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Silylation of saponite with 3-aminopropyltriethoxysilane

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ABSTRACT

A series of saponites (Sap) with a fixed Si/Mg ratio and varied Al contents were synthesized by using hydrothermal methods. The spectral, structural and morphology characters of the obtained products were characterized by a combination of XRD, FTIR, TG-DTG, TEM, ²⁹Si MAS NMR, ¹³C NMR etc. before and after 3aminopropyltriethoxysilane (APTES) grafting. XRD patterns showed that well-ordered Sap were obtained with starting Si/Al ratios of 5.43 and 7.89. Silylation reactions have little or no effect on the layered structure of Sap at the used dosage of APTES. The existence of the –CH₂ stretching bands at around 2937 cm⁻¹ in IR spectra clearly showed the incorporation of silane in the grafted samples. TG–DTG curves revealed that the samples with higher crystallinity displayed higher dehydroxylation temperature, as expected. A new mass loss located at around 420 ° C in silylated Sap was ascribed to the volatilization of the alkyl group in silane. The ²⁹Si NMR spectroscopy showed a series of signals of T structures, ascribed to the different silylation modes between silane and Sap. Furthermore, silylation procedures led to a decrease of the intensity of the signals at ca. – 84 ppm along with an increase of the intensity of Q³ signals. A further increase in the silane concentration did not decrease the resonance at – 84 ppm any further. This phenomenon confirmed the coexistence of Q² structure with Q³Si(2Al) structure, which resulted from the broken bonds at the edge surfaces of the synthesized Sap.

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1. Introduction

The polarity of clay minerals is one of the key concerns during their industrial applications in clay–polymer nanocomposites (Wypych and Satyanarayana, 2005; Ha et al., 2008; Park et al., 2009), environmental materials (Tonlé et al., 2003; Sayılkan et al., 2004), drug delivery and enzyme immobilization (An et al., 2015). Ion exchange method was proven as an easily operated and efficient method to modify the surface of clay minerals and change their surface polarity to hydrophobic (de Paiva et al., 2008). However, the long alkyl chain cationic surfactant, e.g. hexadecyltrimethylammonium bromide, might leach in to the surrounding medium when organoclays are used in solutions (Waddell et al., 1981).

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Silylation, also known as silane grafting, is a promising modification method, providing covalent linkages between organic components and clay mineral surface (Ruiz-Hitzky and Fripiat, 1976; Tao et al., 2011). Compared with the traditional organic cation exchange modification method, silvlation method enables a durable immobilization of the reactive organic groups in the resultant products, preventing their leaching. More importantly, by introducing special functional groups (e.g. -NH₂, -SH), in the used silanes, the affinities and adsorption selectivity of the resultant materials to the special target molecules, such as organic and metallic contaminants, the amount of loaded enzyme and drugs etc., could be greatly improved (Ruiz-Hitzky and Fripiat, 1976; Tonlé et al., 2003; Sayılkan et al., 2004; Wypych and Satyanarayana, 2005; Ha et al., 2008; Park et al., 2009; An et al., 2015). On the other hand, these functional groups can react with the polymer matrix, resulting in the formation of a network of clay mineral, silane and polymer through covalent bonding. This can greatly improve the mechanical properties of the resulting clay-polymer nanocomposites and may lead to a breakthrough in synthesis of novel materials (Ha et al., 2008; Park et al., 2009; Wypych and Satyanarayana, 2005).

