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Study of the dehydroxylation-rehydroxylation of pyrophyllite

J.L. PEREZ-RODRIGUEZ¹, A. DURAN^{1,2}, P.E. SÁNCHEZ JIMÉNEZ^{1,3}, M.L. FRANQUELO¹,

A. PEREJÓN¹, J. PASCUAL⁴, L.A. PÉREZ-MAQUEDA^{1*}

¹*Instituto de Ciencia de Materiales de Sevilla (C.S.I.C. – Univ.Sevilla). c/ Americo Vesputio, 49.
41092 Seville, Spain.*

²*Centre de Recherche et de restauration des musées de France –CNRS UMR 171, Palais du Louvre,
Porte des Lions, 14 Quai François Mitterrand, 75001 Paris, France*

³*Department of Mechanical Engineering. Engineering Center - ECME 150
University of Colorado at Boulder, Boulder CO 80309-0427, USA*

⁴*Depart. de Ingeniería Civil, Materiales y Fabricación, ETSII, U. de Málaga. 29013 Málaga, Spain.*

Abstract.

It has been observed that the partially or totally dehydroxylated pyrophyllite suffers a partial reversible rehydroxylation when cooled down at room temperature. This rehydroxylation was substantiated by thermogravimetric measurements by a mass increase, while IR spectroscopic studies have shown that during the rehydroxylation the intensity of some OH bands increase as two new bands appear. This rehydroxylation process is also very much influenced by the particle size of the pyrophyllite.

Keywords- Pyrophyllite, Particle Size, Dehydroxylation, Rehydroxylation, Thermogravimetry, FTIR Spectroscopy, X-ray diffraction,

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* Author to whom correspondence should be addressed. e-mail: maqueda@cica.es

1. INTRODUCTION

Pyrophyllite is a 2:1 aluminosilicate $[Al_2Si_4O_{10}(OH)_2]$ clay that in nature appears in beds with different proportions of pure pyrophyllite, maximum about 90%, accompanied by other minerals such as kaolinite, quartz, mica, etc. Pyrophyllite has a dioctahedral layer structure with an octahedrally coordinate Al ions sheets in-between two sheets of SiO_4 tetrahedra.¹⁻³ Pyrophyllite has many industrial applications, mostly due to its good technological properties produced by thermal treatment. Thus, it has been mainly used as a raw material in glass, ceramic and refractory industries, for applications such as insulating firebrick or foundry specialities and also in various white-ware bodies.^{4,5} New applications, such as its use in geopolymers, have been also recently reported.⁶ The technological application of pyrophyllite, demands their proper workability, which may be improved by a decrease in particle size.⁷⁻¹⁹ Due to its interest, the thermal dehydroxylation of pyrophyllite has received significant attention in literature.^{17,20-36} Wardle and Brindley³ have suggested that the dehydroxylated pyrophyllite consists of 5-coordinate, distorted, trigonal bipyramidal AlO_5 structural units in the aluminium oxide layer sandwiched between two distorted tetrahedral silica layers.²⁷ Al NMR-MAS studies have shown the 6-coordinated Al in pyrophyllite change their structural arrangement to 5-coordinate Al in dehydroxylated pyrophyllite.^{21,22,37} It has been reported that grinding of pyrophyllite favours the formation of pentacoordinated Al³². ²⁹Si MAS-NMR data have confirmed that the tetrahedral SiO_4 sheets remain unchanged, indicating that dehydroxylated pyrophyllite maintains the 2:1 layer structure.²² The formation of 5-coordinate aluminium sites in dehydroxylated pyrophyllite is consistent with a homogeneous reaction of the adjacent OH groups to liberate water and the formation of a bridging oxide midway between adjacent aluminium atoms.²⁷

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4 The dehydroxylated pyrophyllite may suffer a rehydroxylation process. Heller et al.³⁸ have
5 shown that infrared spectrum of rehydroxylated pyrophyllite provides evidence for the
6 formation of layers that may be composed of regions with pyrophyllite-like structure
7 associated with dehydroxylated materials. Rehydroxylation of pyrophyllite appears to be a
8 function of particle size, since coarsely crystalline dehydroxylated samples showed little or
9 not rehydroxylation after steam treatment whereas dehydroxylated 100-mesh material ground
10 under a vibratory mill was rehydroxylated to the extent of 48 per cent. The grinding of the
11 pyrophyllite produces structural alteration^{30,39} that may affect the rehydroxylation. The
12 rehydroxylation of pyrophyllite involved heating samples in water vapour or left at room
13 temperature for several months.^{20,38,40-42} The structural transformation of other clay minerals
14 such as illite, montmorillonite, glauconite and celadonite during dehydroxylation-
15 rehydroxylation reaction has been also studied by Muller et al.²⁹

