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Dedicated to Professor Dr. H. J. Seifert on the occasion of his 60^{th} birthday

THE INFLUENCE OF THE DRY GRINDING ON THE THERMAL BEHAVIOUR OF PYROPHYLLITE

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The differences of the thermal curves (DTA-TG) of pyrophyllite measured before and after grinding have been studied to obtain quantitative information about the alteration of the structure of this layer silicate.

The mechanical treatment by dry grinding of pyrophyllite produces a decrease in the particle size of the original material. This strongly influences the thermal behaviour of weight losses on the TG curves decrease, and the endothermic DTA effects shift to lower temperatures, until the mechanochemical limit in particle size reduction is reached.

Further grinding produces a disruption of the 2:1 aluminosilicate structure giving an exothermic DTA effect, and also reagglomeration processes of the amorphous and activated material accompanied by a decrease in specific surface area.

Mechanical treatment by grinding (wet or dry) of materials are of great interest in the preparation and processing of ceramic raw materials, because fine mineral particles are so obtained. However, this treatment produces several important changes in the structure, textural properties and chemical reactivity of the powdered material [1, 3]. Thus the reactivity of solids is enhanced and high temperature solid state reactions can be achieved at lower temperatures.

The processes involved in the grinding of clay minerals have been studied by many authors, especially for kaolinite [4, 6] montmorillonite and bentonite [7, 8] and illite [9]. However, little is known about the alteration by grinding of the aluminium silicate pyrophyllite [$Al_2Si_4O_{10}(OH)_2$] and its effect on the thermal behaviour. In previous papers [10, 11} we have studied

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the effects of mechanical dry grinding and thermal treatment on pyrophyllite. It has been shown that low-temperature mullite precursors may be obtained from this silicate after mechanical treatment. These results are important because pyrophyllite is applied in many industries, mainly in refractories, ceramics and foundries [12].

In the present work, the differences of the thermal curves (DTA-TG) of pyrophyllite measured before and after grinding were investigated to obtain quantitative information about the alteration of the structure of this layer silicate.

Experimental

Material

A sample of pyrophyllite from Hillsboro* (North Carolina, USA) was used as starting material. The natural material as received was crushed, lightly ground and sieved to 50 μm before further study. This sample was composed of 90 wt% pyrophyllite, 5 wt% kaolinite and 5 wt% mica [13].

Grinding

Grinding was carried out in a planetary ball mill (RETSCH S-1 model), at a rate of 250 r. p. m. from 5 to 325 minutes, using a grinding vessel made of hard porcelain containing ten balls of 20 mm diameter made of the same material.

X-ray powder diffraction

X-ray powder diffractograms were obtained using a Siemens Kristalloflex D-500 diffractometer with Ni-filtered CuKα radiation and a goniometer speed of 1 /10 2Θ/min, at 26 mA and 36 KV.

The samples were prepared to avoid preferential orientation, as described previously [4, 13].

The average crystallite size (D) was computed from the corrected integral breadths (β) obtained from the X-ray diffractograms, according to the Jones' method [14] by the Eq.

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$$D = \frac{K\lambda}{\beta \cos\theta}$$

where K is the Scherrer constant, Θ is the angle of the (*hkl*) reflection.

DTA-TG

Thermogravimetric (TG) and differential thermal analysis (DTA) curves were obtained simultaneously in static air with an automatic thermal analyzer Rigaku PTC-10 A model. A data processor DPS-1 was fitted to the apparatus.

Pyrophyllite sample of known weight (about 33 mg) was packed gently in a platinum holder and thermally treated from 20 to 1050° (Pt/Pt-Rh 13% thermocouple).

The heating rate was 12 deg/min and calcined Al_2O_3 was used as a reference material. The DTA sensitivity was $\pm 25\,\mu V$ and 5 mg in TG, the chart speed 2.5 mm/min.

The temperatures of the endothermic and exothermic peaks were estimated from the position of the top and bottom of the peak on the chart. The areas under the experimental DTA curves were determined by tracing them on to drawing paper of uniform weight and cutting out the inscribed area. The weights of the cut-outs were subsequently determined on an analytical balance. Runs were made in triplicate.

SEM

Selected samples dispersed in acetone were dried, coated with Au and examined under a scanning electron microscope ISI, model SS-40. From the micrographs, the average particle size was estimated.

