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Preparation and characterization of micron and submicron-sized vermiculite

Abstract The effect of ultrasounds on natural macroscopic vermiculite flakes has been studied. Conditions for the preparation of submicron vermiculite particles of narrow particle-size distribution by sonochemistry are described. The resulting material is crystalline, as assayed by X-ray diffraction. Effects of ultrasound treatment on the mean particle size, crystal structure, crystallite dimensions in different directions, and specific surface area of the resulting particles are investigated. Under the conditions used in this work, there is a practical limit at 40 h in the sonication time for the preparation of submicron particles; longer treatment times promoted aggregation.

Key words Vermiculite · Submicron particles · Ultrasounds · Sonication · Sonochemistry

Introduction

Vermiculite is a clay mineral of significant commercial importance. In its natural state it has few useful applications. However, when it is delaminated and its particle thickness and length are decreased and controlled, it has many important applications: it is used as acoustic or fireproof insulator, lightweight and aggregate additive in concrete and plaster, coating, raw material in the preparation of flexible inorganic films, in conditioning of soils, as fertilizer carrier, absorbent, etc (Ballard and Rideal 1983; Konta 1995).

Several methods have been proposed for dissociating the macroscopic crystal of vermiculite into its fundamental layers (Garret and Walker 1962). The best-known procedure consists in heating rapidly. By heating, water between layers is vaporized, forcing the structure to expand. The layer separation using this method is imperfect and the majority of the packets formed are several orders of magnitude thicker than the fundamental layer. Ballard and Rideal (1983) have carried out the preparation of vermiculite suspensions. Magnesium ions located originally in the interlamellar space are exchanged by sodium ions. Then the sodium ions are replaced by n-butylammonium ions. During the washing of the excess of alkylammonium ions, the complex n-butylammonium-vermiculite adsorbs a large amount of water when n-butylammonium salt solution is present, and vermiculite expands as water is imbibe into the interlamellar space. During this process, the volume increases up to 30 times. The n-butylammonium vermiculite produces the well-known clay colloid system. It leads to the formation of a coherent gel at T < 14 °C. The gel collapses at T > 14 °C, forming a tactoid (Garret and Walker 1962). The tactoid gel evolution has been extensively studied as a function of the salt concentration, temperature, hydrostatic pressure, uniaxial stress along the swelling axis, and volume fraction of the clay in the condensed matter system (Smalley 1994; Williams et al. 1994). The swollen vermiculite can be mechanically delaminated in a higher shear mixer or a suitable colloidal mill. The remaining large particles of vermiculite are removed by a sedimentation process or by sieving through a 50-μm sieve. Using this method, vermiculite layers of several microns in diameter and exceedingly thin have been obtained (Ballard and Rideel 1983). The experimental process in this method is, however, complex and time-consuming, and similar alternative methods have been proposed. In these methods vermiculite is swelled and delaminated by applying a shearing force (Ou and Yang 1987; Nelson 1988).

Mechanical treatments of clays are of great importance in the preparation and processing of raw materials (Somasundaran 1978; Ovadyahu et al. 1998). Progressive amorphization takes place when grinding time increases (Sánchez Soto et al. 1995). This mechanical
treatment produces a heterogeneous material and also the formation of hard agglomerates with modified chemical reactivity. Ground clays are useful in some processes such as synthesis of ceramics, but not for the most important application of vermiculite, in which the delamination and decrease of the thickness and particle diameter are substantial while maintaining its initial crystal in order to retain properties such as insulating.

A feasible technique for particle-size reduction is ultrasound. The extended application of ultrasound as a tool for material chemistry began only in 1980. Cavitational collapse sonication on solids leads to microjet and shock-wave impacts on the surface, together with interparticle collisions, which can result in particle-size reduction (Peters 1996; Doktycz and Suslick 1990). The use of ultrasound for precipitation of fine particles (Gasgnier et al. 1994), treatment of solid surfaces (Peters 1996; Ma et al. 1995), dispersion of solids (Kathigamathan 1993), and preparation of colloids (Hobson et al. 1994) is already extensive. The effect of sonication on vermiculite could be a matter of great interest. Thus, Hinds et al. (1996), studying the particle size of clays by electrically induced birefringence, observed an average particle-size reduction in vermiculite (from 24 to 1.7 μm) for dispersions treated in a 50-W sonication bath for 25 min. In the present study, the effect of ultrasound on vermiculite is extensively studied. Changes in particle size (as measured by different techniques), structure, crystallite size, and specific surface area have been analyzed. Under certain conditions, submicron particles of vermiculite with a relatively narrow particle-size distribution have been prepared.

