Synthesis of Layered Silicate-Polyoxyethylene Alkyl Ether Intercalation Compounds from Kanemite

Nobuyuki Takahashi¹, Hiroaki Tamura¹, Dai Mochizuki¹, Tatsuo Kimura² and Kazuyuki Kuroda¹,³

1. School of Science and Engineering, Waseda University, Tokyo, Japan
2. National Institute of Advanced Industrial Science and Technology (AIST), Nagoya, Japan
3. CREST, Japan Science and Technology Agency (JST), Saitama, Japan

Abstract: Intercalation behavior of poly(oxyethylene) alkyl ether such as C_{16}EO_{10} into layered silicates was investigated by using hexadecyltrimethylammonium (C_{16}TMA) intercalated silicates as intermediates which were prepared from kanemite. The density of Si–OH/Si–O– groups of the C_{16}TMA intercalated kanemite was varied according to the preparation temperature. Lower Si–OH/Si–O– densities of the silicate sheets induced higher degree of intercalation of C_{16}EO_{10} molecules with lower amount of C_{16}TMA cations because of the hydrophobic interaction between alkyl chains of C_{16}EO_{10} molecules and the silicate surface with increased hydrophobicity. The elimination of C_{16}TMA cations during the intercalation of C_{16}EO_{10} molecules seems to be consistent with the charge density of the silicate sheets because of intralayer condensation of Si–OH groups. The intercalation of C_{16}EO_{10} into layered silicates is controllable by this method.

Keywords: Layered Silicate, Nonionic Surfactant, Brij56, Lamellar structure, Inorganic-Organic Nanocomposites

1. INTRODUCTION

Intercalation compounds based on layered silicates have received considerable attention as green and sustainable materials such as catalysts, catalyst supports and adsorbents because of the expandable nanospaces and the inherent high surface areas [1,2]. Such applications have been achieved by controlling interlayer environments including organic modification as well as the variations in layer charge, Si–OH density, and polarity. Therefore, a precise control of layered structures is suggested that the density of Si–OH/Si–O– groups, which is related to the intensity of Q̃ peaks in ²⁹Si MAS NMR spectra, influences the intercalation of nonionic surfactants. The control of the Si–OH/Si–O– density would lead to the precise design of interlayer spaces by intercalation of nonionic surfactants.

In this study, we investigated the intercalation behavior of C_{16}EO_{10} molecules into C_{16}TMA–kanemite with different Si–OH/Si–O– densities, and the intermediates were obtained by changing the reaction temperature of kanemite with C_{16}TMA cations [8]. The intercalation behavior of C_{16}EO_{10} molecules has been investigated only for C_{16}TMA–kanemite prepared at room temperature as an intermediate [7]. Therefore, the insight obtained in this study is useful for further understanding of the intercalation behavior of C_{16}EO_{10} molecules into layered silicates.

2. EXPERIMENTAL SECTION

2.1. Materials

Kanemite (NaHSi₂O₅·3H₂O) was obtained by dispersing δ-Na₂Si₂O₅ (1.0 g) in deionized water (50 mL) with stirring for 0.5 h [7,8]. Hexadecyltrimethylammonium chloride (C₁₆H₃₃N(CH₃)₃Cl, denoted as C₁₆TMACl, Tokyo Kasei Kogyo) and C₁₆EO₁₀ (C₁₆H₃₃(OC₂H₄)₁₀OH, Aldrich) were used as received.

2.2. Synthesis of C₁₆TMA–kanemite (L₁)

The synthetic pathway is summarized in Fig. 1. C₁₆TMA–kanemites with different Si–OH/Si–O– densities were prepared by the reactions of kanemite with C₁₆TMA cations at temperatures ranging from room temperature (r.t.) to 90 °C [8]. Kanemite (1.0 g) was added to an aqueous solution (200 mL) of 0.1 M
C_{16}TMAI and the mixture was stirred for 2 days at room temperature, 50 °C, 70 °C, and 90 °C. The resultant solid products were separated by centrifugation and air-dried, which are denoted as \( L1(\text{r.t.}) \), \( L1(50) \), \( L1(70) \), and \( L1(90) \), respectively.

