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Grafting of montmorillonite with different functional silanes via two different reaction systems

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Abstract

Silane grafted montmorillonites were synthesized by using 3-aminopropyltriethoxysilane and trimethylchlorosilane via two different grafting reaction systems: (a) ethanol–water mixture and (b) vapor of silane. The resulting products were investigated using Fourier transform infrared (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TGA). XRD patterns demonstrate that silane was intercalated into the montmorillonite gallery, as indicated by the increase of the basal spacing. The product prepared by vapor deposition has a larger basal spacing than that obtained from solution, due to the different extent of silane hydrolysis in various grafting systems. TGA curves indicate that the methyl groups penetrate into the siloxane clay are the primary reason for the decrease of the dehydroxylation temperature of the grafted products. 3-Aminopropyltriethoxysilane in the grafted montmorillonite adopts a bilayer arrangement while trimethylchlorosilane adopts a monolayer arrangement within the clay gallery.

Keywords: Montmorillonite; Grafting; 3-Aminopropyltriethoxysilane; Trimethylchlorosilane; Fourier transform infrared; X-ray diffraction; Thermogravimetric analysis

1. Introduction

Expandable clay minerals such as smectites have extensive applications in various fields due to its swelling behavior, adsorption properties, ion exchange property and high surface areas [1–5]. The most commonly used swelling clay is the dioctahedral clay: montmorillonite, which has two siloxane tetrahedral sheets sandwiching an aluminum octahedral sheet. Due to isomorphic substitution within the layers (for example, Al^{3+} replaced by Mg^{2+} or Fe^{2+} in the octahedral sheet; Si^{4+} replaced by Al^{3+} in the tetrahedral sheet), the clay layer is negatively charged, which is counterbalanced by the cations within the interlayer space. The hydration of inorganic cations on the exchange sites causes its surface to be hydrophilic. Thus it is difficult for some organic molecules to be intercalated into montmorillonite by conventional ion exchange methods because of the highly hydrophobia and bulk of the organic molecules. Recently, their potentials have been greatly expanded by being grafted with a variety of biologically active organic substances [6–9]. Hydrophobic modification of the clay intrasurface allows many hydrophobic guest molecules to be readily intercalated.

As is well known, there are various ways to modify clay minerals, i.e., adsorption, ion exchange with organic/inorganic cations, grafting with organic compounds [10]. Organoclays are usually synthesized by modifying clays with surfactants via ion exchange [11,12]. In this way the hydrophobic partition medium within the clay interlayer can be formed and functions analogously to a bulk organic phase. The organoclays can be used to remove toxic compounds from the environment and reduce the dispersion of pollutants in soil, water, and air. In the organoclays, the cationic surfactant is fixed by the electrostatic

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force and may be released in the aqueous medium [13], resulting in secondary pollution. However, in the case of silane grafted clays, the organic molecule is tightly bonded onto the clay surface by the condensation between silane and clay minerals. Thus the release of the organic molecule into the aqueous medium is excluded. The silane grafted clays will be useful in the fields of remediation of polluted environments.

Previous studies have detailed the effects on the grafted products resulting from the used clay materials and silylating agents [14,15]. Less attention was paid to the effects from the grafting methods and media. The main objective of this work is to elucidate the possible variations resulting from different preparation methods. In the present work, two different silanes (3-aminopropyltriethoxysilane and trimethylchlorosilane) were used and two different reaction systems were employed. In the first method, the grafting reaction was carried out in a mixture of ethanol/water while the second method is exposing Na-MMT samples to saturated vapor from refluxing silane. The resultant products were characterized by FTIR, XRD, and TGA, providing some new insights about structure of silane grafted clays and the effects from the various grafting ways. This is of high importance for synthesis and application for silane grafted clays.

