



Thermal treatment of mechanochemically activated kaolinite

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Abstract

The mechanochemical activation of a high defect kaolinite has been studied using a combination of high-resolution thermogravimetry and DRIFT spectroscopy. The effect of grinding causes a decrease in the dehydroxylation temperature and an increase in the amount of adsorbed/coordinated water. The temperature of dehydration also increases with grinding time. It is proposed that this dehydroxylation occurs through a homogenous process involving proton transfer through point heating. The amount of adsorbed water decreases with the increase in temperature of the thermal treatment.

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1. Introduction

Studies of the dry grinding of minerals such as kaolinite have been undertaken for some considerable time [1–6]. Early studies were concerned with the effects of grinding soils of which kaolinite was a constituent. Such studies showed that the surface areas of the materials were increased and that this resulted in a higher ion exchange capacity in the soils. Differences in the grinding of kaolinite by wet and dry methods were found [7–10]. Differences were also found between the dry grinding of the different kaolin polytypes [8,10]. Studies have shown that the dry grinding of kaolinite termed mechanochemical activation results in the delamination of the kaolinite [11–13]. This delamination is observed as a decrease

in intensity of the $d(001)$ spacing as a function of grinding time [14–17]. Such delamination depends on the presence of quartz [17,18]. With sufficient grinding, the material becomes X-ray amorphous in the c -direction. In fact, it has been suggested that the (001) spacing is changed to the (020) spacing which is then most resistant to damage by dry grinding [19].

A number of techniques have been used to study the delamination of kaolinite through mechanochemical treatment [20]. These include X-ray diffraction, nitrogen adsorption and infrared spectroscopy. It has been proposed that two processes occur during the mechanochemical activation [21]. Firstly, the delamination of the kaolinite occurs and secondly the agglomeration of the synthesized particles [13]. The delaminated particles combine to form large spheroidal particles [21]. The delamination process occurs with point heating. This results in partial dehydroxylation. The OH units combine to form water,

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which adsorbs and coordinates the high surface-active sites of the delaminated kaolinite. Thermoanalytical studies have been undertaken but have often focussed on the effects of mechanochemical treatment on the high temperature phase reactions after dehydroxylation [15,22,23]. Few studies have focussed on the role of water in the delamination process and the effect of mechanochemical activation on the dehydroxylation of kaolinite. In this work we report the use of modern high-resolution thermogravimetry techniques for the study of the thermal treatment of mechanochemically activated kaolinite.

2. Experimental techniques

2.1. The kaolinite mineral

The kaolinite used in this experiment was a high-grade natural kaolinite from Hungary. The kaolinite used was selected for this experiment because of the low quartz content and high purity. The Szeg chemical composition as determined by X-ray fluorescence in wt.% is MgO, 0.71; CaO, 0.53; SiO₂, 46.89; Fe₂O₃, 3.1; K₂O, 0.35; Na₂O, 0.16; Al₂O₃, 33.51; TiO₂, 0.06; loss on ignition, 14.69. The major mineral constituent is high defect kaolinite (95 wt.%) with a Hinckley index of around 0.4. Some minor amounts of quartz (2 wt.%) and feldspar (3 wt.%) are also present.

2.2. Milling procedure

A Fritsch pulverisette 5/2-type laboratory planetary mill was used to grind the kaolin. Samples were ground for 0–4, 6 and 10 h. Each milling was carried out with a 10 g air-dried sample in an 80 cm³ capacity stainless steel (18% Cr + 8% Ni) pot using eight (31.6 g) stainless steel balls (10 mm diameter). The applied rotation speed was 374 rpm.

2.3. Thermal analysis

Thermoanalytical investigations have been carried out under dynamic heating conditions (10 °C/min) in a Netzsch (Germany) TG 209-type thermobalance in flowing argon atmosphere of 99.995% purity (Messer Griesheim, Hungary). The samples of approximately

10 mg were heated in a ceramic crucible up to 1000 °C.