Specific surface areas

The specific surface areas (S BET) were determined with an automatic Micromeritics system model 2200 A using pure nitrogen gas as adsorbate, at liquid nitrogen temperature (77.35 K). Samples were run in triplicate.

Results and discussion

X-ray diffraction

X-ray diffraction patterns of (001), (005) and (131) reflections of pyrophyllite, before and after grinding for different times, are shown in Fig. 1. It is clear that grinding increases the structural disorder of this silicate producing total degradation of the crystal structure after 30 minutes and yielding a more amorphous material.

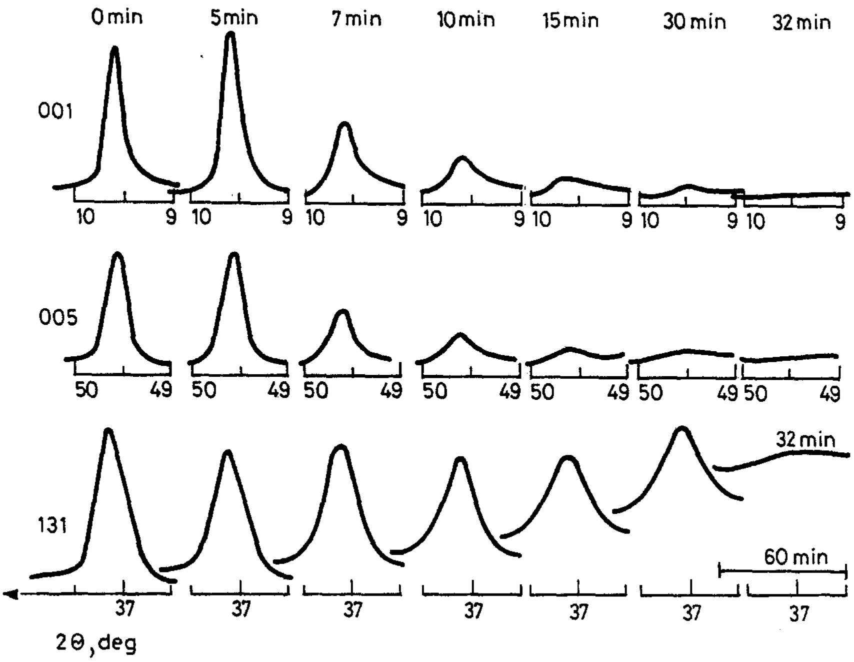

Fig. 1 X-ray diffraction profiles of the (001), (005) and (131) reflections of pyrophyllite, original and ground for various times

As expected, after 7 minutes the broadening of these diffraction bands increases with grinding time and their intensities decrease. Lattice distortion (microstrains) and crystallite size both influence the X-ray line broadening, but the general (*hkl*) reflections (131) change to a lesser extent than the basal reflections (001) because the alteration by grinding is greater along the "*c*" axis of the crystal structure. Assuming that the main contribution to line breadth is due to particle size (crystalline domain), the average crystallite size can be calculated from Scherrer's equation.

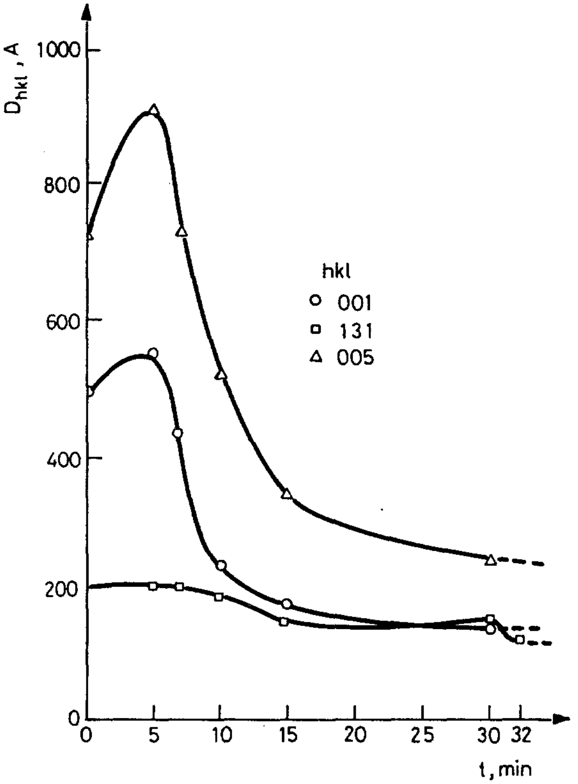

Fig. 2 Average crystallite size (Scherrer) according to (001), (005) and (131) reflections of pyrophyllite as a function of grinding time