2. Experimental

2.1. Materials

The swelling clay used in this work is a montmorillonite (Ca-MT), provided by Nanhai Mining Ltd., China. The cation exchange capacity (CEC) of montmorillonite is 60 meq/100 g. The structural formula of Ca-Mt can be expressed as $(Na_{0.009}Ca_{0.193}Mg_{0.064})(Fe_{0.086}Mg_{0.475}Al_{1.440})(Si_{3.96}Al_{0.04})$-$O_{10}(OH)_{10}\cdot nH_2O$, deduced from the chemical analysis result.

The silanes used in this research are 3-aminopropyltriethoxysilane (γ-APS, with a purity of 99%, from Aldrich) and trimethylchlorosilane (TMCS, with a purity of 98%, from Sinopharm Chemical Reagent Co., Ltd.). Both silanes were used as received without any further purification. Fig. 1 shows the schematic of the used silanes.

2.2. Preparation of sodium exchanged montmorillonite

In the preparation of Na-Mt, 10 g of the mixture of Ca-Mt (9.4 g) and Na_2CO_3 (0.6 g) was added into 100 ml of deionized water and stirred at 80 °C for 3 h. Na-Mt was collected by centrifugation and washed with deionized water. The Na-Mt was dried at 105 °C, ground and sieved through 200 mesh and then placed in a bottle and sealed for further use.

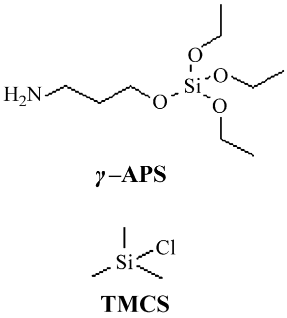

Fig. 1. The schematic of the used silanes.

2.3. Grafting methods

In the present study, two different grafting methods were used. One is that the grafting reaction was carried out in a mixture of ethanol/water (75/25 by volume). Na-MMT (2.5 g) was firstly dispersed in a mixture solution (200 ml), and then 2 g of γ-APS was introduced into the above-mentioned mixture and sheared for 8 h at 80 °C. The resultant product was washed using the mixture of ethanol/water in order to remove the residual silane and dried at 60 °C in a vacuum oven. The product of γ-APS grafted montmorillonite prepared using the above-mentioned method was denoted as M-APS-1. Similarly, the product prepared from TMCS is marked as M-TMCS-1.

The second method for grafting reaction was carried out by exposing Na-MMT samples to saturated vapor from refluxing silane (γ-APS and TMCS, respectively) for 6 h. The temperature was maintained at the boiling point of the used silane. The grafted products were washed with ethanol to remove the residual silane and evacuated at 60 °C. The grafted montmorillonites were denoted as M-APS-2 and M-TMCS-2, respectively.

2.4. Characterization

Fourier transform infrared (FTIR) spectra using the KBr pressed disk technique were performed on a Bruker Vector 33 Fourier transform infrared spectrometer. 32 scans were collected for each measurement over the spectral range of 400–4000 cm^{-1} with a nominal resolution of 4 cm^{-1}.

X-ray diffraction (XRD) patterns were obtained using Bede D1 system diffractometer (CuK_α radiation under target voltage of 35 kV and current of 30 mA, $\lambda = 0.154$ nm). The basal spacings were calculated from the 2θ values using the EVA software.

Thermogravimetric analysis (TG) of montmorillonite and the grafted products were performed on a TG209 thermobalance. Samples were heated from 30 to 900 °C at ramp 15 °C/min under a N_2 flow (25 mL/min) to quantify and distinguish the amount of silane in the grafting products.

3. Results and discussion

3.1. Powder X-ray diffraction

With grafting silane onto montmorillonite, the expansion of the montmorillonite layers was demonstrated by X-ray diffraction. The XRD patterns of the montmorillonite before and after grafting are shown in Figs. 2 and 3. The basal spacing for the Na-MMT is 1.26 nm, the characteristic d(001) value of sodium montmorillonite as reported in literature [15,16]. As shown by the XRD patterns, the basal spacings of the silane grafted montmorillonites are obviously bigger than that of Na-MMT,