2.4. DRIFT spectroscopy

Diffuse reflectance infrared Fourier transform spectroscopic (commonly known as DRIFT) analyses were undertaken using a Bio-Rad FTS 60A spectrometer. The 512 scans were obtained at a resolution of 2 cm⁻¹ with a mirror velocity of 0.3 cm/s. Spectra were co-added to improve the signal to noise ratio. Approximately, 3 wt.% ground kaolinite was dispersed in 100 mg oven dried spectroscopic grade KBr with a refractive index of 1.559 and a particle size of 5–20 μm. Reflected radiation was collected at ~50% efficiency. Background KBr spectra were obtained and spectra ratioed to the background. The diffuse reflectance accessory used was designed exclusively for Bio-Rad FTS spectrometers. It is of the so-called “praying monk” design, and is mounted on a kinematic baseplate. It includes two four-position sample slides and eight sample cups. The cup (3 mm deep, 6 mm in diameter) accommodates powdery samples mixed with KBr using an agate mortar and pestle in 1–3% concentration. The reflectance spectra expressed as Kubelka–Munk unit versus wavenumber curves are very similar to absorbance spectra and can be evaluated accordingly.

Spectral manipulation such as baseline adjustment, smoothing and normalization was performed using the Spectralcalc software package GRAMS[®] (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel ‘Peakfit’ software package, which enabled the type of fitting, function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentz–Gauss cross-product function with the minimum number of component bands used for the fitting process. The Gauss–Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

3. Results and discussion

The particular kaolinite used in this study differs from that previously published [24–26]. In previous

work low defect kaolinites from Zettlitz and Kiralyhgy were used. These kaolinites had a Hinckley index of 0.78 and 1.35, respectively, thus these kaolinites were highly ordered kaolinites with few stacking faults. In this study we have chosen a kaolinite with a high defect structure and a low Hinckley index of 0.15. Electron microscopy shows the kaolinite to be highly disordered with many particles with a curved morphology. The kaolinite has a *b*-axis disorder. The kaolinite resembles a broken-up halloysite in morphology. The reason for this work is to study the effects of structural degradation through mechanochemical treatment of a high defect kaolinite.

3.1. Thermal analysis

One method of determining the water content of kaolinite is to use thermal analysis methods. Fig. 1 shows the thermogravimetric (TG) and differential thermogravimetric analyses (DTG) of the ground kaolinite. A small weight loss is observed below 100 °C and is attributed to adsorbed water. The Szeg kaolinite shows halloysite like properties and such minerals contain interlayer water or water held between the disordered particles. This is the water lost around 100 °C. The TG curve for the pure kaolinite shows a single weight loss at around 490 °C. Curves

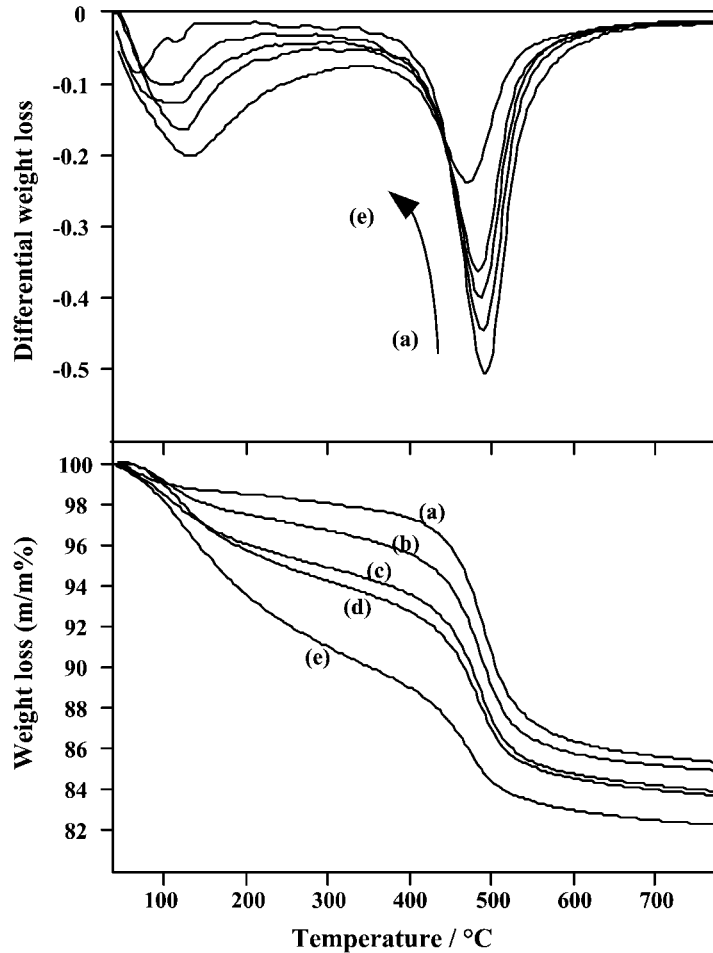


Fig. 1. TG and DTG curves for mechanochemically activated kaolinite after grinding for 0–3 and 6 h.

