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Research paper

Al_{13}-pillared montmorillonite modified by cationic and zwitterionic surfactants: A comparative study

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ABSTRACT

A series of inorganic–organic montmorillonites (IOMts) were synthesized by modifying polyhydroxy-aluminum (Al_{13})-pillared montmorillonites (AlPMts) with the cationic surfactant, hexadecyltrimethyl ammonium bromide (C16), and the zwitterionic surfactant, hexadecyldimethyl(3-sulphonatopropyl)ammonium (Z16). The products prepared using different surfactant concentrations (0.4–5.0 CEC) were characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TG), and C, H, and N elemental analyses. The results showed that the structure of the IOMt was strongly influenced by surfactant type. In the case of C16-modified AlPMt (C-AlPMt), the surfactant molecules entered and expanded the interlayer space, leading to the partial release of pre-intercalated Al_{13} cations. At high surfactant concentrations (>2.0 CEC), the basal spacing of C-AlPMt showed no further expansion although the *gauche*/*trans* conformer ratio of the intercalated surfactant decreased. In the case of Z16-modified AlPMt (Z-AlPMt), however, the amount of Z16 intercalated did not increase when the surfactant concentration exceeded 1.0 CEC, while the basal spacing was identical with that measured for the unmodified AlPMt. This observation could be attributed to a difference in the capacity of AlPMt for intercalating C16 and Z16. It was proposed that C16 was intercalated through both cation exchange (with Al_{13}) and physisorption, while the intercalation of Z16 was primarily mediated by electrostatic attraction between the interlayer Al_{13} cation in AlPMt and the negatively charged group of Z16.

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1. Introduction

Montmorillonite is a naturally occurring layer silicate with excellent swelling capacity, a large specific surface, and a high cation exchange capacity (CEC). The physical and chemical properties of natural montmorillonites can be modified by cation exchange reactions with metal complex cations and organic cations, e.g., pillared interlayered clays (PILCs) (Pinnavaia, 1983) and organo-montmorillonites (OMts) (He et al., 2014). Because of the large specific surface area, high pore volume, and strong surface acidity, PILCs have significant applications in environmental remediation (Li et al., 2013; De León et al., 2014), such as being used as efficient adsorbents for oxyanionic contaminants and heavy metals (Zhou et al., 2010; Zhu et al., 2014). PILCs, however, do not efficiently remove the hydrophobic organic compounds from water because of its hydrophilic surface (Zhu et al., 2009b). In contrast, OMt shows excellent hydrophobicity and can be used as efficient adsorbents for organic pollutants (Stockmeyer, 1991; He et al., 2006; Liu et al., 2012; Fatimah and Huda, 2013).

Wastewater in the environment, however, contains both organic and inorganic contaminants. Therefore, developing novel adsorbents that can efficiently remove both organic and inorganic contaminants is urgent. Inorganic–organic montmorillonites (IOMts), obtained by intercalating cationic metal complexes and organic cations, are capable of removing a wide range of inorganic and organic contaminants (Zhu and Zhu, 2007; Zhu et al., 2009b; Li and Wu, 2010; Ouellet-Plamondon et al., 2012). IOMt can also serve as novel adsorbents of volatile organic compounds (Zhu et al., 2007a), and as catalysts in the degradation of adsorbed organic compounds (An et al., 2008). Little information, however, is available regarding the interlayer structure of IOMt that holds the key to understanding their interactions with pollutants, and to developing novel industrial applications.

Organo-montmorillonites (OMts) are commonly prepared by the intercalation of organic modifiers. Previous studies have shown that the type of organic modifier used can markedly influence the structural characteristics and adsorptive behavior of OMt (Dentel et al., 1998; Heinz et al., 2007; Zhou et al., 2007; Chitrakar et al., 2011; Liu et al., 2012). Thus, modifiers containing special functional groups, such as zwitterionic surfactants, can significantly improve the adsorption capacity of OMt (Shen, 2002). Sulfobetaine, containing both positively charged (quaternary ammonium) and negatively charged (sulfonate) groups

