

Study on Intercalation of Organic Mica with $\text{CnH}_{37}(\text{CH}_3)_3\text{NCl}$ ($n=12, 14, 16, 18$) and Its Independent Interlayer Spacing

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Abstract. We have prepared a special organic mica composite by inserting $\text{CnH}_{37}(\text{CH}_3)_3\text{NCl}$ ($n=12, 14, 16, 18$) surfactant into previously prepared sericite. This complex exhibits a unique interlayer spacing feature. As the surfactant concentration increases, the interlayer spacing will remain unchanged. So far, similar reports haven't been reported. In addition, FT-IR showed that the organic molecules in this material will adopt different structural arrangements at different concentrations.

1. Introduction

Lamellar organosilicate complexes possess special adsorption properties, which is a hot research topic in fields like industrial catalysis [1-2], membrane [3-4], and waste-water absorbent [5-7].

The height and stability of the layer space are two key factors that determine its application: the space determines the number of molecules and its corresponding stable efficiency. According to reports, the filling position of organic molecules and the extension of layer spacing are related to the concentration of organic substances. Organic molecules usually adopt a single-layer oblique ortho-arrangement at low concentrations, and turn to two-layer or even pseudo-three-layer arrangement at high concentrations.

Besides, due to the hydrophobic nature of organic matter, the interlayer space is also very hydrophobic. This means that its application will be limited, for example as an inorganic catalytic material.

This article describes the preparation of an organic mica composite by intercalating the surfactant $\text{CnH}_{37}(\text{CH}_3)_3\text{NCl}$ ($n=12, 14, 16, 18$). We have unexpectedly found that increasing the inter-layer space has nothing to do with the concentration, but it is related to the length of the carbon chain. This particular property implies its potential application.

2. Experiments

2.1 Method

The Ba-mica (Ba-M) prepared by Ba-K ion exchange method was used, and its basic interlayer space was expanded to 1.206 nm [8]. Each time 0.2 g of Ba-M was weighed into a clean flask, the corresponding amount of $\text{CnH}_{37}(\text{CH}_3)_3\text{NCl}$ ($n=12, 14, 16, 18$) ($\geq 95\%$, Aladdin) was added to the flask. Mix with 40.0 ml distilled water. The flask was then sealed and placed in water at 60 °C, and heated in a water bath while stirring with magnetic force for 5 hours. At the end of the reaction, filtration was



immediately carried out. The filter residue was washed with a mixture of alcohol and water (1:1) until it was neutral. The washed filter residue was then washed three times with distilled water and dried in a vacuum drying oven at 95 °C for 12 hours. Finally, the dried organic mica was stored in a sealed vacuum box.

The surfactant concentration was set to: 0.05 CEC, 0.15 CEC, 0.20 CEC, 0.25 CEC, 0.50 CEC, 0.75 CEC, 1.00 CEC, and 1.50 CEC. And the organic mica (O-M) samples obtained were named as M-0.05, M-0.15, M-0.20, M-0.25, M-0.50, M-0.75, M-1.00, and M-1.50 with different carbon chain length ($n = 12, 14, 16, 18$).

2.2. Characterizations

A powder X-ray diffractometer (D8 ADVANCE, Bruker, Germany) was used to characterize the basal spacing of crystalline planes of the samples. The acceleration voltage was 40 kV and the acceleration current was 40 mA. The X-ray wave length was 0.1540 nm. The scanning angle is from 2 to 50 degree, the scanning velocity was 0.01023 degree per step.

A thermo gravimetric analyzer (STA449F3, NETZSCH, Germany) was used to find out the organic quantity swallowed into interlayers. The TGA tests were under oxygen environment with a heating rate of 5 °C /min and from room temperature to 1000 °C.

A fourier transform infrared spectrometer (Nicolet Impact 6700) with a resolution of 4 K was used to examine the interaction between the organic groups and the aluminosilicate sheets. The sample was amounted on a KBr disc, and the sample used was measured as 2% wt. of the KBr.

