



Influence of montmorillonites exchange capacity on the basal spacing of cation–anion organo–montmorillonites



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ABSTRACT

With cationic and anionic surfactants cetyltrimethylammonium bromide (CTAB) and sodium dodecylsulfonate (SDS) as modifiers, Ca-montmorillonites (Ca-Mt), artificial Na-montmorillonites (R-Na-Mt) and natural Na-montmorillonites (Na-Mt) with different cation exchange capacity (CEC) were modified by solution intercalation method, respectively. Then cation–anion organo–montmorillonites (OMt) were prepared. The influence of CEC on the basal spacing of cation–anion OMt and the influence mechanism were discussed by X-ray diffraction (XRD) and zeta potential testing. The results indicate that the basal spacing of cation–anion OMt is related to CEC. For the same type montmorillonites, the basal spacing of cation–anion OMt decreases with the increase of CEC and it is easier to get cation–anion OMt with greater basal spacing when CEC is lower. Moreover, the CEC of Na-Mt has the greatest influence on the basal spacing of cation–anion OMt.

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1. Introduction

Montmorillonites (Mt) has two siloxane tetrahedral sheets sandwiching an aluminum octahedral sheet. Because of the isomorphous substitution within the layers (e.g., Al³⁺ replaced by Mg²⁺ or Fe²⁺ in the octahedral sheet and Si⁴⁺ replaced by Al³⁺ in the tetrahedral sheet), the clay layers have permanent negative charges, which must be counterbalanced by exchangeable cations such as Na⁺ and Ca²⁺ in the interlayer [1,2]. The content of exchangeable cations can be expressed as cation exchange capacity (CEC).

Due to its unique structure, Mt can be modified easily and then has wide applications in many fields [3–5] which have attracted a great deal of interest. Most of the scholars mainly aimed at organic modification with cationic surfactants, such as dodecyl trimethylammonium bromide (DTAB), cetyltrimethylammonium bromide (CTAB) and octadecyl trimethylammonium bromide (OTAB) [6–8]. The adsorption capacity of cationic organo–montmorillonites (OMt) to nonpolar pollutant is greater than the original clay and is increased with increasing the amount of surfactants and the length of organic carbon chain [9]. Although cationic surfactants are easily intercalated into the Mt interlayer by cationic exchange, the poor thermal stability limits its applications in clay-based polymer

nanocomposites, such as rubbers and plastics [10]. Furthermore, there is some work on modifying Mt with anionic surfactants [11,12]. Since the driving force for the adsorption and intercalation of anionic surfactants in clays is limited, it is difficult to prepare anionic OMt. However, the anionic surfactants can be intercalated into Mt interlayer space through the interaction with cationic surfactants and exist stably. In our previous study, cation–anion OMt with 5.30 nm basal spacing had been prepared successfully [10]. The basal spacing is much higher than those of cation–anion OMt reported by Chen et al. (4.10 nm) [13] and cationic OMt reported by Zhu et al. (4.12 nm) [14]. The cation–anion OMt has good heat resistance, high basal spacing and excellent dispersion property. When cation–anion surfactants are intercalated into Mt at the same time, the formed strong distribution medium can remove pollutants cooperatively. Therefore, the adsorption property of cation–anion OMt is better than single cationic or anionic OMt [15] and some other properties are also improved significantly. The application prospect of cation–anion OMt is extensive, and will become the study focus in the future.

It is well known that the structure and properties of the resultant OMt are affected by the used surfactant. But the clay mineral properties (such as CEC) also can not be ignored. Ma et al. [16] and He et al. [17] found that the CEC of Mt has little influence on the maximum basal spacing of cationic OMt, but Mt with a small CEC requires relatively less surfactant to reach its maximum basal spacing. At present, there is no research on the influence of CEC on cation–anion OMt. Cation–anion OMt had been prepared

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successfully by intercalation with CTAB and sodium dodecylsulfonate (SDS) in our previous work [10]. The objective of the present study is to investigate the influence of Mt CEC on the basal spacing of cation–anion OMT and then propose the possible influence mechanism of CEC.

2. Experimental

2.1. Materials

The Ca-montmorillonites (Ca-Mt) were taken from Xuanhua, Hebei province (purified by sedimenting under gravity, the purity is more than 90%). The artificial Na-montmorillonites (R-Na-Mt) were prepared by Na_2CO_3 from Xuanhua Ca-Mt. And natural Na-montmorillonites (Na-Mt) from Xiazijie, Jilin province and Kelamayi, Xinjiang Autonomous Region were used.

The cationic surfactant (99% purity) was CTAB and the anionic surfactant (99% purity) was SDS. Both of them were purchased from Xilong Co., Ltd., Shantou, China.

2.2. Measurements of Mt CEC

The CEC of Mt was measured by $\text{NH}_4\text{Cl}-\text{CH}_3\text{CH}_2\text{OH}$ method. The Ca-Mt were marked as Ca-Mt-1, Ca-Mt-2, Ca-Mt-3, Ca-Mt-4, respectively. The R-Na-Mt were marked as R-Na-Mt-1, R-Na-Mt-2, R-Na-Mt-3, R-Na-Mt-4 and Na-Mt were marked as Na-Mt-1, Na-Mt-2, Na-Mt-3, respectively. The CEC is shown in Tables 1 and 2.

