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Structures and dynamics of *n*-dodecyltrimethylammonium ions intercalated into sodium octosilicate and tetrasilicicfluoromica

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Abstract

Structures and dynamics of *n*-dodecyltrimethylammonium ions intercalated into sodium octosilicate and tetrasilicicfluoromica were studied by powder x-ray diffraction, and ^{13}C CP/MAS and ^1H NMR measurements. In the octosilicate, cations form a 2D-crystalline state in which long axes of intercalated alkylammonium ions were shown to be inclined to silicate layers and polymethylene chains $(-\text{CH}_2-)_n$ take the *all-trans* conformation. On the other hand, in the tetrasilicicfluoromica, cations form disordered arrangements with random conformations of alkyl-chains, considered to be in a 2D-amorphous state. Based on the NMR results, the dynamic behaviour of these ions in 2D space is discussed.

1. Introduction

Phyllosilicates consisting of 2D silicate layers include inorganic cations between layers. These cations can easily be exchanged by organic cations, and form various intercalation compounds. Recently, much attention has been directed to nanospaces made in layered silicates, where guest molecules contained in the interlayer space are expected to form 2D molecular aggregates having different structures and dynamics from those in 3D molecular assemblies in bulk.

Octosilicate ($\text{NaSi}_4\text{O}_8(\text{OH})$) and tetrasilicicfluoromica (ideal composition: $\text{NaMg}_{2.5}\text{Si}_4\text{O}_{10}\text{F}_2$) are phyllosilicates with different structures. The octosilicate consists of homogeneous $\text{Si}_4\text{O}_8(\text{OH})$ layers that contain densely packed negatively charged sites with ordered distributions. On the other hand, tetrasilicicfluoromica consists of layers of MgO_4F_2 octahedra sandwiched between two layers formed by SiO_4 tetrahedra. In the layers, one of every six Mg^{2+} ions is missing, giving negatively charged sites, randomly distributed. In the present study, we intend to show the influence of structures in host clay minerals by properties of intercalated molecules, and selected *n*-dodecyltrimethylammonium ions as a guest system that can take various conformations and has many degrees of freedom, so it can fit into different interlayer environments. Structures and dynamics of the cationic aggregate intercalated into these two

phyllosilicates were investigated by using x-ray powder diffraction (XRD), differential thermal analysis (DTA) and solid state NMR.

2. Experimental details

Sodium octosilicate (abbreviated to Na-OS) was synthesized hydrothermally from a mixture of silicon dioxide, sodium hydroxide and water with a molar ratio of $\text{SiO}_2:\text{NaOH}:\text{H}_2\text{O} = 4:1:25.8$ [1]. The mixture was sealed in a Teflon-sealed stainless autoclave and kept at 100 °C for two weeks. The product was washed with an NaOH solution of pH 9.5 and dried at 40 °C for two days. The colourless powder obtained was identified by XRD. Synthetic sodium tetrasilicifluoromica (abbreviated to Na-MC) ($\text{Na}_{0.6}\text{Mg}_{2.7}\text{Si}_4\text{O}_{10}\text{F}_2$, CO-OP Chemical Co., Ltd) was used as purchased. The intercalation of *n*-dodecyltrimethylammonium (C_{12}TMA) ions into silicates was performed by the ion exchange method using an aqueous solution of C_{12}TMA chloride with its concentration adjusted to twice that of the cation exchanging capacity of each compound. The product was centrifuged and washed with distilled water repeatedly until a negative AgNO_3 test was obtained. To determine the effect of differences in the alkyl-chain length, the intercalation of *n*-hexadecyltrimethylammonium (C_{16}TMA) ions to OS and MC was performed using the same method.

