

Some physico-chemical alterations caused by mechanochemical treatments in kaolinites of different structural order

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Abstract

Two kaolinites of different structural order designated KGa-2 and KC were milled for variable times (15, 30, 45, 60, 75, 90, 105 and 120 min). The ensuing changes were monitored using particle size distribution (PSD) analyses, pH measurements and thermal methods [thermogravimetric analysis (TGA), and differential thermal analysis (DTA)]. The size mode for the initial particles ranged from 0.31 to 0.36 μm in KGa-2 and from 6.6 to 7.7 μm in KC. After 120 min of milling, however, both kaolinites exhibited similar PSD results and modes (26.2–30.5 μm). Milling caused the transformation of surface charges and produced water molecules. This resulted in a decreased pH in KC and an increased one in KGa-2; however, both tended to converge on pH 6 after several minutes of milling. The new larger particles were formed by bonding between the new water molecules formed. Based on the temperature at which they disappeared, the water molecules were coordinated as zeolitic or interlayer water. The effects of milling became apparent at an earlier stage in the less ordered kaolinite. In well-ordered kaolinites consisting of large particles, the inner-to-inner surface hydroxyl ratio results in a symmetric dehydroxylation effect; thus, milling increased structural disorder and decreased the peak temperature, symmetry and width. Also, $T_p - T_{on}$ increased by effect of an increased presence of edges and inner surface hydroxyls, whereas $T_{off} - T_p$ decreased with decreasing proportion of inner hydroxyls relative to other types of OH groups.

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1. Introduction

Kaolinite is one of the most abundant minerals in the Earth crust. Some of its properties (viz. colour, particle size, morphology, surface chemistry and charge) are exploited by the papermaking, paint and pharmaceutical industries, among others [1].

A number of techniques have been developed in recent years in order to alter the physical, chemical, structural and surface properties of kaolinite with a view to expanding or improving its applications. The treatments used to this end in-

clude (a) calcination at different temperatures [1]; (b) application of ionic and/or polar surfactants to turn its hydrophilicity into hydrophobicity or organophilicity [1]; (c) amorphization by milling [2]; (d) zeolitization by treatment with Na, Ca, Mg and K oxides at 100 °C [1]; (e) acidification [3]; (f) various combinations of the previous ones [4].

Milling an inorganic material causes the disintegration of particles and the consequent formation of new active surfaces in addition to changes in its physico-chemical properties that decrease its crystallinity (through amorphization) and increase its surface reactivity [5,6]. These “mechanochemical” effects are observed mainly when the material is milled using equipment involving friction and impaction forces on particles (e.g. vibratory, oscillating or planetary mills). Mechanochemical reactions can be classified into four broad categories [7], namely: (a) atom diffusion (prototropy), (b)

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displacement between layers (delamination), (c) layer disruption and (d) adsorption of atmospheric water by the amorphous product.

The physical disintegration of kaolinite crystalline grains results in its gradual destruction via alterations in properties such as specific surface area, ion-exchange capacity, water absorption capacity and acid solubility, as well as through the formation of spherical aggregates of fine particles [2,8–15]. Changes in surface area with milling occur in three steps [14], namely: (a) the formation of new surfaces, (b) aggregation (viz. a monotonic decrease in the area change with milling time) and (c) agglomeration (which decreases the surface area).

The mechanochemical amorphization of kaolinite [11] involves layer disruption and grouping, rearrangement of coordinated polyhedra and proton transfer to other sites in the structure (an effect known as “prototropy” [16]); the result is an array of tetrahedral residual layers, and of octahedra and tetrahedra distorted to an extent dependent on the particle size and initial order [17], as well as on the particular milling method used.

