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Effect of Intercalation Agents on Morphology of Exfoliated Kaolinite

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Abstract: Kaolinite intercalation compounds were prepared by intercalating fatty acids and quaternary ammonium salts into kaolinite layers, using methanol-grafted kaolinite as the precursor. Meanwhile, massive lamellas were exfoliated during the intercalation process. The interlayer structure, chemical bonding and morphology of kaolinite before and after intercalation were characterized in detail. As the alkyl chain length increases, the basal spacing of kaolinite increases gradually. The morphology analysis indicated that the ionic type of intercalation agent has a more important influence on the morphology change of kaolinite than their alkyl chain length. The initial kaolinite layers were mostly transformed into nanoscrolls in the product intercalated with stearyl trimethyl ammonium chloride (STAC). The present study demonstrates the arrangement model of intercalated molecules between kaolinite layers using X-ray diffraction (XRD) in conjunction with Fourier transform infrared (FTIR) and stereochemical calculation. On the basis of a probed arrangement model, the mechanism of effect of the alkyl chain length and ionic type of intercalation agent on the morphology of exfoliated kaolinite is suggested.

Keywords: kaolinite; intercalation and exfoliation; morphology; alkyl chain length; ionic type

1. Introduction

Kaolinite is a widely studied and applied class of phyllosilicate minerals [1–6]. Because of its specific physical and chemical properties, it has been used as a pigment for coatings, a filler for paper and polymers, an extender for water-based paints and inks, and a major component of ceramics [7–11]. Recently, the exfoliation of kaolinite has received a lot of attention because of its ability to greatly enhance certain properties of the resulting nano kaolinite. Typically, existing exfoliating methods include high-pressure extrusion, mechanical grinding, chemical intercalation, and so on [12–14]. Among these, chemical intercalation is considered the most effective way to achieve the exfoliation of kaolinite.

It is well known that the research on the intercalation of kaolinite began in the 1960s. However, the negligibly small cation-exchange capacity of kaolinite makes it very difficult to intercalate organic guest species into basal space. This is because any two contiguous layers of kaolinite are linked through strong hydrogen bonds arising from the interactions between Al–OH and Si–O groups. The limited guest species that are directly intercalated, only including *N*-methylformamide [15], dimethylsulfoxide [16,17], urea [18], potassium acetate [19,20], and hydrazine hydrate [21], can enter into the kaolinite interlayer directly. With explorations into the intercalation mechanism of kaolinite, however, an intercalation method has been developed from early direct intercalation to displacement and entrainment intercalation. Simultaneously, the variety of the guest species that are intercalated into

kaolinite layers has also been extended. As an intermediate to further intercalate large guest species, methoxy-modified kaolinite has been paid great attention to [15,22–25]. So far, the intercalation of kaolinite by inserting series alkylamines [15,22,26], series quaternary ammonium salts [23,27], series silanes with an amino group, benzyl alkyl ammonium chlorides [28,29], series fatty acids and salts [30,31] into kaolinite layers by taking a methanol-grafted kaolinite compound as a precursor has been successfully performed. When *n*-docosanamine was intercalated into kaolinite, the basal spacing of the corresponding intercalation compound was the largest, increasing up to 6.42 nm [26]. It is widely accepted that remarkable interfacial adhesion, such as hydrogen bonds, van der Waals forces and dipole–dipole interactions, impedes kaolinite lamella exfoliation. However, the organic guest species that are intercalated into kaolinite do not only increase the interlayer spacing greatly but also destroy hydrogen bonds between kaolinite lamellas effectively. The weaker interfacial adhesion makes kaolinite lamella exfoliation easier.

Additionally, an intercalation agent can be divided into two types depending on the characteristics of the charge generated, that is, an anionic or cationic intercalation agent. Expanded interlamellar spacing could weaken the binding force of kaolinite lamellas. This provides an effective way for the exfoliation of kaolinite lamella. During the exfoliation process, the morphology of kaolinite changes from platy stacks particles to nanoscrolls [32]. Moreover, previous research indicates that the change in kaolinite morphology is caused by intercalation with cationic long-chain macromolecules [23,33]. On the contrary, an anionic intercalator would not. Thus, in intercalation exfoliation of kaolinite, interlayer structure and morphology changes are closely related with the ionic type of the intercalation agent. However, research on the relationship between the type of intercalation agent and kaolinite interlayer structure as well as morphology has not been reported yet.

In this paper, the changes in the kaolinite interlayer structure and morphology were studied by taking series of fatty acids and quaternary ammonium salts as intercalation agents. The selected fatty acids were anionic intercalation agents, while the quaternary ammonium salts were intercalation agents. The resulting products were evaluated by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and transmission electron microscopy (TEM). Finally, the arrangement model of intercalated molecules in kaolinite lamellas was determined using XRD in conjunction with FTIR and stereochemical calculation. The mechanism of the effect of anionic and cationic intercalation agents on the morphology of exfoliated kaolinite was explored.

