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Surface modification of mechanochemically activated kaolinites by selective leaching

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Abstract

Low- and high-defect kaolinites mechanochemically activated for different periods of time have been treated with sulfuric acid solution. These modified materials were analyzed using a combination of X-ray diffraction, thermogravimetry, chemical analysis, diffuse reflectance Fourier transform infrared spectroscopy, as well as specific surface area and pore size distribution measurements. In addition to the mechanochemically amorphized part, the disordered and the adequately distorted phases also reacted with sulfuric acid. The specific surface areas of the leached samples of the partially or the completely amorphized materials were found to be greater than those of the thermally amorphized ones. The acid treatment results in a greater total pore volume for the partially amorphized materials than for the totally amorphized mineral. The partially amorphized high-defect kaolinite was proved to be more soluble than the low-defect kaolinite under similar conditions.

Keywords: Dry grinding; Kaolinite; Mechanochemical activation; Selective leaching

1. Introduction

The industrial utilization of kaolin minerals covers a wide range of applications including the production of ceramics, paper, paints, plastics, rubber, ink, cracking catalysts, adsorbents, etc. [1]. The physical, chemical, structural, and surface properties of kaolinite determine it's applicability. These properties can be significantly modified by mechanochemical activation through dry grinding [2–20]. Earlier studies [2–5] showed that dry grinding considerably increases the surface area, the ion-exchange capacity, the heat of immersion and the solubility in hydrochloric acid. It has been found that the grinding of kaolinite brings about a progressive lowering of the temperature at which the structural water is evolved. It was inferred [4] that grinding caused a distortion, but not an actual decomposition, of the kaolinite lattice. Takahashi [5] and Schrader [6] found that prolonged dry grinding resulted in a disordered phase which yielded an amorphous material due to the complete destruction of the kaolinite structure. This disintegration of kaolinite crystals should be seen as a real amorphization of the structure characterized by the cleavage of bonds between clusters of atoms and the irreversible displacement of atomic groups which do not revert on release of the external load [6,8,9]. Numerous authors [7–11] reported that the mechanical amorphization of kaolinite is accompanied by the rupture of O–H, Al–OH, Al–O–Si, and Si–O bonds. The product of such amorphization is a water-containing xerogel with random structure, in which the original hydroxyl groups of kaolinite are converted into coordinated water bonded to the kaolinite ‘backbone’ [7,9,10,13,17–20]. This phenomenon is known as prototropy, which is based upon the interaction of two hydroxyl groups in a two step process to form a water molecule by proton migration [7,17–19]. It has been shown that the properties of the ground product as well as the effec-

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tiveness of mechanochemical amorphization depend on the crystallinity of the original kaolinite [9,12,14,17]. Reynolds and Bish [16] demonstrated that there is no evidence for the occurrence of an intermediate disordered phase during grinding. Instead, grinding apparently creates an increased amount of disordered kaolinite that coexists with the relatively unaffected material.

The solubility of the clay minerals in acids is of fundamental importance because it reveals certain attributes of the clay minerals [21]. From a practical standpoint, solubility characteristics are important in determining the utility of various clays as sources of aluminum and for the production of porous materials [21–24]. The solubility of kaolinite in acids varies with the nature and concentration of the acid, the acid-to-kaolinite ratio, the temperature, and the duration of treatment [4,9,11,21–24]. Grim [21] reviewed some other studies related to acid–kaolinite reactions. Most of these investigations have indicated that the kaolinite is more soluble in sulfuric than in hydrochloric acid. Under similar condition of acid treatment, but after amorphization by heating or grinding, all or substantially all the alumina of the kaolinite is soluble [11,21–24]. Temuujin et al. [23,24] examined porous silica prepared from mechanochemically and thermally amorphized kaolinites by sulfuric acid leaching. It was suggested that the SiO_4 tetrahedral sheet of the porous silica basically maintains the original layered structure and is different from the general framework structure of silica gel [24]. The mechanically amorphized acid-treated kaolinite showed a uniform pore size distribution in the mesopore region [23].