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33 Nevertheless, Wang et al.³³ have recently found, using infrared spectroscopy, that the
34 dehydroxylation of pyrophyllite in the temperature range 550-900 °C is characterized by a
35 decrease in the intensity of the OH signals and phonon bands of pyrophyllite as well as the
36 appearance of extra signals at 3690 and 3702 cm⁻¹, that they attribute to an intermediate
37 partially dehydroxylated phase. Thus, these authors suggested that the dehydroxylation of
38 pyrophyllite is a two-stage process with a defined intermediate stage. Based on these
39 observations, it has been theoretically proposed the presence of different possible
40 intermediates.^{43,44} Nevertheless, it has not been considered that pyrophyllite samples after
41 annealing were cooled down, ground and dried at 110°C during 12 h. Thus, the contact with
42 laboratory atmosphere may produce rehydration of the samples and be responsible of the
43 intermediates phases that cannot be necessarily attributed to the heating process.
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4 The thermally-induced dehydroxylation and later rehydroxylation of pyrophyllite
5 remains only partially understood. The aim of this study is to investigate the thermally-
6 induced dehydroxylation and rehydroxylation of pyrophyllite paying special attention to the
7 effect of particle size.
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13 14 15 16 **II. Experimental Procedure**

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20 The studied sample was a pyrophyllite from Zalamea la Real, Spain, that is a mixture of
21 pyrophyllite, kaolinite, mixed layer illite-smectite and illite, and a small content of rutile and
22 quartz. This pyrophyllite was purified following a procedure previously described in
23 literature.^{45,46} After this treatment the sample was constituted by pure pyrophyllite
24 accompanied by a small proportion of rutile. This sample was selected because it has already
25 different particles sizes, while the mechanical treatment required by other natural pyrophyllite
26 samples to obtain different particle sizes may produce structural alterations^{7,11,12,14,15,18,19,47}
27 and, therefore, are not suitable for the present study. The different fractions were separated
28 using an aqueous gravity sedimentation procedure for separation of the coarser fractions and a
29 centrifugation procedure for collecting the smallest ones.⁴⁸ Thus, several fractions with
30 different particle sizes, i.e. 20-40 μm , 10-20 μm , 5-10 μm , 2-5 μm and $<1 \mu\text{m}$ were obtained.
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47 *(2) Thermal heating*

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49 Thermal treatments of pyrophyllite samples with different particle sizes were carried out
50 between 500 and 1000°C for periods of 1 hour and 5 days in a tubular furnace (carbolite
51 furnaces type RHF 1600, Hope Valley, UK).
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(3) Thermogravimetric study

Thermogravimetric analyses (TG) were carried out with an automatic thermal analyser system (model TG/DTA 6300, SII Nanotechnology, Japan). Experiments were performed in static air at a heating rate of 10 °C min⁻¹. Samples were maintained in an oven at 110 °C overnight before the thermal analysis experiments to remove any hydration water.

Dehydroxylation-rehydroxylation cycles in a water saturated air flow were performed in a simultaneous thermal analysis instrument (model Q600, TA instruments, New Castle, DE).

(4) Kinetic analysis

The activation energy of the dehydroxylation was obtained by means of the isoconversional method.^{49,50} The method is based in the following equation:

$$\ln\left(\frac{d\alpha}{dt}\right)_\alpha = C_\alpha - \frac{E_\alpha}{RT_\alpha} \quad (1).$$

being α the reacted fraction (a parameter that changes with the reaction from 0 before the process has started to 1 when it is totally finished), $(d\alpha/dt)_\alpha$ the reaction rate at a particular value of α , R the gas constant and C_α , E_α and T_α the values of a constant, activation energy and temperature for each value of α . Thus, the values of the activation energy can be determined from a set of thermogravimetric curves obtained under different linear heating rates. The procedure implies of plotting the values of $\ln(d\alpha/dt)_\alpha$ as a function of $1/T_\alpha$, in such a way that the activation energy is obtained directly from the slope of the resulting line. This method allows determining the activation energy of the process as a function of the reacted fraction from a series of experimental curves obtained under different linear heating rate conditions, without any assumption or previous knowledge about the kinetic model obeyed by the solid-state reaction.

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(5) X-ray diffraction analysis

Diffraction patterns were obtained using a diffractometer (model, X'PERT PRO, PANalytical, Almelo, The Netherlands) at 40 kV and 40 mA with $\text{CuK}\alpha_1$ radiation, with a HTK 1200 high temperature chamber and Philips X'Celerator detector.

