EFFECT OF INTERCALATED AMIDE MOLECULES ON INTERLAYER CONDENSATION OF LAYERED SILICATE RUB-15

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(Received September 22, 2017. Accepted December 23, 2017)

ABSTRACT

Topotactic conversion of layered silicates into zeolites through interlayer condensation is advantageous for the synthesis of zeolites with unusual compositions, structures, and/or morphologies that have not been obtained using conventional hydrothermal methods. Recently, layered silicate RUB-15 was successfully converted to sodalite with relatively few defects through interlayer condensation by refluxing in N-methylformamide (NMF). However, the effect of NMF, an amide molecule, on the interlayer condensation of RUB-15 is not yet fully understood. In this study, RUB-15 was refluxed or heated in one of four amides: NMF, formamide (FA), N,N-dimethylformamide (DMF), and N-ethylformamide (NEF) to understand the effect of amide molecules on the interlayer condensation in terms of both the size of the amide molecules and their interactions with the layered silicate. On the basis of the powder X-ray diffraction patterns and solid-state \textsuperscript{29}Si MAS NMR spectra of refluxed or heat-treated products, both NMF and DMF are well suited for interlayer condensation of RUB-15, and the most optimal amide is NMF because it produces the fewest defects. FA (smaller than NMF) and NEF (larger than DMF) are less suitable as interlayer organic species for sodalite formation. It was also found that interlayer condensation of layered octosilicate proceeded in the presence of NMF by refluxing, whereas the condensation did not proceed in DMF by refluxing. These results strongly suggest that the matching in size of the amide molecules with respect to the surface structures of the layered silicates and their interactions play major roles in the interlayer condensation.

Key words: RUB-15, interlayer condensation, topotactic conversion, silica sodalite, layered silicates, zeolites

INTRODUCTION

Layered silicates composed of crystalline silicate layers possess exchangeable cations between the layers and reactive silanol groups on the layer surfaces. Silanol groups can be used for covalent modifications (Takahashi and Kuroda, 2011), such as esterification (Mitamura et al., 2001; Kiba et al., 2010), interlayer condensation (Leonowicz et al., 1994; Schreyeck et al., 1996; Ikeda et al., 2004; Zanardi et al., 2004; Marler et al., 2005; Wang et al., 2005; Marler et al., 2006; Moteki et al., 2008; Marler and Gies, 2012; Roth, 2013; Asakura, 2014c; Rojas and Camblor, 2014; Schmidt, 2015a, 2015b; Kasneryk, 2017), and silylation (Ruiz-Hitzky and Rojo, 1980; Ruiz-Hitzky et al., 1985; Yanagisawa et al., 1988; Ogawa et al., 1998; Shimozima et al., 2001; Mochizuki et al., 2002; Fujita et al., 2003, 2005; Mochizuki et al., 2005, 2006; Mochizuki and Kuroda, 2006; Takahashi et al., 2010, 2011; Asakura et al., 2011, 2014a; Ide et al., 2011). Si–O–Si bonds form between adjacent layers through interlayer condensation by calcination, which can yield zeolites; the formed zeolites show the platy morphology of pristine layered silicates, indicating topotactic conversion. The interlayer condensation method is advantageous to synthesize zeolites with unusual...
compositions, structures, and/or morphologies that have not been obtained using conventional hydrothermal methods (Marler and Gies, 2012). Silanol groups on layers must be faced with those in adjacent layers to facilitate their condensation, and their positions must be retained for successful condensation. Therefore, controlling the relative positions of silanol groups in the adjacent layers by shifting the layers in a lateral direction is quite important for interlayer condensation, and it is often achieved by intercalating organic species between silicate layers. One of the drawbacks of this method is the formation of defects based on stacking disorder of the layers and their irregular/incomplete condensation (Marler and Gies, 2012). Such defects should be ascribed to uncontrollable condensation processes in which the interlayer organic species are simultaneously removed during interlayer condensation by calcination. These defects may unfavorably affect their performances as catalysts and separation media.