b–d show a two-step weight loss. With increased grinding time, the curves shift to lower temperatures. Further, it appears that the weight loss in the first step (>100 and <400 °C) increases as the weight loss in the second step decreases (>400 °C). Such observations are confirmed by the DTG curves. Two weight losses are observed as minima in the DTG curves. The first weight loss is attributed to the liberation of water formed as a result of mechanochemical dehydroxylation of the kaolinite, while in the second stage (above 450 °C) water is lost in the thermal dehydroxylation process. Both processes are observed as minima in the DTG curves (DTG curves in Fig. 1). Fig. 2a displays the change in the dehydroxylation temperature with grinding time and the associated weight loss. This dehydroxylation temperature decreases with grinding time. The area of this peak decreases concomitantly as the area of the first weight loss peak centred at approximately 150 °C increases.

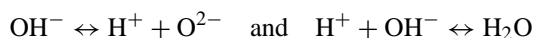
This weight loss profile ascribed to a water weight loss is rather complex, because of different types of water present in the mechanochemically-synthesized material. Fig. 2b shows the increase in the temperature for the loss of water during the dehydration process. The weight loss parallels the increased temperature of dehydration. The dehydration step in the DTG curves is asymmetric. The significance of this asymmetry on the high temperature side means that the water molecules are becoming more strongly hydrogen bonded with the length of grinding time. Two types of water are identified: firstly water that is removed at low temperatures, namely adsorbed water and secondly water which is coordinated to the kaolinite surface and is removed at the higher temperatures. The DTG pattern suggests that a range of bonding strengths is involved and as a consequence the water is removed over a range of temperatures. It is noteworthy that the removal of water from the ground kaolinite will not be the same as the removal of water from the unground kaolinite surfaces. The ground kaolinite no longer possesses the kaolinite structure but is a high surface area material.

The effect of mechanochemical activation is the point heating of the kaolinite, which causes the dehydroxylation of the kaolinite at contact points between the grinding medium and the kaolinite layers. It is probable that this occurs when the kaolinite layers are compacted between the stainless steel grinding

spheres during the grinding. This is why the kaolinite dehydroxylation increases with grinding time. The temperature of the bulk material may only increase by a very small amount and yet the temperature at the contact between two kaolinite layers during grinding may be intense.

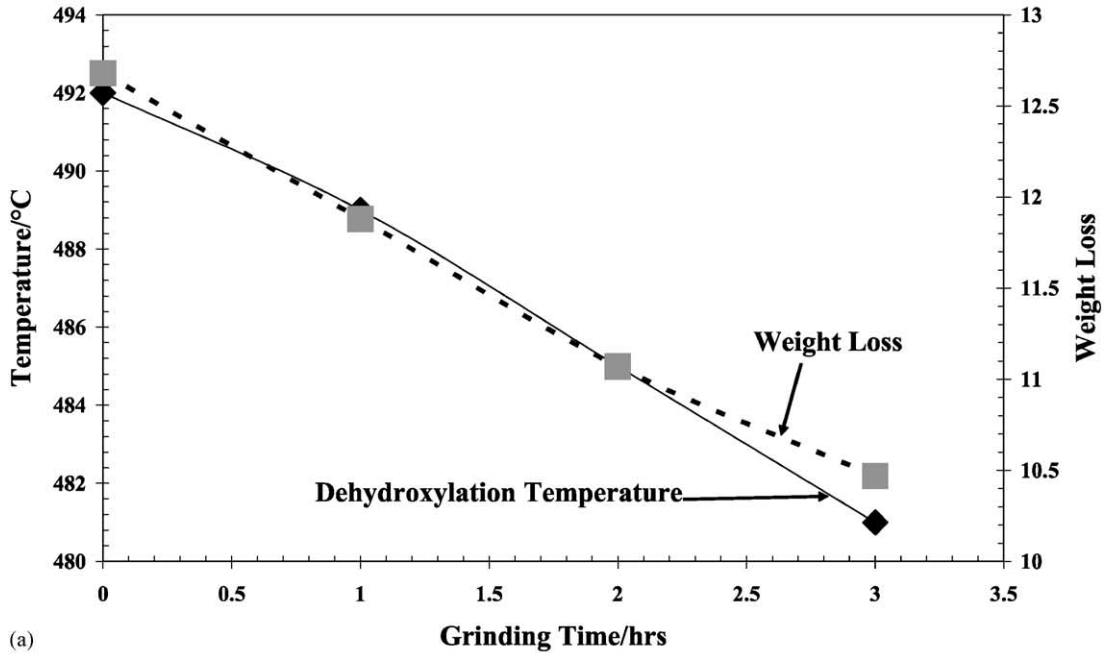
The concept of proton migration through percussive grinding and their combination with hydroxyl units has been known for sometime [27]. The generally accepted concept for the dehydroxylation of kaolinite is based upon the interaction of two hydroxyl groups in a two-step process to form a water molecule by proton transfer leaving a chemically bonded oxygen, as a superoxide anion, in the lattice. This phenomenon is known as prototropy.