(6) IR spectroscopy study

Two different IR spectroscopy measurements were performed in the samples. Thus, temperature-programmed diffuse reflectance infrared Fourier transform spectroscopy (model Nexus FT-IR, Thermo-Nicolet, Newington, NH) was used for collecting spectra under in-situ conditions of heating. Only a few of milligrams of these samples were used for these measurements, and heating was performed in static air. No KBr was used for the preparation of the sample. Additionally, for room temperature IR measurements, samples of 3 mg of fine samples powders after heating at different temperatures were thoroughly mixed with 900 mg of dry KBr powder; 200 mg of the sample/matrix mixtures were pressed into disc shaped pellets at room temperature under vacuum. After this, pellets were heated for 24 hours at 110°C to remove adsorbed water. Measurements were performed between 400 and 4000 cm^{-1} with a spectrometer with a DTGS detector coupled with a KBr beam splitter (model Nicolet 510, Thermo-Nicolet, Newington, NH). A total of 200 scans with an instrumental resolution of 4 cm^{-1} were collected for each spectrum. Commercial software OMNIC and PEAK FIT were used for data analysis. Integrated absorbance was obtained by curve-fitting, using the secondary derivative method with Gaussian functions and linear baselines.

III. Results and Discussion

Pyrophyllite minerals are classically identified as trans-vacant with a dehydroxylation maximum between 550 and 680°C.^{3,17,29,30,51,52} However, some authors identified up to three kinds of pyrophyllite populations.^{34,53,54} The first one identified as a trans-vacant structure showed a DTG dehydroxylation peak with a maximum temperature near 650°C. The second one identified as a cis-vacant structure showed a DTG dehydroxylation peak at about 880°C. The third one attributed to cis- and trans- mixture or interstratification of pyrophyllite phases showed two dehydroxylation effects.

Figure 1 displays the thermogravimetric curves in the temperature range 250-950 °C as obtained for the purified pyrophyllite sample at different heating rates. The curves show only one step with a resulting mass loss percentage (4.95%) corresponding to the release of structural OH (dehydroxylation) of an ideal pyrophyllite with a DTG dehydroxylation peak with a maximum temperature about 650°C. These results are in agreement with only a vacant type in the structure of the sample selected for this work. It is quite clear from Fig. 1 that the thermal dehydroxylation of pyrophyllite is very much affected by the heating rate. Thus, thermal dehydroxylation temperature increases upon increasing heating rate. This behaviour is characteristic of a kinetically driven process. Kinetic analysis of curves in Fig. 1 has been conducted by means of the differential isoconversional method. The resulting values for the activation energy are displayed in Fig. 2 versus the reacted fraction. Results in Fig. 2 shows that the activation energy values are independent of the reacted fraction and, therefore, an unique activation energy of $224 \pm 16 \text{ kJ mol}^{-1}$ describes the entire dehydroxylation process.

In order to substantiate the effect that particle size may have in the thermal dehydroxylation of pyrophyllite, thermal analysis has been performed on samples of different particle size

