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DETECTION OF FOUR DIFFERENT OH-GROUPS IN GROUND KAOLINITE WITH CONTROLLED-RATE THERMAL ANALYSIS

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Abstract

The thermal behaviour of mechanochemically treated kaolinite has been investigated under dynamic and controlled rate thermal analysis (CRTA) conditions. Ten hours of grinding of kaolinite results in the loss of the *d*(001) spacing and the replacement of some 60% of the kaolinite hydroxyls with water. Kaolinite normally dehydroxylates in a single mass loss stage between 400 and 600°C. CRTA technology enables the dehydroxylation of the ground mineral to be observed in four overlapping stages at 385, 404, 420 and 433°C under quasi-isobaric condition in a self-generated atmosphere. It is proposed that mechanochemical treatment of the kaolinite causes the localization of the protons when the long range ordering is lost.

Introduction

Kaolinite dehydroxylation is an important factor in a number of industrial processes, e.g. the extraction of oil from oil shales and coals [1, 2]. A single kaolinite layer contains a siloxane tetrahedral sheet linked via oxygen atoms to an octahedral sheet containing aluminium, oxygen and hydroxyl-groups. Each unit cell shows four hydroxyl-groups. The inner hydroxyl-group lies between the tetrahedral and octahedral sheet, while three inner surface hydroxyl-groups lie between adjacent kaolinite layers forming hydrogen bonds to the oxygen atoms of the next siloxane sheet. Kaolinite dehydroxylation is thought to re-

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sult from the interaction of two hydroxyl-groups to form a water molecule leaving a chemically bonded oxygen in the lattice [3, 4].

The concept of kaolinite dehydroxylation involves the interaction of two hydroxyl-groups in a two-step process forming a water molecule by proton transfer leaving a chemically bonded oxygen, as a superoxide anion, in the lattice [4–6]. These steps require proton delocalisation at specific hydroxyl-sites. For water formation, these protons must migrate to a second hydroxyl-site. If two adjacent hydroxyl-groups are involved then this process will be homogenous [4]; if, however, non-adjacent hydroxyl-groups are involved, this process would require proton diffusion (proton hopping) and probably counteractive cation diffusion with the water molecules being produced at the outer surface [7]. It has been argued that kaolinites dehydroxylate by this homogenous process [4, 6]. Infrared and conductivity measurements on phyllosilicates at predehydroxylation temperatures have shown proton delocalisation [8]. Deuterium exchange readily occurring in kaolinite at elevated but predehydroxylation temperatures substantiates this process [9].

The effect of grinding on the properties of kaolinite has long been investigated. Yariv and Cross classified the reactions occurring during the grinding of kaolinite in four groups: thermal diffusion, delamination, layer breakdown and sorption of water [10]. Migrating protons as a result of thermal diffusion interact with structural hydroxyls and give water at a relatively low temperature. As a result of delamination by grinding the oxygen and hydroxyl planes become increasingly exposed. Breakdown of the kaolinite layers increases the number of exposed functional groups. Freshly exposed kaolinite surfaces adsorb water from the atmosphere. Here we show that by combining dry grinding and Controlled Rate Thermal Analysis (CRTA) it is possible to distinguish between not only hydration and dehydroxylation water molecules, but, more importantly, between the water molecules removed during the four-step dehydroxylation associated with each individual hydroxyl-group in the kaolinite structure.

Experimental

The clay used is a low defect kaolinite (with a Hinckley index of approx. 0.7) from Sedlec (Zettlitz) in Slovakia. The chemical composition is 0.26% MgO, 0.54% CaO, 46.97% SiO_2, 0.37% Fe_2O_3, 1.21% K_2O, 36.32% Al_2O_3 and 0.05% TiO_2. The air-dry clay used for the experiments contained 0.17% moisture. Minor impurities observed are illite and quartz. A Fritsch pulverisette 5/2 type stainless steel planetary mill was used to grind the kaolinite for 10 h. The milling was carried out with a 10 g air-dried sample in an 80 cm^3 container using 32.6 g stainless steel balls (10 mm diameter).