Figure 2 shows the plot of the average crystallite size (crystalline domain) of the original and ground pyrophyllite as a function of grinding time. The greatest change was observed in the (005) reflection of pyrophyllite. These changes indicate that a delamination effect started during the first minutes of grinding, as in other layer silicates, e. g. , kaolinite [5, 6]. It is clear from Fig. 2 that a limit in mechanochemical reduction of the original particles was reached after about 30 minutes' grinding.

Thermogravimetric analysis and specific surface areas

TG diagrams of ground samples are shown in Fig. 3. Selected data or specific surface areas and weight losses in original and ground samples calculated from these TG curves are summarized in Table 1.

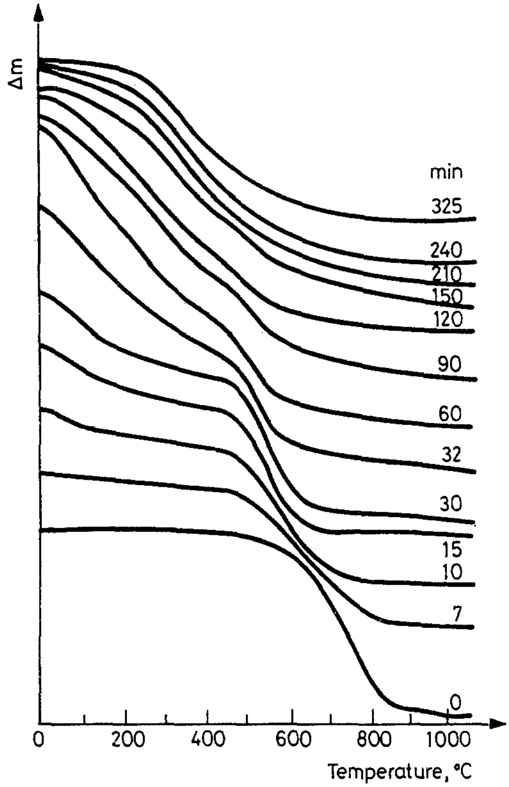

Fig. 3 TG curves of original and ground pyrophyllite up to 325 minutes grinding (β = 12°C × min^{-1})

The weight loss of unground samples begins at 500° (Fig. 3) at a low rate. The rate increases gradually with temperature and the reaction terminates at 1500°. The total weight loss agrees with that calculated for an ideal pyrophyllite (5.0%). This is assumed to be due entirely to structural water loss by dehydroxylation. As expected from the crystal structure, the OH groups in pyrophyllite need higher temperature than kaolinite for dehydroxylation [15], due to different bonding energies in the crystal structure. In pyrophyllite there is no isomorphic substitution in the tetrahedral sheets of silicate layer (2:1).

As can be seen in Table 1 and Fig. 3 after 15 min the grinding treatment produces as increased weight loss on heating at 200 °, i. e. an increase in "free moisture" of the samples, suggesting some extremely weakly bound hydroxyl groups of an amorphous phase are being lost within this temperature range (see Table 1). Also, the high increase in specific surface area from a minimum value of 0.5 m^2g^{-1} to ≈ 60 m^2g^{-1} can cause some hydroxylation processes by adsorption of atmospheric water molecules. Both adsorbed water molecules and extremely weakly bound OH groups escape at lower temperatures than in unground pyrophyllite (Fig. 3). These results are similar to those reported by several authors for ground clay minerals (Miller and Oulton [4], Hlavay *et al.* [5] and Juhasz [6]).

