



Research paper

The formation mechanism of organoammonium-kaolinite by solid-solid reaction

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ABSTRACT

Solid-solid reactions and its corresponding solution method have been utilized to study the formation and intercalation mechanism of organoammonium-kaolinite formed from quaternary ammonium salt and kaolinite (Kaol) by using a methoxy-modified Kaol as an intermediate. The products were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermogravimetry and differential scanning calorimetry (TG–DSC) analysis. Results showed that butyl trimethylammonium and hexyl trimethylammonium ions were successfully intercalated into the silicate layers, while the larger ions ($C_nH_{2n+1}N(CH_3)_3^+$, $n \geq 8$) were not. The intercalated alkylammonium ions were lying flat and poorly packed between the interlayer spaces of Kaol. In addition, a similar thermal behavior in the products obtained by both methods was also revealed. During the intercalation process, the alkylammonium ions were introduced by ion-dipole intercalation. In addition to the ion-dipole force, some other factors may contributed to these results, such as the geometrical constraint, the pH value of the mixed solution, the adsorbed water molecules, and the charge distribution at the external surfaces (the latter three will play a role if solutions are used). When solid-state reaction was used, the attraction caused by ion-dipole force was not strong enough to overcome the geometrical constraints, therefore larger alkylammonium ions were not intercalated.

1. Introduction

Compared with original clay minerals or others after modification, organoclay nanocomposites have attracted substantial attention because of its excellent physical and chemical properties. Modified clays can be used as reinforcing fillers for electric materials (Sand et al., 2003), refractory varnish (Beall and Goss, 2004), rheological control agents (Xi et al., 2005), and 2D nanofluidic (Cheng et al., 2017). Various guest substances have been widely utilized to prepare clay mineral-organic intercalation complexes such as polar molecules (Cheng et al., 2010; Frost et al., 2000; Komori et al., 1998), alkylammonium ions (mainly quaternary ammonium ions) (Favre and Lagaly, 1991; He et al., 2004a; Kuroda et al., 2011; Makó et al., 2016), cationic dyes and cationic complexes (Annabi-Bergaya, 2008; Nedelčev et al., 2008), and different types of polymers (Armstrong and Chesters, 1964; Aranda and Ruiz-Hitzky, 1999; Chaiko, 2003). Among the guest species, quaternary alkylammonium salts, as an important modifier, have been extensively used to prepare organoclays because of its excellent properties (Bergaya et al., 2006; Yuan et al., 2015). The reaction between the clay minerals and quaternary alkylammonium salts were usually proceed in the form

of liquids or solid-state with ion-exchange or ion-dipole intercalation (de Paiva et al., 2008; Li and Ishida, 2002), particularly in liquid phase. Vermiculites (Ghabru, 1989), micas (Tamura, 1996), hectorite (Gorrasi et al., 2003), montmorillonite (He et al., 2004a; Lee and Lee, 2004), bentonite (Majdan et al., 2005), and Kaol (Cheng et al., 2016; Kuroda et al., 2011; Yuan et al., 2013) are the commonly used layer silicates to react with quaternary alkylammonium salts, especially montmorillonite.

Some efforts have been made to synthesize organoammonium-montmorillonite through both in normal solution method and solid state reaction during the past 3 decades (Breakwell et al., 1995; He et al., 2010; Lagaly, 1981; Li and Ishida, 2003; Ogawa et al., 1989, 1990, 1992; Tang et al., 2003). Quantitative exchange of the montmorillonite interlayer cations by quaternary alkylammonium ions provides a method for characterization of organoammonium-Kaol. Kaol has poor ability of ion exchange and only a few attempts to synthesize organoammonium-Kaol in solution or melting by step-wise expansion of the interlayer space (Cheng et al., 2016; Kuroda et al., 2011; Letaief and Detellier, 2009; Liu et al., 2015; Long et al., 2012). Letaief and Detellier (2009) investigated the alkylammonium ionic liquids on the

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functionalization of the interlayer space of Kaol by using melting-intercalation process. In this experiment, the ammonium salts were synthesized to avoid decomposing of neat surfactant. They found that the synthesized alkylammonium salts with a short alkyl chain were grafted directly using Kaol/dimethylsulfoxide intercalation complexes (Kaol-DMSO), while the grafting of longer chains was done in two steps. Kuroda et al. (2011) proposed another approach, by using solution method, to intercalate organoammonium cations in Kaol. These researchers introduced hexadecyl trimethylammonium chloride into Kaol from a Kaol-methanol pre-intercalate (Kaol-MeOH). According to the authors the Kaol layers rolled simultaneously with its exfoliation (one-step route). Furthermore, the intercalation reaction was significantly influenced by the reaction temperature (Yuan et al., 2013). Makó et al. (2016) employed molecular simulation analyses to reveal the possible compositions of the Kaol-cetyl trimethylammonium chloride intercalation complex. While there are a few literatures on the intercalating of alkylammonium cations in Kaol, mainly in solution method, little information is known about the mechanism of formation. Simultaneously, no systematic attempts to synthesize Kaol/quaternary ammonium salt complexes by solid-solid reaction. Therefore, further studies are still necessary to investigate the possible formation of organoammonium-Kaol by the solid-solid reaction and its formation mechanism.

Herein, we explored the formation of Kaol/quaternary ammonium salt complexes by the solid-solid reaction. Moreover, the formation mechanism of organoammonium-Kaol complexes was investigated as well. In the present work, methoxy-modified Kaol was used as precursors for further displacement reaction with series quaternary ammonium salts by solid-solid reaction and solution method (as a reference). The products obtained both methods were carefully compared, and the related interaction mechanisms between the Kaol host and the organic guests were investigated. The results of this study are useful in explaining the formation mechanism of this type of reaction.