DTA measurements were performed with a home-made apparatus between 85 and 331 K to detect possible phase transitions. Powder XRD patterns were measured with a Philips X'pert PW 3040/00 diffractometer using $\text{Cu K}\alpha$ radiation. The data were collected from 1° to 30° in Na-OS and Na-MC as well as the above four intercalated systems at 290 K and also at 350 K in $\text{C}_{12}\text{TMA-OS}$ and $\text{C}_{12}\text{TMA-MC}$. ^{13}C CP/MAS NMR spectra were measured at a Larmor frequency of 75.47 MHz, a contact time of 5 ms and a spinning rate of 7 kHz with a Bruker MSL-300 NMR system at 290 and 350 K. Temperature dependences of the second moments (M_2) of ^1H NMR absorption lines were measured with a Bruker SXP-100 spectrometer. M_2 values were determined using the solid echo method [2].

3. Results and discussion

3.1. Elemental analysis and differential thermal analysis (DTA)

Elemental analysis of C, N and H in the intercalated compounds showed that about 70% and 66% of Na^+ ions were exchanged by C_{12}TMA ions in Na-octosilicate (Na-OS) and Na-mica (Na-MC), respectively, i.e., a C_{12}TMA ion occupies an area of 38 Å² in Na-OS and 47 Å² in Na-MC. This indicates that Na-OS affords somewhat denser intercalation of the layers than Na-MC.

DTA measurement showed no phase transitions in these two systems over the temperature range studied.

3.2. X-ray diffraction (XRD) and ^{13}C CP/MAS NMR spectra

Powder XRD patterns of Na-OS, $\text{C}_{12}\text{TMA-OS}$, $\text{C}_{16}\text{TMA-OS}$, Na-MC, $\text{C}_{12}\text{TMA-MC}$ and $\text{C}_{16}\text{TMA-MC}$ at 290 K are shown in figure 1. By introducing C_{12}TMA ions, *d*-spacings were extended, indicating the intercalation of long-chain cations into layers. From (001) reflections, *d*-spacings in $\text{C}_{12}\text{TMA-OS}$ and $\text{C}_{12}\text{TMA-MC}$ were derived to be 23.7 ± 1.7 Å and 19.4 ± 0.7 Å, respectively. By subtracting the layer thickness of 9.5 Å in Na-OS [3] and 9.6 Å in Na-MC [4], the interlayer distances in $\text{C}_{12}\text{TMA-OS}$ and $\text{C}_{12}\text{TMA-MC}$ were obtained to be 14.2 ± 1.7 Å and 9.8 ± 0.7 Å, respectively. This difference, which gives information

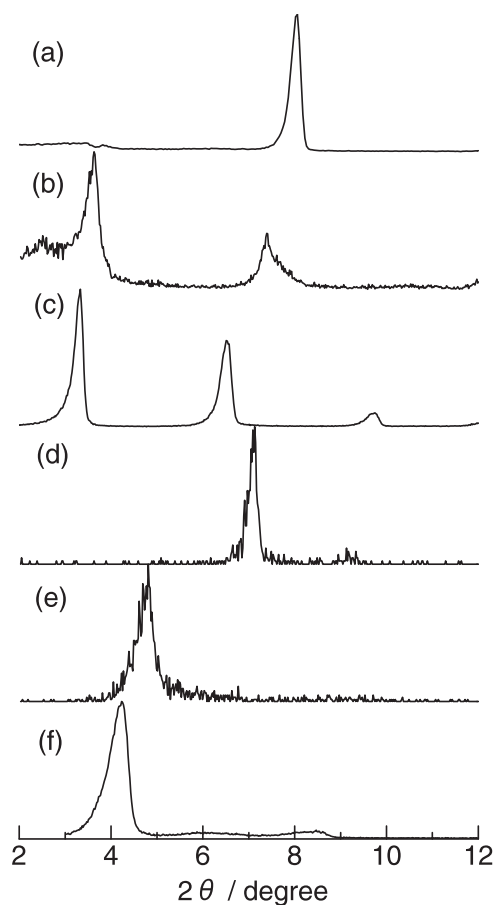


Figure 1. Powder x-ray diffraction patterns observed in (a) sodium octosilicate (Na-OS), (b) dodecyltrimethylammonium-octosilicate (C_{12} TMA-OS), (c) hexadecyltrimethylammonium-octosilicate (C_{16} TMA-OS), (d) tetrasilicicfluoromica (Na-MC), (e) dodecyltrimethylammonium-tetrasilicicfluoromica (C_{12} TMA-MC) and (f) hexadecyltrimethylammonium-tetrasilicicfluoromica (C_{16} TMA-MC).