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4 separated from the same pyrophyllite sample. Fig. 3 shows the thermogravimetric traces
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6 obtained for different fractions ($< 1 \mu\text{m}$; $5\text{-}10 \mu\text{m}$; $10\text{-}20 \mu\text{m}$; $20\text{-}40 \mu\text{m}$). It is quite clear from
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8 this figure that the particle size has an important influence on the temperature of the
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10 dehydroxylation. Thus, smaller particles dehydroxylate at considerable lower temperatures
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12 than larger ones.
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16 High-temperature X-ray diffraction is also a suitable method for studying the thermal
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18 dehydroxylation of pyrophyllite. Thus, Fig. 4a displays the diffraction pattern at room
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20 temperature for the $<1 \mu\text{m}$ pyrophyllite sample in the range $27.5^\circ\text{-}29.75^\circ$ of 2θ . In this range,
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22 only a single diffraction peak is recorded at 28.5° ($d=3.13\text{\AA}$) that corresponds to the 003 peak
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24 of the pyrophyllite. As temperature increases, the intensity of this peak decreases, while a new
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26 peak corresponding to dehydroxylated pyrophyllite is recorded at 29° ($d=3.08\text{\AA}$), eventually, at
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28 640°C , the peak corresponding to pyrophyllite disappears and only that of dehydroxylated
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30 pyrophyllite is detected (Fig. 4b). In any case no other diffraction peaks were observed during
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32 the dehydroxylation that could be attributed to intermediate phases. The reacted fraction of
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34 the dehydroxylation can be determined from the ratio of intensities of the two diffraction
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36 peaks. Thus, Fig. 5 includes the plots of the reaction fraction as a function of temperature for
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38 the $<1 \mu\text{m}$ and $20\text{-}40 \mu\text{m}$ fractions under linear heating rate conditions. As it can be seen from
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40 this figure, the behaviour is quite similar to that reported by thermogravimetric method. Thus,
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42 smaller particles dehydroxylate at much lower temperature than larger ones. Fig. 6 displays
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44 the evolution of the reaction fraction with time for the same two fractions of Fig. 5 but under
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46 isothermal conditions ($T= 520^\circ\text{C}$). In this latter case, the smaller particles are totally
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48 dehydroxylated in less than 1 hour while the larger ones, even after 40 h, are not totally
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50 dehydroxylated.
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Figure 7 displays the temperature-programmed diffuse reflectance infrared spectroscopy measurements for the $<1 \mu\text{m}$ fraction at different temperatures in the spectral range of wavenumbers from 3725 to 3600 cm^{-1} . For the spectrum recorded at room temperature (Fig 7a) only a band at 3675 cm^{-1} is observed in this spectral range, assigned to Al_2OH stretching mode due to the interaction between OH and Al.⁵⁵ The presence of a single band in this spectral range could be attributed to a trans-vacant structure unlike the partially cis- and trans-vacant structure that shows two OH-stretching bands (3674 and 3668 cm^{-1}).²⁶ At 550°C (Fig. 7b), the band at 3675 is broadened and shifted at 3660 cm^{-1} . As the sample is cooled down at room temperature and maintained at room conditions during twelve hours, the spectra (Fig. 7c) shows not only the typical band of pyrophyllite at 3675 cm^{-1} , but two extra bands at 3690 cm^{-1} and at 3702 cm^{-1} that were not observed in the original pyrophyllite neither at 550°C . Therefore, these two new bands that appear after cooling and maintaining the sample a room temperature for several hours, and were not present in the IR spectra of the sample registered a 550°C , could be attributed to a rehydroxylation process and not to a dehydroxylation process as was assigned by Wang et al.³³

In order to study the effect of particle size and dehydroxylation temperature in the rehydroxylation of pyrophyllite, a set of samples with different particle sizes ($<1 \mu\text{m}$, $2\text{-}5 \mu\text{m}$, $5\text{-}10 \mu\text{m}$, $10\text{-}20 \mu\text{m}$ and $20\text{-}40 \mu\text{m}$) were at first heated for one hour at different temperatures, then cooled at room temperature and maintained at room conditions during twelve hours, and finally the FTIR spectra were recorded at room temperature. The intensity of the OH absorption bands at 3675 , 3690 and at 3702 cm^{-1} for the different particle sizes and dehydroxylation temperatures are shown in Figs. 8, 9 and 10, respectively. These figures show a decrease in the intensity of the three absorption bands in the range of temperature below 600°C for the $<1 \mu\text{m}$ fraction and below 700°C for the other fractions. This decrease in

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4 band intensity is followed of an increase in the range up to 750 °C and again of a decrease in
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6 the range 750-900 °C. At 900 °C rehydroxylation is hindered.
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10 In order to follow the dehydroxylation-rehydroxylation process under in situ
11 conditions of heating, thermogravimetric experiments were performed in water saturated air
12 flow. Thus, temperature was increased from room temperature to 750°C at 10 °C min⁻¹, then
13 cooled down at room temperature at 10 °C min⁻¹, and finally maintained at this temperature
14 for five hours while the sample was maintained under a flow of water saturated air. The entire
15 cycle was repeated several times. Fig. 11a shows the resulting curves for the <1 μm sample
16 and Fig. 11b shows a detail of one of the cycles. In the first heating cycle, the dehydroxylation
17 of the material takes place in the temperature range from about 450 °C to 645 °C with a 5.95%
18 mass loss, while in the range from 645 °C to 750 °C, no further mass loss is observed. As
19 temperature decreases from 750°C to room temperature, a mass increase is recorded; this
20 mass increase continues at room temperature but at a smaller rate. The total amount of mass
21 gain of the dehydroxylated sample is about 1.6 %. When the sample is again heated, water is
22 released in two steps clearly discriminated in the DTG signal, one from room temperature to
23 370 °C and another from 370 °C to 750 °C, that correspond to 1.01 % and 0.59 % mass loss,
24 respectively. The low temperature mass loss could be attributed to the release of hydration
25 water, while the one at higher temperature could be assigned to the dehydroxylation of the
26 rehydroxylated pyrophyllite. Thus, the dehydroxylated pyrophyllite suffers hydration and a
27 partial rehydroxylation. This partial rehydroxylation is reversible, as observed in the different
28 cycles of Fig. 11a. A similar behaviour was observed in terms of dehydroxilation-
29 rehydroxylation for other pyrophyllite fractions, although the amount of rehydration and
30 rehydroxylation were affected by the particle size. Thus, for the larger fraction, i.e. 20-40 μm,
31 the total amount of mass gain of the dehydroxylated sample is about 0.4%, in such a way that
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4 the rehydration correspond to 0.32% and the rehydroxylation to 0.08%. The maximum
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6 temperature used for the dehydroxylation cycles also plays an important role in the amount of
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8 water gained during the cooling (Fig. 12). Thus, the maximum mass gain is obtained for 750
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10 °C, similarly to the IR study that showed the highest intensity of the OH bands for the sample
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12 previously heated at such temperature (Figs. 8-10).
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18 **IV. Conclusions**

