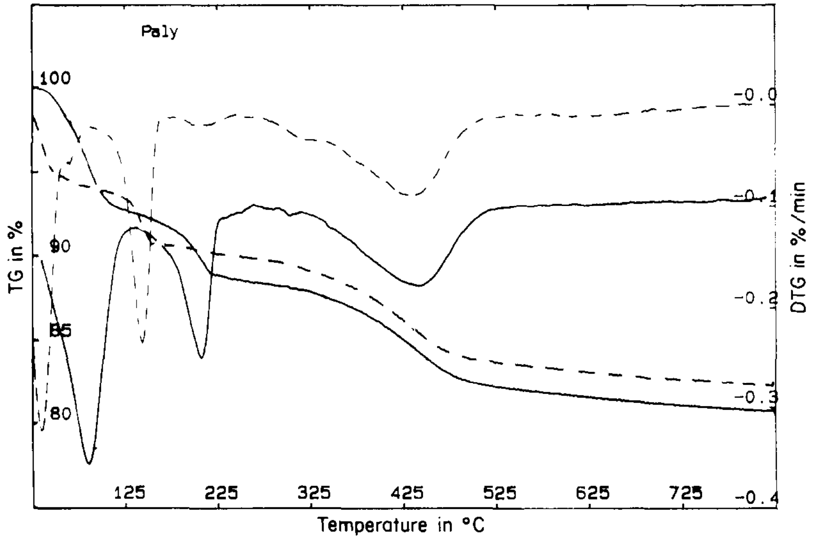

Fig. 2. TG and DTG curves of palygorskite: broken line, under vacuum; solid line, under He atmosphere.

one. This is because the sample had already lost surface-adsorbed and zeolitic water in the preparatory heating before the analysis. Therefore, the silicate reaches step two at 100°C. However, for the rehydrated sample, step one appears in the graph, just as it does in the graph for the natural sample.

In Fig. 5, the graph for Paly-150 shows only step three. This implies that in the preparatory heating when the first two coordinated water molecules were lost, the structure began folding. The data for the rehydrated sample, Paly-150-rehy, show all three steps (as in the natural sample), indicating that all classes of water molecules reappear after exposure to atmospheric conditions. Therefore, the folding produced at this temperature is reversible.

Figure 6 indicates what happens in the third step when there is some irreversible folding during the preparatory heating. Paly-300 shows only the

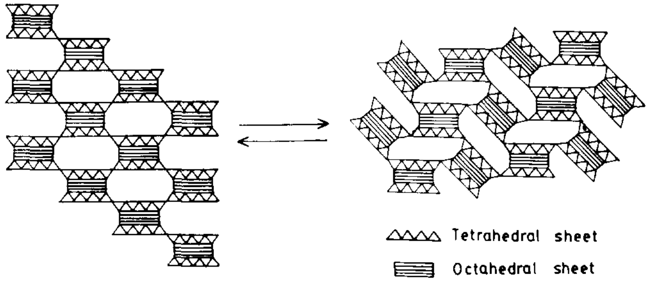

Fig. 3. Scheme showing the structural folding of palygorskite during thermal treatment.

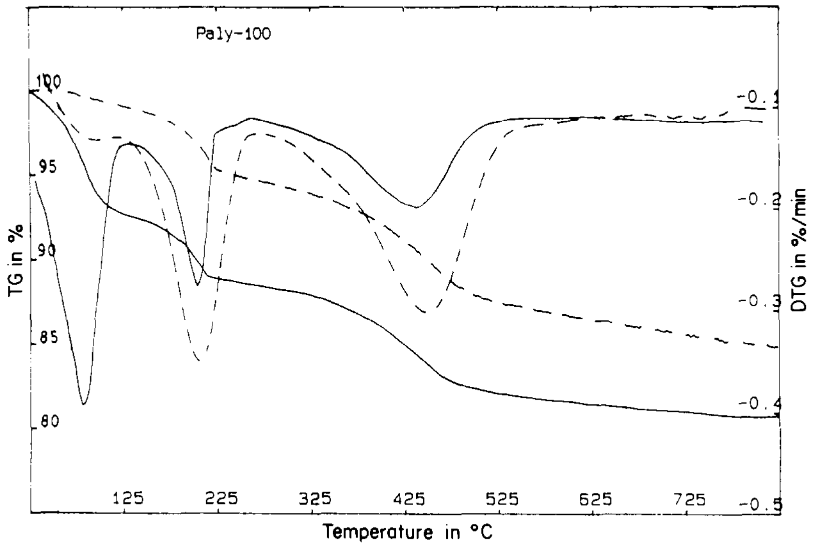

Fig. 4. TG and DTG curves of palygorskite treated at 100°C: broken line, Paly-100; solid line, Paly-100-rehydrated.