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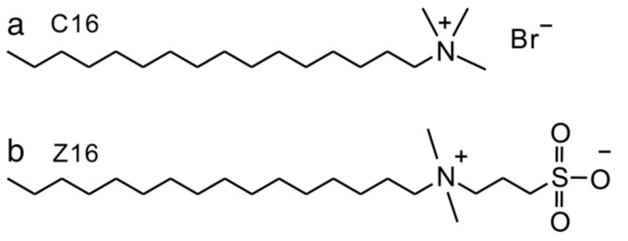

Fig. 1. Chemical structures of the surfactants used. (a) Cationic hexadecyltrimethylammonium bromide (HDTMAB), denoted as C16; and (b) zwitterionic hexadecyldimethyl(3-sulphonatopropyl)ammonium (HDDMSA), denoted as Z16.

(Fig. 1) is an example of a zwitterionic surfactant. Besides being highly water-soluble, biodegradable, and biologically safe, sulfobetaine can readily intercalate into the interlayer space of montmorillonite (Zhu et al., 2011).

When the interlayer space of montmorillonite already contains a cationic metal complex, sulfobetaine intercalation is promoted through electrostatic attraction between the positively charged metal complex and the negatively charged group of the surfactant. It might therefore be expected that IOMt, intercalated with both a zwitterionic surfactant and a cationic metal complex, has properties and interlayer structures that are different from those found in organoclays. Likewise, the capacity of these materials for adsorbing charged organic and inorganic pollutants would differ from that of OMt. Previous studies have also shown that the interlayer structure and properties of OMt and pillared interlayered clays (PILCs) are strongly dependent on surfactant configuration and dosage as well as pretreatment conditions (Khalaf et al., 1997; Heinz et al., 2007; He et al., 2010). By analogy, this observation would also apply to IOMt.

This study reports on the properties of a series of IOMt prepared by modifying Al_{13}-pillared montmorillonite (AlPMt) with different concentrations of a cationic (C16) and a zwitterionic (Z16) surfactant (Fig. 1). Al_{13} denotes the polyhydroxy-aluminum (Keggin) cation ($[Al^{IV}Al^{VI}_{12}O_4(OH)_{24}(H_2O)_{12}]^{7+}$). The basal spacing, chemical composition, thermal stability, and structure of the IOMt were determined by X-ray diffraction (XRD), X-ray fluorescence (XRF), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TG), and C, H, and N elemental analysis.

2. Experimental

2.1. Materials

The sample of calcium montmorillonite (Ca-Mt; purity > 95%) was obtained from Inner Mongolia, China. The chemical composition of Ca-Mt was as follows (wt.%): SiO_2 58.16%, Al_2O_3 16.95%, Fe_2O_3 5.26%, CaO 2.29%, MgO 3.57%, K_2O 0.15%, Na_2O 0.19%, MnO 0.027%, TiO_2 0.2%, and P_2O_5 0.08%, and the loss on ignition is 13.23%. Its chemical formula was written as $Ca_{0.168}Na_{0.025}K_{0.013}[Si_{3.984}Al_{0.016}][Al_{1.352}Fe_{0.271}Mg_{0.365}Ti_{0.010}]O_{10}(OH)_2\cdot nH_2O$. The cation exchange capacity (CEC), measured by the adsorption of $[Co(NH_3)_6]^{3+}$ (Zhu et al., 2007b), was 110.5 meq/100 g. The C16 and Z16 surfactants ($C_{19}H_{42}BrN$ and $C_{21}H_{45}NO_3S$, respectively) (Fig. 1), with a purity of 99%, were supplied by Nanjing Robiot Co. Ltd., China. $AlCl_3\cdot 6H_2O$ and Na_2CO_3 were analytically pure and obtained from Guangzhou Chemical Reagent Factory, China.

2.2. Preparation of inorganic–organic montmorillonites (IOMts)

Hydroxy-aluminum solutions, containing Al_{13} cations, were obtained by slowly adding a solution of 0.5 M Na_2CO_3 to a 1.0 M $AlCl_3$ solution at a rate of 1 mL/min with vigorous stirring in water for 24 h at 60 °C, giving a final ratio of $OH^-/Al^{3+} = 2.4$. Montmorillonite (10 g) was added to the hydroxy-aluminum solution, and the Al/clay ratio was 10 mmol/g. The mixture was stirred for 24 h, and allowed to stand ('aged') for 24 h at 60 °C (Zhu et al., 2009a). The product was collected by centrifugation, washed 8 times with distilled water, and freeze-dried for 48 h. The Al_{13}-pillared montmorillonite was denoted as AlPMt.

