

Research Progress in Microstructure Research Methods of Palygorskite Mineral Nanomaterials

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Abstract. Palygorskite mineral nanomaterials are typical porous materials widely existing in nature and have many micropores and mesopores, which could play an active role in many fields such as thermal insulation functional additive for composite materials. Based on the above reason, this paper briefly summarized the microstructure research progress of palygorskite mineral nanomaterials, and related research orientations were also proposed.

Introduction

Palygorskite, also called as attapulgite, is a natural fibrous nanoscale clay mineral and belongs to sepiolite group minerals [1-3]. The ideal crystal structure of palygorskite and a unit cell formula of $(\text{Al}_2\text{Mg}_2)\text{Si}_8\text{O}_{20}(\text{OH})_2(\text{OH})\cdot 4\text{H}_2\text{O}$ was firstly proposed by Bradley(1940)[4]. Palygorskite with a 2:1 phyllosilicate ribbon-layer structure is linked to two continuous SiO_4 tetrahedron sheets along a set of Si-O-Si bonds and a discontinuous octahedron sheet [5-6].

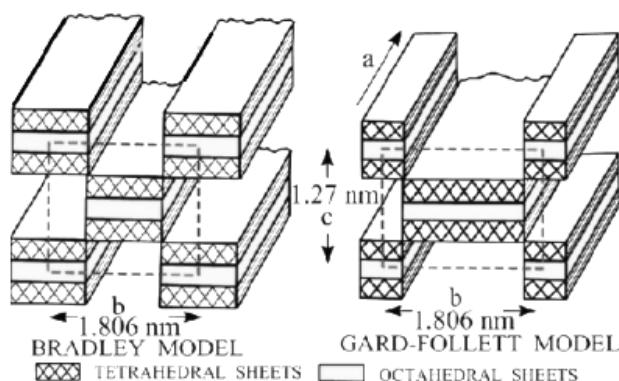


Fig.1 Diagram of crystal structure of palygorskite

The ideal crystal structure of palygorskite endows it with a dioctahedral character in which Mg ions occupy the octahedral sites. However, many researches have found that di- or tri-valent cations (Mg^{2+} , Al^{3+} , Fe^{3+} or Fe^{2+}) can replace partially the octahedral cations in the formation process of minerals due to the isomorphic phenomenon, and these cations usually inhabit four of the five octahedral sites with $\text{R}^{2+}/\text{R}^{3+}$ ratio close to 1 [7-9]. Thus, this unique nanorod-like crystal structure of porous palygorskite empowers itself with higher specific surface area, better ion-exchange capacity, and superior thermal and mechanical stability. It has been applied in many industrial fields,

such as a potential absorbent to remove dyes, reinforcing fillers, color matters and versatile carriers [10-16]. The diagram of crystal structure of palygorskite is shown in Fig.1.

In primitive cell of palygorskite, different kinds of atoms or molecule are arranged according to certain rules, as shown in Fig.2. The above peculiar structure of palygorskite results in good performance of adsorption, rheology and catalysis.

