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Research paper

Novel intercalation mechanism of zwitterionic surfactant modified montmorillonites

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ABSTRACT

In this present work, a novel intercalation mechanism of zwitterionic surfactant modified montmorillonites (ZSMMt) has been introduced. Using 3-(*N*,*N*-dimethylpalmityl-ammonio) propane sulfonate (SB16) and montmorillonite (Mt), a series of zwitterionic surfactant modified Mt were synthesized. The resulting organoclays were investigated by X-ray diffraction (XRD), Fourier transformed infrared spectroscopy (FTIR), and thermogravimetric (TG) analysis, corroborated by the useful information provided by the element analysis. As revealed by XRD results, the basal spacing of ZSMMt increases from 1.47 nm to 4.13 nm with the increase of zwitterionic surfactant loading from 0.2 to 4.0 times of the cation exchange capacity (CEC). According to chemical composition analysis results, the number of Ca^{2+} ions released during the process of ZSMMt preparation is very limited and the ratios of Ca/Si and Ca/Al of ZSMMt are comparable with those of raw Mt. These results suggest that Ca^{2+} still remain in the interlayer spaces of Mt. There is no noticeable exchange reaction that takes place between the zwitterionic surfactant and the interlayer Ca^{2+}. After the zwitterionic surfactant intercalation, the IR vibration shifts from 1194 to 1191 cm^{-1}, which implies a new bonding between the Ca^{2+} and sulfonate group of SB16. The decomposition temperature of the ZSMMt, almost 60–80 °C higher than that of bulk surfactants, clearly reflects the strong interaction force after intercalation. The present study thus concludes that the intercalation mechanism of ZSMMt is not an exchange process but an ion-dipole interaction between Mt and zwitterionic surfactant, thereby, a novel cross-coupling intercalation mechanism of preparing organoclays has been proposed.

1. Introduction

In the past four decades, growing attention has been paid to organoclay (OC) complexes in wide range of applications (Yariv and Cross, 2002; Bergaya et al., 2006), and the exploration of novel modification methods on clay mineral has never stopped (Kedzierski et al., 2016; Mansa et al., 2016; Merino et al., 2016; Su et al., 2016). There are a number of swelling clays, which are the most popular ones for OC preparation, such as montmorillonite (Mt), vermiculite, saponite, hydrobiotite, and so on. These clay minerals are mostly TOT-type. Their structural layers are negative charged because of isomorphic substitution, resulting the existence of exchangeable hydrated cations in the interlayer space to balance the negative charges of clay layers (Bergaya et al., 2006). The most common surfactants employed to modify the swelling clay minerals are cationic surfactants, such as quaternary ammonium. This kind of surfactant consists of two distinct moieties – a positive charged hydrophilic head and a hydrophobic hydrocarbon chain tail. After modification, cationic surfactant molecules attach on the inner and outer surface of clay minerals, and thus change the surface properties of clay minerals from hydrophilic to hydrophobic (He et al., 2014). Such modification improves their efficiencies as adsorbents for organic contaminant (Zhu et al., 2015), geotechnical barriers (Liao and Lin, 2016), filling of nanocomposite (Alvi et al., 2016), etc.

Based on numerous previous studies, the mechanism of cationic surfactant modification on clay minerals has been clearly clarified (He et al., 2014). The fundamental intercalation mechanism is the cation replacement or cation exchange, i.e. water soluble surfactant cations enter into the interlayer space of clay minerals and replace the counterion metal cations, which are dissolved in aqueous solution and removed by subsequent washing.

Though the edge faces of clay minerals may be positively charged, it is generally accepted that an anionic surfactant cannot enter into the interlayer of clay mineral due to the electrostatic repulsion between

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negatively charged clay layers and hydrophilic heads of the surfactant. For most swelling clay minerals, the contribution of the 001 planes to the total surface area of a clay mineral dominates over other planes, and the interactions on the edge face are normally negligible (Yariv and Cross, 2002). As for nonionic surfactants, there are no intercalating force at all between surfactant molecules and clay minerals.

Since the available surface sites of clay minerals for bonding anionic or nonionic surfactants are extremely limited, these two kinds of surfactants are much less considered for modification of swelling clay mineral (Fu et al., 2016).

Zwitterionic surfactants, such as sulfobetaines, have similar properties in solution in some respects to both ionic and nonionic surfactants. Fox example, many sulfobetaines exhibit Krafft points which are usually associated with ionic surfactants, in addition, they are highly water-soluble over a wide range of concentration, pH, hardness, and salinity (Weers et al., 1991). Lagaly once used betaine to modify Mt and investigated the betaine-Mt's rheological and colloidal properties, however, only a brief description on replacement of exchangeable cations of Mt with betaine was included without intercalation mechanism discussion (Schmidt and Lagaly, 1999).

In our previous study, a novel OC, zwitterionic surfactant modified Mt (ZSMMt) was reported (Zhu et al., 2011). Sulphobetaine is a kind of zwitterionic surfactant or inner salt, which contains both positively charged trimethylammonium and negatively charged sulfonate group. It can retain its zwitterionic characteristics over a broad pH range. A zwitterionic surfactant can intercalate into the interlayer spacing of Mt, and the influences of alkyl chain length and loading levels of the zwitterionic surfactant on the basal spacing of ZSMMt have been extensively discussed (Zhu et al., 2011; Ma et al., 2015b, 2016). Our previous study has also demonstrated that ZSMMt have more complicated structure and higher thermal decomposition temperature compared with cationic surfactants modified Mt (Zhu et al., 2011). However, to the best of our knowledge, the intercalation mechanism of a zwitterionic surfactant into the interlayer of swelling clay is still unclear. This work aims to investigate and identify the intercalation mechanism of zwitterionic surfactant into the interlayer of Mt. A series of ZSMMt with different surfactant loadings have been synthesized, the swelling processes and molecule microenvironment of ZSMMt were investigated. Accordingly, the modification mechanism of ZSMMt has been proposed.