2. Materials and Methods

2.1. Materials

Classical kaolinite (denoted as K) with high purity was obtained from Zhangjiakou, China. Its Hinckley index of 1.31 indicated a high degree of crystallinity. The chemical composition of the sample was the same as that of the reference [27]. High-purity (purities of greater than 98%) reagents were obtained from Sinopharm Chemical Reagent Company, Ltd. (Shanghai, China), and decyl trimethyl ammonium chloride, dodecyl trimethyl ammonium chloride, tetradecyl trimethyl ammonium chloride, hexadecyl trimethyl ammonium chloride, and stearyl trimethyl ammonium chloride were denoted as DETAC, DTAC, TTAC, HTAC, and STAC, respectively.

2.2. Preparation

The kaolinite/dimethylsulphoxide (DMSO) intercalation compound (denoted as K-D) was prepared according to the method described by Olejnik et al. [16]. The preparation of methoxy-grafted kaolinite compound (K-M) followed the procedure described by Komori et al. [15]. Afterwards, the K-M was centrifuged and closed in a test tube to prevent methanol evaporation. To prepare the kaolinite/quaternary ammonium salts intercalation compounds (K-Qas), approximately 1 g of methoxy-modified kaolinite was added into a 20 mL of 1 mol/L solution of quaternary ammonium salts in methanol and stirred under room temperature for 72 h. The precipitations were centrifuged

and the excess quaternary ammonium salt was removed by washing six times with fresh ethanol. Then the resulting products were dried at 80 °C for 24 h. The dried products were denoted as K-Qa- C_n ($n = 4, 6, 8, 10, 12, 14, 16, 18$). To prepare the kaolinite/fatty acid intercalation compounds (K-Fas), a 1 mol/L solution of fatty acid in water was prepared at 80 °C firstly; 2 g of wet methoxy-modified kaolinite was added into 20 mL of the prepared solution and stirred for 72 h at the same temperature. The resulting products were washed with water to remove the additional fatty acid in the surface and then dried at 80 °C for 24 h. In this way, kaolinite/fatty acid intercalation compounds were prepared. The dried products were denoted as K-Fa- C_n ($n = 10, 12, 14, 16, 18$).

2.3. Characterization

XRD patterns were recorded with $\text{CuK}\alpha$ ($\lambda = 1.54178 \text{ \AA}$) irradiation on a D/max-2500PC diffractometer from RIGAKU Company, Akishima, Japan. Operational conditions of 40 KV, 100 mA and from 1° to 15° were used. Typically, one XRD run took 14 min. FTIR spectra were taken by using a Nicolet6700 FTIR spectrometer made by Thermo Company, Waltham, MA, USA. The FTIR test was performed in the mid-IR range from 4000 to 600 cm^{-1} using 32 scans with a resolution of 4 cm^{-1} . The morphological study of the prepared samples was conducted by a FEI-Tecnaï G2 F30 S-TWIN TEM (FEI Company, Eindhoven, The Netherlands), operating at 300 kV for the accelerating voltage.

3. Results and Discussion

3.1. XRD Analysis

The interlayer structure of the kaolinite intercalation compounds with different guest species can be conveniently monitored by XRD. In this study, the dependence of the interlayer structure on the chain length has been investigated. Because the XRD patterns of K-D and K-M have been reported in previous literature [34], they are not presented in this paper. Figure 1 shows the XRD patterns of kaolinite/fatty acid intercalation compounds and kaolinite/quaternary ammonium salt intercalation compounds, respectively. XRD data of the intercalation products show that their basal spacings are expanded to a length much longer than 0.72 nm, the basal spacing of K-Fas and K-Qas, indicating that Fas and Qas intercalate into kaolinite layers. Figure 1 also displays that the 001 reflection of the two types of intercalation compounds shifted to a low angle (2θ) with the increase in the alkyl chain length. In the case of Fas, the XRD patterns presented a narrow and intense 001 reflection, suggesting that the layer structure of kaolinite remains intact during the intercalation and exfoliation processes. Moreover, reflection at 0.86 nm for K-Fas, corresponding to K-M, was still observed. This indicated that the intercalation efficiency of fatty acids into kaolinite was incomplete. In addition, the other reflections were assigned to the second- and third-order diffractions of K-Fas. The basal spacings varied between 2.36, 2.79, 3.27, 3.68, and 4.13 nm in K-Da, K-La, K-Ma, K-Pa, and K-Sa, respectively. Similarly, the interlamellar spaces of K-Qas varied between 3.66, 3.50, 3.80, 4.09 and 4.24 nm.

The d-spacing Δd of different kaolinite intercalation compounds was obtained by using the value of the d-spacing in the compound and subtracting that of the corresponding compound prepared with an intercalation agent of less than two carbon atoms (Table 1). For K-Fas, the d-spacing Δd varied between 0.41 and 0.48 nm as the carbon atoms of the intercalator increased. Except for K-DTAC, however, the d-spacing Δd of K-Qas ranged between 0.15 and 0.30 nm. The dependence of the d-spacing on the chain length revealed that the arrangement model of the fatty acid and quaternary ammonium salt in kaolinite lamellas was similar. However, the rate of the interlamellar spacing increase was related to the type and properties of the guest species. For both complexes, the relation curves between the basal spacing and carbon number are presented in Figure 2. In comparison with K-Qas, it was found that a linear relationship between the number of carbon atoms of the fatty acid and the kaolinite interlamellar spacing was more apparent.

