Applied Clay Science xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Applied Clay Science

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

Research paper

Surface organo-functionalization of palygorskite nanorods with γ-mercaptopropyltrimethoxysilane

Peng Liu*, Hongxing Wang, Changou Pan

State Key Laboratory of Applied Organic Chemistry, Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China

ARTICLE INFO

Keywords:
Surface functionalization
Palygorskite
Silane modification
Dispersibility, microstructure

ABSTRACT

Palygorskite (Pal) nanorods have attracted more and more interests in polymer-based nanocomposites. Surface modification with silane is the main approach to improve their dispersibility in organic matrices. In the present work, the functionalization of Pal nanorods with silane was optimized in detail, aiming to the high dispersibility in organic matrices, including the reaction condition (temperature and time) and feeding ratio of silane (e.g. γ-mercaptopropyltrimethoxysilane, MPS). The morphology of the products was analyzed with TEM technique. Based on the characterization results and the sedimentation phenomena of their dispersions in toluene, the microstructure of the organo-functionalized palygorskite (OPAL) was established, in which locking effect and welding effect of silane were proposed.

1. Introduction

As an abundant clay mineral, palygorskite has attracted more and more interests in polymer-based nanocomposites, due to its unique shape of nanorod and high aspect ratio (Ruiz-Hitzky et al., 2015). However, due to its strong polar surface, the palygorskite (Pal) nanorods should be surface modified to improve their dispersibility in polymeric matrices, with small organic molecules or polymers (Kango et al., 2013; Liu, 2007; Wang and Wang, 2016).

Organo-silanes are one kind of the most widely used coupling agents for the surface organo-functionalization of the hydroxyl terminated substrates (Haensch et al., 2010). They could covalently anchor onto the substrates to introduce functional groups, e.g. as in grafted polymer (Ruckenstein and Li, 2005). After modification with silane, inorganic nanoparticles usually exhibit efficiently enhanced dispersibility in liquid media (Kumiya and Iijima, 2010). The effect of the modification conditions on the dispersibility of the nanoparticles have been thoroughly investigated, including pH value (Campelj et al., 2009; Pazokifard et al., 2015; Wang et al., 2011), reaction temperature (Campelj et al., 2009), reaction time (Wang et al., 2011), solvents (Iijima et al., 2009), etc. The silane modification has become the most used surface functionalization method to improve the dispersibility of the nanoparticles. During the process of silane modification, the amount of silane usage is a very important parameter. The excessive coupling agent would lead to polycondensions between the nanoparticles and silanes via silica bridges and form aggregations (Palmai et al., 2013), which would decrease their dispersibility.

The silylation has been widely studied with the layered clay minerals, such as montmorillonite, kaolinite, saponite, etc. (He et al., 2013; 2014). Therein, locking effect was generally observed, as the neighboring clay layers were connected and fixed by the simultaneous condensation of silane (or silane oligomer) (Su et al., 2012; Yang et al., 2012). Furthermore, the polarity of the solvents has been revealed to have an important influence on the locking effect during the organo-functionalization (Su et al., 2013). For polar-protic solvents, the numbers of hydrogen bonds between the amino groups of the silane and solvents, and hydrolysis extent of the silane decreased, leading to a low loading of silane and a low condensation degree among the silane molecules. Silylation methods had been intensively used to improve the dispersibility of palygorskite nanorods (Wang and Wang, 2016), and the silylated palygorskite nanorods have been widely used as adsorbents for heavy metal ions and dyes (Han et al., 2015; Liang et al., 2013; Moreira et al., 2017). However, to the best of our knowledge, there is no comprehensive study on the effect of the silylation condition on the microstructure and dispersibility of the silylated clay minerals with high aspect ratio.

In the present work, surface modification of palygorskite (Pal) nanorods by γ-mercaptopropyltrimethoxysilane (MPS) was reported. The effects of the modification conditions on the morphology and microstructure of the product were emphasized. Based on TEM, TG, and sedimentation analysis results, the locking effect and welding effect were proposed.

* Corresponding author.
E-mail address: pliu@lzu.edu.cn (P. Liu).

http://dx.doi.org/10.1016/j.clay.2017.08.010
Received 1 May 2017; Received in revised form 26 July 2017; Accepted 7 August 2017

Table 1
Reaction conditions for the organo-modification of Pal nanorods.