Saponite (Sap), generally presented as M_x^+ [Si₄ – $_x$ Al_x] [Mg₃]O₁₀(OH)₂·nH₂O (M = Na, Li, K etc.), is a 2:1 type trioctahedral

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clay minerals of the smectite group. Its layer contains a central brucitelike $[Mg_3(0,OH)_6]$ octahedral sheet sandwiched by two $[Si(0)_4]$ tetrahedral sheets on both sides (Brigatti et al., 2006). Four out of six OH⁻ groups are replaced by oxygen atoms in octahedral sheet of saponite. These oxygen atoms are shared by the tetrahedral sheets. Sap has much higher surface acidity and thermal stability than its dioctahedral smectite counterpart, montmorillonite (Casagrande et al., 2005; Vogels et al., 2005). The edge surfaces of clay minerals are covered by the "undercoordinated" metal ions such as, Si^{4+} , Al^{3+} , Fe^{3+} , Mg^{2+} etc. This broken edge bond was evidenced by the adsorption of negatively charged gold colloids, as observed by Thiessen (1942) through electron microscope. However, due to the low edge surface area in the natural clay minerals such as montmorillonite, kaolinite etc., the broken bond related signal is generally absent in their ²⁹Si NMR spectra. Pioneering work by Herrera et al. (2004) showed that Sap subgroup minerals generally have a higher ratio of lateral thickness/particle diameter than montmorillonites. This kind of broken edge bonds induce Q² environments for the Si atoms, which can be confirmed by a ²⁹Si NMR chemical shift at ca. - 85 ppm (Herrera et al., 2004; He et al., 2014). These sites readily react with silane and produce materials that are silvlated on the edges (Herrera et al., 2005). Although previous studies showed the possibilities of silvlation of hectorite, only limited research was focused on the silvlation of Sap, which is related to silvlation sites and bonding function between silane and Sap surface.

Therefore, in this study a series of Sap with a fixed Si/Mg ratio (4:3) were synthesized using hydrothermal methods, and subsequently silylated with 3-aminopropyltriethoxysilane (APTES). The structures and properties of the Sap before and after silylation were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), and thermogravimetric analysis (TG–DTG). The bonding modes between Sap and APTES were further determined by solid-state magic angle spinning nuclear magnetic resonance (²⁹Si MAS NMR and ¹³C MAS NMR) spectroscopy. The new insights obtained in this study are of high importance for advancing our fundamental understanding of the mechanisms underlying the silylation of clay mineral surfaces.

1.1. Experimental methods

1.1.1. Preparation methods

1.1.1.1. Synthesis of Sap. Sap samples with a fixed Si/Mg ratio were prepared by modifying a previously reported method (Kawi and Yao, 1999; He et al., 2014). A mixture of 18.00 g of NaOH and 32.80 g of NaHCO₃ was dissolved in 250 mL of deionized water. Then, 38.65 g of sodium metasilicate (Na₂SiO₃·9H₂O) were added under vigorous stirring (Solution A). Desired amounts of AlCl₃·6H₂O and 30.80 g of MgCl₂·6H₂O were dissolved in 25 mL of deionized water (Solution B). Solution B was slowly input into Solution A under continuous stirring to form a uniform gel. The fresh gel was then sealed into a Teflonlined stainless steel autoclave and treated at 160 °C for 24 h. The obtained precipitates were washed by centrifuge–washing cycles until the supernatant reached neutral pH, then dried at 80 °C and ground for the further treatments. The obtained products were marked as Sap-X (X = Si/Al ratio in the starting material).

1.1.1.2. Grafting Sap with organosilane. The grafting reaction was carried out in a mixture of water/ethanol (25/75 by volume) (He et al., 2005). A mixture of 3.00 g of synthetic Sap and desired amount of APTES (99%, Aldrich) were put into 60 mL of water/ethanol and dispersed by stirring at 80 °C for 24 h. After washing by centrifuge–washing cycles using the water/ethanol solution and drying at 80 °C, the resultant products were ground and stored before characterization. The grafting products prepared from Sap-X were denoted as Sap-X-nAP, where nAP represents silylated sample synthesized using n·mmol APTES. For example, Sap5.43-30AP represents the silylated sample of Sap-5.43 reacted with 30 mmol APTES.

1.1.2. Analytical techniques

X-ray diffraction patterns (XRD) of the samples, were collected between 1° and 80° (2 θ) at a scanning rate of 1° (2 θ) min⁻¹ on a Bruker D8 Advance diffractometer with Ni-filtered CuK α radiation (λ = 0.154 nm, 40 kV and 40 mA).