It is proposed that the properties of kaolinites prepared by mechanical activation combined with selective leaching depend on the nature of the starting material and the duration of mechanochemical treatment. The present paper examines the alterations of low- and high-defect kaolinites due to acid treatment after dry grinding for different intervals of time.

2. Materials and methods

2.1. Materials

Two high-grade natural kaolins were used in the experiments: the Zettlitz kaolin from the Czech Republic, and the Szegi kaolin from Hungary. These kaolins were selected for this experiment because of their low quartz content and high purity.

The chemical composition of the Zettlitz kaolin in wt% is: MgO, 0.28; CaO, 0.80; SiO_2, 46.23; Fe_2O_3, 0.88; K_2O, 0.66; Al_2O_3, 36.74; TiO_2, 0.05; loss on ignition, 13.36. The major mineral constituent is a low-defect kaolinite (91 wt%) with a Hinckley index [25] of around 0.8. Some minor amounts of quartz (2 wt%) and muscovite (7 wt%) are also present. The specific surface area is 19.4 m^2/g.

The chemical composition of the Szegi kaolin in wt% is: MgO, 0.15; CaO, 0.55; SiO_2, 46.73; Fe_2O_3, 3.21; K_2O, 0.22; Na_2O, 0.1; Al_2O_3, 33.94; TiO_2, 0.06; loss on ignition, 14.12. This natural kaolin mainly consists of a high-defect kaolinite (95 wt%) with some impurities of feldspar (2 wt%) and quartz (3 wt%). The Hinckley index of the Szegi kaolinite is 0.3. The specific surface area is 31.3 m^2/g. (The symbols of the Zettlitz and Szegi material are “Z” and “Sz”, respectively.)

Clays were ground (mechanochemically activated) for 0, 1/4, 1, and 2 h using a Fritsch pulverisette 5/2 type laboratory planetary mill. Each milling was carried out with a 5 g air-dried sample in an 80 cm^3 capacity stainless steel (18% Cr + 8% Ni) pot using 30 (114.1 g) stainless steel balls (10 mm diameter). The applied rotation speed was 374 rpm. (The symbols of materials ground for 0, 1/4, 1, and 2 h are “0”, “1/4”, “1”, and “2”, respectively.)

After grinding, 6 g of mechanically activated materials were selectively leached with 300 cm^3 of 20 wt% H_2SO_4 solution for 2 h at 90 °C, followed by the addition of distilled water. The leached material was filtered through a G4 type glass filter, washed three times with distilled water and dried at 110 °C overnight. (The leached materials are marked by “L”.)

For comparison, the original kaolins were heat treated at 600 °C for 24 h. The calcined materials were also leached as it was described above. (The heat treated materials are marked by “H”.)

2.2. Methods

The X-ray diffraction (XRD) analyses were carried out on a Philips PW 3710 type diffractometer equipped with a PW 3020 vertical goniometer and curved graphite diffracted beam monochromator. The radiation applied was Cu$K\alpha$ from a broad focus Cu tube, operating at 50 kV and 40 mA. The samples were measured in step scan mode with steps of 0.02° 2θ and a counting time of 1 s. Data collection and evaluation were performed with PC-APD 3.6 software. Philips X’Pert program was applied to determine the full width at half maximum (FWHM) value and the total area of an individual peak in a diffraction pattern. The back-packed mounts of finely powdered samples were used to eliminate preferential orientation.

Thermogravimetric analyses (TGA) were carried out in a Netzsch (Germany) TG 209 type thermobalance under dynamic heating conditions (10 °C/min heating rate) in flowing nitrogen atmosphere of 99.995% purity (Messer Griesheim, Hungary). A ceramic crucible was used for the experiments filled with approximately 10 mg sample in each case.

Diffuse reflectance Fourier transform infrared spectroscopic (DRIFT) analyses were undertaken using a Bruker Equinox 55 spectrometer; 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 5-mg samples were dispersed in 50 mg oven-dried spectroscopic grade KBr with a refractive index of 1.559