The results show that the difference between K-Qas and K-Fas in the arrangement model of the guest species may be due to the K-Qas being easily influenced by the solvent concentration and temperature of the intercalator.

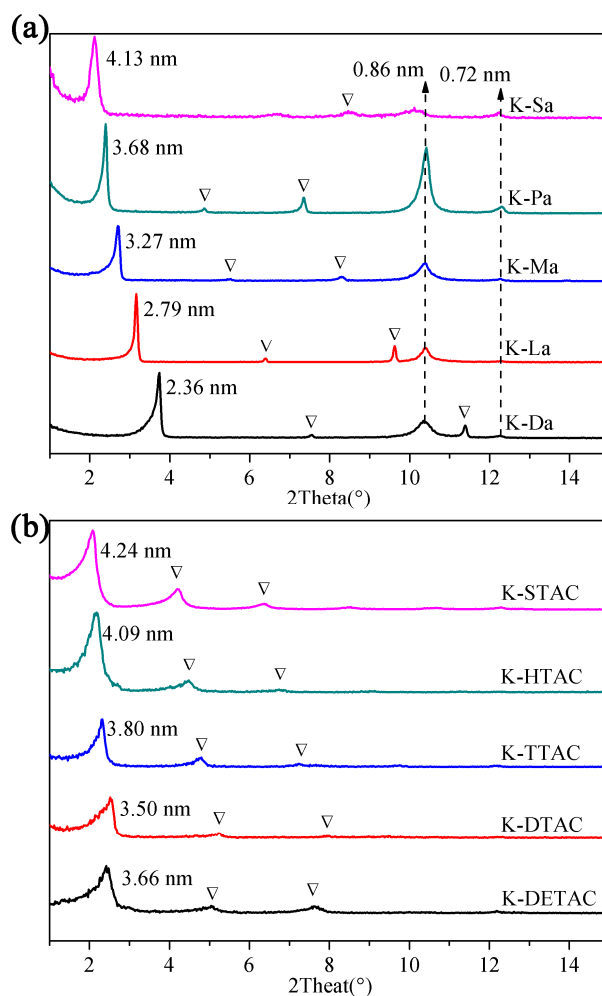


Figure 1. XRD patterns of (a) kaolinite/fatty acid intercalation compounds (K-Fas) and (b) kaolinite/quaternary ammonium salts intercalation compounds (K-Qas).

Table 1. Basal spacing values (d_{001}), expansion of d-spacing Δd of different kaolinite intercalation compounds, and molecular chain length of intercalated guest species.

Fatty Acid	Molecular Chain Length (Å)	d_{001} (Å)	Δd (Å)	Quaternary Ammonium Salt	Molecular Chain Length (Å)	d_{001} (Å)	Δd (Å)
Decanoic acid	12.42	23.6	-	DETAC	14.60	36.6	-
Lauric acid	14.97	27.9	4.3	DTAC	17.15	35.0	-1.6
Myristic acid	17.52	32.7	4.8	TTAC	19.70	38.0	3.0
Palmitic acid	20.07	36.8	4.1	HTAC	22.25	40.9	2.9
Stearic acid	22.62	41.3	4.5	STAC	24.80	42.4	1.5

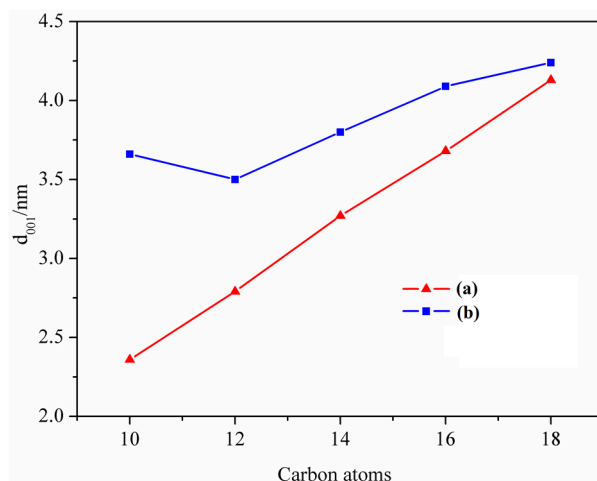


Figure 2. Relation curves of basal spacing and number of carbon atoms in the alkyl chain: (a) kaolinite/fatty acid intercalation compounds (K-Fas); (b) kaolinite/quaternary ammonium salts intercalation compounds (K-Qas).

3.2. Morphology Characteristics of Kaolinite upon Intercalation and Exfoliation

The transformation process of the kaolinite morphology from layer sheets to nanoscrolls by intercalation and exfoliation treatment has been reported by previous literatures. However, the effect of the guest species' type and alkyl chain length on the change in the kaolinite morphology has not been reported. TEM images of K and K-Qas with different alkyl chain lengths are illustrated in Figure 3. As indicated by the TEM image of K, the raw kaolinite is mainly composed of a typical pseudo-hexagonal morphology (Figure 3a). After the intercalation with K-Qas, the morphological changes of kaolinite are clearly evident in the TEM images (Figure 3b–f). The TEM images of K-Qa-C₄ and C₆ products both show the mere existence of partially curled kaolinite layers. At a higher magnification, it was clearly found that some semi-closed tubes exist in K-Qa-C₆, which indicates that the kaolinite layers were more easily exfoliated when intercalated with butyltrimethylammonium chloride. As the chain length increased, the curl degree of kaolinite sheets increased and some kaolinite sheets even curled into nanoscrolls. Moreover, the initial kaolinite particles were mostly transformed to nanoscrolls in the product prepared with stearyl trimethyl ammonium chloride (STAC; Figure 3f). Although the validity of the summary of morphological data was limited by characterizations in the microscopic observations, the change trend of the kaolinite morphology was sufficiently clear to examine the effect of the alkyl chain length on the transformation of the kaolinite morphology.