Table 1 Specific surface areas and TG (β = 12°C/min) data of unground and ground pyrophyllite samples

Grinding time (min)	Surface area ($m^2 \times g^{-1}$)	Weight losses from TG curves (%)				Total weight loss (%)
		20–200	200–400	400–700	700–1000°C	
0	0.52	0	0	1.54	3.48	5.02
5	14.01	0.20	0.20	2.14	2.49	5.03
7	21.02	0.25	0.25	3.08	1.45	5.03
15	56.57	1.28	0.67	3.96	0.18	6.09
30	58.12	1.40	1.10	4.28	0.37	7.15
32	46.24	2.63	1.84	3.44	0.55	8.46
60	27.75	3.32	2.55	2.97	0.41	9.25
120	12.05	1.81	2.72	2.17	0.55	7.25
240	–	0.59	2.57	2.61	0.36	6.13
325	7.04	0.18	2.30	2.43	0.48	5.39

As shown in Fig. 2 the largest particle size reduction by grinding is reached at 30 min. The DTA (Fig. 5) curve of the sample ground for 30 min shows the endothermic effect at lower temperature than after shorter grinding time. This decrease in particle size causes the elimination of hydroxyl groups at lower temperatures in the ground than in the unground material. In addition, in the crystal structure stressed by mechanical treatment, the bond energy of these OH groups tend to decrease, so that they are lost at lower temperatures.

At longer grinding time, as a consequence of the enhanced surface energy provided by the grinding treatment, the particles become agglomerated and the specific surface area begins to decrease. This falls to a value of 7 m^2g^{-1}, which is, in any case, higher than that of the original sample (Table 1). This decrease in specific surface area is well-known in grinding operations [1, 2].

At longer grinding times, these agglomeration processes probably impede the water elimination caused by thermal treatment and water diffusion is hindered. This is indicated by the TG traces showing a decrease in weight loss when the grinding time increases (Fig. 3). The simultaneous loss in the remaining regions of structural OH also decreases and occurs at lower temperatures. Finally, after more than 60 minutes' grinding, the slopes change gradually to positive values, as a result of the agglomeration processes and reduced diffusion of water molecules by heating. All these effects are probably due to the mechanochemical activation of the ground material.

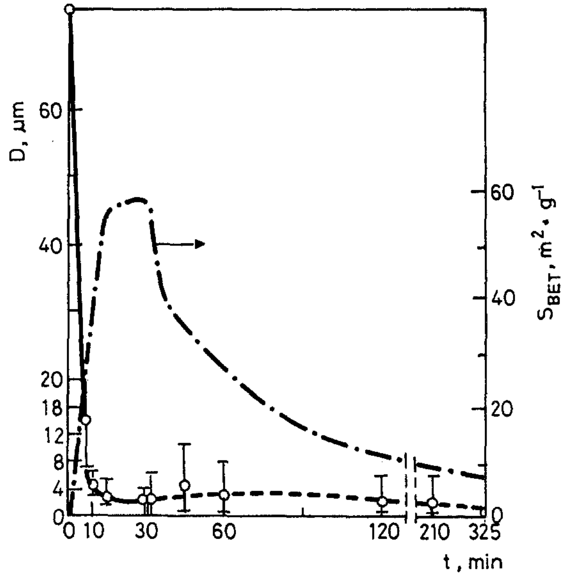

Fig. 4 Average particle size, estimated by SEM, and surface area (BET) of original and ground pyrophyllite

In a previous electron microscopic study [10], it was shown that the shape and size of pyrophyllite plates were more regular with increasing grinding time, i. e. when they reached lower particle size. In a more detailed study, we have been able to estimate the average particle size from microphotographs. Figure 4 shows a plot of that estimation as function of the grinding time. It is clear that this evolution is opposite to the increase and evolution of surface area, as also shown by Fig. 4. After a 30 minutes' grinding, the limit in mechanochemical reduction of pyrophyllite is reached because the activated particles start a reaggregation process that leads to a decrease in the surface area of the material.

Differential Thermal Analysis

The DTA curve of the original pyrophyllite sample (Fig. 5) shows a single broad endothermic peak in the 600–800° region due to OH elimination, with a maximum peak temperature at 760°. At short grinding times, this broad endothermic effect is shifted to lower temperatures and becomes sharper (Fig. 5). At 30 minutes' grinding the DTA diagram is similar to that of kaolinite. This is related to the decrease in bond energy of OH groups of pyrophyllite, due to mechanical treatment. The high-temperature decomposition of large particles occurs at lower temperatures as the bonds are broken or altered by grinding. Besides, the decrease in the starting temperatures for dehydroxylation of ground pyrophyllite may be caused simply by reduction in particle size producing a pronounced increase in surface area, helping OH groups to leave the strained crystalline structure, and increasing the weight loss at that temperature.