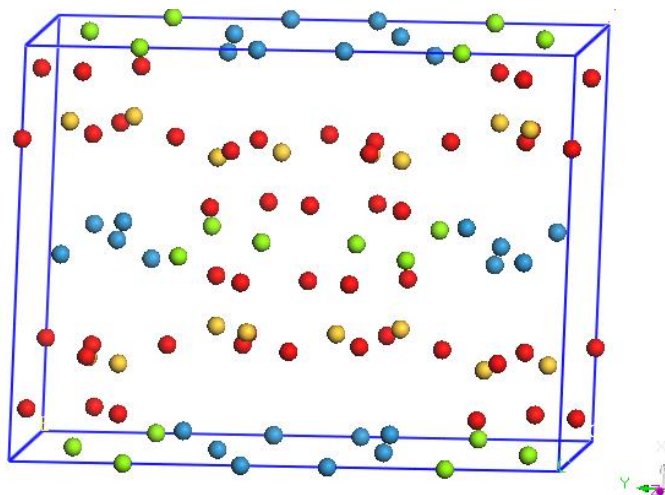


Fig. 2 Diagram of atom position in primitive cell of palygorskite

Research Methods on the Microstructure of Palygorskite Mineral Nanomaterials

Many efforts focused on the palygorskite characterization via the technique of TEM until now. Esquivel et al. explored the massive mountain leather from a Lanitos mining district mine in Chihuahua, Mexico, which was characterized through the analytical techniques of XRD, SEM, TEM, and SAED and found to be a complex mineral composite composed of intermixed nanofibers of palygorskite $((Mg, Al)_a(SiO_x)_b(OH)_c \cdot nH_2O)$ and birnessite $(Ca_a(MnO_2)_b \cdot nH_2O)$ and intercalated with cleavage flakes of hematite (Fe_2O_3). This complex nanofiber mass was fabricated from an extremely tough material which could not be crushed in the rock crusher. The material was of interest especially in light of the fact that this natural nanocomposite was formed from a hydrothermal regime that dated to roughly 30 million years ago. Mark et al. [18] devoted to defect structures contained within individual fibers through the observation technique of transmission electron microscopy (TEM). They discovered that defects were common, and three major kinds had been observed: omission of groups of 2:1 layer ribbon modules that created open channel defects, planar defects, and stacking disorder observed as 180° rotations of the entire polysomes. And they also proposed these defects may enhance crystallization rates of fibers and some defects obviously sealed parts of channels within a fiber and probably blocked exchange of cations, H_2O , and organic molecules. The defects detected in the study may elucidate variations in many properties of palygorskite minerals, including exchange properties about large organic molecules and chemical composition. Darvishi et al. [19] fabricated palygorskite nanoparticles via the facile sonochemical method, and characterized by the techniques of X-ray fluorescence analysis (XRF), X-ray powder diffraction (XRD), thermal gravity analysis (TGA), differential thermal analysis (DTA) and infrared spectroscopy. The morphology and size of the nanorods were inspected by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

Xie et al. [20] investigated the morphological characteristics and microstructures of the authigenic palygorskite occurring with smectite and carbonate minerals in the Late Miocene Red Clay Formation, on the Chinese Loess Plateau, monitored by the techniques of the powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (TEM). SEM analyses indicated that palygorskite was a common component. Delicate palygorskite fibers radiate from the margins of platy smectite, indicating a pedogenic origin during

the weathering of pre-existing smectite, a process that involved intense dissolution of the smectite and an adjustment in its structure. Moreover, palygorskite emerges as coatings, pore-fillings, and pore-bridging cements among dolomite rhombs, suggesting that the fibrous palygorskite is produced by a direct dolomite precipitation from pore fluids, mostly after dolomite crystallization. Their studies interpret that the red clay sediments undergo a steady dry–warm climate with periods of high rainfall and evaporation. The warm climate would have increased the rate of weathering of minerals, and subsequently enhanced the ions content and pH in the soil solutions during dry periods. This soil environment is favorable for smectite transformation and palygorskite deposition. On account of their study, the influence of the environmental and paleoclimatic changes on the formation of palygorskite in the arid soils of the Chinese Loess Plateau has been understood further. Tazaki et al. [21] discovered the smectite-to-palygorskite transition in North Pacific deep-sea sediments by transmission electron microscopy (TEM). The original smectite was characterized by showing crinkled thin films whereas well crystallized palygorskite formed elongated lath-shaped crystals. Palygorskite formation appeared to be initiated on the surface of smectite films. The initial short needles of palygorskite exhibited predominantly 4.0–4.2-Å layers which evolved into fibres and lath-shaped crystals. At a later stage, crystals with well defined mozaic structure exhibited 6.3-Å and 3.15-Å spacings, (200) and (400) planes of palygorskite. Electron diffraction patterns of elongated laths presented a combination of smectite (15.3 Å), chlorite (7.4 Å) and palygorskite (10.2 Å and 6.3 Å) spacings. The mozaic structure was not regarded as the final product, which was composed of Si:Al:Fe:Mg in an approximate ratio 5.1:1.2:1:1 via the detection of EDX, while for the initial smectite the ratio was 5.1:2.3:1:0.4. Their study also illustrated the successful application of high resolution electron microscopy in the mineral transformations determination.

Development Trend of Microstructure Research of Palygorskite Mineral Nanomaterials

In recent decades, there are many reports about microstructure feature, crystal structure and thermal stability; however, the studies on inner surface, adsorption and channel structure of palygorskite are mainly performed by BET analysis. The tested size and distribution of pores are different significantly from theoretical results due to the limitation of testing methods and accuracy. The experimental research such as TEM analysis combined with cutting technique on inner channel should be emphasized in future research, because the microstructure could be observed directly rather than previously indirect research [22-23].

Conclusions

Palygorskite mineral nanomaterials possess many micropores and mesopores, which could play an active role in many fields such as adsorptive functional additive for composite materials. The work summarizes the related research progress of microstructure of palygorskite mineral nanomaterials, and points out the experimental method based on the TEM analysis is the appropriate method for directly testing palygorskite mineral nanomaterials.

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