on cationic arrangements in the interlayer space, is discussed later together with the ^{13}C NMR data. The (001) reflection angle derived from the XRD pattern observed in C_{12} TMA-OS at 353 K was the same as that at 290 K, indicating no marked thermal effect on the intercalation structure in this temperature range. By subtracting the layer thickness mentioned above from the *d*-spacings of $26.6 \pm 0.9 \text{ \AA}$ observed in C_{16} TMA-OS and $20.7 \pm 0.3 \text{ \AA}$ in C_{16} TMA-MC, the interlayer distances were determined to be 17.1 ± 0.9 and $11.1 \pm 0.1 \text{ \AA}$, respectively.

^{13}C CP/MAS NMR spectra of C_{12} TMA-OS and C_{12} TMA-MC are shown in figure 2. Signal assignments given in table 1 and figure 3 were carried out by referring to data observed in the aqueous solution of C_{12} TMA chloride [5]. Since sharp spectra were observed in C_{12} TMA-OS, ordered arrangements of alkyl chains in C_{12} TMA ions are expected. Observed chemical shift values for C4–C9 in C_{12} TMA-OS at 290 K suggest the polymethylene chains in C_{12} TMA ions are extended with keeping the *all-trans* zigzag conformation [6, 7]. New peaks at 30.06 and 27.04 ppm observed at 350 K upon heating were assignable to the *liquid-like* and *gauche* conformation [6, 7] formed by thermal excitation. The low relative intensity

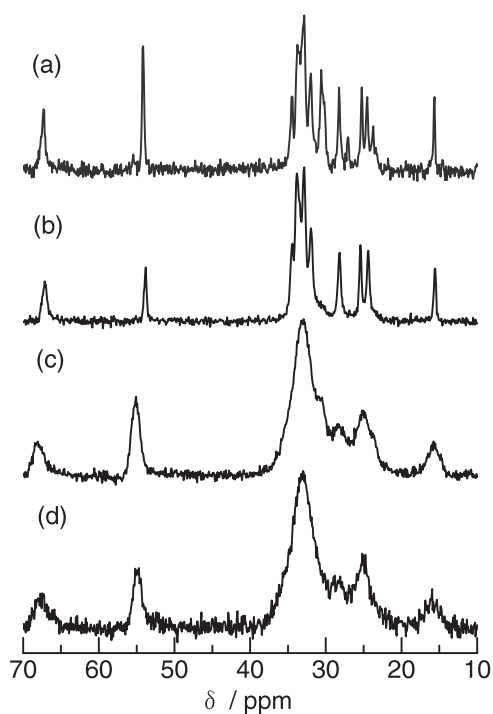


Figure 2. ^{13}C CP/MAS NMR spectra observed in dodecyltrimethylammonium-octosilicate ($\text{C}_{12}\text{TMA-OS}$) at 350 K (a) and 290 K (b), and dodecyltrimethylammonium-tetrasilicicfluoromica ($\text{C}_{12}\text{TMA-MC}$) at 350 K (c) and 290 K (d).

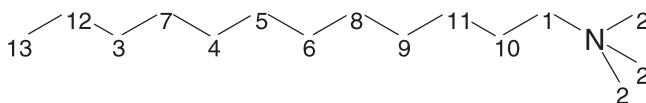


Figure 3. C numbering in the dodecyltrimethylammonium ion.

of the peak assigned to ammonium terminal methyl carbons at 290 K implies a short $T_{1\rho}$ for these carbon nuclei arising from the *tert*-ammonium group rotation.