We reported suppression of defect formation during interlayer condensation of layered octosilicate (Asakura et al., 2014b) and RUB-15 (Koike et al., 2017) into RWR- and SOD-type (sodalite) zeolites, respectively. In this method, the framework formation process by refluxing in an appropriate organic solvent and subsequent calcination process are strictly separated. The first step induces interlayer condensation at a relatively milder temperature than calcination, while retaining the organic species between the layers. In both of the cases, the zeolite frameworks are formed by refluxing in N-methylformamide (NMF). Subsequently, the organic species in the formed pores are eliminated by calcination. Interlayer condensation through refluxing in NMF yields zeolite structures with relatively fewer defects (Asakura et al., 2014b; Koike et al., 2017) than those reported previously (Oumi et al., 2007; Moteki et al., 2008, 2011). The role of NMF in the process is to adjust the stacking order between the layers. In addition, the retention of NMF within the silicate layers during the interlayer condensation contributes to the lower degree of defects formation. Accordingly, it is important to explore other amide molecules that are applicable to interlayer condensation and investigate the effect of various amide molecules for optimal interlayer condensation of layered silicates to further understand the condensation. However, the application of amide molecules, other than NMF, is scarce; only two reports have reported successful synthesis of AST-type zeolite and interlayer condensation of layered silicate magadite (Asakura et al., 2014c, 2015).

In this study, the effect of the kind of amide molecule on the interlayer condensation of layered silicate RUB-15 and layered octosilicate was investigated to understand the relations between the amide molecule characteristics and the layer structures (Figure 1). Three amides with different substituents and molecular sizes, formamide (FA), N,N-dimethylformamide (DMF), and N-ethylformamide (NEF), were used in addition to NMF. This study has clarified that NMF and DMF are applicable to interlayer condensation of RUB-15. NMF is the most effective organic agent to form a sodalite with fewer defects, suggesting the importance of both the size of the amide molecules and their interactions with the silicate layers. Layered octosilicate, possessing one-dimensional nanogrooves on its layer surfaces, was chosen as another layered silicate for comparison with RUB-15, which possesses cup-like surface cavities. The structure of the layered silicates and the interactions between the layer surfaces and amide molecules are crucial for interlayer condensation of layered silicates because interlayer condensation did not proceed for layered octosilicate during refluxing in DMF.
MATERIALS AND METHODS

Materials

Tetramethylammonium hydroxide (~25% in water, Tokyo Chemical Industry Co., Ltd.) and tetramethoxysilane (>99.0%, Tokyo Chemical Industry Co., Ltd.) were used without further purification to prepare RUB-15. Acetic acid (special grade, min. 99.7%, Wako Pure Chemical Industries, Ltd.), NMF (special grade, min. 99.0%, Wako Pure Chemical Industries, Ltd.), FA (extra pure reagent, min. 97.0%, Wako Pure Chemical Industries, Ltd.), DMF (>99.5%, Tokyo Chemical Industry Co., Ltd.), and NEF (>98.0%, formyl-ethylamine, Tokyo Chemical Industry Co., Ltd.) were used as received.

Fumed silica (99.8% SiO₂, Aldrich) and NaOH (97.0%, Wako Pure Chemical Industries, Ltd.) were used to prepare the layered octosilicate (denoted as Na-Oct). Hydrochloric acid (Wako Pure Chemical Industries, Ltd.) was used without further purification to prepare the protonated layered octosilicate (denoted as H-Oct).

RUB-15, RUB-15 intercalating acetic acid (Ac-RUB), and NMF(180rf)-RUB obtained by refluxing Ac-RUB in NMF

RUB-15 was synthesized according to a reported method (Koike et al., 2017). The powder X-ray diffraction (XRD) pattern and ²⁹Si magic angle spinning (MAS) NMR spectrum of the obtained sample are the same as those of RUB-15 (Oberhagemann et al., 1996). Ac-RUB was synthesized by stirring RUB-15 in 6 M acetic acid to protonate SiO⁻ groups on the layer surfaces and control the stacking sequence (Moteki et al., 2008, 2011). The powder XRD pattern and ²⁹Si MAS NMR spectrum of the obtained sample (Figure 2(a) and Figure 3(a), respectively) are the same as those of Ac-RUB (Moteki et al., 2008, 2011). Refluxing Ac-RUB in NMF was performed to form an interlayer-condensed compound with NMF (NMF(180rf)-RUB) according to the procedure in our previous paper (Koike et al., 2017). The powder XRD pattern and ²⁹Si MAS NMR spectrum of NMF(180rf)-RUB are shown in Figure 2(c) and Figure 3(c), respectively.