3. Results and Discussion

3.1. Slight change of enlarged interlayer space

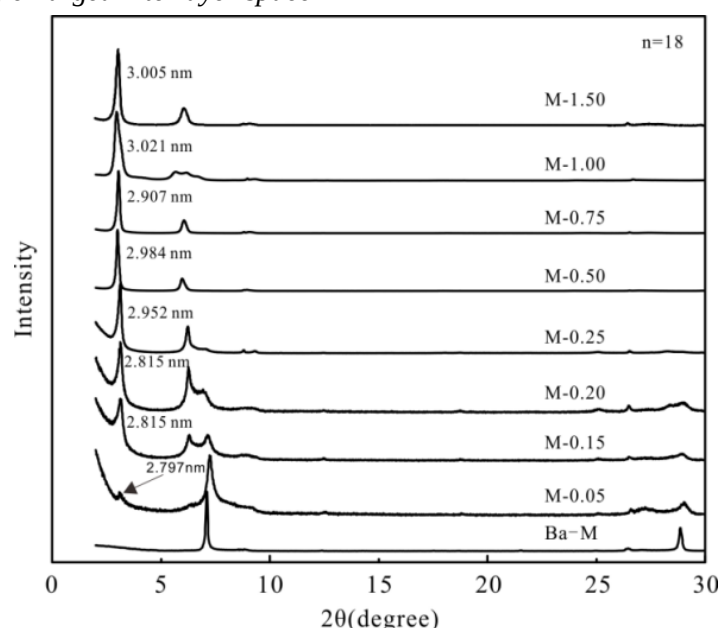


Figure 1. XRD patterns of $C_{18}H_{37}(CH_3)_3NCl$ ($n=18$) intercalated O-M.

As shown in Figure 1, the new peak appears gradually, and the original sericite peak gradually disappears, indicating that the sericite has been successfully intercalated. When the concentration of surfactant ($n = 18$) ranged from 0.05 CEC to 1.50 CEC., the size of d_{001} increased from 2.797 to 3.005 nm. According to reports, as the surfactant concentration increases, the substrate spacing also increases from about 1.4 nm to 4.0 nm. Therefore, the d_{001} for preparing organic mica in this paper seems to be independent of the surfactant concentration.

The space height between the interlayers is equal to the thickness of the sheet d_{001} minus 0.96 nm,

and the increase range is 1.837-2.045 nm. The difference is 0.208 nm, and the thickness of a monolayer of water molecules is about 0.2 nm. Therefore, the slight difference in d_{001} may be caused by water molecules. We will discuss this further in FTIR analysis.

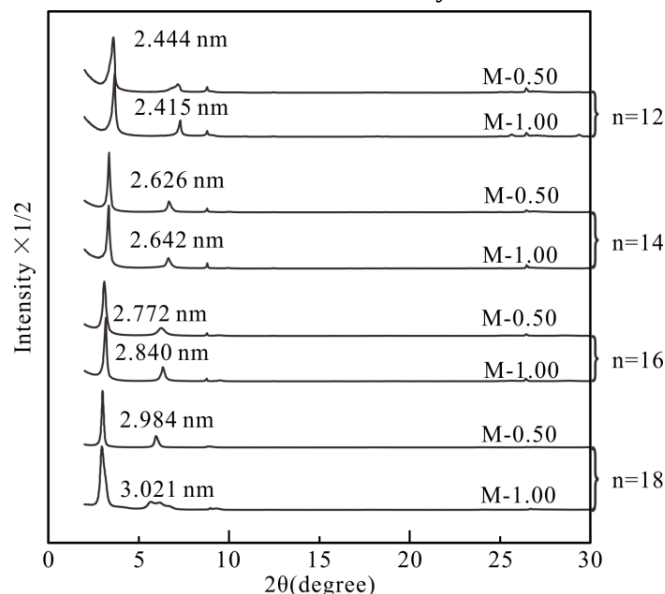


Figure 2. XRD patterns of $C_nH_{37}(CH_3)_3NCl$ ($n=12, 14, 16, 18$) intercalated O-M

The concentration independence can also be observed in O-M pillared with different carbon lengths ($n=12, 14, 16$) (Figure 2). At 0.50 CEC and 1.00 CEC of same carbon length, the d_{001} are nearly same that the height of the basal spacing floated only 0.17-0.2 nm. And, the length of the long carbon chain shortens about 0.2 nm as every two carbon atoms cuts, which is in accordance with our observation.