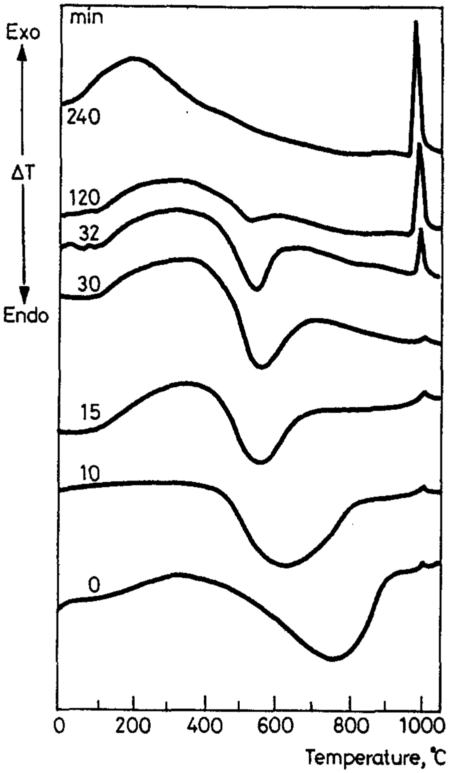

Fig. 5 Selected DTA of time diagrams of original and ground pyrophyllite.

The formation of one or two endothermic peaks at low temperatures (below 300°) could mean that some extremely weakly bound hydroxyl groups or adsorbed water molecules of an amorphous phase are being lost at lower temperatures. This is in agreement with TG and specific surface area measurements described above (Table 1).

As shown by the DTA diagrams (Fig. 5), grinding for more than thirty minutes does not cause any further change in the temperature of the principal endothermic peak, confirmed by the plot shown in Fig. 6. This is in disagreement with reported results for ground kaolinite [4]. However, the area of this peak decreases and disappears after long grinding times, as observed also for kaolinite [4, 6].

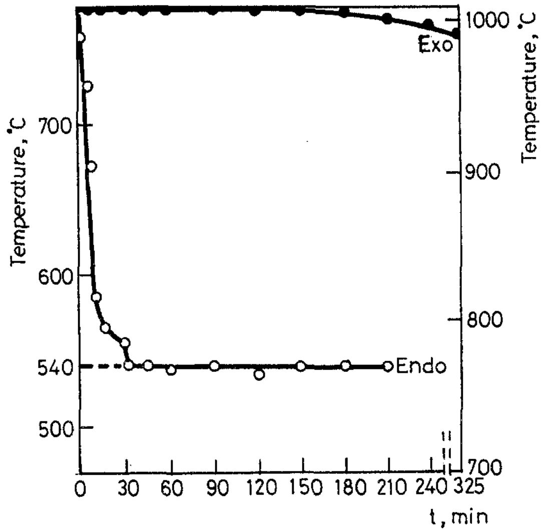

Fig. 6 Plot of endothermic and exothermic temperatures of DTA effects against grinding time for original and ground pyrophyllite

The unground pyrophyllite (Fig. 5) shows a small exothermic effect at ≈1000°, probably due to a low proportion of kaolinite (≈5 wt%) present as an impurity, as pure pyrophyllite does not show it [15]. This exothermic effect increases markedly after mechanical treatment by grinding, especially from 30 minutes to longer grinding times, when structural breakdown is very important (Fig. 1).

The areas of the endothermic and exothermic peaks calculated from DTA diagrams are shown in Fig. 7. The endothermic effect diminished when the grinding time increased, although it is difficult to calculate the "peak" areas. There is a discontinuity between the 30 and 32 minutes and then a progressive decrease. It disappears at 240 minutes of grinding (Fig. 5). On the contrary, the exothermic effect shows a small linear increase up to 30 minutes and increases drastically from 30 to 32 minutes and longer grinding times. Finally, it becomes practically constant after more than 240 minutes, forming a plateau-shaped curve. We are conscious that precise measurement of this area is difficult as some diffraction shows in Fig. 1, but the results obtained with pyrophyllites from other origins (Australia and Huelva (Spain)) have given similar results. The relationship of the exothermic peak and the endothermic effect is currently under research in our laboratory. Henmi and Yoshinaga [16] suggest that a high temperature exothermic DTA peak can be considered as an indication of the presence of Si-O-Al linkages in non-crystalline aluminosilicate materials, such as in ground pyrophyllite. For that reason the increase in intensity of the exothermic effect is related to disrupted aluminosilicate structure. In fact, it was demonstrated in a previous paper that formation of high-temperature phases is associated with this exothermic effect in ground pyrophyllite [11].

