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Research paper

Solvothermal evolution of red palygorskite in dimethyl sulfoxide/water

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ABSTRACT

Red clay deposit with palygorskite (Pal) as the main component is abundant on the earth, but it is not yet fully utilized in industrial fields because of its deep color. In this paper, we employed a facile one-step solvothermal process to treat red Pal using water, dimethyl sulfoxide (DMSO) and DMSO/water as solvents and studied the effect of this process on the structure, physico-chemical characteristics and color of red Pal. It was revealed that the brick-red Pal still remain its color unchanged after solvothermal reaction in water or DMSO solvent, but it converted to white after reaction in dimethyl sulfoxide (DMSO)/water mixture. When the volume ratio of DMSO to water is 2:1, the product has the best whiteness of 83.3%. The associated minerals such as quartz, feldspar and muscovite did not change significantly and the rod-like crystalline morphology of Pal still remains intact after solvothermal reaction. The leaching of Fe(III) in Pal, the dissolution of α-Fe_2O_3 and the reduction of Fe(III) by the dimethyl sulfide (the reaction product of DMSO with water) to Fe(II) contributed to the conversion of red Pal to white one. The conversion of brick-red Pal to white would lay a foundation for the applications of deep-colored clay minerals in the fields of chemical industries and composite materials.

1. Introduction

Palygorskite (Pal) is a kind of naturally abundant magnesium, aluminium-rich silicates with nanorod-like crystal morphology, nanopores and active surface groups (Bradley, 1940; Galán, 1996; Suárez and García-Romero, 2011). It has been widely applied in many fields such as adsorption (Wang et al., 2015; Berhane et al., 2016), colloids (Xu et al., 2013), nanocomposites (Huang et al., 2012; Zhang et al., 2016a; Tang et al., 2016), sealing materials (Galán et al., 2011), catalysis (Papoulis et al., 2013; Shi et al., 2016), hybrid pigment (Giustetto et al., 2014; Tian et al., 2017), antibiotic materials (Cai et al., 2013), animal feeding (Chen et al., 2016), pharmaceutical product (López-Galindo et al., 2011) and so on. Unlike the common two-dimensional clay minerals, Pal has a 2:1 ribbon-layer structure composed of two continuous tetrahedral sheets and one discontinuous octahedral sheet, which are joined together by Si—O—Si bonds to form nano-tunnels with the size of 0.37 nm × 0.64 nm along *c* axis (Bradley, 1940; Drits and Sokolova, 1971). There are three types of different sites in the octahedral sheet that can accommodate metal ions: edge (M3), middle (M2) and interior (M3) (Suárez et al., 2007). The M3 sites can be occupied by Mg(II) and Al(III) and Fe(III), while the M2 sites are usually occupied by Mg(II) and Al(III). The cations in the octahedral sheets can be replaced with the similar ion species due to isomorphism substitution phenomenon, of cations on octahedral sites, natural Pal with different composition, so that the composition and structure of natural Pal are different from the theoretical ones, and the actual formula of Pal is expressed as $(Mg_{5-y-z}R_{y\square z}^{3+})(Si_{8-x}R_x^{3+})O_{20}(OH)_2(OH_2)_4R^{2+}_{(x-y+2z)/2}(H_2O)_4$ (where, □ is a vacant site, and *R* represents Mg, Al or Fe) (Bailey, 1984; Newman and Brown, 1987), or $(Mg_2R_2^{3+}\square_1)(Si_{8-x}Al_x)O_{20}(OH)_2(OH_2)_4{\cdot}R_{x/2}^{2+}(H_2O)_4$ (where x = 0–0.5) (Galán and Carretero, 1999; Ruiz-Hitzky et al., 2011).