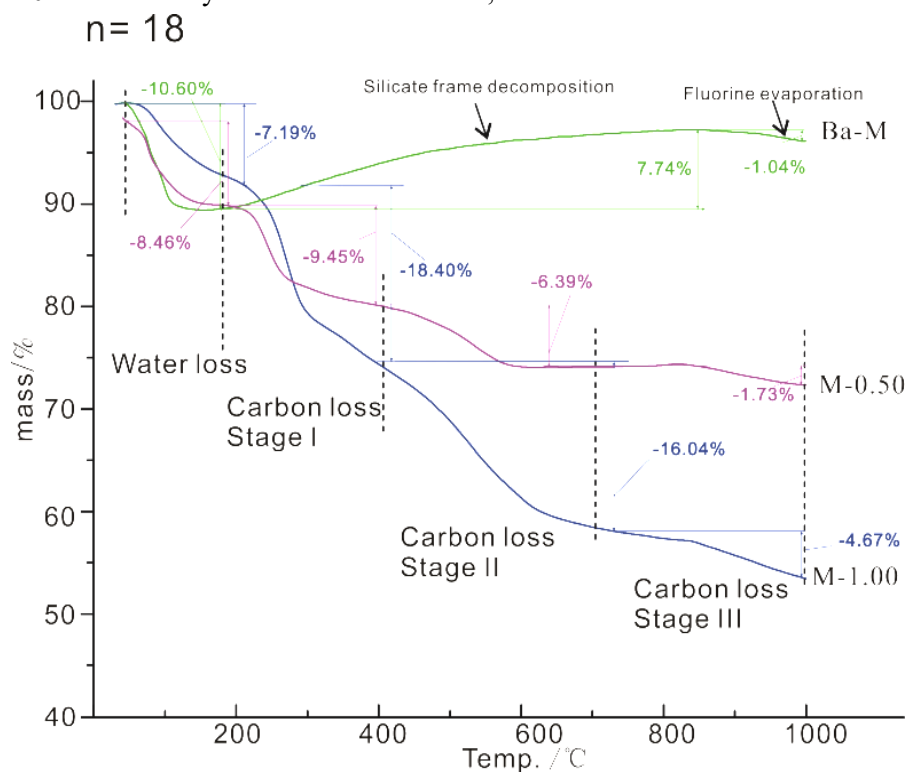


Figure 3. Mass loss of samples of Ba-M, M-0.50 and M-1.00

TGA tests were to conform if the concentration independence was caused by the saturation of surfactant molecules in the gallery space, as exemplified $C_{18}H_{37}(CH_3)_3 NCl$ (STAC) pillared O-M (Figure 3). In oxygen environment, the surfactant will burn out when heating. The mass loss between the 80-200 °C accounts for the structural water. The water loss is about 10.60% in Ba-M, 8.46% in M-0.50, and 7.19% in M-1.00. And the mass loss between the 200-1000 °C is due to the silicate frame decomposition in Ba-M, and in O-M it is the combination of organics and silicate frame decomposition.

The organics content in O-M, which is equal to the mass loss between 200-1000 °C minus the corresponding mass loss in Ba-M, was 24.27% in M-0.50 and 45.81% in M-1.00. And ideally, the maximum of organics content was about 33.33% in M-0.50 and 50.00% in M-1.00. Therefore, the gallery space hasn't been completely soaked by the organic molecules below 1.00 CEC. It is then fair to say that the d001 of the O-M prepared is independent to the surfactant concentration.