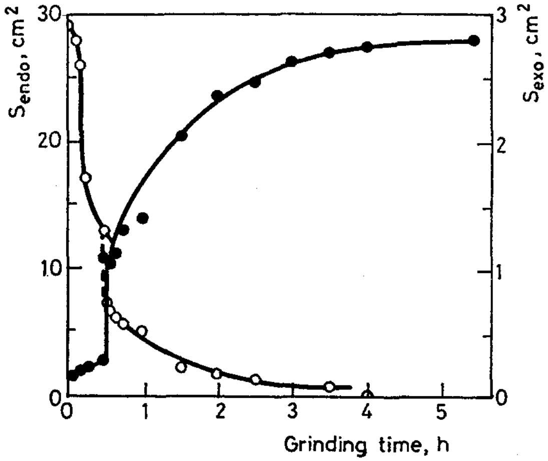

Fig. 7 Plot of endothermic and exothermic DTA peak areas of original and ground pyrophyllite.

From a structural point of view, pyrophyllite contains aluminium octahedra perfectly sandwiched between silica tetrahedra, with no cationic isomorphous substitution. Changes in DTA curves during the first minutes of grinding are attributed here to a decrease in particle size. Further grinding of pyrophyllite would produce complete structural breakdown resulting in a matrix consisting mainly of the residual tetrahedral sheets and deformed tetrahedra and octahedra, as was also suggested by Cicel and

Kranz for ground montmorillonite [8], which is isostructural with pyrophyllite.

Thus, the temperature of the endothermic peak decreases up to 30 minutes due to particle size reduction, and becomes constant after longer grinding time (Fig. 6), when the mechanochemical limit in particle size reduction is reached and the crystal structure undergoes a more significant alteration.

On the other hand, the particle size does not change the temperature of the exothermic peak appreciably but the sharpness and height increase with the grinding time. Only when the endothermic peak is small and practically disappears is there a slight lowering in the temperature of the exothermic peak (Fig. 6).

Conclusion

The mechanical treatment by dry grinding of pyrophyllite produces a decrease in the particle size of the original material. This strongly influences the thermal behaviour of the resultant product, decreasing the temperatures of weight losses on the TG curves, and shifting the endothermic DTA effects to lower temperatures, until the mechanochemical limit in particle size reduction is reached.

Further grinding produces a disruption of the 2:1 alumino-silicate structure giving an exothermic DTA effect and also reagglomeration processes of the amorphous and activated material accompanied by a decrease in specific surface area.

This is of great importance when considering the effect of particle size on the thermal properties of natural pyrophyllites, but needs further study of the behaviour of samples of different crystallochemical nature.

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Zusammenfassung — Es wurden vergleichbare Änderungen an thermischen Kurven (DTA, TG) von Pyrophyllit vor und nach Zerkleinerung untersucht, um quantitative Angaben über die Änderung dieses Schichtensilikates zu erhalten.

Durch die mechanische, trockene Zerkleinerung von Pyrophyllit kam es gegenüber dem Ausgangsmaterial zu einer Abnahme der Partikelgröße. Durch diesen Umstand wird das thermische Verhalten des erhaltenen Produktes stark beeinflußt. Bis zum Erreichen der mechanochemischen Grenze der Minderung der Partikelgröße nehmen in den TG-Kurven die Temperaturen für die Massenverluste ab, und die endothermen DTA-Effekte werden zu niedrigeren Temperaturen verschoben.

Weiteres Zerkleinern führt zu einer Störung der 2:1-Aluminosilikatstruktur, was einen exothermen DTA-Effekt verursacht, sowie auch zu Reagglomeration des sehr amorphen und aktivierten Materiales, begleitet von einer Minderung des spezifischen Oberfläche.