2.3. Preparation of the cation–anion OMT

The cation–anion OMT were prepared by the following method. 5 g Mt was dispersed in 100 g distilled water, and stirred at 600 rpm and 70 °C for 1 h. After adding a desired amount of CTAB, the reaction mixtures were stirred for 1.5 h at 70 °C. The amount of CTAB was equivalent to 2.0 times the CEC of Mt. Next, a desired amount of SDS was added, lasting stirring for another 1.5 h. The mass ratio of CTAB/SDS is 5:3. The products were centrifuged and washed two times with distilled water, dried at 60 °C, grounded in an agate mortar and passed through a 200-mesh sieve.

2.4. Testing and characterization

The zeta potential of Mt was conducted on a zeta potential analyzer. Before measurement, all samples were dispersed in water. And the pH of the tested solution is about 6.50.

X-ray diffraction (XRD) analysis was performed on a D/max-rA 12 kW diffraction at 40 kV and 100 mA using a Cu tube (Cu $\text{K}\alpha$ radiation, $\lambda = 0.154$ nm) at a scanning rate of 4°/min and scanning width of 3–70°, 1–25°.

3. Results and discussion

3.1. Influence of Mt CEC on the basal spacing of cation–anion OMT

Three different types of Mt were modified by cation–anion surfactants and the cation–anion OMT were characterized by XRD.

Table 1
CEC of Ca-Mt and R-Na-Mt.

Sample	CEC (mmol/100 g)	Sample	CEC (mmol/100 g)
Ca-Mt-1	49.69	R-Na-Mt-1	68.88
Ca-Mt-2	68.89	R-Na-Mt-2	89.08
Ca-Mt-3	90.03	R-Na-Mt-3	114.09
Ca-Mt-4	115.85	R-Na-Mt-4	138.14

Table 2
CEC of Na-Mt.

Sample	CEC (mmol/100 g)
Na-Mt-1	61
Na-Mt-2	71.1
Na-Mt-3	78.28

3.1.1. Ca-Mt

Figs. 1 and 2 show the XRD patterns of four purified Xuanhua Ca-Mt (Ca-Mt-1, Ca-Mt-2, Ca-Mt-3, Ca-Mt-4) and four cation–anion OMT samples (O-Ca-Mt-1, O-Ca-Mt-2, O-Ca-Mt-3, O-Ca-Mt-4) modified by CTAB and SDS, respectively.

Comparing the Ca-Mt CEC, the maximum basal spacing (d_{001}) of cation–anion OMT and the differences of CEC and d_{001} (ΔCEC and Δd_{001}) in Table 3, it can be found that the CEC of Ca-Mt-1 is the minimum (49.7 mmol/100 g) while the d_{001} of O-Ca-Mt-1 ($d_{001} = 6.05$ nm) is the maximum. And the OMT with the smallest d_{001} (5.19 nm) was made from the Ca-Mt-4 (CEC = 115.85 mmol/100 g) with the largest CEC. Along with the increase of CEC, the basal spacing of OMT decreases. The larger the ΔCEC is, the less the Δd_{001} decreases. And the d_{001} changes larger when the CEC is smaller. The experimental results indicate that the Ca-Mt CEC has influence on the basal spacing of cation–anion OMT. The Ca-Mt with smaller CEC can reach its relatively larger basal spacing through intercalation with CTAB and SDS. When the CEC is smaller, the influence on the basal spacing of cation–anion OMT is larger.

3.1.2. R-Na-Mt

XRD patterns of four Xuanhua R-Na-Mt (R-Na-Mt-1, R-Na-Mt-2, R-Na-Mt-3, R-Na-Mt-4) and four cation–anion OMT samples (O-R-Na-Mt-1, O-R-Na-Mt-2, O-R-Na-Mt-3, O-R-Na-Mt-4) modified by CTAB and SDS are shown in Fig. 3 and Fig. 4.

Table 4 displays the R-Na-Mt CEC, the d_{001} of cation–anion OMT and the differences of CEC and d_{001} . The CEC of R-Na-Mt-1 is the minimum (68.9 mmol/100 g) and the d_{001} of O-R-Na-Mt-1 is the maximum (5.52 nm). The basal spacing of cation–anion OMT decreases with the increase of CEC. And the Δd_{001} changes little as the ΔCEC increases. Therefore, the CEC of R-Na-Mt has a little influence on the basal spacing of cation–anion OMT. The cation–anion OMT with larger basal spacing can be obtained easily by R-Na-Mt with smaller CEC.

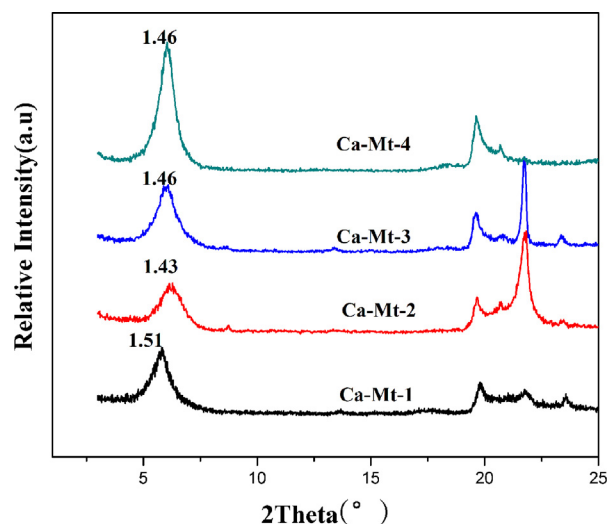


Fig. 1. XRD patterns of Xuanhua Ca-Mt.

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