The reaction process may be envisaged chemically as follows:

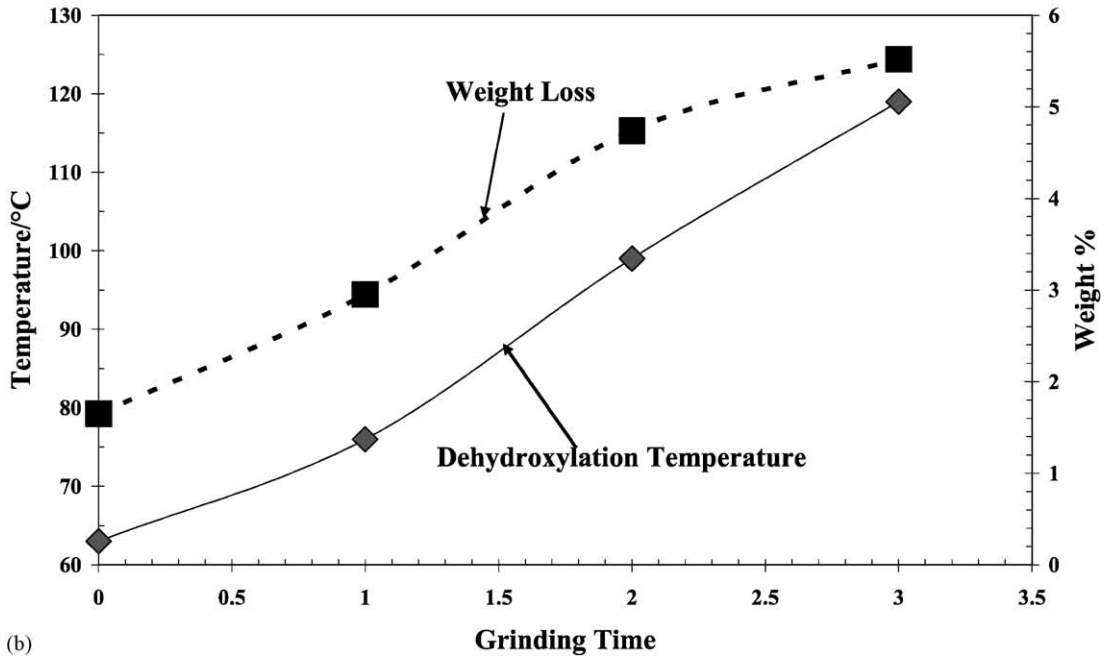


These reactions take place when mechanochemical activation of the kaolinite occurs. It is highly likely that point contact heating at specific sites results in the attainment of high temperatures sufficient to cause dehydroxylation. This results in the increase in dehydroxylation with grinding time. These steps require proton delocalization at specific hydroxyl sites. Such delocalization may occur when the mechanochemical treatment of the kaolinite causes heating at the point of contact between two particles. For water to form, these protons must migrate to a second hydroxyl site. Such proton diffusion is enabled if the temperature is sufficiently high. It is expected that not all point contacts would reach the dehydroxylation temperature. If two adjacent hydroxyls are involved in the two-step process then this process will be homogenous; if, however, non-adjacent hydroxyls are involved, such a process would require proton diffusion (sometimes referred to as proton hopping) and probably counteractive cation diffusion with the water molecules being produced at the outer surface. Where hydroxyls of different acidities are to be found, the homogenous process is more likely. It can be argued that kaolinites dehydroxylate by this homogenous process during mechanochemical activation.