2.3. Intercalation of \( \text{C}_{16}\text{EO}_{10} \) into \( L1 \)

\( L1 \) was dispersed in an aqueous solution of \( \text{C}_{16}\text{EO}_{10} \) (0.1 M, 40 mL). The mixture was stirred for 2 days at room temperature and centrifuged to recover the resultant product. The slurry was washed by dispersing in deionized water, stirred for 5 min, and centrifuged. This procedure was repeated twice to remove residual \( \text{C}_{16}\text{EO}_{10} \) molecules completely and air-dried. The products are denoted as \( L2(\text{r.t.}) \), \( L2(50) \), \( L2(70) \), and \( L2(90) \), respectively.

2.4. Acid treatment of \( L2(\text{r.t.}) \)

The wet slurry of \( L2(\text{r.t.}) \) (0.2 g as dried \( L1(\text{r.t.}) \)) was dispersed in an aqueous solution of \( \text{C}_{16}\text{EO}_{10} \) (0.1 M, 40 mL). The pH value was decreased to 3.0 by adding HCl (1.0 M) slowly over 0.5 h. The mixture was stirred for 1 day. The slurry was centrifuged, washed twice with deionized water, and air-dried. The product is denoted as \( L3(\text{r.t.}) \).

2.5. Characterization

Powder X-ray diffraction (XRD) measurements were performed on a Rigaku Rint 2000 powder diffractometer with a radiation of Ni-filtered Cu Kα under the operating conditions of 40 kV and 40 mA. The amounts of organic constituents were determined by CHN analysis (Perkin Elmer, 2400 Series II). Thermogravimetry (TG) measurements were carried out with a Rigaku Thermo Plus 2 instrument under a dry air flow at a heating rate of 10 °C min\(^{-1}\), and the amounts of SiO\(_2\) fractions in the products were calculated from the residual weights after heating up to 900 °C. Two-dimensional (2D) \(^{29}\text{Si}\{\text{\textsuperscript{1}H}\}\) HETeronuclear chemical shift CORrelation (HETCOR) NMR experiments [9] were performed under conditions of magic-angle sample spinning at 5–6 kHz, using a \( \mu s \) \( \pi/2 \text{H} \) pulse, followed by a 4.0 ms contact time.

3. RESULTS AND DISCUSSION

3.1. Intercalation of \( \text{C}_{16}\text{EO}_{10} \) into \( L1 \)

The XRD patterns of \( L2s \) are shown in Fig. 2. As reported previously, \( L2(\text{r.t.}) \) has a layered structure having the \( d \)-spacings of 3.3, 1.6 and 1.1 nm [7]. The XRD patterns of \( L2(50) \) (3.3, 1.7 and 1.1 nm), \( L2(70) \) (3.6, 1.8 and 1.2 nm) and \( L2(90) \) (3.7, 1.8 and 1.2 nm) exhibit successful intercalation into \( L1s \) because these three peaks are assignable to layered structure and the \( d \)-spacings of the main peaks are larger than those observed for the corresponding intermediates.

The \( \text{C}_{16}\text{TMA}/\text{Si} \) and \( \text{C}_{16}\text{EO}_{10}/\text{Si} \) ratios calculated from the CHN and TG data are summarized in Table 1. The carbon contents of \( L2(50) \), \( L2(70) \), and \( L2(90) \) (45.4, 44.8, and 44.3 mass%) are larger than those of \( L1(50) \), \( L1(70) \), and \( L1(90) \) (41.4, 40.1, and 40.0 mass%). The results also support the intercalation of \( \text{C}_{16}\text{EO}_{10} \) molecules into \( L1s \). The \( \text{C}_{16}\text{EO}_{10}/\text{Si} \) molar ratios of \( L2(50) \), \( L2(70) \), and \( L2(90) \) are 0.09, 0.10 and 0.10, respectively. The ratios are increased with the increase in the synthetic temperature of \( L1s \). The \( L1s \) obtained at higher
temperatures showed higher $Q^4/(Q^3+Q^4)$ ratios, suggesting the proceeding of intralayer condensation of Si−OH groups [8]. Therefore, the decrease in the Si−OH/Si−O density enhances the intercalation of C16EO10 molecules into L1.