2. Experimental

2.1. Materials

The raw Ca^{2+}—Mt (purity > 95%) was obtained from Inner Mongolia, China. The cation exchange capacity (CEC) is 110.5 meq/100 g. The zwitterionic surfactant, 3-(*N*,*N*-dimethylpalmityl-ammonio) propane sulfonate (SB16), with a purity of 99%, was purchased from Nanjing Robiot Co., Ltd., China. The solubility of SB16 is about 10% in water and the critical micelle concentration is 0.06 mM at 25 °C.

2.2. Preparation of the ZSMMt

Organo-Mt (OMt) was synthesized following the generalized procedure outlined below. A specific amount of SB16 was dissolved in distilled water by ultrasound at 60 °C for 0.5 h. Then, 30 g of Ca^{2+}—Mt was slowly added to a solution with a concentration (11.05, 22.1, 33.15, 44.2, 55.25, 82.88, 110.5, 138.13, and 165.75 mM) corresponding to 0.2, 0.4, 0.6, 0.8, 1.0, 1.5, 2.0, 2.5, 3.0, and 4.0 times of the CEC, respectively. The water: Mt mass ratio was kept at 20:1. The reaction was carried out at 60 °C for 15 min by ultrasonic method with 100 Hz. All products were washed twice with distilled water, dried at 80 °C, ground in an agate mortar, and passed through a 100-mesh sieve. The resulting ZSMMt prepared with Ca^{2+}—Mt and 0.5CEC SB16 is labeled as SB16-0.5, others are labeled following the same way.

2.3. Measurement

Powder X-ray diffraction (XRD) patterns were collected using Cu Kα radiation on a Bruker D8 Advance X-ray diffractometer, which was operated at 40 kV and 40 mA with a scanning speed of 2°/min between 1° and 20°.

FTIR spectra were obtained on Bruker Vertex-70 Fourier transform infrared spectrometer. The KBr pressed disk technique was adopted. To get well-proportioned mixture, each sample was prepared with a ZSMMt/KBr ratio of approximate 1:100, and ground in an agate mortar for 10 min. The spectra were collected over 400–4000 cm^{-1} with a resolution of 4 cm^{-1}.

Thermogravimetric (TG) analysis was performed on a Netzsch STA 409 PC instrument. About 20 mg of finely ground sample was heated in a corundum crucible from 30 to 900 °C at 10 °C/min under pure N_2 atmosphere (60 cm^3/min).

Major element oxides were analyzed using a Rigaku RIX 2000 X-ray fluorescence spectrometer (XRF) on fused glass beads. Calibration lines used in quantification were produced by bivariate regression of data from 36 reference materials encompassing a wide range of silicate compositions, and analytical uncertainties are mostly between 1% and 5%.

3. Results and discussion

3.1. XRD of ZSMMt

The XRD patterns of raw Ca^{2+}—Mt and ZSMMt prepared at different SB16 concentrations (0.2–3.0 CEC) are shown in Fig. 1.

The basal spacing of raw Mt is 1.47 nm, which is a typical d-value of calcium Mt. Compared with raw Mt, ZSMMt have increased basal spacings. The *d* (001) values (~1.5 nm) and intensity of the reflections do not substantially increase for the ZSMMt at low concentrations (0.2–0.4 CEC), which could be attributed to the size and the lateral monolayer arrangement of the SB16 surfactant molecules in the interlayer spaces. At higher surfactant concentrations (0.6–1.0 CEC), the main reflections shift to smaller angles, and the shape is gradually broadened. The broadening of reflections indicates a disordered structure. In addition, the secondary reflection appears, suggesting that more surfactants are intercalated into the interlayer space with multiple arrangement models. With an increase of surfactant dose from 2.0 to 4.0 CEC, the 001 reflections turn to be shaper and sharper (Fig. 1), indicating that the layers of OMt become ordered.

3.2. Chemical composition analysis of ZSMMt

The content of three major element oxides CaO, Al_2O_3 and SiO_2 in ZSMMt is shown in Table 1. The intercalation process of SB16 in Mt is very different from that of a cationic surfactant. The interlayer exchangeable cations Ca^{2+}, Na^+, etc. can be replaced by cationic surfactants. For zwitterionic surfactant, our blank experimental result shows that the molecules do not precipitate with Ca^{2+} in the solution. Hence, the ratio of interlayer exchangeable Ca^{2+} to Al or Si content in the crystal structure of Mt can be used as a guide to monitor whether Ca^{2+} cations are replaced or not. The ratios of CaO/SiO_2 and CaO/Al_2O_3 are almost unchanged after the intercalation of surfactant into the interlayer space of Mt, suggesting that Ca^{2+} still exist in the interlayer space. Furthermore, the solution concentration of Ca^{2+} after modification was determined by ICP-AES for SB16-1.0. The release amount of Ca^{2+} is about 1.74 mg/g, equal to 0.07 CEC of Mt, which comparable with that of Ca^{2+}—Mt in distilled water (0.03 CEC). That is to say, no obvious exchange reaction takes place between the zwitterionic surfactant and the interlayer exchangeable cations.