Some previous studies have shown that prototropy occurs when the kaolinite is diluted with salts [28–31]. It has been suggested that this proton migration leads to lattice defects [29]. In this study, we have started



(a)



(b)

Fig. 2. (a) Changes in the dehydroxylation temperature and dehydroxylation weight loss with grinding time; (b) changes in the dehydration temperature and the dehydration weight loss with grinding time.

with a highly disordered kaolinite and it appears that proton migration readily occurs without any diluants.

3.2. DRIFT spectroscopy

Another means of identifying water in structures is the use of infrared, in this case, DRIFT spectroscopy. The water may be observed as OH stretching bands and as water HOH bending modes. The water OH stretching modes occur over a range of wavenumbers

from around 3000 to 3550 cm^{-1} . Adsorbed water is normally observed as a band at 3550 cm^{-1} where as coordinated water is observed at wavenumbers around 3300 cm^{-1} . Water bending modes are observed as bands in the 1595–1680 cm^{-1} region. The DRIFT spectra of the OH stretching modes of water and of the mechanochemically activated kaolinite at 0 and 6 h of grinding are shown in Figs. 3 and 4. These figures show the DRIFT spectra of the thermally treated mechanochemically activated kaolinite

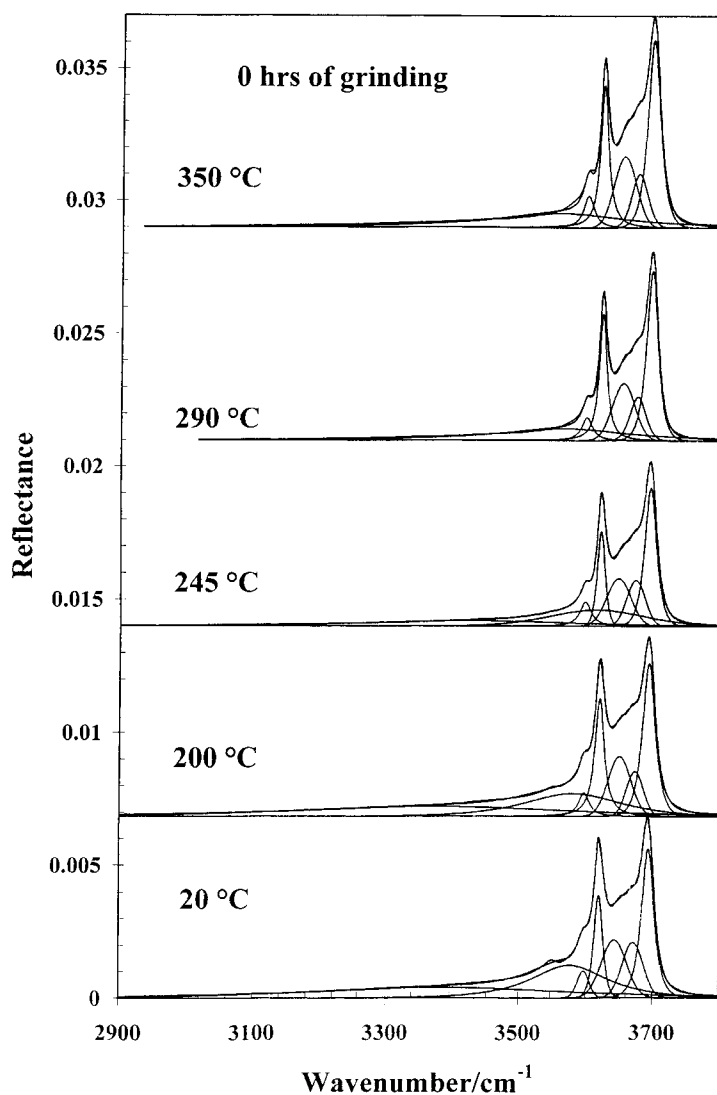


Fig. 3. DRIFT spectra of the hydroxyl stretching region of kaolinite after 0h of grinding.