Thermogravimetric analyses under dynamic heating conditions (10 and 0.1°C min^{-1}) were performed in a Netzsch (Germany) TG 209-type thermobalance in flowing argon atmosphere of 99.995% purity (Messer Griesheim, Hungary). The controlled rate thermal analysis (CRTA) of the raw and mechanochemically treated mineral was carried out in a Derivatograph PC-type thermoanalytical instrument (Hungarian Optical Works, Hungary) at a slow, pre-set, constant decomposition rate of 0.05 mg min^{-1}. Below this threshold value the samples were heated under dynamic conditions at a uniform rate of 1°C min^{-1}. The samples were heated in a closed labyrinth-type platinum crucible in a self-generated atmosphere under quasi-isobaric conditions at a rate of 1°C min^{-1} up to 800°C. With the quasi-isothermal, quasi-isobaric heating program of the instrument the furnace temperature was regulated precisely to provide a uniform rate of decomposition in the main decomposition stage.

Diffuse reflectance Fourier transform infrared spectroscopic (commonly known as DRIFT) analyses were undertaken using a Bio-Rad (USA) 60A type spectrometer. 512 scans were obtained at a resolution of 2 cm^{-1} with a mirror velocity of 0.3 cm s^{-1}. Spectra were co-added to improve the signal to noise ratio. Approximately 3 mass% ground kaolinite was dispersed in 100 mg oven-dried KBr. Background KBr spectra were recorded and the spectra were ratioed to the background. The DRIFT accessory 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 cups (3 mm deep and 6 mm in diameter) accommodate powdery samples mixed with KBr using an agate mortar and pestle in 1–3% concentration. The reflectance spectra expressed as Kubelka-Munk units *vs*. wavenumber curves are very similar to absorbance spectra and can be evaluated accordingly.

Results and discussion

The thermogravimetric and derivative thermogravimetric curves of the untreated kaolinite and of the ground form are shown in Fig. 1. While the thermal decomposition of the raw kaolinite occurs in a single stage at 495°C resulting in a total mass loss of 13.85% up to 900°C (a), the pattern of the ground clay differs significantly (b). The kaolinite is partially dehydroxylated due to dry grinding. The amount of hydration water lost up to 362°C is 11.56%. In the dehydroxylation stage a mass loss of 7.01% was observed. This means that about 4.7% of moisture was picked up from the atmosphere and some 60% of the OH groups dehydroxylated during grinding. The fact that hydration water was liberated in a rather wide temperature range (from ambient up to 362°C) indicates that – in accordance with literature data – part of the water is chemisorbed to the clay surface.

After 10 h of grinding the kaolinite is almost amorphous as indicated by X-ray diffraction. Partial dehydroxylation of the kaolinite (metakaolinite formation) and the strong adsorption of water are observed in the DRIFT spectra as well (Fig. 2). In addition to the loss in intensity of the kaolinite OH-stretching bands (3695, 3670, 3650 and 3620 cm^{-1}) [11–14] and the appearance of water OH-stretching and deformation bands in the 3500 to 3600 cm^{-1} region and around 1600 cm^{-1} respectively, drastic changes can be seen in the range from 700 to 1200 cm^{-1} [15]. To investigate the reversibility of this partial dehydroxylation process, the ground clay was heated to 300°C and (after cooling to room temperature) exposed to humid air (*RH*=50%). After one day the amount of water adsorbed was 2.05%, while after one month the amount of water increased to 3.31%. Further exposure to humid air did not result in observable changes in the moisture content of the ground mineral. Mixing the ground clay with water for 24 h did not result in any changes in the DRIFT spectra.