3.2. Identical Conformational Arrangement of Surfactant Molecules

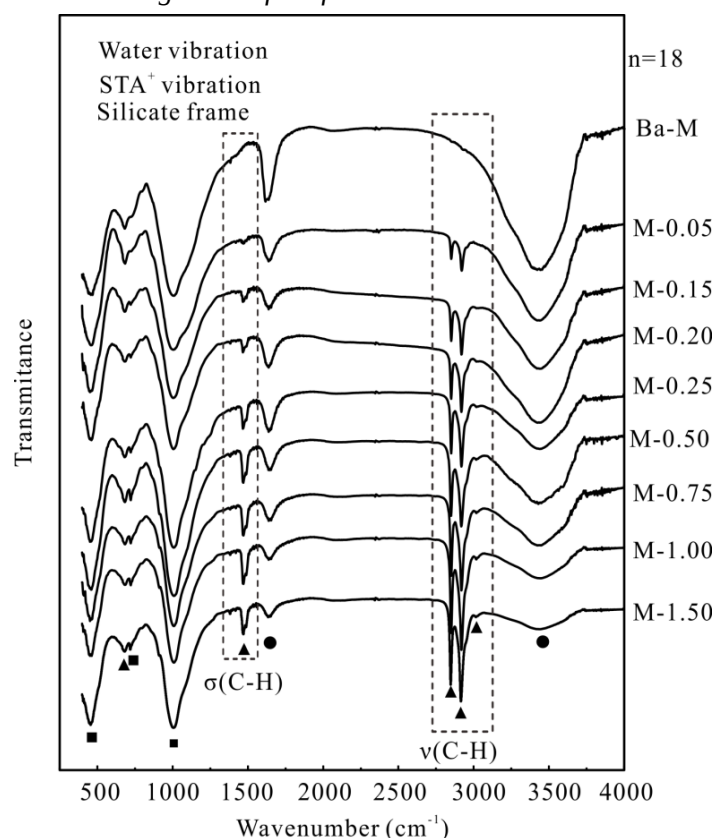


Figure 4. Mid-FTIR spectrums of Ba-mica and O-M intercalated with STAC.

The FTIR spectrums are shown in figure 4. The intensity of water stretching band (3442 cm^{-1}) and bending band (1618 cm^{-1}) gradually weakened with the increase of STAC quantity. This is due to the hydrophobic effect conferred by the carbon chains. As more surfactant molecules intercalated into the gallery space, the water repellency grew stronger, resulting in the reduction of water content. TGA results also prove this point.

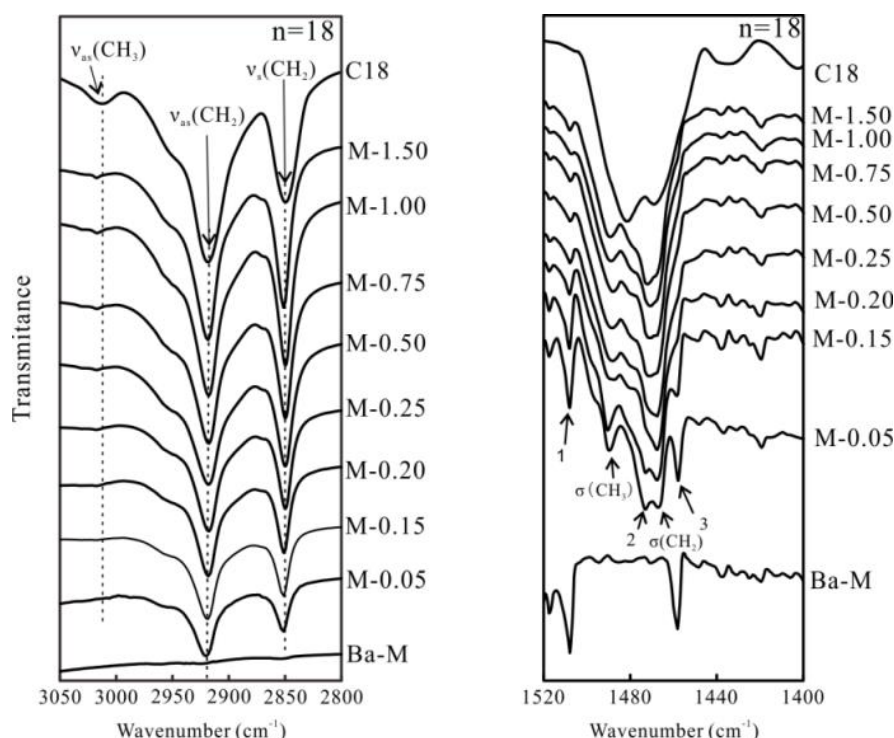


Figure 5. FTIR spectrums in the 3050-2800 cm^{-1} and 1520-1400 cm^{-1} regions of Ba-mica and O-M intercalated with STAC

Compared with crystalline state of STAC, the band frequencies of STAC in O-M associated with methylene (CH_2) were almost same, while the band frequencies associated with the methyl in the head ammonium group ($\text{N}(\text{CH}_3)_3$) shifted towards a higher wave number (Figure 5) though the peaks were weak. The exact data are shown in table 1.