Fourier transform infrared (FTIR) spectra were obtained using a Bruker VERTEX 70 Fourier transform infrared spectrometer. All spectra were collected at room temperature over the range of 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹ and 64 scans.

Thermogravimetric (TG) analysis was carried out on a Netzsch STA 409 PC/PG instrument, employing a heating rate of 10 °C min⁻¹ from 30 to 900 °C under a nitrogen flow of 60 mL min⁻¹.

Transmission electron microscopy (TEM) images were collected on a JEOL 2010 high resolution transmission electron microscope operated at an accelerating voltage of 200 kV. Specimens were prepared by dispersing the sample in ethanol and ultrasonically treating for 5 min. A drop of the resultant dispersion was placed on a holey carbon film supported by a copper grid, after which the ethanol was evaporated.

All the solid-state NMR experiments were carried out at $B_0 = 9.4$ T on a Bruker AVANCE III 400 WB spectrometer with an H-X BL4 double-resonance probe. The corresponding resonance frequency of ²⁹Si was 79.5 MHz. Samples were packed in a 7 mm ZrO₂ rotor and spun at the magic angle (54.7°) with the spin rate of 7 kHz. ²⁹Si MAS NMR spectra were acquired using direct excitation with ¹H high power decoupling using a 90° pulse of 6.0 µs and a recycle delay of 60 s. The ²⁹Si chemical shift was referenced to kaolinite at - 91.5 ppm. The resonance frequency of ¹³C was 100.6 MHz. Samples were packed in a 4 mm ZrO₂ rotor and spun at the magic angle (54.7°). The spin rate was 6 kHz. ¹H—¹³C CP MAS NMR spectra were recorded with a contact time of 2.0 ms and a recycle delay of 5 s. The ¹³C chemical shift was externally referenced to tetramethylsilane at 0 ppm.

2. Results and discussion

2.1. FTIR spectroscopy

For Sap (Fig. 1a), the –OH stretching bands were at around 3691 cm^{-1} (narrow and sharp, structural –OH) and $3600-3448 \text{ cm}^{-1}$ (–OH in water). The band corresponding to the water bending mode was observed at 1642 cm^{-1} . The strong and broad band at around 1000 cm^{-1} is due to the stretching mode Si—O—Si. The bands in the region of $430-460 \text{ cm}^{-1}$ were attributed to deformation vibrations of Si—O—Mg. These bands were very similar with those for natural montmorillonite (Fig. 1) (Xue et al., 2007).

The bands in the range of $457-467 \text{ cm}^{-1}$ were used to distinguish the smectites between di- and trioctahedral structures. Because Mg²⁺ has higher electronegativity than Al³⁺, the location for the deformation vibration region of Si—O—Mg in Sap ($457-465 \text{ cm}^{-1}$) is generally lower than that of Si—O—Al in montmorillonite (above 467 cm^{-1}). In dioctahedral montmorillonite, this band might split, due to the differences in nearest neighbor environment of the octahedral Al³⁺ such as the number of vacancies (Yao et al., 2005). In the present samples, all such deformation vibrations located in the region of $452-463 \text{ cm}^{-1}$ did not show any splitting (Fig. 1). This strongly suggests that all these synthetic Sap are of trioctahedral structure. The most intense Si—O—Si stretching vibrations were observed in the Sap products Sap-5.43 (Fig. 1c) and Sap-7.89 (Fig. 1e), which suggested that these samples are of higher crystallinity than the other samples in this study.

Generally, four main changes are expected in the IR spectra of silylated products corresponding to the stretching vibrations of the surface –OH, surface water, the alkyl chain and Si—O vibrations (Figs. 1b, d and e) (Herrera et al., 2005). First, the shape and width of the Si—O stretching related absorptions were changed in the region of 1000–

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