Milling is highly likely to cause a large enough temperature change at a specific contact point for Al–OH and O–H bonds to be distorted or even broken, thereby leading to dehydroxylation and the formation of water molecules [14]. The water is formed by interaction of two hydroxyl groups in a two-step process: in the first, one hydroxyl group dissociates by proton transfer (prototropy) leaving a chemically bonded oxygen, as a superoxide anion, in the lattice; in the second, the proton released in the first step bonds to the other hydroxyl group to form a water molecule. If the process involves two adjacent OH groups, then it is *homogeneous*; otherwise, diffusion occurs and the water molecule is formed on the outer surface, the process being *heterogeneous* [18].

Despite the previous evidence, some aspects of the changes induced by milling in kaolinite are still obscure. Thus, the following questions remain unanswered: (a) do particle aggregates behave as a single particle or are they easily disintegrated? (b) why does reactivity increase with increasing particle size? The aim of this work was to acquire new information with a view to facilitating the interpretation of mechanochemical changes in kaolinite.

2. Material and methods

2.1. Material

The well-ordered kaolinite (KC) was supplied by Caosil (Guadalajara, Spain) with a Hinckley index of 1.19; the disordered kaolinite (KGa-2) was from Georgia (USA) and obtained from the Source Clay Repository of the Clay Minerals Society (MO, USA) with a Hinckley index of 0.43. Both were of sedimentary origin and the major mineral component was kaolinite (>95%) with a minor amount of quartz and mica in KC, and a small amount of anatase and mica in KGa-2.

The chemical composition, in wt.% as oxides, is SiO₂ 45.82, Al₂O₃ 37.65, Fe₂O₃ 0.97, K₂O 0.80, loss on ignition 14.76 in KC; SiO₂ 43.49, Al₂O₃ 38.14, Fe₂O₃ 1.15; TiO₂ 1.91, K₂O 0.02, P₂O₅ 0.32, loss on ignition 14.97 in KGa-2.

To study if the changes were due to the particle size or to structural modifications, the kaolinite from Georgia was separated into >20, 20–10, 10–5, 5–2 and 2–1 μm fractions by sedimentation, and into 1–0.5, 0.5–0.1 and <0.1 μm fractions by centrifugation.

2.2. Milling procedure

The solids were subjected to mechanical treatment in a Fritsch Pulverisette-7 planetary mill. Samples were milled for 15, 30, 45, 60, 75, 90, 105 or 120 min. In each test, an amount of 3 g of air-dried sample was milled in a 25 cm³ stainless steel pot with the aid of three stainless steel balls; one ball was 15 mm in diameter and 13.6 g in weight, and the other two 12 mm in diameter and 7 g in weight. The rotation speed used was 730 rpm.

2.3. Particle size distribution

The particle size distribution (PSD) of the natural and milled samples was determined on a Malver Instruments Mastersizer-S instrument. Test was conducted in suspension. In order to avoid flocculation, samples were supplied with sodium polyphosphate (3.6%) and sodium carbonate (0.8%) as dispersants and ultrasonicated for 5 min. Then, in the compartment of small volume, the suspension was stirred at 3510 rpm and ultrasonicated. The lens used was 300 mm in focal length, so the measuring range was 0.05–900 μm. Each sample was analysed eight times.

2.4. pH measurements

The pH of the samples was measured with a Mettler 340 pH-meter following stirring of a 1:2.5 sample/de-ionized water suspension for 10 min and standing for 30 min.

2.5. Thermal methods

The thermal methods used (viz. TG, DTA and DTG) were implemented in a Setsys-16 instrument from Setaram, using 100 μl platinum crucibles, Pt/Pt10% Rh thermocouples, an argon stream at a flow-rate of 6.3 l/h, milled alumina as reference sample. Both the alumina and the samples were compacted in the absence of applied pressure. Prior to heating (at a rate of 10 °C/min), an isotherm was recorded at 25 °C for 1000 s.

The Setsoft 2000 module coupled to the thermal analyser allowed us to determine the mass change between two points in the TG curve or the areas of the peaks (by integration, using DTG and DTA). Also, the DTA curves gave the onset and offset points, which were bound by the intersect of the baseline with the tangent at the inflection point between the rising and falling segments (Fig. 1). Peak width was taken to

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