Samples	Reaction temperature and time	Amount of MPS (mL)
OPal-1	20 °C, 24 h	1.00
OPal-2	Refluxing (about 70 °C), 8 h	1.00
OPal-3	Solvothermal (80 °C), 8 h	1.00
OPal-4	Refluxing (about 70 °C), 8 h	0.50
OPal-5	Refluxing (about 70 °C), 8 h	0.25
OPal-6	Refluxing (about 70 °C), 8 h	0.10
OPal-7	Refluxing (about 70 °C), 8 h	0.05

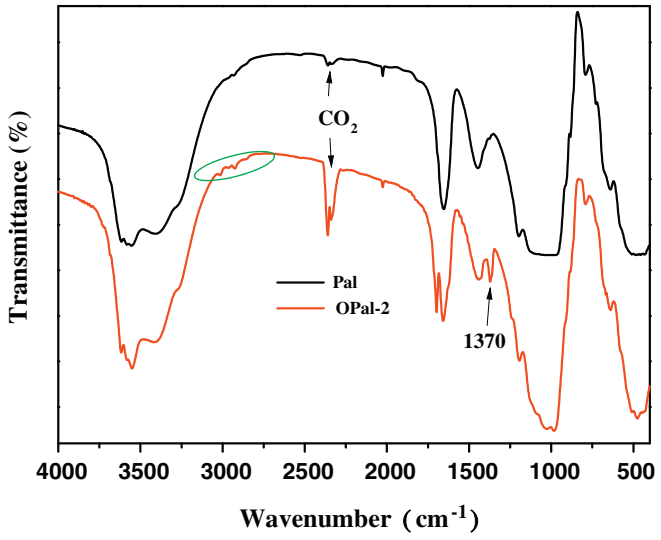


Fig. 1. FT-IR spectra of the bare Pal and the OPal-2 nanorods.

Fig. 2. Digital photo of the dispersion of the OPal samples prepared under different temperatures after standing for 30 min.

2. Experimental section

2.1. Materials and reagents

Pal nanorods (Jiangsu Goldstone Attapulgite R & D Center Co. Ltd., Xuyi, China) were dried at 120 °C for 24 h before the further use. MPS (97%) was purchased from J & K Scientific Co. Ltd., Beijing, China. Absolute ethanol, toluene and other reagents were analytical grade and used as received.

2.2. Modification of the Pal nanorods

1.00 g Pal nanorods were dispersed into 20 mL absolute ethanol with ultrasonication for 2 h. Then certain amount of MPS was added and the mixture was heated with stirring for the surface modification (Table 1). After the reaction, the product was separated by centrifugation (10,000 rpm for 8 min), and washed with ethanol by ultrasonication 30 min. After the centrifugation-washing cycles were repeated three times, the product was dried at 40 °C for 24 h.

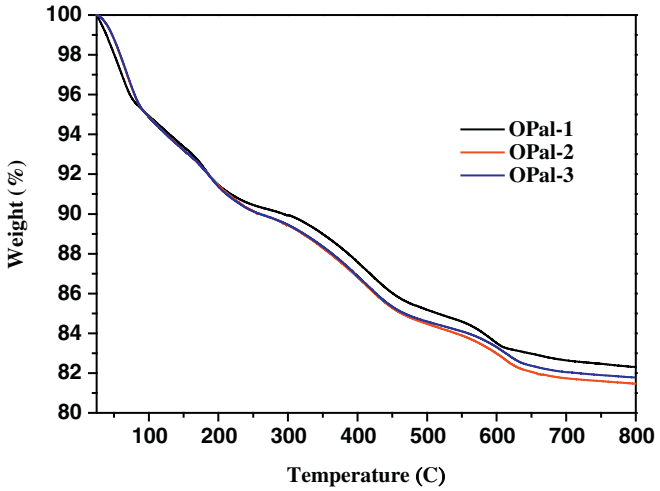
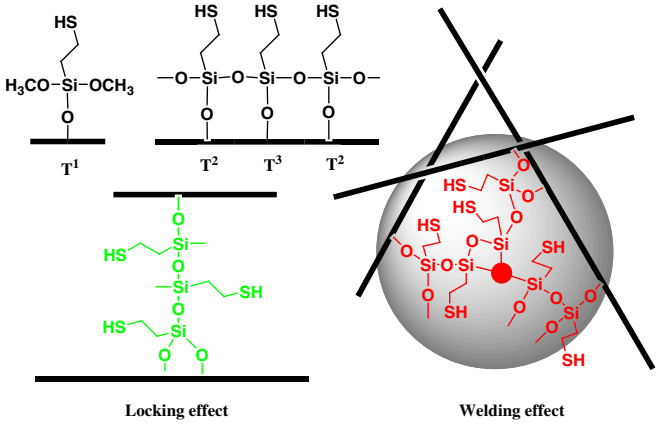


Fig. 3. TG curves of the OPal-1, OPal-2 and OPal-3 samples.



Scheme 1. Schematic illustration of the surface coupling reaction, the locking effect and welding effect.

2.3. Analysis and characterizations

Fourier Transform Infrared (FTIR) Spectrometer (NEXUS 670, Nicolet, Germany) was used to confirm the feature groups of samples in the range of 400–4000 cm^{-1}, using KBr pellet method.

The morphological analysis of the OPal products was carried out on a JEM-1200 EX transmission electron microscope (TEM). The samples were dispersed in ethanol. The carbon-coated copper grid was dip-coated in the dispersions of the samples, and dried at room temperature before observation.

Thermogravimetric (TG) analysis was performed with a Perkin-Elmer TGA-7 system at a scan rate of 10 °C/min to 800 °C in N_2 atmosphere.

3. Results and discussion

3.1. Effect of reaction condition

Due to the polar surface of the Pal nanorods, ethanol was selected as