In fact, most of the natural Pal is mainly formed in the Tertiary sediments through the deposition mechanism in marine, bay, lagoon, and lake conditions (Verrecchia and Le Coustumer, 1996). Xie et al. (2008) firstly reported an authigenic Pal found in the sediments of Lingtai red clay, and discussed its occurrence and paleoclimatic implications. Xie et al. (2013) also reported that there are huge reserves of red Pal minerals in western China, associated with quartz, feldspar, illite, chlorite and muscovite. In this type of clay mineral, the Mg(II) or Al(III) in the octahedral sheet of Pal were partially replaced by Fe(III), making it appears brick-red color (Akbulut and Kadir, 2003; Xie et al., 2013). Although this kind of clay mineral is extremely rich in reserves on earth, the complex components and deep color make it difficult to get large-scale applications in the industrial fields. Therefore, it is significant to study the structure evolution and color transformation of natural red Pal under different conditions, and thus to extend its

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applications in industrial field.

It has been reported that the solvothermal process is an effective way to improve the structure of Pal and enhance its performance because in this process the inert *Si*-O-M bonds can be broken to form new active groups (Wang et al., 2015, 2016; Zhang et al., 2016b). The morphology and physicochemical properties of Pal were also changed with the change of microscopic structure. However, changing the color of Pal from deep color to white is still challenging. It is expected that the brick-red Pal can be transformed into white through a simple solvothermal process, thereby enhancing their application values in industrial fields.

In order to clarify the change of structure and physico-chemical properties of Pal after solvothermal treatment, and to lay a foundation for the transformation of brick-red Pal into white, we treated the brick-red Pal in three different medium under solvothermal condition. It was found that Pal shows no color change after treated in sole water or common organic solvents, but it changes to white after treatment in dimethyl sulfoxide (DMSO)/water mixture. The change of structure and physico-chemical properties of Pal after solvothermal treatment was studied systematically in this paper.

2. Experimental

2.1. Materials

Natural brick-red Pal was from Jingyuan Mine located at Jingyuan County of Gansu Province in China. The main chemical compositions are Al_2O_3 16.01%, Na_2O 2.42%, MgO 5.02%, CaO 3.96%, SiO_2 52.38%, K_2O 3.72% and Fe_2O_3 7.46%. The cation exchange capacity (CEC) is 12.8 mmol/100 g, and the amount of methylene blue adsorbed is 13.9 mmol/100 g. Dimethyl sulfoxide (DMSO, $SO(CH_3)_2$) with analytical grade was purchased from Tianjin Chemical Reagent Factory (Tianjing, China). All other reagents used in this study are of analytical grade and all solutions were prepared with deionized water.

2.2. Solvothermal processing of brick-red Pal

Firstly, the brick-red Pal was treated with 5 mass% of the aqueous solution of HCl at the solid/liquid ratio of 1/10 for 240 min to remove the associated carbonates. Then, the resultant aqueous dispersion was passed through a 200-mesh sieve to remove large-size grains and quartz. Finally, the solid product was separated by centrifugation at 5000 r/min, fully washed to pH around 7 with deionized water, and dried to constant mass in an oven at 105 °C for 4 h. The dried product was crushed and passed through a 200-mesh sieve.

The pretreated brick-red Pal was uniformly dispersed in 60 mL solvents (water, DMSO or DMSO/water mixture (v/v = 2/1)) at the solid-liquid ratio of 1/5 (m/v) by vigorous stirring for 5 min. The resulting dispersion was transferred to 100 mL of autoclave with Teflon lining, and then allowed to react at 180 °C for 24 h. After the autoclave was naturally cooled to room temperature, the solid product was separated by centrifugation at 5000 r/min, and then thoroughly washed with deionized water and ethanol in turn. Finally, the solid product was dried under vacuum and at 60 °C to a constant mass. The brick-red raw Pal was marked as RPal, and the solvothermal treated Pal in water, DMSO and DMSO/water mixture solvent are marked as WPal, DPal and DWPal, respectively.