The alkyl chain length of intercalators has a significant influence on the morphology change of kaolinite in intercalation and exfoliation processes. Thus the effect of the intercalated molecules' type on the transformation of the kaolinite morphology was examined. Figure 4 shows the TEM images of K-Fa-C₁₈ and K-Qa-C₁₈ with a different magnification. Comparing with K-Fa-C₁₈ (anionic intercalators), the K-Qa-C₁₈ samples showed a more extensive degree of rolling. They contained some kaolinite layers with a recognizable pseudo-hexagonal morphology, some damaged layers, thin plates and a large number of nanoscrolls. However, the TEM images of K-Fa-C₁₈ products were composited of a considerable number of platy particles and few partially curled kaolinite layers. These morphological changes resulted from the incomplete exfoliating and curling of platy kaolinite particles. From the above analysis, we know that the ionic type of the guest species has a significant influence on the morphology change of kaolinite in intercalation and exfoliation processes. In order to exclude alkyl-chain-length effects, the TEM images of K-Fa-C₁₈ and K-Qa-C₁₆ (Figure 3e) were selected to be compared. It was clearly found that more nanoscrolls and semi-closed tubes or partially curled kaolinite layers existed in K-Qa-C₁₆.

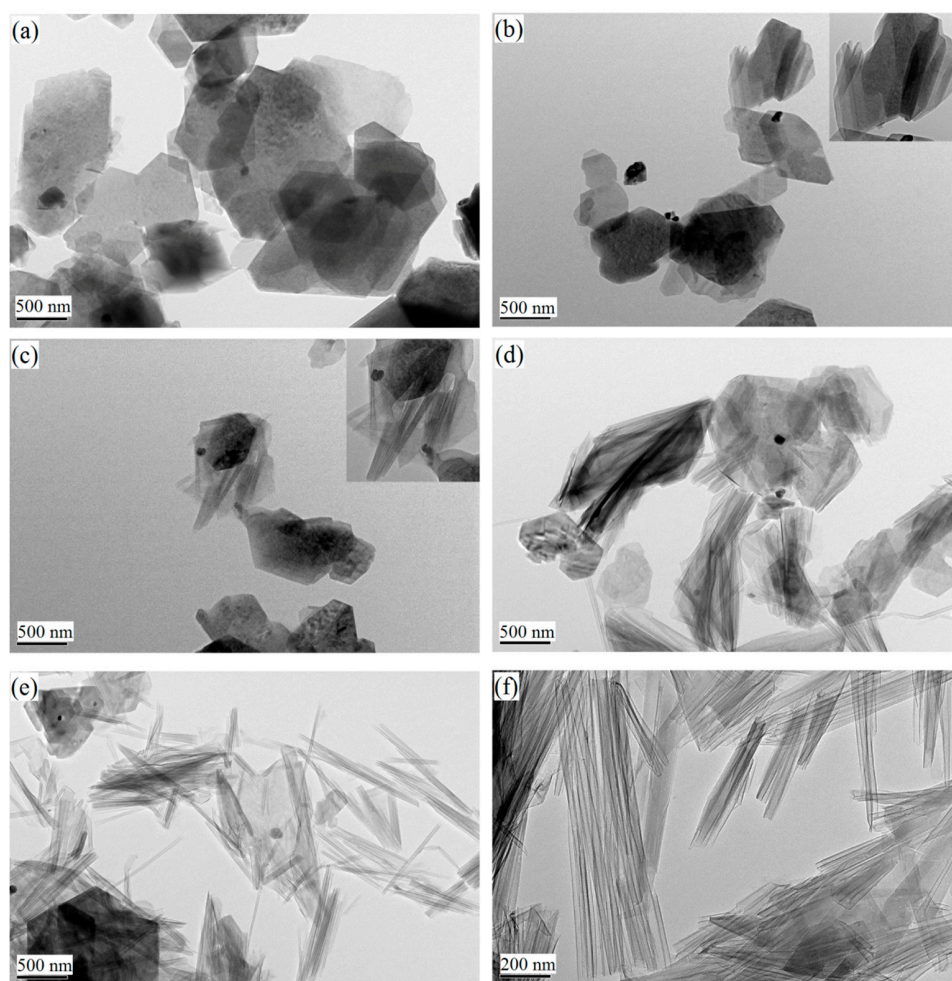


Figure 3. TEM images of (a) K, (b) K-Qa-C₄, (c) K-Qa-C₆, (d) K-Qa-C₈, (e) K-Qa-C₁₄, and (f) K-Qa-C₁₈.