On the other hand, $\text{C}_{12}\text{TMA-MC}$ showed both at 290 and 350 K broadened peaks compared with those in $\text{C}_{12}\text{TMA-OS}$, suggesting disordered molecular arrangements or conformations in alkyl chains. The observed differences in interlayer structures of OS and MC can be explained by the following reasons. The fact that the cation exchange capacity of Na-OS (2.84 mmol g^{-1}) is larger than that of Na-MC (1.80 mmol g^{-1}) indicates that cations are more loosely packed in MC, giving alkyl-chain arrangements that are more disordered than in OS. The second reason is that negative charges in silicate layers are randomly distributed in mica, whereas they are ordered in OS. Since ammonium groups in C_{12}TMA cations are expected to be pointed to the negative charged sites in the layer, the more ordered arrangement in OS is acceptable.

Here, we combine the above ^{13}C CP/MAS NMR results in $\text{C}_{12}\text{TMA-OS}$ with the interlayer spacing of 14.2 \AA determined by XRD and the total length of about 21 \AA in an *all-trans* C_{12}TMA ion. From these results, the double layered and inclined arrangements of C_{12}TMA ions to the silicate layer are expected in octosilicate, and the angle of inclination to the silicate layer was estimated to be about 20° by considering the *all-trans* conformation of the alkyl chain as shown

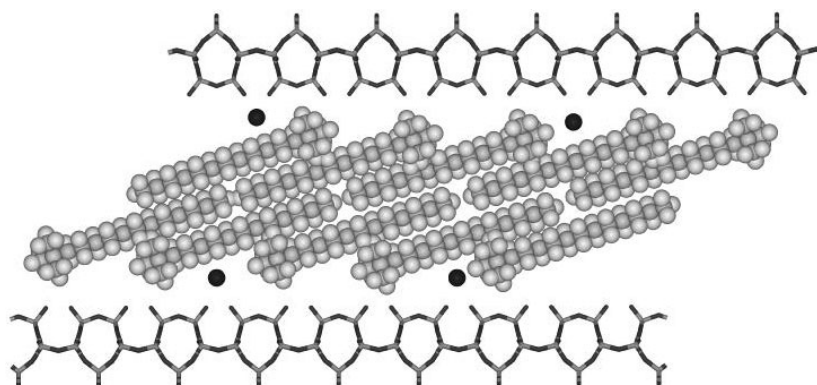


Figure 4. A schematic model of arrangements of dodecyltrimethylammonium ions in octosilicate. The frameworks and black spheres represent silicate lattices and the remaining Na^+ ions.

Table 1. ^{13}C NMR chemical shifts observed in dodecyltrimethylammonium chloride ($\text{C}_{12}\text{TMA-Cl}$) and dodecyltrimethylammonium-octosilicate ($\text{C}_{12}\text{TMA-OS}$).

Assignment	$\text{C}_{12}\text{TMA-Cl}$	$\text{C}_{12}\text{TMA-OS}$ (350 K)	$\text{C}_{12}\text{TMA-OS}$ (290 K)
C1	66.98	67.32	67.15
C2	53.41	54.13	53.80
C3	31.93	34.48	34.40
C4–C9	29.62	33.75	33.83
	29.50	33.51	32.86
	29.44	32.86	31.97
	29.31	31.97	
C10	26.37	30.60	
		28.25	28.17
C11	23.31	27.04	
		25.26	25.42
C12	22.68	24.53	
		23.72	24.37
C13	14.06	15.63	15.55

in figure 4. The extended interlayer spacing obtained in $\text{C}_{16}\text{TMA-OS}$ compared with that in $\text{C}_{12}\text{TMA-OS}$ originating from the difference in the carbon number also supports the inclined alkyl-chain with the ordered structure. The remaining 30% of Na^+ ions in the included total cations, determined by the elemental analysis, are considered to play the role of a buffer for the close distance predicted between alkyl-TMA ions, which can be assumed to be equal to the distance between anionic centres in the OS-layer [3], being 7.3 Å. This is because the alkyl-TMA ions inclining at 20° to the layer require an inter-ionic space of about 10 Å as roughly estimated from van der Waals contacts (figure 4).