third step. When the samples in He are reheated, there is a loss of water molecules; this loss of mass is less for Paly-300 than for Paly-150 or Paly-100. This is because during the preparatory heating, the material had already lost much of the water left over after step two. Only part of the folding at 300°C is irreversible, as can be seen in analysis of the rehydrated

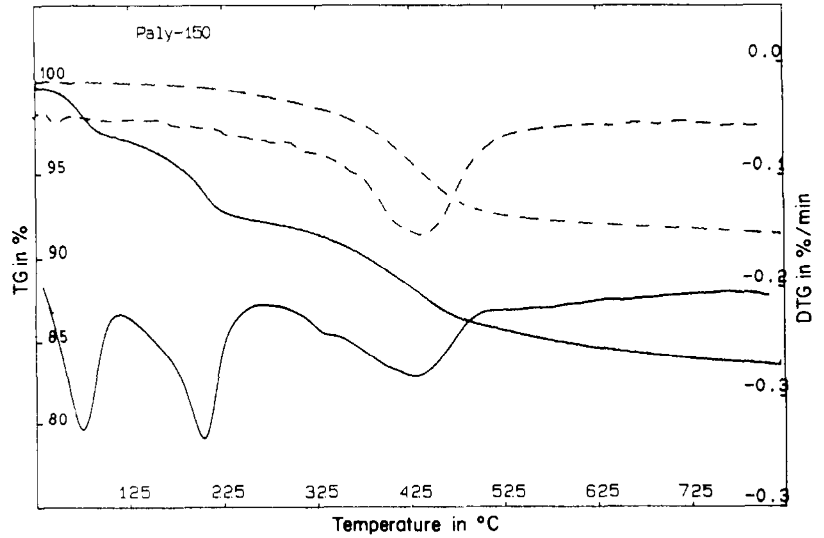

Fig. 5. TG and DTG curves of palygorskite treated at 150°C: broken line, Paly-150; solid line, Paly-150-rehydrated.

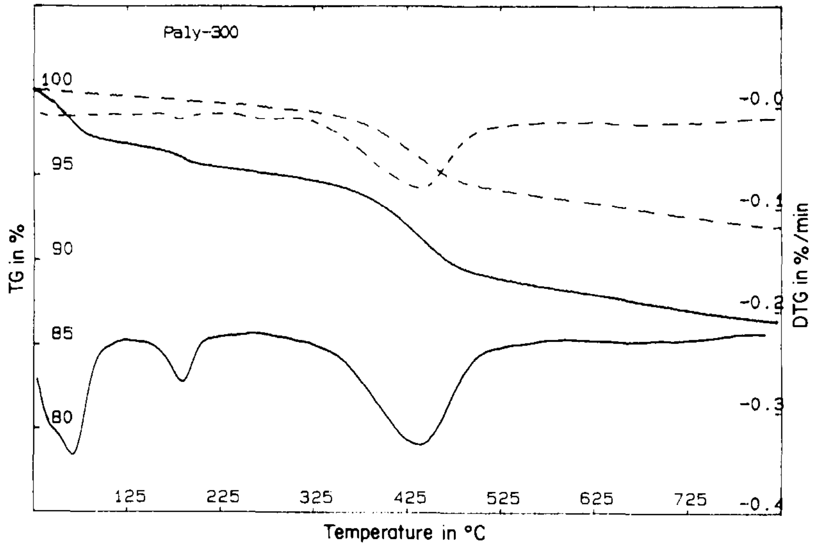

Fig. 6. TG and DTG curves of palygorskite treated at 300°C: broken line, Paly-300; solid line, Paly-300-rehydrated.

sample, where steps one and two do not completely reappear. Thus at 400°C, irreversible folding to a greater extent is to be expected.

Figure 7 confirms this expectation: in Paly-400 there is an even smaller loss of mass during the analysis, signifying that the coordinated water was lost completely that dehydroxylation had taken place. For the sample that was allowed to rehydrate, the TG is similar to that of the sample which was not allowed to rehydrate, except for a small loss of water below 100°C, due to the surface-adsorbed water on the external surface. This indicates that the folding was extensive and irreversible, because there is no rehydration at all.

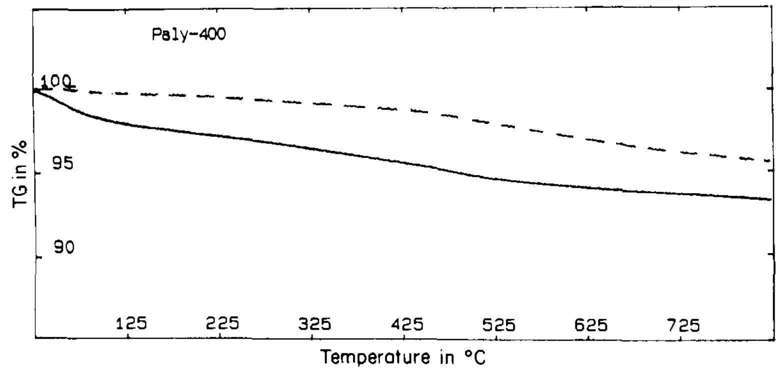

Fig. 7. TG curves of palygorskite treated at 400°C: broken line, Paly-400; solid line, Paly-400-rehydrated.

