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Structural and thermal behavior of proclay kaolinite using high energy ball milling process

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ABSTRACT

Planetary ball mill is used to process kaolinite clay powder under a commercial name of proclay kaolinite. Influence of milling time on structure and thermal behavior of proclay kaolinite are presented and discussed. X-ray powder diffraction shows that peak intensities, at kaolinite characteristic positions, decrease gradually and decay after 3 hours of milling. Amorphous structure of kaolinite forms with a nanocrystalline quartz. The mean crystallite size of nanocrystalline quartz is found to decrease from $D = 30 \pm 2$ nm for unmilled powder to $D = 7 \pm 1.5$ nm after 9 hours of processing. For the same time shift, thermal analysis shows that specific heat capacity of unmilled powder increases from 0.93 J/g.K to 1.65 J/g.K for milled powder.

1. Introduction

Clays are widely used as additives or fillers due to their specific mineralogical composition that allows adsorption properties and chemical reactivity [1–3]. Rheological properties and chemical reactivity of clays all depend on the nature and content of minerals composing the clay [4,5]. Kaolinite as a clay mineral is particularly used for pollutants removal [3,6,7]. It is the objective of this work to understand the structural modification of kaolinite during its processing to better improve its physical and chemical properties. Ball milling is an efficient mechanical process that induces major structural and chemical changes of materials through an energetic mechanical treatment [8].

Among possible high energy ball mill designs, planetary ball mill is characterized by large centrifugal forces, which can reach up to 20 times the gravitational acceleration. Centrifugal forces are a result of the rotation of a supporting disc and vial (45–500 ml) containing the charge. These two parts of the mill setup rotate in opposite direction, causing the milling media (balls) and charge powder to roll off the inner wall of the vial and thereby to be thrown across the bowl [9–11]. Planetary ball milling involves a repeated fracturing and rewelding of particles leading to size reduction and particle shape change. The main parameters that affect particle size reduction include rotation speed, ball size, ball-to-powder weight ratio, milling environment and milling time [9,11]. A wide variety of powders can be processed using ball milling to achieve nanostructured materials such as Fe-Ni [12,13], Mg_2Ni [8] but also different clays: beidellite and ripidolite [14], Na^+-montmorillonite, organo-montmorillonite clays [15], kaolin [16,17] and kaolinite [18–20].

Kaolinite clays structure are composed of alternating silica and octahedral sheets [21,22]. In the plane of atoms common to both sheets, two-thirds are oxygen atoms; one third is composed of hydroxyls. Because of slight differences in the oxygen-to-oxygen distances in the tetrahedral and octahedral layers, there is some distortion of the ideal tetrahedral network. As a result, kaolinite appears as triclinic instead of being monoclinic. The bonding between successive kaolinite layers is composed of both van Der Waals forces and hydrogen bonds. The bonding is sufficiently strong to prevent interlayer swelling in the presence of water [22,23].

Kaolin, which contains generally from 85% to 95% of kaolinite [21,24], is widely used in many applications such as cement and ceramic processing. It plays a role of filler in polymer-nanocomposite, paints, paper and rubbers [16,24]. Crystal structure implications in clay minerals is elucidated since early works such us those implying base-exchange reactions [25]. More specifically, rapid prototropy is related to major changes in spectra for kaolinite subject to percussive grinding [26]. Crystalline structure deterioration by mechanical process is described as an intermediate state between original crystalline and

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final amorphous state [27]. Recently, the influence of ball milling on kaolinite structure and its main physicochemical properties is investigated [28–33].

Makò and co-workers [30] processed natural kaolin composed of 92% of kaolinite and quartz using planetary ball mill. They showed that the mechanochemical activation causes destruction in the crystal structure of kaolinite by the rupture of the O – H, Al – OH, Al – O – Si and Si – O bonds. They also pointed out that quartz content of kaolin accelerates mechanochemical amorphization of kaolinite.

Frost et al. [31] have studied the effect of mechanochemical activation upon the intercalation of a high-defect kaolinite with formamide. The authors [31] have used planetary ball mill to process natural kaolin where the major mineral constituent is a high-defect kaolinite (95 wt%) combined with a low quartz content. Milling times of 1 h to 6 h are selected with 30 cm^3 of concentrated formamide solution. The authors [31] have found that the intensity of the $d(001)$ spacing decreases with milling time with the intercalated high-defect kaolinite expanding to 10.2 Å. The intensity of the peak of the expanded phase of the formamide-intercalated kaolinite decreases with milling time. In the same study, thermal analysis reveals that the evolution temperature of the adsorbed formamide and loss of the inserting molecule increases with increased milling time. The temperature of the dehydroxylation of the formamide-intercalated high-defect kaolinite decreases from 495 °C to 470 °C with mechanochemical activation. Ding et al. [18], have discussed the relationship between kaolinite structure and the temperature of thermal transformation of kaolinite powders milled using planetary ball mill for 0-2 h and heated for 900 °C, 1000 °C and 1400 °C. The authors [18] have found that the crystallinity of kaolinite decreases and the kaolinite structure is destroyed gradually with the milling time. Also, the authors [18] have shown that both endothermic peak strength (500 °C to 700 °C) and temperature decrease with the increase of milling time due to dehydroxylation. The authors [18] have noticed a vanishing endothermic peak after 1 h of milling. Such vanishing peak indicates that the dehydroxylation process develops during milling and becomes almost completed after 1 h.