IOMts were obtained by stirring a given amount of surfactant into distilled water at 60 °C for 0.5 h, and adding a specified amount of fresh (nonfreeze-dried) AlPMt. The amount of surfactants added was equivalent to 0.4, 1.0, 1.5, 2.0, 3.0, 4.0 and 5.0 times the CEC of montmorillonite. The mixture was stirred for 12 h at 60 °C, and then the products were collected by centrifugation, washed 8 times with distilled water, and freeze-dried for 48 h. The products prepared from AlPMt by adding 1.0 CEC of C16 and Z16 surfactants were denoted as $C_{1.0}$-AlPMt and $Z_{1.0}$-AlPMt, respectively. Similarly, the other IOMt samples were marked by subscripts indicating the CEC multiplier.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer with Ni-filtered CuKα radiation ($\lambda = 0.154$ nm, 40 kV and 40 mA) with a 0.01 2θ step size and a 0.65 s counting time with 2.3° Soller slits, 1.0 mm divergence slit and 0.1 mm receiving slit. Samples used for XRD were random powder.

Fourier-transform infrared (FTIR) spectra of the samples were obtained using pressed KBr disks and a Bruker VERTEX 70 spectrometer. The disks were prepared by pressing a mixture of powdered sample (0.9 mg) and KBr (80 mg). All spectra were recorded at room temperature over the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1} and 64 scans.

Thermogravimetric analysis (TG) was performed on a Netzsch STA 409PC instrument. The samples were heated from 30 to 1000 °C at a rate of 10 °C/min under a flow of high-purity nitrogen (60 mL/min). The differential thermogravimetric (DTG) curves were directly derived from the corresponding TG curves.

Major elemental analysis was conducted on a Rigaku RIX 2000 X-ray fluorescence (XRF) spectrometer. Calibration lines used in quantification were obtained through bivariate regression of data from 36 reference materials encompassing a wide range of silicate compositions, giving a standard error of 1–5%.

The C, H, and N elemental microanalyses were performed in an Elementar Vario EL III Univeral CHNOS Elemental Analyzer. The amount of loaded surfactant (M_S), expressed as mmol/g, was derived from the relationship $M_S = W_C / (M_C \times N)$, where W_C is the mass percentage (wt.%) of organic carbon obtained by CHN analysis, M_C is the molar mass of carbon (12.0 g/mol), and N is the number of carbon atoms in the surfactant molecule (for C16, N = 19; for Z16, N = 21).

3. Results and discussion

3.1. X-ray diffraction

The d_{001}-value of 1.88 nm for the parent (unmodified) AlPMt corresponded to an interlayer space of 0.92 nm (Fig. 2). This value was close to the dimension of the Keggin cation (0.9 nm), indicating the successful intercalation of Al_{13} into Ca-Mt (Plee et al., 1985).

The variation in the d_{001}-values clearly depended on surfactant configuration and dosage. In the case of C-AlPMt, the d_{001}-values increased with the concentration of C16 surfactant (Fig. 2a). The d_{001}-value of 1.79 nm for $C_{0.4}$-AlPMt was slightly smaller than value recorded for the unmodified AlPMt. However, when the amount of C16 added was increased to 1.0 CEC, the d_{001}-value expanded to 2.07 nm (Fig. 2a). At a dosage of 2.0 CEC, a d_{001}-value of 3.80 nm was recorded together with a weak second-order reflection near 1.90 nm. No further increases in d_{001}-value were observed for surfactant dosages in excess of 2.0 CEC. These observations may be explained in terms of the intercalation of C16 in a paraffin-type configuration (He et al., 2014). For dosages of equal to or less than 1.0 CEC, the surfactant might be intercalated in the cationic form (by cation exchange with

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