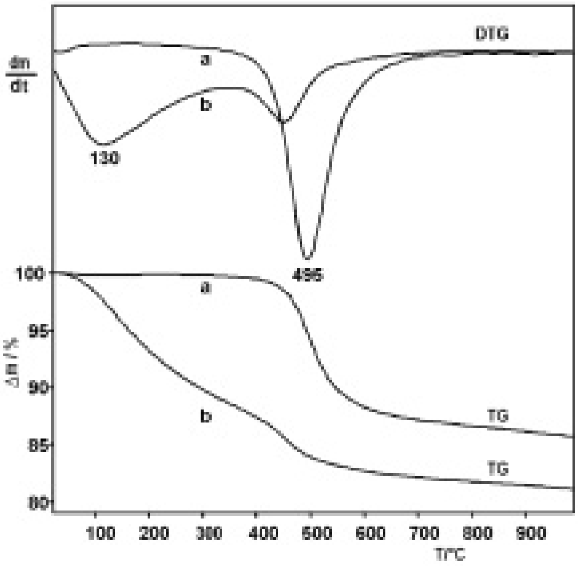

Fig. 1 Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of a – raw kaolinite and b – raw kaolinite dry-ground for 10 h

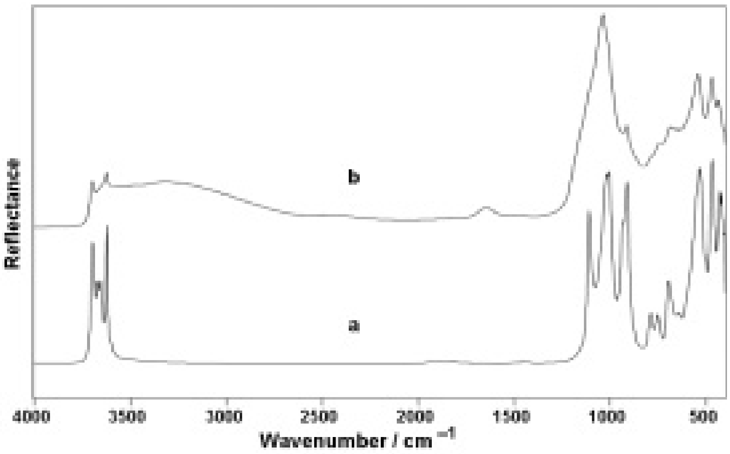

Fig. 2 FT-IR (DRIFT) spectra of a – raw kaolinite and b – raw kaolinite dry-ground for 10 h

Under the conditions of extremely slow heating (0.1°C min^{-1}) the raw kaolinite starts to dehydroxylate at 393°C and this process is finished by 466°C (Fig. 3). The DTG peak temperature shifts from 495 to 433°C. An additional mass loss stage at 474°C belongs to the dehydroxylation of illite impurities. Under 'normal' heating – i.e. at 10°C min^{-1} – these two processes cannot be resolved. Thus, the dehydroxylation of kaolinite is indeed a one-step process, in spite of the fact that four different OH environments can be identified by vibrational spectroscopy [16–20]. The dehydr-

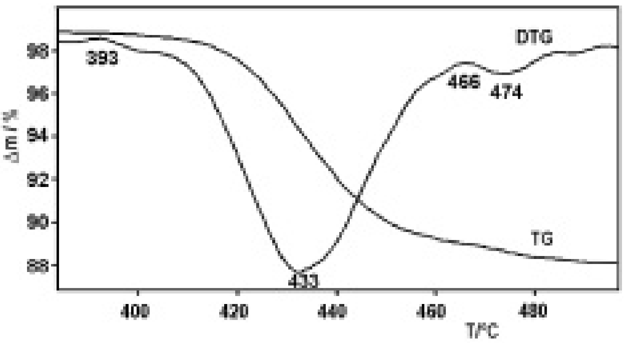

Fig. 3 Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of the raw kaolinite heated at a rate of 0.1°C min^{-1}

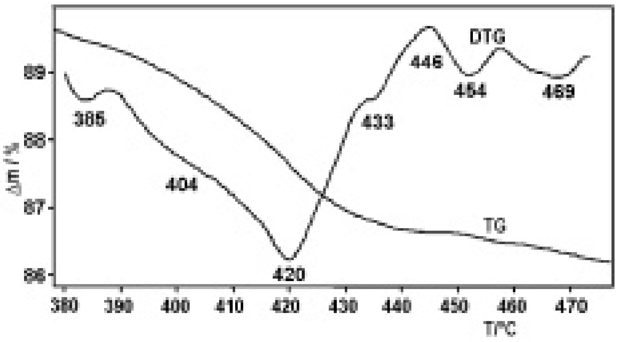

Fig. 4 Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of the ground mineral heated at a rate of 0.1°C min^{-1}

oxylation of the ground kaolinite, however, takes place in four overlapping stages at 385, 404, 420 and 433°C (Fig. 4). It means that with extremely slow heating the four different OH environments can indeed be distinguished in the thermoanalytical curves. Thus, the delocalisation of protons on heating no longer occurs when the long-range ordering of kaolinite – as a result of grinding – is lost.

