

Near-infrared investigation of folding sepiolite

MARIA TSAMPODIMOU¹, VANESSA-JANE BUKAS^{1,*}, ELIZABETH T. STATHOPOULOU^{1,†},
VASSILIS GIONIS¹ AND GEORGIOS D. CHRYSOSIKOS^{1,‡}

¹Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vass. Constantinou Avenue, Athens, 11635, Greece

ABSTRACT

Sepiolite is an industrially important clay mineral of the palygorskite-sepiolite group with alternating 2:1 ribbons and hydrated tunnels. Dry sepiolite, $\text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4(\text{OH}_2)_4$, loses half of its OH_2 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, $\text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4(\text{OH}_2)_2$, reveals a new spectrum of fundamental and higher-order OH_2 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_3OH (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 OH_2 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 OH_2 -deficient and contains unstable, fivefold-coordinated Mg^{2+} .

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