Powder Technology 280 (2015) 173–179

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Effect of grinding time on fabricating a stable methylene blue/palygorskite hybrid nanocomposite

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ARTICLE INFO

Article history:
Received 18 November 2014
Received in revised form 22 March 2015
Accepted 20 April 2015
Available online 26 April 2015

Keywords:
Palygorskite
Hybrid nanocomposites
Grinding
Microstructure
Stability

ABSTRACT

The nanoscale dispersion of the crystal bundles or aggregates of natural palygorskite (PAL) is the key factor to prepare a stable PAL-based hybrid nanocomposite. The appropriate grinding process can effectively disaggregate the crystal bundles of PAL as dispersed nanorods and promote its interaction with organic molecules. In this study, a series of methylene blue/palygorskite (MB/PAL) hybrid nanocomposites were prepared by a facile mortar grinding process, and the effects of grinding time on their structure and stability were intensively investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectra, Brunauer–Emmett–Teller (BET), thermal gravimetric analysis (TGA) and UV–vis techniques, as well as the resistance tests to acid, heat and UV-light. It was found that the control of grinding time is the key point affected the stability of hybrid structure, because it greatly influenced the removal of the water molecules, the change of *d*-spacing of (110) crystal plane and the organic/inorganic interaction between MB molecules and PAL. The aggregates of PAL crystals were highly dispersed as individual nanorods after being ground for 30 min, and the MB molecules are more easily to be adsorbed on the nanorods of PAL or be encapsulated in their channels, so the thermal stability, acid and UV-light resistance of the nanocomposites were evidently enhanced.

1. Introduction

Organic–inorganic hybrid materials have recently received growing attention in both academic and industry areas owing to their superior stability enhanced by the "host/guest" hybridization interaction [1–3]. This kind of hybrid materials are similar with the famous "Maya Blue" pigment prepared by ancient Mayas for decorating mural paintings, pottery and statues [4], which still carry a beautiful blue to turquoise color even though they have been exposed to environment for more than thousands of years [5,6]. In the last decade, the unusual features of Maya Blue inspired researchers to develop stable hybrid materials by hybridizing organic molecules with clay minerals, e.g., palygorskite, sepiolite, montmorillonite, kaolinite, and zeolites, and it has been confirmed that palygorskite is the irreplaceable candidate to fabricate a hybrid material with superior stability as the Maya Blue [3,7–10].

Palygorskite (PAL) is a hydrous Mg-, Al-rich silicate clay mineral with a rod-like crystal morphology. It has a ribbon-layer structure constructed of ribbons of 2:1 phyllosilicate modules comprised of linked double silicate chains that sandwich Mg, Al-(O,OH) octahedral strips [11]. Large amounts of channels parallel to the phyllosilicate ribbons exists in the crystal structure, and are usually filled by the zeolitic water molecules that are weakly attached to the Mg, Al-OH by H-bonding [12]. The special structure features of PAL make it easily to strongly interact with small organic molecules (i.e., dye, organic solvents [13]) to form stable hybrid structure, such as the highly stable Maya Blue pigment derived from indigo and PAL [14–16]. In such hybrid materials, organic molecules may exist in the following forms: (a) adsorbed onto the external surface of PAL [17]; (b) blocking the entrances at the edges of PAL channels [18,19]; or (c) enter into the channels of PAL [20–22]. It has been recognized that the stability of such hybrid materials is derived from and is also dependent on the stronger interaction between dye molecules and PAL. The dye molecules have usually been loaded onto PAL by an adsorption process and then the resultant dye-loaded PAL was grinded and treated by heating to form a hybrid structure. The grinding process is especially important to the formation of hybrid structure, because it can improve dispersion of PAL crystal bundles, release the pores or channels of PAL, and thus may intensify the interaction between dye and PAL. Therefore, the dispersion scale of PAL nanorods is important to the formation of an stable organic–inorganic hybrid materials.

In general, better dispersion of the PAL nanorods, with more available pores or channels, can make sure the dye molecules entirely cover on their surface and then be encapsulated in the channels after heating treatment. However, natural PAL exists as "woodpile-like" aggregates or crystal bundles owing to the strong hydrogen bonding and

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http://dx.doi.org/10.1016/j.powtec.2015.04.046
0032-5910/

Van der Waals interactions among rods [23,24], the single PAL nanorods are hardly obtained even they were dispersed in the solution [25]. In that case, the covering of the dye molecules on the surface of PAL is extremely limited, and the derived dye/PAL hybrid materials are hardly to reach a satisfactory performance. Hence, the disaggregation of PAL crystal bundles into individual rods becomes the key factors to affect the stability of the PAL-based hybrid materials.

Grinding is a conventional method used to change the physicochemical features of the powder materials in many cases [26–29]. For instance, it has been demonstrated that mortar grinding is more effective to realize the intercalation modification of the aminomontmorillonite compared with the solution stirring and the microwave heating [30]. The mortar grinding process is also an effective technique to mix the dye with the clay mineral in preparation of the PAL-based hybrid material [10,19,31]. But these studies are mainly focused on the effects of dye concentration or heating treatment on the properties of the hybrid materials, and rarely paid attention to improve the performance by altering the dispersion scale of the PAL. When the external force overcomes the hydrogen-bonding or van der Waals forces existed among rods, the aggregates or crystal bundles can be disaggregated. But excessive mechanical treatment may break the nanorods. The difference in the dispersion scale of the PAL rods, resulted from different grinding action, can affect the property of the dye/PAL hybrid materials. Therefore, it is essential to explore the optimum grinding condition for preparing the stable dye-PAL nanocomposite.