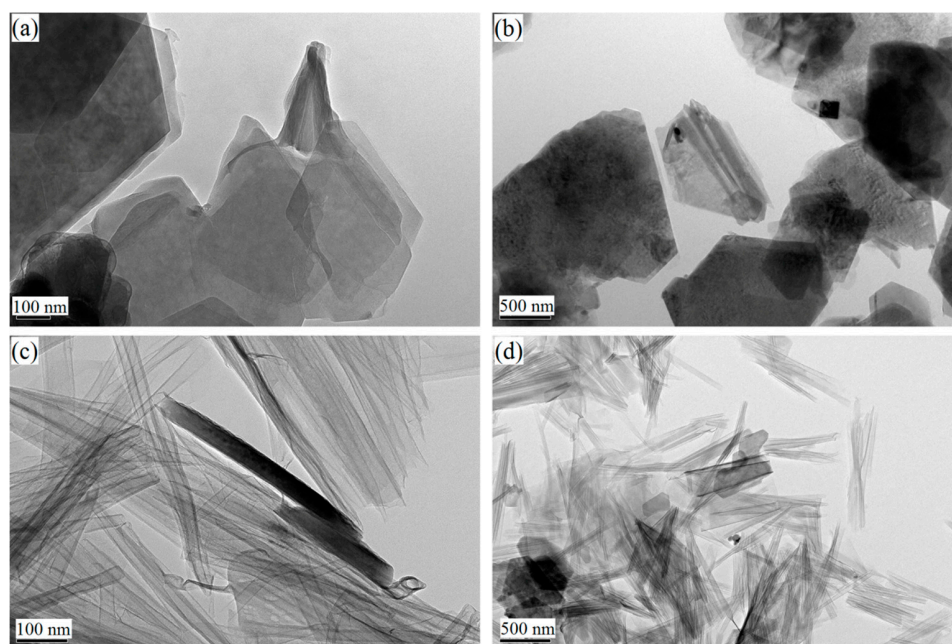


Figure 4. TEM images of (a,b) K-Fa-C₁₈, and (c,d) K-Qa-C₁₈.

3.3. FTIR Analysis of Exfoliated Kaolinite

It is well known that FTIR spectroscopy is an important method to analyze group interactions. In order to reveal the interactions of different types of guest species with kaolinite groups, the fatty acid and quaternary ammonium salt were selected as anionic and cationic intercalated molecules. Because the intercalation compounds used in this paper were prepared using K-M as an intermediate, FTIR spectrograms of K, K-D and K-M are also shown in Figure 5. FTIR spectra of K-Fas and K-Qas are shown in Figures 6 and 7, respectively. When fatty acids and quaternary ammonium salts were introduced into the kaolinite layers, bands in the range of $2800\text{--}3000\text{ cm}^{-1}$ arose from the antisymmetric and symmetrical CH_2 stretching vibrations of the alkyl chains. In detail, the antisymmetric CH_2 stretching vibrations of alkyl chains of quaternary ammonium salt shifted from 2924 to 2917 cm^{-1} with the increase in the carbon number of the alkyl chains. However, kaolinite/fatty acid intercalation compounds were almost unchanged. This indicated that the chemical environment of CH_2 of fatty acids in kaolinite layers was hardly affected. Bands at 3544 and 1651 cm^{-1} , as a result of the OH stretching and H–O–H bending vibrations of the water molecules adsorbed on the intercalators, were observed. The IR spectrum of K-Fas exhibited new peaks at $\sim 1700\text{ cm}^{-1}$, assigned to stretching vibrations of C=O . In the case of K-Qas, bands at 1477 cm^{-1} arose from the bending vibrations of the NH_2 group.

As shown in Figure 5, the two bands at 3692 and 3620 cm^{-1} are the characteristic OH-stretching vibration bands of K-M. The two bands were attributed to inner-surface hydroxyls (3692 cm^{-1}) and internal hydroxyls (3620 cm^{-1}), respectively. Previous studies have confirmed that it is difficult for the internal hydroxyls to be affected by the guest species intercalated into kaolinite interlayers. In contrast, the inner-surface hydroxyls were easily influenced by intercalation and modification processes. After methoxy-grafted kaolinite compounds reacted with fatty acids and quaternary ammonium salts, stretching vibration peaks of the inner-surface hydroxyl group varied similarly (Figures 6 and 7). The inner-surface hydroxyl stretching bands of K-Fas and K-Qas all increased sharply and shifted to a high wavenumber. However, the positions of internal hydroxyls at 3620 cm^{-1} had nearly no change between the two processes. On the other hand, the IR spectra of both compounds exhibited some slight differences in the shape of the bands at 3620 cm^{-1} . The characteristic peak of K-Fas was sharper than that of K-Qas, reflecting that quaternary ammonium salt interacted with internal hydroxyl groups of kaolinite. This may be caused by the insertion of $-\text{CH}_3$ at the N-end of quaternary ammonium salt into ditrigonal pyramid caves of kaolinite silica tetrahedron.