The thermoanalytical curves of raw kaolinite recorded under CRTA conditions indicate that dehydroxylation starts at 437°C and the temperature remains spontaneously constant at 506°C when the rate of mass loss reaches the pre-set level (0.05 mg min^{-1}). This means that dehydroxylation of the mineral – in accordance with earlier findings – takes place under quasi-isothermal and quasi-isobaric conditions [21]. The thermal behaviour of the ground kaolinite under CRTA conditions is shown in Fig. 5. The thermal decomposition pattern of the ground clay is completely different. Although the pre-set rate of decomposition (0.05 mg min^{-1}) is already reached at about 100°C, the liberation of water hydrated to the partially dehydroxylated mineral takes place in a self-generated (water vapour) atmosphere in a non-isothermal process. The fact that the temperature does not remain spontaneously constant during this constant rate decomposition process means that higher and higher energy (i.e. higher and higher temperature) is necessary to maintain the water

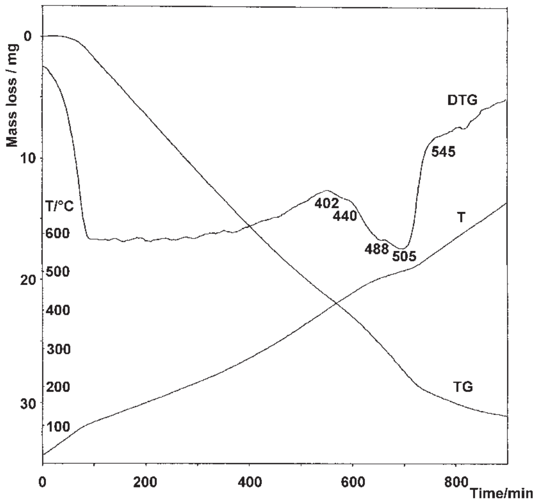

Fig. 5 Thermoanalytical curves of the ground kaolinite heated under quasi-isobaric conditions (sample mass is 188.00 mg). *T* represents the heating curve

liberation process at the same constant rate. A slight decrease in the decomposition rate can only be observed after 300°C, and the process reaches a minimum rate at 402°C. If the water present were simply adsorbed (like in the case of the unground sample), it would liberate under these conditions at about 100°C in an isothermal process. The extremely wide temperature range of dehydration (between 100 and 402°C) and the non-isothermal nature of the process indicate that water formed in the grinding-induced dehydroxylation reaction is bonded very strongly to the clay (most likely to the aluminium ion). In addition, the energies of hydration cover a very wide range.

Removal of residual OH-groups (i.e. dehydroxylation of the intact portion of the kaolinite) takes place above 402°C in a self-generated atmosphere under quasi-isobaric conditions. This is a rather slow process and the pre-set rate is reached only around 500°C. The most striking observation regarding dehydroxylation is that water is formed in three closely overlapping steps at 440, 488 and 505°C, i.e. the dehydroxylation process can be resolved to three closely overlapping stages (the fourth one cannot be distinguished in the falling part of the DTG curve). A separate mass loss due to the dehydroxylation of illite appears as a shoulder in the DTG curve at 545°C.

Conclusion

Under the conditions of extremely slow heating and those of controlled-rate thermal analysis in a self-generated atmosphere, the distorting effects of heat and mass transfer processes on the thermoanalytical curves can be eliminated. In this way a better resolution of closely overlapping thermal decomposition processes can be obtained offering an insight in the subtle nature of kaolinite dehydroxylation.

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