The C16TMA/Si molar ratios of L2(50), L2(70), and L2(90) (0.19, 0.13 and 0.13) are lower than those of L1(50), L1(70), and L1(90) (0.27, 0.23 and 0.25), respectively. C16TMA cations were eliminated partially by the reaction with an aqueous solution of C16EO10. The decrease of C16TMA cations was also observed in the case of L1(r.t.); the C16TMA/Si molar ratio decreased from 0.30 to 0.26 [7]. The decreased amount of the C16TMA/Si molar ratio ($\Delta$C16TMA/Si) in L2(r.t.), L2(50), L2(70), and L2(90) are 0.04, 0.08, 0.10 and 0.12, respectively. Because the intralayer condensation within the individual sheets of kanemite causes the decrease of the Si−OH/Si−O density, the electrostatic interaction of C16TMA cations with silicate layers decreases with the condensation. Therefore, the intralayer condensation of the silicate layers can enhance the elimination of C16TMA cations.

The XRD patterns of L2s showed that the $d$ value of the main peak increased when L1s with much condensed frameworks were used. The $d$ value and the C16EO10/Si ratio of L2(r.t.) also increased with the decrease in the pH value during the acid treatment in an aqueous solution of C16EO10 [7]. We explain the increase in the $d$ value by the assumption that weak interaction between C16EO10 molecules and silicate surfaces is dominant in the interlayer region. Similarly, in this study, the increase of the $d$ value with the increase of the amount of condensed silicate species in L1s arises from the increase of the amount of intercalated C16EO10.

### 3.2. Intercalation mechanism

L2(r.t.) was treated with hydrochloric acid in an aqueous solution of C16EO10 to remove C16TMA cations completely and to precede the intralayer condensation of Si−OH groups (Fig. 1). We analyzed the interactions between C16EO10 molecules and silicate layers of L3(r.t.) by using HETCOR NMR. The 2-D NMR spectrum of L3(r.t.) (Fig. 3) showed the correlation between water (at 5.0 ppm, $^1$H) and $Q^3$ species, showing the presence of adsorbed water on the silicate surfaces [10]. We observed the correlations arising from the dipole-dipole couplings between methylene protons (1.3 ppm, $^1$H) and the $Q^3$ species, and between oxyethylene protons (3.0 ppm, $^1$H) and the $Q^3$ species. The correlations display that both oxyethylene chains and alkyl chains are located closely to the $Q^3$ species. The intensity of the peak due to methylene protons is higher than that due to oxyethylene chains, despite the number of protons in alkyl chains is less than that in oxyethylene chains. Therefore, it is suggested that alkyl chains are more closely located to the silicate layers than oxyethylene chains. This closer location of alkyl chains with the silicate layers can be explained by assuming the hydrophobic interaction between the alkyl chains and the silicate layers. L3(r.t.) has a higher

### Table 1. Amount of organic fractions and SiO2 in the kanemite-based products

<table>
<thead>
<tr>
<th>Sample</th>
<th>C/mass%</th>
<th>N/mass%</th>
<th>SiO2/mass%</th>
<th>C16TMA/Si</th>
<th>C16EO10/Si</th>
<th>$\Delta$C16TMA/Si***</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1(r.t.)*</td>
<td>42.7</td>
<td>2.6</td>
<td>36.2</td>
<td>0.30</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>L1(50)</td>
<td>41.4</td>
<td>2.4</td>
<td>38.4</td>
<td>0.27</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>L1(70)</td>
<td>40.1</td>
<td>2.2</td>
<td>41.0</td>
<td>0.23</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>L1(90)</td>
<td>40.0</td>
<td>2.4</td>
<td>40.7</td>
<td>0.25</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>L2(r.t.)*</td>
<td>46.7</td>
<td>1.9</td>
<td>33.9</td>
<td>0.26</td>
<td>0.07</td>
<td>0.04</td>
</tr>
<tr>
<td>L2(50)</td>
<td>45.4</td>
<td>1.5</td>
<td>33.2</td>
<td>0.19</td>
<td>0.09</td>
<td>0.08</td>
</tr>
<tr>
<td>L2(70)</td>
<td>44.8</td>
<td>1.1</td>
<td>36.9</td>
<td>0.13</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>L2(90)</td>
<td>44.3</td>
<td>1.1</td>
<td>36.4</td>
<td>0.13</td>
<td>0.10</td>
<td>0.12</td>
</tr>
</tbody>
</table>