FA(180)-RUB, DMF(155rf)-RUB, and NEF(180)-RUB synthesized by refluxing or heating Ac-RUB in FA, DMF, or NEF, respectively

Ac-RUB (0.1 g) was refluxed in 40 mL of DMF (boiling point: 153°C) at approximately 155°C in an oil bath for 1 h. Ac-RUB (0.1 g) was heated (not refluxed) in 40 mL of FA or NEF at 180°C for 1 h because the boiling points of FA and NEF are 210°C and 202°C, respectively. On the basis of the condensation temperature (170°C) of silanol groups of RUB-15, as determined by TG data (Moteki et al., 2011), the temperature was set at 180°C for the progress of interlayer condensation, and the temperature is same as that used in our previous study (Koike et al., 2017). When FA or NEF was used, the reaction temperature was also set at 180°C, and the heating actually worked out in the same way as refluxing. The boiling temperature of DMF is 153°C, so the refluxing at 155°C in an oil bath was chosen. Although the rates of condensation reaction may be different among the four amides, the condensation reaction proceeded for all the cases.

Fig. 2. XRD profiles of (A) RUB-15 ((a) Ac-RUB, (b) FA(180)-RUB, (c) NMF(180rf)-RUB, (d) DMF(155rf)-RUB, (e) NEF(180)-RUB, (f) FA(180)-RUB-cal, (g) NMF(180rf)-RUB-cal, (h) DMF(155rf)-RUB-cal, (i) NEF(180)-RUB-cal, (j) FA-RUB, (k) NMF-RUB, (l) DMF-RUB, and (m) NEF-RUB) and (B) layered octosilicate ((n) H-Oct, (o) FA(180)-Oct, (p) NMF(180rf)-Oct, (q) DMF(155rf)-Oct, (r) NEF(180)-Oct, (s) FA(180)-Oct-cal, (t) NMF(180rf)-Oct-cal, (u) DMF(155rf)-Oct-cal and (v) NEF(180)-Oct-cal).

Fig. 3. ²⁹Si MAS NMR spectra of (a) Ac-RUB, (b) FA(180)-RUB, (c) NMF(180rf)-RUB, (d) DMF(155rf)-RUB, (e) NEF(180)-RUB, (f) FA(180)-RUB-cal, (g) NMF(180rf)-RUB-cal, (h) DMF(155rf)-RUB-cal, (i) NEF(180)-RUB-cal, (j) NMF(180rf)-Oct, (k) DMF(155rf)-Oct, (l) NMF(180rf)-Oct-cal, and (m) DMF(155rf)-Oct-cal.
The color of FA changed to black during heating because FA thermally decomposes above 180°C. Then, the samples were centrifuged and dried under a reduced pressure. The treated samples are denoted as FA(180)-RUB, DMF(155rf)-RUB, and NEF(180)-RUB. The color of FA(180)-RUB was dark brown while the other two samples were white. All the thermally treated samples were heated at a heating rate of 10°C min⁻¹ and then calcined at 800°C for 5h in an air atmosphere. The calcined white samples are denoted as NMF(180rf)-RUB-cal, FA(180)-RUB-cal, DMF(155rf)-RUB-cal, and NEF(180)-RUB-cal.

FA-RUB, DMF-RUB, NEF-RUB and NMF-RUB synthesized by stirring Ac-RUB at room temperature in FA, DMF, NEF, or NMF, respectively

Ac-RUB (0.1 g) was stirred in 40 mL of FA, DMF, NEF, or NMF at room temperature for 1h. Then, the samples were centrifuged and dried under reduced pressure. The treated samples are denoted as FA-RUB, DMF-RUB, NEF-RUB, and NMF-RUB.

Layered octosilicate (Na-Oct) and protonated octosilicate (H-Oct)

Layered octosilicate (Na-Oct) was synthesized on the basis of the conditions reported previously (Mochizuki et al., 2006). Fumed silica, NaOH, and deionized water were mixed in the composition of SiO₂ : Na₂O : H₂O = 4 : 1 : 25.8. The mixture was treated hydrothermally at 100°C for 4 weeks in a Teflon-sealed vessel. The powder XRD pattern and ²⁹Si MAS NMR spectrum of the obtained sample are the same as those of Na-Oct reported previously (Mochizuki et al., 2006). Protonated layered octosilicate (H-Oct) was obtained by treating Na-Oct with 0.1 M HCl for 2 d according to a literature (Kiba et al., 2010). The powder XRD patterns of the obtained sample (Figure 2(n)) are the same as those of H-Oct reported previously (Kiba et al., 2010). H-Oct (0.1 g) was refluxed or heated in 40 mL of FA, NMF, or NEF at 180°C for 1 h based on conditions reported previously (Asakura et al., 2014b). H-Oct (0.1 g) was refluxed in 40 mL of DMF at 155°C for 1 h. Then, the samples were centrifuged and dried under a reduced pressure. The treated samples are denoted as FA(180)-Oct, NMF(180rf)-Oct, NEF(180)-Oct, and DMF(155rf)-Oct. All the refluxed/heated samples were heat-treated at a heating rate of 2.5°C min⁻¹ and then calcined at 550°C for 6 h in an air atmosphere. The calcined samples are denoted as FA(180)-Oct-cal, NMF(180rf)-Oct-cal, NEF(180)-Oct-cal, and DMF(155rf)-Oct-cal.