Table 1. Vibration frequencies related to surfactant in O-M (Frequency unit: cm^{-1})

Assignment of group *	M-0.05	M-0.15	M-0.20	M-0.25	M-0.50	M-0.75	M-1.00	M-1.50	STAC
$\nu_{\text{as}}(\text{N}(\text{CH}_3)_3)$	~	~	~	3018.23	3017.96	3017.6	3017.44	3017.81	3012.58
$\sigma(\text{N}(\text{CH}_3)_3)$	1489.85	1490.52	1487.65	1488.22	1489.00	1488.53	1488.08	1489.38	1481.53
$\nu_{\text{as}}(\text{CH}_2)$	2919.94	2918.43	2917.75	2918.09	2918.16	2918.1	2918.09	2918.03	2918.06
$\nu_{\text{s}}(\text{CH}_2)$	2850.29	2850.27	2849.89	2850.00	2850.08	2849.96	2849.87	2850.50	2849.70

* This is referred to Barman et al. 2003, Venkataraman et al. 2000, Venkataraman et al. 2001.

At different STAC loadings, the four important vibrations of STA^+ , including $\nu_{\text{as}}(\text{N}(\text{CH}_3)_3)$ (Asymmetric stretching vibration of the methyl in the head ammonium group) and $\sigma(\text{N}(\text{CH}_3)_3)$ (the corresponding bending vibration), $\nu_{\text{as}}(\text{CH}_2)$ (Asymmetric stretching vibration of the methylene) and $\nu_{\text{s}}(\text{CH}_2)$ (symmetric stretching vibration), altered insignificantly, indicating that STA^+ was in a similar environment once it was accommodated between sheets regardless its concentration.

Compared with pure STAC, the $\nu_{\text{as}}(\text{CH}_2)$ and $\nu_{\text{s}}(\text{CH}_2)$ in O-M fluctuated very little, demonstrating the carbon chains adopted the same conformational mode as the crystalline STAC in which the carbon chains are fully stretched (Venkataraman et al. 2001), i.e., the STAC dose had no influence on its conformational model in O-M.

However, compared with the crystal state of STAC, the $\nu_{\text{as}}(\text{N}(\text{CH}_3)_3)$ and $\sigma(\text{N}(\text{CH}_3)_3)$ in O-M moved to higher frequency, meaning the head ammonium group was immobilized. This was caused by the positively charged head ammonium group interacting with negatively charged aluminosilicate sheets.

It is also noticeable that the scissor vibration of the methylene $\sigma(\text{CH}_2)$, which reflects the interaction between carbon chains, was split (Figure 5b). The splitting was clear in M-0.05 and M-0.15, and blurred at higher STAC quantity, but it still could be resolved comparing with it in crystalline state, representing that the STA^+ had two different chain interactions. This was due to the uneven distribution of structural water. The STA^+ in water concentrated terrain were hydrated stronger. And the water was repelled out gradually as more STA^+ moved in, which therefore weakened its interaction with STA^+ .

4. Conclusion

Organic mica composites were prepared with pre-prepared Ba-mica by intercalating $\text{C}_n\text{H}_{37}(\text{CH}_3)_3\text{NCl}$ ($N=12, 14, 16, 18$). The evidences in FTIR showed that the STA^+ in O-M adopted an identical conformational arrangement at different concentrations. Combining with XRD analysis, it is believed that this organic mica composite has a unique property that its basal space is regardless to the organics concentration. Even in a very low loading, the organic molecules are still strong enough to support the whole interspace from crashing that was believed to happen, i.e., the organics structure is robust so that it will not change easily even though a certain number of organics dissolve out. In addition, the remaining water molecule is helpful to adjust the hydrophilic-hydrophobic property on the premise of retaining this structure. According to this character, potentially, demanded layered silicate composite with certain height or hydrophilic feature can be precisely prepared.

Acknowledgments

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