Dry-state grinding was commonly used to prepare the dye/PAL hybrid nanocomposite, and the effect of zeolitic water was mainly concerned. In fact, the existence of moderate adsorbed water during grinding may play more important role for the dispersion of the aggregates or crystal bundles of PAL. PAL show higher adsorption capacity for the water soluble dye such as methylene blue (MB) in solution [32–35]. In order to study the effect of grinding time, the optimal water content of 37% was determined by our experiments. At this optimal water content, the effect of grinding time on the microstructure and stability of MB/PAL nanocomposite to resist acid and UV-light was investigated by combining Fourier transform infrared (FTIR) spectra, X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), Brunauer–Emmett–Teller (BET), UV–vis–NIR spectra and thermal gravimetric analysis (TGA) techniques.

2. Experimental

2.1. Materials

Palygorskite (PAL) is produced in Huangnishan mine, Jiangsu province, China, with the chemical composition of SiO_2 (71.43%), Al_2O_3 (12.35%), Fe_2O_3 (7.69%), MgO (8.91%), K_2O (1.48%), CaO (1.79%), Na_2O (0.66%). Methylene blue (MB, indicator grade) was purchased from Alfa Aesar and used as received. Distilled water was used for all the experiments.

2.2. Preparation of MB/PAL hybrid nanocomposites

50 g of PAL powder was dispersed in 500 mL of distilled water under vigorous stirring at 800 rpm for 1 h to obtain a homogeneous suspension. Then, 8 g of MB powder was slowly added into the suspension under continuous stirring. After the MB dye being dissolved completely, the stirring speed was adjusted to 200 rpm and continued for 24 h at room temperature to reach the saturation adsorption. Then, the solid was separated from the solution by centrifugation at 5000 rpm for 10 min. The maximum adsorption amount of MB onto PAL is 158 mg/g, as calculated by the method reported by Liu et al. [32]. The wet MB/PAL sample was firstly dried at 105 °C for 60 min to reach the water content of 37%, and then it was divided into six equal parts. One part was only heated at 105 °C for 4 h without grinding, named as MB/PAL. The other five parts were ground at room temperature in a mortar-type grinding apparatus (Beijing Grinder instrument equipment Co., Ltd.) for 10, 20, 30, 45, and 60 min at 60 rpm/min, respectively, and then were heated at 105 °C for 4 h. The resultant samples were denoted as MB/PAL-10, MB/PAL-20, MB/PAL-30, MB/PAL-45, and MB/PAL-60 according to the different grinding time, respectively.

2.3. Acid resistance

0.05 g of the sample was mixed with 25 mL of 1.0 mol/L aqueous solution of hydrochloric acid in a 50 mL conical flask and shaken at 120 rpm (30 °C) for 24 h to reach the desorption equilibrium. Then the suspension was centrifuged at 5000 rpm for 10 min, and the concentration of the MB dissolved in the supernatant was measured using a Specord 200 UV–vis spectrophotometer (Germany) with a wavelength range of 190–1100 nm.

2.4. UV-light resistance

0.5 g of the MB/PAL sample was smooth-spread in a 4-centimeter aluminium foil box and sealed in a Fluorescent UV test chamber (LX-UV, Xin Lang Electronic Inc., China), irradiated with a UV-B spectrum of 320 W/m^2 at 60 °C for 240 h. The acid resistance of the final irradiated MB/PAL samples was evaluated according to the process of 2.3.

2.5. Characterization

The Fourier transform infrared (FTIR) spectra were recorded in the range of 4000–400 cm^{-1} on a Nicolet NEXUS FTIR spectrometer using the KBr pellets. The X-ray diffraction patterns were collected on a X'pert PRO diffractometer with Cu-Ka radiation (40 kV, 30 mA), the samples were scanned at a rate of 2°/min from 3 to 70°. Thermal gravimetric analysis (TGA) was tested on a Diamond TG-DTA 6300 thermal analyzer with the heating temperature from 35 to 900 °C and heating rate of 10 °C min^{-1} under a nitrogen atmosphere. The specific surface area, pore volume and pore size distribution of the samples were measured on an Accelerated Surface Area and Porosimetry System (Micromeritics, ASAP2020, Atlanta, USA) using N_2 as an adsorbate at 77 K. The FESEM morphology of the MB/PAL samples was observed on a Field Emission Scanning Electron Microscope (JSM-6701F, JEOL, Ltd., Japan) after coating a thin golden film on the sample. UV–vis–NIR spectra were obtained on a Perkin Elmer Lambda 900UV–vis–NIR Spectrometer (USA).

3. Results and discussion

3.1. FESEM analysis

The FESEM images of the raw PAL, MB/PAL-10, MB/PAL-30 and MB/PAL-60 samples are shown in Fig. 1. The nanorods in raw PAL tightly packed together to form a lot of bulk aggregates due to the strong hydrogen bonding and Van der Waals interaction existed among rods (Fig. 1a) [36]. After adsorbing MB and grinding for 10–30 min, the aggregates of PAL rods were evidently dissociated, and many individual nanorods with the length of 0.5–1 μm could be observed (Fig. 1b and c). However, the length of many rods obviously becomes shorter after being grinded for 60 min, despite the dispersion degree of PAL rod crystals becomes better (Fig. 1d). Also, a lot of submicrometer particles can be observed, which suggest that the PAL rod crystal bundles have been seriously damaged. The grinding process can generate strong compression, shearing stress and looping stress, which may tear up the crystal bundles into single nanorods. However, the single crystals of PAL would be seriously damaged if imposing the strong shearing stress on them for a long time. Therefore, it is crucial to explore the role of grinding time on the dispersion scale, microstructure, and the host/guest interaction between MB and PAL. The appropriate grinding time is the key to dissociate the aggregates of PAL rod crystals for preparing the stable MB/PAL hybrid nanocomposite.