3.3. ^1H NMR second moment (M_2)

Temperature dependences of ^1H NMR M_2 -values observed for $\text{C}_{12}\text{TMA-OS}$ and $\text{C}_{12}\text{TMA-MC}$ are shown in figure 5. An observed M_2 -value of 19 G^2 in $\text{C}_{12}\text{TMA-OS}$ at 100 K was smaller than the calculated value of 21.2 G^2 for the methyl group rotation in the terminal alkyl group,

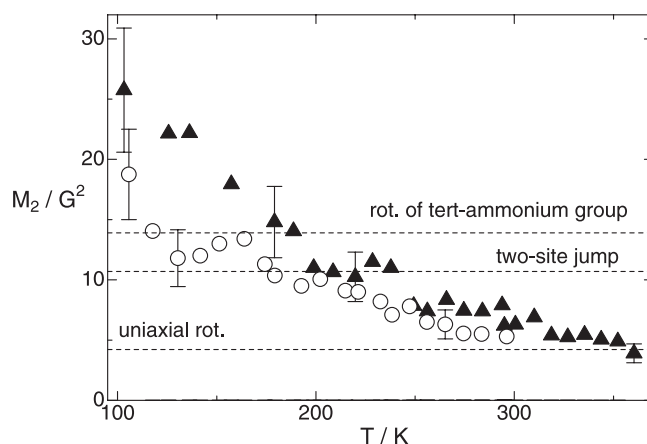


Figure 5. Temperature dependences of ^1H NMR second moment M_2 observed in dodecyltrimethylammonium-octasilicate (open circle) and dodecyltrimethylammonium-tetrasilicicfluoromica (closed triangle). Calculated M_2 -values are shown by dashed lines.

indicating that this motion was already activated at this temperature. A plateau value of about 12 G^2 observed between 120 and 160 K is explainable by the onset of the *tert*-ammonium group rotation by comparing the calculated value of 13.8 G^2 for an isolated cation as shown in figure 5. The observed value gradually decreased on heating above 160 K and reached 5.5 G^2 at room temperature, implying the onset of the cationic uniaxial rotation as a whole that gives the calculated value of 4.2 G^2 .

C_{12}TMA ions in MC showed a more gradual M_2 decrease than in OS in the low-temperature range studied. This implies distributed rates of the molecular motions explainable by disordered arrangements and conformations of alkyl chains in the layer consistent with the x-ray and ^{13}C NMR data.

4. Conclusion

From measurements of XRD, elemental analysis, ^{13}C NMR spectra and M_2 in ^1H NMR absorptions, we showed in OS that C_{12}TMA ions form a double layered and an inclined arrangement to the clay layer, keeping the *all-trans* conformation of alkyl-chains up to room temperature. Above room temperature, the disordered alkyl-chain structure characterized by mixing of the *gauche* conformation was obtained. Upon heating from 100 K to room temperature, cationic motions were activated and uniaxial reorientation of chains is observed at room temperature. These results indicate that C_{12}TMA ions intercalated into OS behave like a 2D rotator phase or liquid crystal.

In C_{12}TMA -MC, disordered molecular arrangements and conformations of alkyl-chains were considered even at low temperatures, as shown by broad spectra in ^{13}C NMR.

These differences in the structure of C_{12}TMA ions in OS and MC, i.e., alkyl-chains in the former are characterized by the 2D-crystalline state, while in the latter by the 2D-amorphous state, can be attributed to differences in the cation exchange capacity and the regularity of the negative charge distribution in the layer in these two kinds of clays. Regular and dense distribution of the negative charges in OS can form the uniform arrangement of cations, whereas random and low-density charge distributions in MC cannot afford the ordered 2D-molecular aggregate, but a disordered packing of cations probably both in arrangements and conformations.

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