**Experimental**

Material

A vermiculite from Santa Olalla (Huelva, Spain) was used as starting material, having a half-unit cell composition of

\[
\text{Si}_{2.64} \quad \text{Mg}_{3.48} \quad \text{Fe}^{3+}_{0.32} \quad \text{Al}_{0.14} \quad \text{Fe}^{2+}_{0.036} \quad \text{Mg}_{0.01} \quad \text{O}_2\text{(OH)}_2 \quad \text{Mg}_{0.436}.
\]

Sonication

A high-intensity ultrasonic horn that consists of a solid titanium rod connected to a piezoelectric ceramic and a 20-kHz, 750-V powder supply was used. The apparatus can be thermostated using a double-jacket reactor.

Flakes of vermiculite were mixed in the reactor with 25 cm³ freshly deionized water and 25 cm³ hydrogen peroxide and subjected to ultrasound for periods ranging between 10 and 100 h.

Particle observation and size distribution

Transmission electron microscopy (Philips) was used for the direct examination of the particles.

Two different laser light methods were used for particle size analyses. The low angle laser light scattering (LALLS) apparatus (Malvern, Mastersizer Model) is based on the fact that when a particle passes through a laser beam it causes light to be scattered at an angle that is inversely proportional to its size. The photon correlation spectroscopy (PCS, Malvern, Zetasizer model) measures the speed of Brownian motion of the particles, calculates the diffusion speed of particles, and relates this to particle size, using the Stokes-Einstein equation. The former apparatus can be used for submicron or larger particles, the latter for submicron or nanometric particles.

**X-ray diffraction analysis**

Diffraction patterns were obtained using a diffractometer (Kristalloflex D-500 Siemens) at 36 kV and 26 mA with Ni-filtered CuKα radiation and a graphite monochromator. Samples were prepared using a side-packed holder made of aluminum. The holder was taped gently with a glass slide to consolidate the powder. To avoid preferential orientation, the results were obtained using a holder with an open window covered by a piece of filter paper between the sample and the glass slide, both being removed before X-raying. The dimensions of the coherently diffracting domains (crystallite size) of vermiculite in different directions were determined from the full width at half-maximum (FWHM) of the X-ray diffraction peaks using the Scherrer equation.

The shape factor, M, was determined from the ratio of intensities of the 004 and 060 X-ray diffraction patterns.

**Specific surface areas**

The specific surfaces areas were determined with an automatic system (Micromeritics 2200 A Model, Norcross, GA) using the BET method, at liquid-nitrogen temperature. Nitrogen gas was used as an adsorbate.

**Chemical analysis**

Chemical analysis of magnesium in supernatant solutions after the ultrasound treatment was performed by atomic absorption.

**Results and discussion**

Before sonication treatment, the original vermiculite sample consists of platelets of about 2.5 cm in length and 0.5 cm in thickness. Figures 1 and 2 show the particle-size distribution versus percentage of particle volume at different sonication times, as estimated by LALLS measurements. After a sonication period of 10 h (Fig. 1a), the median diameter decreases to 15.5 μm with a standard deviation of 12.2 μm, being the extreme particle sizes 0.11 and 76.2 μm. The median diameter decreases to 10.8 μm with a standard deviation of 6.6 μm when the sample is sonicated for 20 h (Fig. 2b). After sonication periods of 30 and 40 h (Fig. 1c, d), the median diameters decrease to 5.4 μm with a standard deviation of 4.6 and 2.4 μm with a standard deviation of 2.6 μm, respectively. Moreover, after a sonication period of 40 h (Fig. 1d), the distribution shows the presence of two types of particles with maximum volume percentages at 0.52 and 2.4 μm. These two types of particles are also detected for shorter sonication times, but the percentages of the smallest particles were very small. These results show that on increasing sonication time from 0 to 40 h, the maximum volume percentages of particle size decrease drastically, changing from macroscopic size to two types of particles at 0.5 and 2.4 μm. On increasing