Textural characteristics

Textural characteristics include microporosity and surface area. The textural characteristics determined for the palygorskite prepared under similar experimental conditions can be explained in terms of the structural changes observed in the thermal analysis.

Figure 8 shows *t*-plots for the samples treated at 75°C and 150°C. The curve for Paly-150 passes through the origin of the coordinates which indicates an absence of microporosity. In contrast, the curve for Paly-75 indicates microporosity.

The changes in the specific surface area at different temperatures can be explained by the structural changes that have been proposed (Fig. 9). The surface area reaches a maximum at 75°C, and then decreases with temperature to 125°C, where it levels off and remains stable between 125 and 500°C. This confirms that the loss of the first two coordinated water molecules (second step) produces folding in the structure. This hinders access of N_2 molecules into the channels of the silicate and, consequently, N_2 adsorption only takes place on the external surface of the mineral. The external surface area remains stable with increasing temperature in spite of the irreversible changes in the material. At 100°C or lower, after total or partial loss of surface-adsorbed and zeolitic water, N_2 adsorption also takes

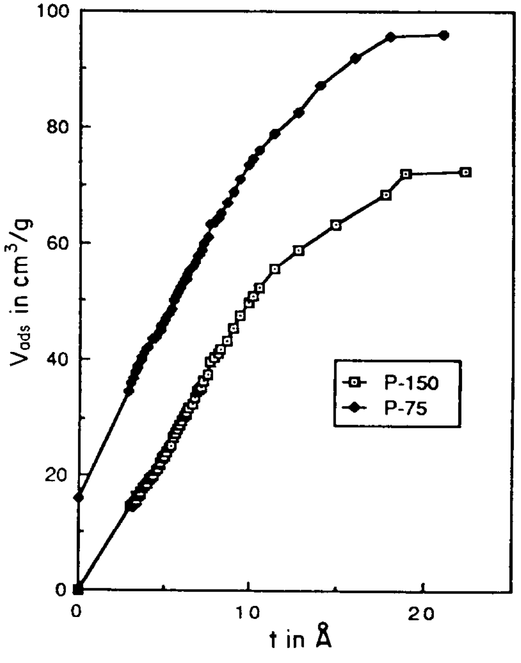

Fig. 8. *t*-Plots for palygorskite treatment at 75°C (Paly-75) and 150°C (Paly-150).

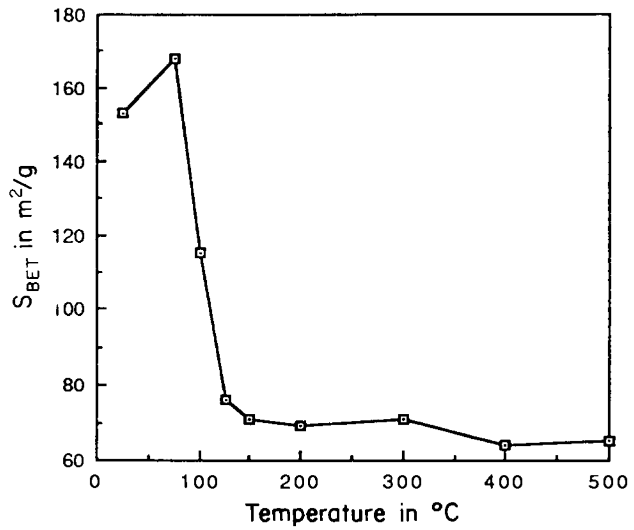

Fig. 9. Variation of specific surface S_{BET} under vacuum thermal treatment of palygorskite.

place in the mouths of the channels because the folding of the structure has not yet occurred.

CONCLUSIONS

The TG-DSC experiments indicate incipient folding at 125°C under vacuum, whereas when the thermal treatment is performed under He flow, the folding starts at 180°C. This folding is reversible up to 300°C. Beyond 300°C, irreversible changes in the structure of the silicate take place.

The surface area increases with temperature, reaching a maximum at 75°C where microporosity is observed in the material due to access of N_2 molecules to the structural channels. Beyond 75°C, folding leads to a progressive decrease in specific surface area until microporosity disappears completely at 125°C. Between 125 and 500°C, the specific surface area remains stable, because only the external surface is measured by N_2 adsorption.

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