2. Experiment

2.1. Materials

The Kaol used in this study was well-crystallized and obtained from Hebei Province, China. DMSO, MeOH, quaternary ammonium salts, butyl trimethylammonium chloride ($C_4H_9(CH_3)_3NCl$), hexyl trimethylammonium bromide ($C_6H_{13}(CH_3)_3NBr$), octyl trimethylammonium chloride ($C_8H_{17}(CH_3)_3NCl$), decyl trimethylammonium chloride ($C_{10}H_{21}(CH_3)_3NCl$), dodecyl trimethylammonium chloride ($C_{12}H_{25}(CH_3)_3NCl$), tetradecyl trimethylammonium chloride ($C_{14}H_{29}(CH_3)_3NCl$), hexadecyl trimethylammonium chloride ($C_{16}H_{33}(CH_3)_3NCl$), and stearyl trimethylammonium chloride ($C_{18}H_{37}(CH_3)_3NCl$) were used in this study. All reagents were of analytical grade purity and used as received.

2.2. Synthesis of intercalation complexes

To prepare the Kaol-DMSO intercalation complexes, 20 g Kaol was added into a mixture of 180 ml DMSO and 20 ml deionized water. The mixture was stirred in a water-bath at 60 °C for 12 h, and then centrifugation was carried out to separate the suspension. Then, MeOH was used to wash the excess DMSO in the solid, and the obtained products were dried in an oven at 60 °C for 12 h for further use.

To prepare the methoxy-modified kaolinite, the pre-intercalation complexes were added into MeOH and stirred for 7 days replacing the MeOH with fresh MeOH each day. The solid in the mixture was separated by centrifugation and dried in an oven at 60 °C for 12 h for the following investigation. The product obtained was denoted as Kaol-MeOH.

Lastly, before the preparation of the organoclays, the Kaol-MeOH and all organic salts were dried in an oven at 100 °C for 6 h to exclude

the effect of absorbed water. Then, 1 g Kaol-MeOH and 0.01 mol butyl trimethylammonium chloride (BTAC), hexyl trimethylammonium bromide (HTAB), octyl trimethylammonium chloride (OTAC), decyl trimethylammonium chloride (DTAC), dodecyl trimethylammonium chloride (DETAC), tetradecyl trimethylammonium chloride (TTAC), hexadecyl trimethylammonium chloride (HTAC), and stearyl trimethylammonium chloride (STAC) were ground with an agate mortar and a pestle for up to 30 min at ambient temperature in air. The solid was dried at 60 °C for 4 h and no further operation was taken to remove the excess organic salts (in order to avoid the formation of intercalation complexes during washing). The products obtained were denoted as Kaol-BTAC-S, Kaol-HTAB-S, Kaol-OTAC-S, Kaol-DTAC-S, Kaol-DETAC-S, Kaol-TTAC-S, Kaol-HTAC-S, and Kaol-STAC-S, where S was stand for the solid-solid reaction.

Simultaneously, a conventional solution method was also carried out as a reference, 1 g Kaol-MeOH was dispersed in a 10 ml solution containing 1 mol/L guest species in MeOH and stirred with a magnetic stirrer for 24 h. The mixture was then separated by centrifugation and dried in an oven at 60 °C for 4 h. The products obtained were denoted as Kaol-BTAC-L, Kaol-HTAB-L, Kaol-OTAC-L, Kaol-DTAC-L, Kaol-DETAC-L, Kaol-TTAC-L, Kaol-HTAC-L, and Kaol-STAC-L, where L was stand for the liquid reaction.

2.3. Characterization

XRD patterns were collected using a Rigaku D/MAX 2500 PC instrument equipped with Ni-filtered and Cu K α radiation operating at 45 kV and 100 mA. The samples were scanned at 2° (2 θ)/min in the range of 2°–30°.

FTIR spectra were recorded on the Thermo Fisher Nicolet 6700 spectrometer by a KBr disk (ca. 2% by mass in KBr) from 600 to 4000 cm^{-1} (32 scans at 4 cm^{-1} resolution).

TG–DSC was carried out in a Mettler-Toledo TG–DSC 1/1600 HT simultaneous thermal analyzer at a heating rate of 10 °C/min under a flowing nitrogen atmosphere (100 ml/min) from 30 to 1100 °C.

3. Results and discussion

3.1. XRD analysis

The XRD patterns of Kaol and its intercalation complexes with DMSO and methanol are shown in Fig. 1. Original Kaol XRD pattern displays a typical and well-ordered layer structure with a basal spacing (d_{001}) of 0.72 nm. Upon treatment with DMSO, a new reflection at 1.13 nm was observed, indicating that DMSO was successfully

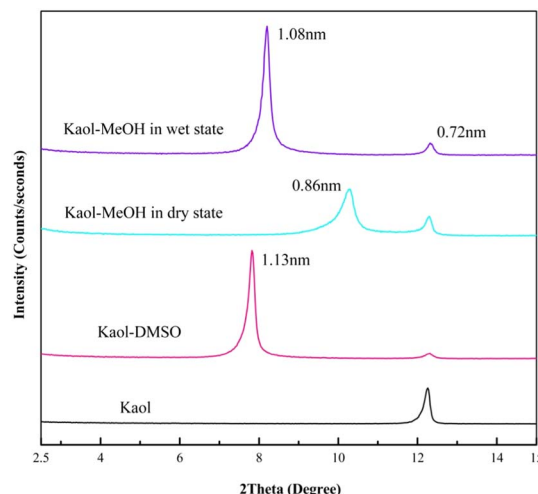


Fig. 1. XRD patterns of Kaol and its intercalation complexes with DMSO and MeOH.

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