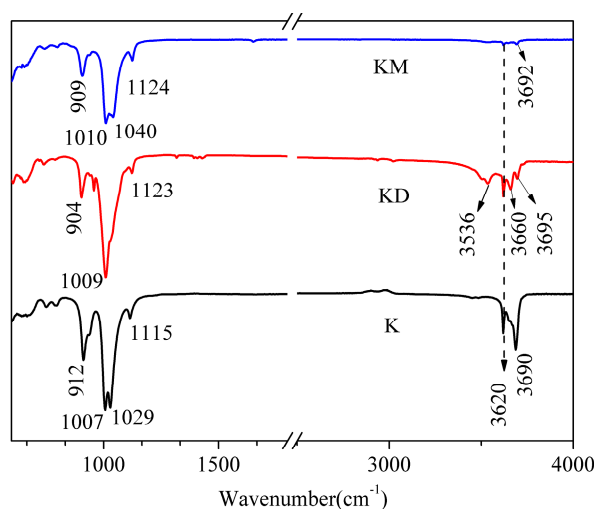


Figure 5. FTIR spectra of K, K-D, and K-M.

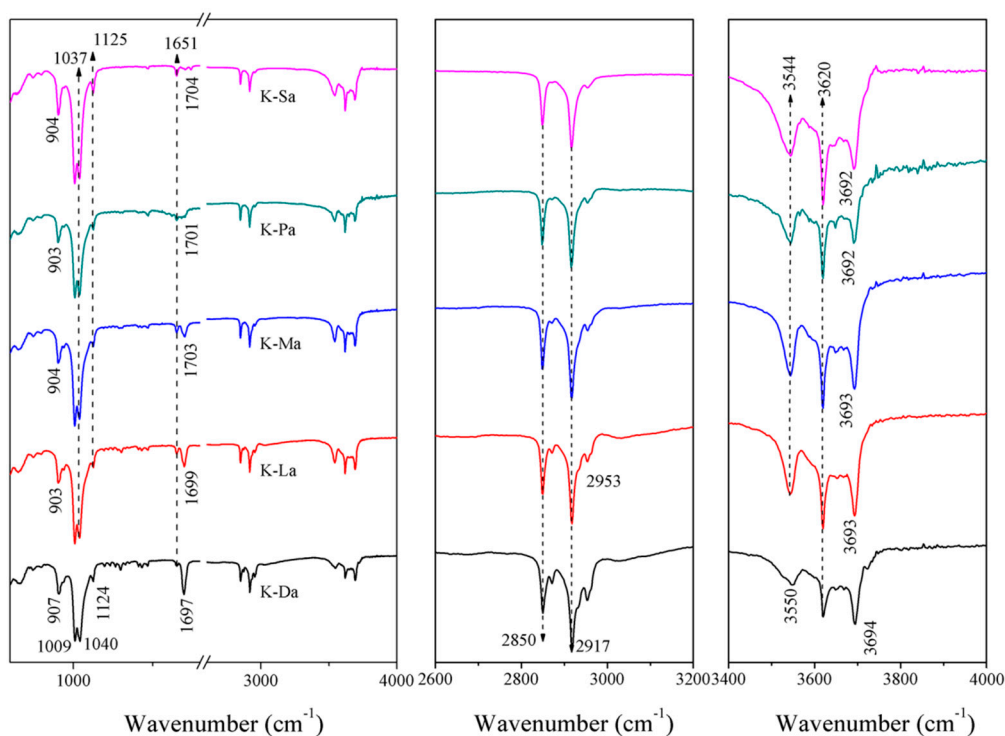


Figure 6. FTIR vibration spectra of kaolinite/fatty acid intercalation compounds (K-Fas).

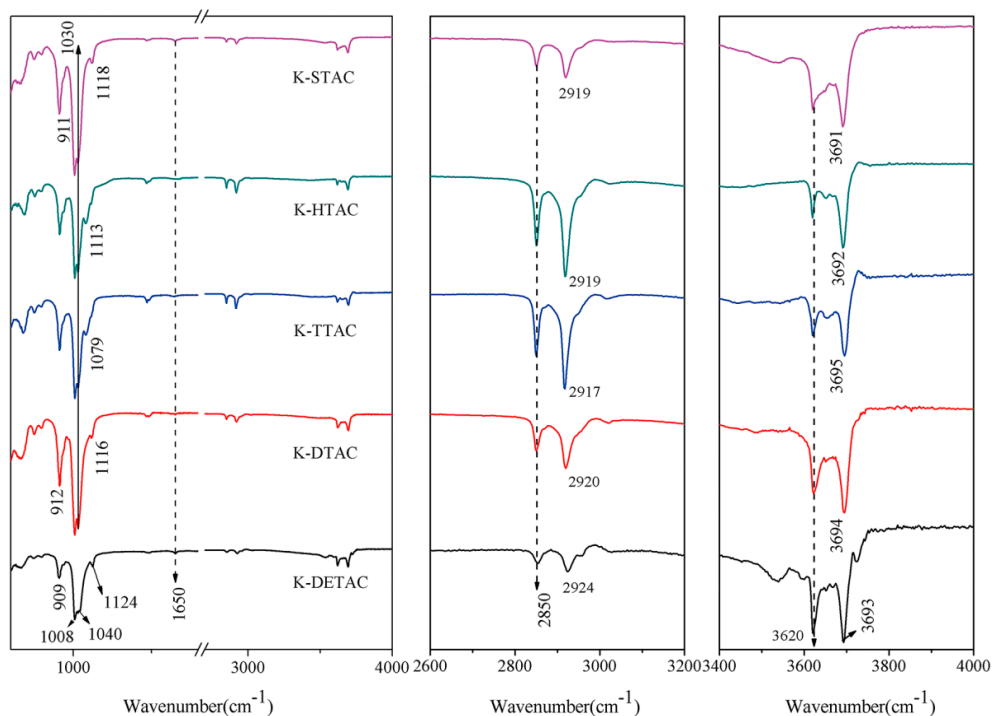


Figure 7. FTIR vibration spectra of kaolinite/quaternary ammonium salts intercalation compounds (K-Qas).