* These data are obtained from our previous paper [7].
** $\Delta$C16TMA/Si equals to C16TMA/Si of L1 minus C16TMA/Si of L2.

---

* Corresponding author: K. Kuroda, kuroda@waseda.jp

---

![Fig. 3. 2-D $^{29}$Si{1$^H$} HETCOR NMR spectrum of L3(r.t.)](image-url)
The \( Q^3/(Q^3+Q^4) \) ratio (0.48) [7] because of intralayer condensation of \( \text{Si-OH} \) during the acid treatment. In general, silica surfaces composed mainly of \( Q^4 \) species are more hydrophobic than those of \( Q^3 \) species. We predict that the hydrophobicity of silicate layers due to the presence of more \( Q^4 \) species enhances the intercalation of \( \text{C}_{16}\text{EO}_{10} \).

The \( \text{C}_{16}\text{EO}_{10}/\text{Si} \) molar ratio of \( \text{L}_2(\text{r.t}) \) was increased with the increase in the synthetic temperature of \( \text{L}_1 \)s (Table 1). The mechanism of intercalation of \( \text{C}_{16}\text{EO}_{10} \) can be explained as follows: \( \text{L}_1 \)s with higher \( Q^3/(Q^3+Q^4) \) ratios can be obtained at higher temperatures because of the progress of intralayer condensation. The surface with larger amount of \( Q^4 \) species can provide hydrophobic interlayer surfaces. The amount of \( \text{C}_{16}\text{EO}_{10} \) adsorbed on the silicate surfaces increased according to the hydrophobic interaction between the surfaces and alkyl chains of \( \text{C}_{16}\text{EO}_{10} \). Therefore, the intralayer condensation of \( \text{Si-OH} \) enhances the intercalation of \( \text{C}_{16}\text{EO}_{10} \) in the interlayer spaces of \( \text{L}_1 \)s. We have already showed the increase of the \( \text{C}_{16}\text{EO}_{10}/\text{Si} \) ratio with the decrease in the pH value of the reaction medium because of hydrogen bonding between \( \text{Si-OH} \) and EO chains [7]. However, the hydrophobic interaction between alkyl chains and silicate surfaces also affects the intercalation property of \( \text{C}_{16}\text{EO}_{10} \) molecules into \( \text{L}_1 \)s.

4. CONCLUSION

Intercalation behavior of \( \text{C}_{16}\text{EO}_{10} \) molecules into layered silicates was investigated by using \( \text{C}_{16}\text{TMA-kanemites (L}_1 \text{s) with different Si-OH/Si-O densities. The decrease in the Si-OH/Si-O densities of C}_{16}\text{TMA-kanemites enhances the hydrophobicity of the interlayer surface. The amount of intercalated C}_{16}\text{EO}_{10} \) molecules is increased according to the intralayer condensation which induces the hydrophobic interaction between alkyl chains and silicate surfaces. The eliminated amount of \( \text{C}_{16}\text{TMA cations is increased when C}_{16}\text{TMA-kanemites with more condensed frameworks are used. The intercalation of C}_{16}\text{EO}_{10} \) molecules into layered silicates is controllable depending on the conditions. The design of the interlayer environments of layered materials is promising for the enhancement of the properties as green and sustainable materials such as catalysts, catalyst supports and adsorbents.

ACKNOWLEDGMENT

We acknowledge Dr. T. Shibue for the 2-D NMR measurement. The work was partially supported by Grants-in-Aids for the Global COE Program “Practical Chemical Wisdom” MEXT, Japan.

REFERENCES