With regards to the huge body of work concerning kaolinite, we are interested to study structural changes related to the mechanical processing of a specific kaolinite. Indeed, the aim of this work is to quantify milling time effect on structure and thermal behavior of proclay kaolinite using planetary ball mill in friction mode process ($\omega >> \Omega$) like detailed in [34]. Ball milling process is, in our case, beneficial to produce amorphous kaolinite without heating and calcination. We propose, in this study, a quantification of proclay kaolinite ball milling processing, where we are able to handle large amount of proclay kaolinite powder compared to previous studies. We demonstrate that our milling configuration is superior to reported milling set-ups to achieve complete structural changes within relatively short milling time.

2. Materials and Methods

Kaolinite powder of Proclay BR500, from Beaujard–Poigny site (France) is used in this study. In order to obtain chemical composition of proclay kaolinite, elemental analysis is conducted by X-ray fluorescence spectroscopy and carried out using S8 TIGER instrument from Bruker which has particularity to combine several crystal analyzers. Table 1 summarizes the chemical composition of proclay kaolinite. Geotechnical properties of our proclay kaolinite, namely liquid limit (65%), plastic limit (30%) and plasticity index (35%) are obtained using Atterberg limits protocol. The milling of proclay kaolinite powder is carried out using a planetary high-energy ball mill (Retsch PM 400). The planetary high energy ball mill is composed of four vials mounted on a planar disc. With the rotation of the disc, the vials move in a circular and in opposite direction compared to the disc rotation. The rotation speeds of the disc and the vials are $\Omega = 400$ rpm and $\omega = 800$ rpm, respectively. Different milling times t are selected, where t = 1 h, 3 h and 9 h. Thirty-millimeter diameter steel balls and 500 ml volume steel vials are used. The weight of powder samples is 260 g per vial. More than 1 kg in total weight obtained after one milling stage. The ball-to-powder weight ratio is 3.1. In order to calculate possible oxygen contamination, we use the following data: 2.26 g/cm^3, 7.85 g/cm^3 and 22.4 l/ mole for proclay kaolinite powder, steel density and molar volume of oxygen, respectively. With these data in hand, we find that, for one vial, the weight ratio of oxygen to the total mass (ball and powder) is 7.65×10^{-3} %. We mention that vials of planetary ball mill (RETSCH PM 400) are adequately sealed excluding, by the way, any risk of air contamination during milling process. Also, in order to avoid iron or chromium contamination of the processed powder by elements from balls or vials, we impose a delay time frame of 30 minutes after 1 h of milling. This contamination can affect properties of kaolinite like the decrease of specific heat Cp in presence of iron [35]. X-ray investigations are performed on a Bruker D2 phaser diffractometer using a continuous scanning mode with Cu K_α radiation ($\lambda = 0.1541$ nm). The lines are measured in the 2θ range (5–100) ° in steps of 0.02° for 10 s. The software used for evaluation is DIFFRAC.EVA with ICDD PDF2. Preliminary analysis shows that the first half of the 2θ range is the most effective one to determine major structural changes.

Table 1
Chemical composition of proclay kaolinite powder.

Species	Weight content (%)
SiO_2	68.58
Al_2O_3	27.23
TiO_2	1.71
Fe_2O_3	1.07
K_2O	0.55
CaO	0.38
MgO	0.12
Others	0.36

The changes in the lattice parameters are calculated from the shift of the high angle diffraction line (different lines mentioned in Fig. 1 are exploited) using Bragg's law. The lattice parameter a is calculated from the mean of two angles at lines (100) and (200). The same holds for the calculation of lattice parameter c with different angles. The accuracy is estimated to 3×10^{-4} nm and 4×10^{-4} nm for lattice parameters a and c, respectively.

Crystallite size and lattice strain are calculated using XRD profile analysis described by Langford [36]. The measurement procedure uses

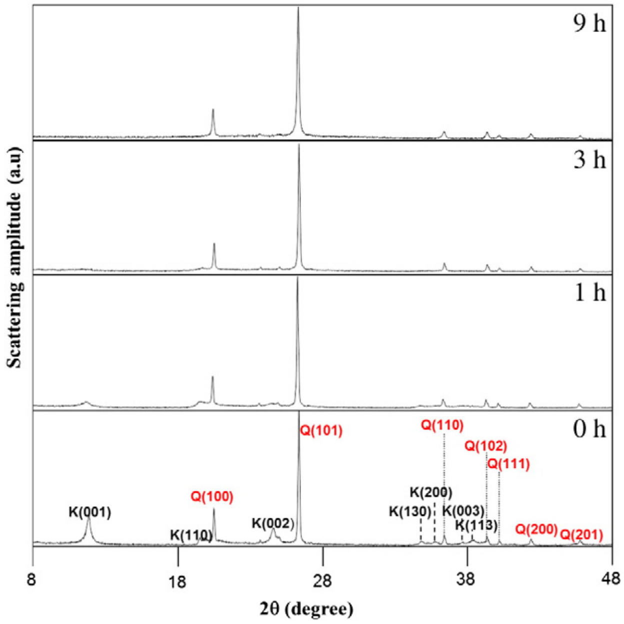

Fig. 1. X-ray patterns of proclay kaolinite as function of milling time.