2.3. Characterizations

FTIR spectra were measured using a Fourier transform infrared spectroscopy (Thermo Nicolet NEXUS TM, USA) in the wavenumber range of 4000–400 cm^{-1} after the samples were pressed as KBr pellets. SEM images were taken by a JSM-6701F Field-emission scanning electron microscope (JEOL, Ltd. Japan) after the samples were dispersed in ethanol, dropped onto a copper stub and treated by spraying gold nanoparticles. TEM images were taken by a TECNAI-G2-F30 transmission electron microscope (FEI, USA). X-ray diffraction (XRD) patterns were collected by an X'pert PRO X-ray powder diffractometer (PAN Analytical Co., Netherlands) equipped with a Cu-Kα radiation source (40 kV, 40 mA) from 3 to 80° with a step interval of about 0.167°, using Cu-Kα radiation of 0.1542 nm. The specific surface area (S_{BET}) was measured using an ASAP 2010 analyzer (Micromeritics, USA) at 77 K, and the values were calculated by the Brunauer-Emmett-Teller (BET) method. The total pore volume (V_{total}) and the micropore volume (V_{micro}) were obtained from the volume of liquid N_2 held at the relative pressure P/P_0 = 0.95 and estimated by the *t*-plot method ultimately. TG and DTG curves were measured from 25 to 800 °C using a STA 6000 (PerkinElmer Instrument Co., Ltd. USA) under N_2 atmosphere at a heating rate of 10 °C/min. The chemical composition was determined using a MiniPal 4 X-ray fluorescence spectrometer (PANalytical Co., Netherland). Mossbauer spectra were obtained at room temperature with a MS-500 (Oxford Company, Britain) electromechanical spectrometer working in a constant acceleration mode. A ^{57}Co/Pd source and a-Fe standard were used. The experimentally obtained spectra were fitted to mathematical processing according to the least squares method. The parameters of hyperfine interaction such as isomer shift (IS), quadrupole splitting (QS), hyperfine magnetic field (Hhf), and the relative area of the partial components in the spectra were determined.

3. Results and discussion

As can be seen from the digital photos shown in Fig. 1, the RPal, WPal and DPal samples are brick-red and the DWPal sample is white. The change in the structure and physicochemical properties of Pal after solvothermal treatment were discussed in detail below.

3.1. XRD analysis

The changes of the crystal phase of Pal before and after solvothermal treatment was studied by XRD analysis. As shown in Fig. 2, several crystal phases can be observed in the XRD curve of RPal. The reflections at 2θ = 8.47° (d = 1.0441 nm), 13.62° (d = 0.6496 nm), 2θ = 19.80° (d = 0.4480 nm) and 2θ = 35.01° (d = 0.2561 nm) can be attributed to the characteristic reflections of (110), (200), (040) and (400) crystal planes of Pal, respectively (Bradley, 1940; Galán et al., 1994). In addition, the reflections at 2θ = 8.86° (d = 0.9972 nm), 2θ = 17.99° (d = 0.4931 nm) and 2θ = 29.95° (d = 0.2982 nm) are ascribed to the reflections of (002), (004) and (115) crystal planes of muscovite, respectively (Standard card: JCPDS NO. 06-0263) (Song et al., 2005; Yu et al., 2006). The reflections of clinochlore at 2θ = 6.22° and 12.40° (Carroll, 1970), the reflections of quartz at 2θ = 20.84°, 26.63°, 50.12° and 59.94° (Zhou et al., 2013), and the reflections of feldspar at 2θ = 27.96° (Su et al., 2016) also appear in the XRD patterns of Pal. These reflections can still be observed in the XRD

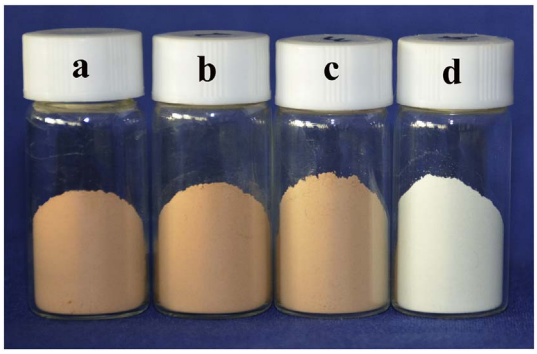

Fig. 1. The digital photos of (a) RPal and the solvothermal products in different solvents: (b) water, (c) DMSO, and (d) DMSO/water (v/v = 2/1) mixture.