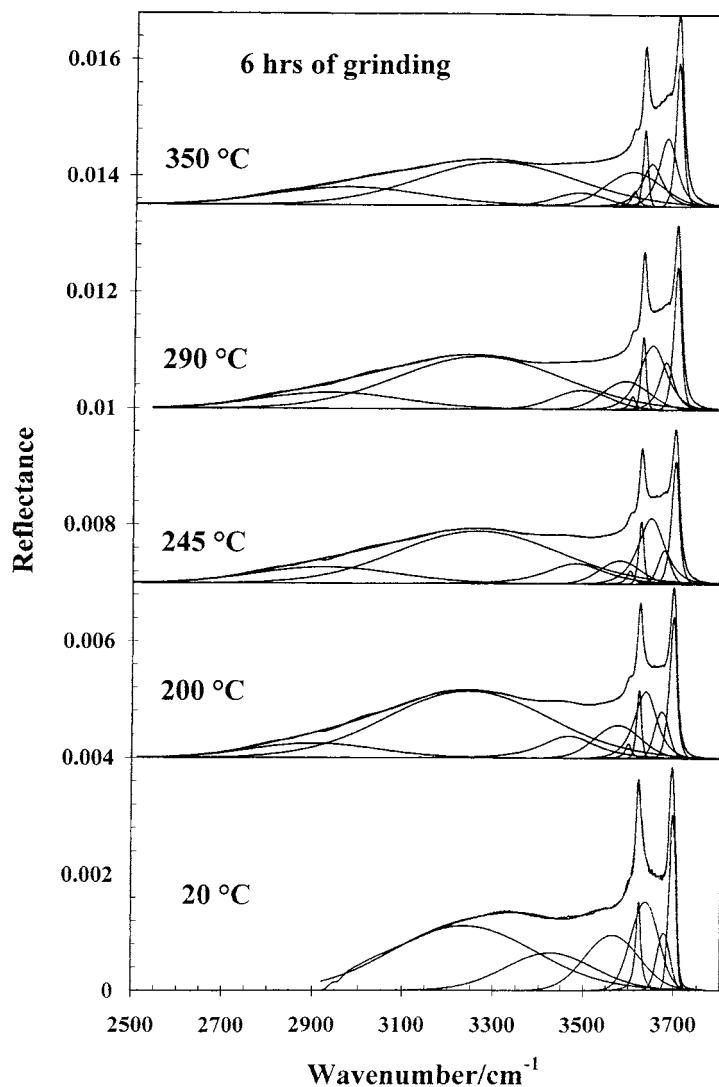


Fig. 4. DRIFT spectra of the hydroxyl stretching region of kaolinite after 6 h of grinding.

after heating to the stated temperature, quenching to room temperature and collecting the spectral data. During the cooling process, water is adsorbed by the surface-active kaolinite.

A band is observed in all of the spectra at 3595 cm^{-1} and is attributed to interlamellar water. The Szeg kaolinite does contain some iron in the octahedral sites (3.1%). The FeOH stretching vibration is observed at this position and may contribute to the overall intensity at 3695 cm^{-1} [32]. However, because of the low

concentration of Fe in the octahedral site, it is considered that the band is due to interlamellar water. At 0 h of grinding a very broad profile is observed centred at 3400 cm^{-1} . The intensity of the band decreases with thermal treatment as may be observed in Fig. 3. After mechanochemical treatment the intensity of the bands centred on 3200 cm^{-1} is of considerable more intensity than for the 0 h spectral patterns. The intensity of the band decreases with increasing temperature. This band is assigned to water bonded to the amorphous

kaolinite material. It is bonded to the amorphous silica–alumina resulting from the destroyed kaolinite surfaces.

It is proposed that the reason for the adsorption of water during the quenching from elevated temperatures after mechanochemical treatment rests with the formation of mesopores into which the water is trapped. Research on this hypothesis is continuing. The effect of mechanochemical action on the kaolinite is to delaminate the kaolinite and in effect synthesize a single layer mineral. These single layers then agglomerate to form the mesopores. It is suggested that kaolinite layers with surface-active sites touch in a V or Y arrangement. These surface-active sites are proton deficient due to the dehydroxylation of the kaolinite and the consequent formation of water. Water then coordinates to these surface-active centres.

4. Conclusions

The mechanochemical treatment of kaolinite results in the dehydroxylation of the kaolinite through point heating. It is proposed that this dehydroxylation occurs through a homogenous process involving proton transfer. The amount of dehydroxylation increases with grinding time. The effect of this point heating results in a decrease in the dehydroxylation temperature with grinding time and an increase in the amount of adsorbed/coordinated water. The temperature of this dehydration also increases with grinding time. Thermal treatment of the mechanochemically activated kaolinite results in the adsorption of water during cooling. The amount of adsorbed water decreases with the temperature of the thermal treatment.

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