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Study of structural properties of ion treated and mechanically deformed commercial bentonite

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Abstract

This study deals with the investigation of the structural changes of Ca-montmorillonite present in a commercial bentonite produced by mechanical deformation via high-energy ball milling or by ionised argon interaction, both in controlled thermodynamic environment.

Scanning electron microscopy (SEM), transmission electron microscopy (TEM), differential scanning calorimetry (DSC), Fourier-transform infra-red (FTIR), X-ray powder diffraction (XRPD), particle size laser diffraction (PSLD) and swelling index (SI) were used for the characterization of the samples.

(i) Ball milling. We have observed that high-energy ball milling produced a progressive reduction of the *d* (001) lattice spacing of the montmorillonite from 1.50 to 1.30 nm as a function of time (at a constant cycle frequency). Simultaneously, a severe decrease and broadening of the XRD spectrum peaks were also detected, indicating a reduction of crystallinity and an increase of microstrain. Analysis by laser-diffraction indicates a bimodal distribution of the particle size, and a progressive increase of the number of particles with size in the range 0.5–1 μm and greater than 20 μm, for the material milled up to 20 h. However, by using increased spatial resolution, sub-micrometric rounded particles were observed after 20 h of milling by SEM analysis, and the presence of nanometric particles by TEM. FTIR and DSC clearly showed a structural destabilization both in the interlayer and in the intralayer and a progressive loss of interlayer water. The swelling index drastically reduced as a function of milling time. Finally, as expected, the more pronounced transformations were observed for milling in medium vacuum of 0.13 Pa (10^{-3} Torr), than for in inert gas or air atmospheres because of the more dehydrating environment.

(ii) Argon-ion treatment. X-ray diffraction analysis showed that the mean *d* (001) montmorillonite lattice spacing shifted from 1.50 to 1.35 nm, whilst the peak intensity decreased and broadened, with a decrease of the crystallite size in the 001 direction. SEM showed an increased presence of sub-micrometric rounded particles at the surface of the treated samples than for the untreated ones. DSC indicated a decrease in water content after the gas treatment. Laser diffraction showed that the ion treatment increased the number of submicron-sized particles with a concomitant reduction of the number of particles with bigger sizes, leading to an increase of the volumetric surface. These very preliminary results suggest that ionised argon treatment performed in a controlled environment can be exploited to reduce the amount of interlayer water molecules in

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montmorillonite, to modify its surface characteristics and particle size distribution in a way to increase the specific surface without particle agglomeration or compaction. Applications to other clay minerals (for example, talc and kaolinite, etc.) are envisaged and in progress. Hence, both mechanical deformation and interactions of particular ionised gases can induce significative changes of the physical and chemical properties of bentonite and other clay minerals and further systematic studies are in progress in order to evaluate the potentiality for low-cost industrial applications.

Keywords: Ca-montmorillonite; Mechanical deformation; Ion treatment; Structural properties

1. Introduction

Nanostructured materials are generally artificially synthesized materials that have the constituent phases or grain structures modulated on a length scale less than 100 nm (Siegel, 1994). They can be produced by means of a wide variety of physical, chemical and mechanical methods.

Nanostructured materials are receiving great attention since their properties are different from, and often superior to, those of conventional materials that have phase or grain structure developed on coarser size scale (Siegel, 1994; Hadjipanayis and Siegel, 1994; Gleiter, 1989; Kear et al., 1989).

Natural nanostructured materials occur mainly as fine particulate minerals at or near the Earth surface (Banfield and Navrotsky, 2001). Most research on natural nanostructures, however, deals with silicate layered structures (e.g., clay minerals) which display size-dependent properties that make them candidates for many applications, such as environmental remediation or protection, industrial raw materials, catalysis, etc. (see for instance, Decarreau, 1990; Newman, 1987; Fodwen et al., 1984; Van Olphen and Fripiat, 1979; Grim, 1968). For example, the cation exchange capacity is related to the particle size and, clays may also exhibit both Bronsted and Lewis acid sites as a function of their small particle size and chemistry (Knozinger, 1993; Newman, 1987).

Recently, many studies were made to evaluate the possible effects of mechanical deformation on the structures of clay minerals, because both in research and industry fields these materials were often used only after grinding that could induce significant changes in chemical, physical and mechanical properties.

Several studies have been concerned with structural and textural changes of kaolinite (see for instance Horvath et al., 2003; Frost et al., 2001; Suraj et al., 1997; Aglietti et al., 1986; Hlavay et al., 1977), talc (Godet-Morand et al., 2002; Aglietti, 1994) especially by planetary ball mill (Kano and Saito, 1998; Filio et al., 1994), but less works have taken into account the properties of bentonites after mechanical deformation (Christidis and Makri, 2003; Filipović-Petrović et al., 2002; Volzone et al., 1987; Novak et al., 1982; Čičel and Kranz, 1981; Mingelgrin et al., 1978; Saltzman and Yariv, 1976), despite of the numerous uses in industrial, pharmaceutical and chemical applications. In addition, some of the available data are incoherent.

Mechanochemical-milling treatment of smectite could enhance the capacity for absorption of organic molecules, closely dependent from exchangeable ion (Saltzman and Yariv, 1976). On the other hand, the swelling index observed in various homoionic forms of montmorillonites before mechanical treatment was increased by mechanical deformation for short times, and reduced for longer times (Volzone et al., 1987). Textural changes lead also to an enhancement of the capacity of absorption water molecules in the interlayer of smectite (Novak et al., 1982), even though a long milling treatment leads to a progressive collapse of the structure (Volzone et al., 1987).

The surface properties of materials can be modified also by gas treatment; however, the literature in this field is less informative, especially when ionised gas interaction to the naturally occurring clays is concerned. For example, some data are available on the effect of neutral gas pressure on the dehydration reaction of interlayer water in Na-montmorillonite, Ca-exchanged and Mg-exchanged montmorillonite (Huang et al., 1994; van Groos and Guggenheim, 1984, 1987). More recent studies suggest the great importance to understand under what circumstances