The IR bands in the range of $900\text{--}912\text{ cm}^{-1}$ correspond to the bending vibration peak of the internal surface hydroxyl group of kaolinite. Compared with the starting kaolinite (Figure 5), the bending vibration bands of Al–OH shifted to a low wavenumber in the spectra of K-Fas, and their intensities decreased. However, there were slight changes for K-Qas. These differences indicated that the fatty

acids had more influence on the surface hydroxyl group of kaolinite than the quaternary ammonium salts. In other words, the interaction between the carboxyl groups of the fatty acid and the inner-surface hydroxyl groups of kaolinite was stronger.

On the basis of the spectrum of the starting kaolinite, the band at 1115 cm^{-1} was assigned to the stretching vibrations of apical Si–O. After intercalation, the stretching vibrations of apical Si–O were perturbed by the guest species. It was observed that the band at 1115 cm^{-1} shifted to 1125 cm^{-1} and then persisted at the same position in K-Fas (Figure 6). For K-Qas, the bands at 1124, 1116, 1079, 1113, and 1118 cm^{-1} were assigned to the apical Si–O stretching band. This implied that the apical Si–O was affected by the intercalation with quaternary ammonium salts. The bands at 1040 and 1010 cm^{-1} observed for K-M were assigned to the in-plane vibrations of Si–O–Si. After kaolinite had intercalated with the fatty acids, the bands at 1040 and 1010 cm^{-1} did not shift. However, when kaolinite was intercalated with quaternary ammonium salts, the 1040 and 1010 cm^{-1} bands shifted with different levels (Figure 7). In other words, the quaternary ammonium salts caused more shifts than the fatty acid. This difference might imply that the quaternary ammonium salts interacted with the top oxygen of the silica tetrahedron. On the other hand, the characteristic peak at $\sim 1040\text{ cm}^{-1}$ in K-Fas was sharper than for F-Qas.

As mentioned in the above analysis, both fatty acids and quaternary ammonium salts were intercalated into kaolinite successfully. Compared with K-Fas, quaternary ammonium salt molecules not only interacted with the internal surface hydroxyl groups of kaolinite but also with Si–O significantly. In the case of K-Fas, the fatty acids mainly interacted with the internal surface hydroxyl groups of kaolinite, and the Si–O was affected slightly.

3.4. Discussion on the Morphology Changes of Exfoliated Kaolinite

On the basis of the morphology analysis, we know that the alkyl chain length and ionic type have a great effect on the change in kaolinite morphology. During the intercalation and exfoliation processes, the kaolinite layers transformed from platy particles to nanoscrolls. The driving force for kaolinite curling from sheets to nanoscrolls arose from the lateral misfit of the smaller octahedral and larger tetrahedral sheet. However, the kaolinite layers needed to be exfoliated firstly. It is well known that kaolinite layers are strongly held by hydrogen bonds, electrostatic forces and van der Waals forces. When kaolinite intercalated with guest species, the hydrogen bonds were broken significantly and provided free space for kaolinite sheets to exfoliate or curl up [32,35]. Consequently, it is easy to understand the effect of the alkyl chain length on the morphology of kaolinite sheets. With the lengthening in the molecular chain of the intercalator and a widening kaolinite interlamellar spacing, the binding force between lamellas weakens, thus resulting in the exfoliating and curling of kaolinite lamellas. The longer the molecular chain is, the wider the kaolinite interlamellar spacing is and the weaker the interlamellar binding force will be, making lamellas easier to exfoliate or curl up. The basal spacings of K-Fa- C_{18} and K-Qa- C_{18} are 4.13 and 4.24 nm, respectively. Although they have a similar interlamellar spacing, their morphology differs significantly. This demonstrates that the type of intercalator plays a more important role in hydrogen bond failure between lamellas. In order to imply the mechanism in this, the arrangement model of the guest species in kaolinite should be revealed first.

To date, the derivation of arrangement models for the kaolinite intercalation compound is still based on XRD analysis and stereochemical calculation. In this paper, XRD was used in conjunction with FTIR and stereochemical calculation to probe the interlayer structure of kaolinite intercalation compounds. The XRD analysis indicated that both quaternary ammonium salts and fatty acids orientated in kaolinite layers with a similar arrangement. The basal spacing of the intercalation compounds and corresponding intercalated molecules' length are shown in Table 1. In addition, on the basis of a stereochemical calculation that is generally used to simulate the arrangement of organic compounds in the interlayer space of clay minerals such as montmorillonite and Kaolinite [23,36,37],

both kinds of intercalators should be arranged in the form of a tilted bilayer in the interlayer space of kaolinite.