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23 It has been observed that the dehydroxylation of pyrophyllite is a kinetically driven process
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25 with an activation energy of $224 \pm 16 \text{ kJ mol}^{-1}$. The process is very much affected by the
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27 particle size of the original pyrophyllite. Thus, smaller particles dehydroxylate at much lower
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29 temperature than larger particles. It has been also observed that the totally or partially
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31 dehydroxylated pyrophyllite suffers hydration and partial rehydroxylation when cooled down
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33 at room temperature. This dehydroxylation-rehydroxylation process is reversible as observed
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35 when the sample is heated and cooled in cycles. The particle size also plays an important role
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37 in the rehydroxylation process, in such a way that the rehydroxylation is more important in
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39 smaller particles than in the larger ones.
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For Peer Review

FIGURE CAPTIONS

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7 Fig.1.- TG (a) and DTG (b) traces for the purified pyrophyllite sample at different heating
8 rates.
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11 Fig.2.- Values of the activation energy of the process as a function of the reacted fraction (α)
12 for the thermal dehydroxylation of the purified pyrophyllite sample.
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15 Fig.3.- TG (a) and DTG (b) traces for different particle size fractions of pyrophyllite.
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18 Fig.4.- 003 diffraction of $<1\mu\text{m}$ fraction in the original pyrophyllite (a) and after heating at
19 600 °C during 30 minutes (b).
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23 Fig.5.- Reaction fraction (α) as a function of temperature for the $<1\mu\text{m}$ (a) and 20-40 μm (b)
24 fractions under linear heating rate conditions.
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27 Fig.6.- Reaction fraction as a function of time for the $<1\mu\text{m}$ (a) and 20-40 μm (b) fractions
28 under isothermal conditions ($T= 520^\circ\text{C}$)
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32 Fig.7.- Diffuse reflectance infrared spectra for the $<1\mu\text{m}$ fraction recorded at different
33 temperatures: a) room temperature, b) during the dehydroxylation at 550 °C, and c)
34 after heating and cooling down at room temperature and maintained at room
35 conditions during twelve hours
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42 Fig.8.- Intensity of OH absorption band at 3675 cm^{-1} for samples of different particle size
43 previously heated for one hour at different temperatures, then cooled at room
44 temperature and maintained at room conditions during twelve hours. (■) $< 1\mu\text{m}$; (X)
45 2-5 μm ; (▲) 5-10 μm ; (●) 10-20 μm ; (†) 20-40 μm .
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52 Fig.9.- Intensity of OH absorption band at 3690 cm^{-1} for samples of different particle size
53 previously heated for one hour at different temperatures, then cooled at room
54 temperature and maintained at room conditions during twelve hours. (■) $< 1\mu\text{m}$; (X)
55 2-5 μm ; (▲) 5-10 μm ; (●) 10-20 μm ; (†) 20-40 μm .
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4 Fig.10.- Intensity of OH absorption band at 3702 cm^{-1} for samples of different particle size
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6 previously heated for one hour at different temperatures, then cooled at room
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8 temperature and maintained at room conditions during twelve hours. (■) $< 1\text{ }\mu\text{m}$; (X)
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11 2-5 μm ; (▲) 5-10 μm ; (●) 10-20 μm ; (⊕) 20-40 μm .
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14 Fig.11.- Cyclic thermogravimetric experiment in water saturated air flow for the $<1\text{ }\mu\text{m}$
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16 fraction. Figure (a) shows the entire experiment, while figure (b) shows a detail of one
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18 of the cycles. T: temperature, TG: %mass, DTG: differential mass loss.
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21 Fig.12.- Mass loss of fraction $<1\mu\text{m}$ previously heated at different temperatures during 1 hour
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23 and cooled down at room temperature for 12 h.
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