Near-infrared investigation of folding sepiolite

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ABSTRACT

Sepiolite is an industrially important clay mineral of the palygorskite-sepiolite group with alternating 2:1 ribbons and hydrated tunnels. Dry sepiolite, Mg₆Si₁₀O₂₆(OH)₁₂(ıH)₂₃, loses half of its OH₂ content upon further heating and undergoes a structural collapse known as folding. This treatment is considered essential for enhancing the absorptive properties of the clay. In this paper, the folding process is studied by near-infrared (NIR) spectroscopy, mid-infrared attenuated total reflectance (ATR), and thermogravimetric analysis (TGA). The folded state, Mg₆Si₁₀O₂₆(OH)₁₂(OH)₂₃, reveals a new spectrum of fundamental and higher-order OH₂ vibrations, as well as systematically split doublets of structural and surface O-H vibrations. Detailed assignments for the stretching, combination, and overtone O-H modes are proposed on the basis of the two non-degenerate populations of Mg-OH (and SiOH) present in the folded state. It is demonstrated that NIR is of particular diagnostic value in monitoring conveniently and non-invasively the folding process, which appears as a simple transition between well-defined dry- and folded-structures. At the level of elementary sepiolite particles (laths), folding is described as a cooperative process requiring the integrity of the ribbons and the inter-ribbon linkages (moderately acid-leached sepiolite does not fold). This is opposed to the skewed and sometimes complex OH₂ desorption trace observed by high-resolution TGA, which appears to indicate a multimodal distribution of laths. It is proposed that the rate-determining step for a sepiolite (also, palygorskite) lath to fold is the creation of a critical zone at mid-particle length, which is OH₂-deficient and contains unstable, fivefold-coordinated Mg²⁺.

Keywords: Sepiolite, palygorskite, folding, acid activation, near-infrared spectroscopy, ATR, high-resolution TGA

INTRODUCTION

Sepiolite is a member of the palygorskite-sepiolite group of clay minerals with main industrial applications as rheology modifier and absorbent, but also as carrier, catalyst support, etc. (Galan 1996; Álvarez et al. 2011). It is a trioctahedral phyllosilicate with ideal formula Mg₆Si₁₀O₂₆(OH)₁₂(OH)₂₃·zH₂O per half unit cell (z ≈ 8 at ambient), a modulated structure and a lath-like particle morphology (Brauner and Preisinger 1956; Post et al. 2007). Modulation is manifested by the periodic reversal of the apical Si-O bonds in the tetrahedral sheet every three pyroxene terminations of the tetrahedral sheet (Fig. 1a). As a result, sepiolite consists of alternating 3-chain, trioctahedral 2:1 ribbons and hydrated tunnels. The term “tunnel” is preferred here over the more commonly used term “channel” because the latter is reserved to describe the grooves (i.e., open “tunnels”) running along the external surface of the particles. Two types of tunnel H₂O are shown in the formula: two coordinated OH₂ per “exposed” Mg²⁺ cation on the edges of the discontinuous octahedral sheet and “zeolitic” (2) H₂O filling the tunnels. In addition to these types, there is also H₂O on the external surface of the particles, interacting with the abundant silanol (SiOH) terminations of the tetrahedral sheet, and physisorbed H₂O. All H₂O except the Mg-coordinated OH₂ species desorb below ~130–150 °C (Nagata et al. 1974; Frost and Ding 2003), leaving the structure open (Post et al. 2007) and the inner surface of the tunnels exposed (Ruiz-Hitzky 2001).

Heating palygorskite-sepiolite clays at higher temperatures (~300 °C) induces the removal of one OH₂ per Mg, causes the folding of the structure (Fig. 1b) and results in the collapse of the tunnels (Preisinger 1963; Post et al. 2007). This folding event is of technological importance (“calcination”) because it marks the loss of microporosity and colloidal properties of the clays, and leads to the enhancement (“activation”) of mesoporous absorptive properties, such as oil bleaching performance (McCart er et al. 1950; Haden and Schwint 1967; Álvarez et al. 2011).

Hayashi et al. (1969) were the first to study systematically the high-temperature transformations of sepiolite by mid-infrared spectroscopy and XRD. In the temperature range of folding, they found that the single Mg₆O-H stretching band of sepiolite splits into two components due to the simultaneous presence of folded and unfolded structures. Subsequent thorough mid-infrared studies by Serna et al. (1975) and Prost (1975) confirm the observations of Hayashi et al. (1969) regarding band splitting, but assign