The interaction of intercalator groups with internal and surface layers of kaolinite can be determined according to the distribution of intercalator molecules between kaolinite lamellas. The distribution patterns of the fatty acid and quaternary ammonium salt molecules in kaolinite lamellas are shown in Figure 8. Combining with FTIR analysis results, quaternary ammonium salt molecules interact with both internal surface hydroxyl groups of kaolinite and Si–O at the bottom of kaolinite lamellas. On the one hand, for ion groups of quaternary ammonium salts, it is easy to form a new acting force with Al–OH through a hydrogen bond. On the other hand, Si–O is negatively charged and attracts positive ion groups through electrostatic force. Carboxylate radical ions of fatty acid are negatively charged, thus repelling Si–O mutually, but interact with hydroxyl groups of kaolinite. Although both anionic (fatty acid) and cationic (quaternary ammonium salt) molecules present a bilayer inclining distribution, –COO– in the anionic intercalator mainly interacts with internal surface hydroxyl groups of kaolinite, while positive ions at the N-end of the cationic intercalator interact with both internal surface hydroxyl groups of kaolinite and the Si–O bond of the silica tetrahedron of kaolinite. Meanwhile, some methyls will enter into ditrigonal pyramid caves of kaolinite silica tetrahedron. Compared to anionic guest species, it is easier for a cationic species to destroy the hydrogen bond between kaolinite lamellas. Particularly, positive ion groups of two layers of quaternary ammonium salt molecules interact with both silica tetrahedron faces and alumina octahedron faces between kaolinite lamellas, enabling the cutting of bonds of Si–O and Al–OH. Furthermore, the interface between two layers of quaternary ammonium molecules is the adjacent surface of like ions that repel mutually. Therefore, the interlamellar binding force of kaolinite disappears gradually with the widening of the interlamellar spacing. As a result of the distortion force caused by structural dislocation, kaolinite lamellas curl up into tubes. Fatty acids not only have a hydrogen bond force and a weak electrostatic attraction between their radicals (carboxyl and methyl) and internal surface groups of kaolinite, but they also have a weak hydrogen bond force between them. Such forces reach a balance state with the distortion force caused by the structural dislocation of kaolinite and connect lamellas together, thus enabling the anionic intercalator to keep its lamellar structure.

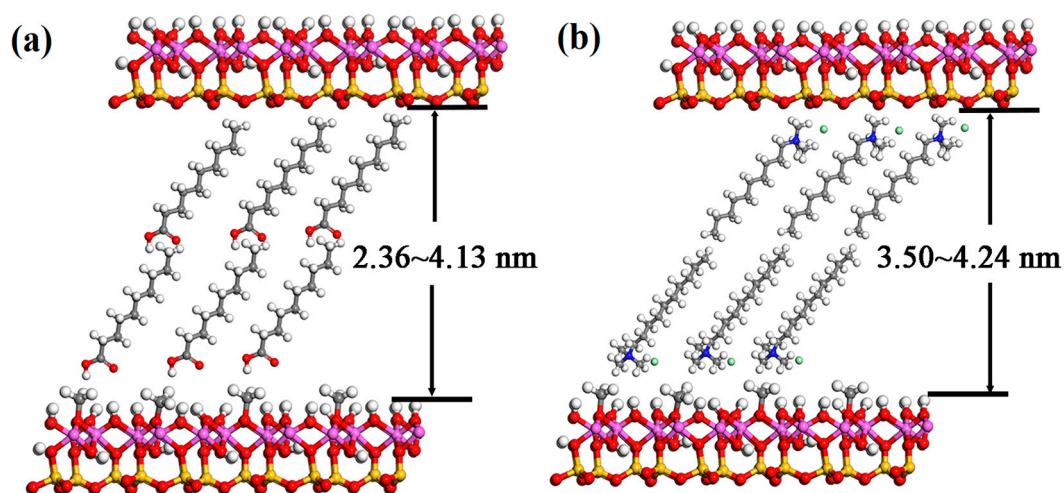


Figure 8. Schematic diagram of arrangement models of (a) kaolinite/fatty acid intercalation compounds (K-Fas), and (b) kaolinite/quaternary ammonium salts intercalation compounds (K-Qas).

4. Conclusions

The interlayer structure, morphology, and chemical bonding of kaolinite intercalation compounds with different guest species are investigated in detail. With the lengthening of the alkyl chain and

gradual expanding of interlamellar spacing, kaolinite lamellas begin to exfoliate and curl up from the edges until they form nanotubes. Compared with the alkyl chain length, the ionic type of the guest species plays a more important role in the changes in the kaolinite morphology. An anionic intercalator could make kaolinite exfoliate but retain its structure and morphology. However, it is easier for an organic cationic intercalator to destroy the hydrogen bond and weaken the binding force between kaolinite lamellas, thus making kaolinite lamellas peel off and curl up. The arrangement models of guest species in kaolinite layers were probed to elucidate the effect mechanism of guest species on the changes in the kaolinite morphology, which could provide the theoretical basis for preparing kaolinite with different microstructures and morphologies.

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