Characterizations

Powder XRD measurements were performed on a Rigaku Rint-Ultima III powder diffractometer with Cu Kα radiation (λ = 0.15418 nm) by a parallel beam geometry equipped with a scintillation detector and a parabolic multilayer mirror. Solid-state ²⁹Si MAS NMR spectra were recorded on a JEOL JNM-ECX-400 spectrometer at a resonance frequency of 79.42 MHz with a 90° pulse and a recycle delay of 500 s. Samples were placed in a 4-mm zirconia rotor spinning at 7 kHz. CHN elemental analysis was performed using a Perkin-Elmer 2400 Series II instrument. 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 up to 900°C. FT-IR spectra were recorded on a JASCO FT/IR 6100 spectrometer using the KBr disk method. Scanning electron microscopy (SEM) images were obtained using a Hitachi S5500 scanning electron microscope at an accelerating voltage of 1 kV. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2010 microscope at an accelerating voltage of 200 kV. First-principle calculations were performed with the CASTEP module in BIOVIA Materials Studio, based on the density functional theory (DFT). The detailed conditions for the calculation are shown in the NOTES below. Geometry optimization calculations by molecular dynamic simulation were carried out using the Forcite module in BIOVIA Materials Studio. The calculations were performed using a PCFF force field to obtain the best configuration and location of the interlayer amide molecules. One amide molecule was added into a unit cell of RUB-15 (and sodalite cage) or four amide molecules were added into the interlayer space of the layered octosilicate as the initial geometries for the simulations.

RESULTS AND DISCUSSION

Characterization of thermally treated samples

Ac-RUB was refluxed or heated in FA, DMF, or NEF to prepare the interlayer-condensed products (denoted as FA(180)-RUB, DMF(155rf)-RUB, or NEF(180)-RUB). The powder XRD patterns of FA(180)-RUB, DMF(155rf)-RUB, and NEF(180)-RUB are shown in Figure 2(b), (d), and (e), respectively. The conversion of Ac-RUB into a sodalite framework through refluxing in DMF is confirmed on the

Table 1. List of samples used in this study.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Comments on the Reactions/Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA(180)-RUB</td>
<td>Incomplete/irregular condensation</td>
</tr>
<tr>
<td>NMF(180rf)-RUB⁴</td>
<td>Sodalite</td>
</tr>
<tr>
<td>DMF(155rf)-RUB</td>
<td>Sodalite</td>
</tr>
<tr>
<td>NEF(180)-RUB</td>
<td>Incomplete/irregular condensation</td>
</tr>
<tr>
<td>FA(180)-RUB-cal</td>
<td>Incomplete/irregular condensation</td>
</tr>
<tr>
<td>NMF(180rf)-RUB-cal⁴</td>
<td>Sodalite</td>
</tr>
<tr>
<td>DMF(155rf)-RUB-cal</td>
<td>Sodalite</td>
</tr>
<tr>
<td>NEF(180)-RUB-cal</td>
<td>Incomplete/irregular condensation</td>
</tr>
<tr>
<td>FA-RUB</td>
<td>Expansion of basal spacing</td>
</tr>
<tr>
<td>NMF-RUB⁴</td>
<td>No change in basal spacing</td>
</tr>
<tr>
<td>DMF-RUB</td>
<td>Expansion of basal spacing</td>
</tr>
<tr>
<td>NEF-RUB</td>
<td>Expansion of basal spacing</td>
</tr>
<tr>
<td>FA(180)-Oct</td>
<td>Decrease in the intensities of the peaks</td>
</tr>
<tr>
<td>NMF(180rf)-Oct</td>
<td>RWR-type zeolite</td>
</tr>
<tr>
<td>DMF(155rf)-Oct</td>
<td>Expansion of basal spacing</td>
</tr>
<tr>
<td>NEF(180)-Oct-cal</td>
<td>Decrease in the intensities of the peaks</td>
</tr>
<tr>
<td>FA(180)-Oct-cal</td>
<td>RWR-type zeolite</td>
</tr>
<tr>
<td>NMF(180rf)-Oct-cal</td>
<td>Decrease in the intensities of the peaks</td>
</tr>
<tr>
<td>DMF(155rf)-Oct-cal</td>
<td>Decrease in the intensities of the peaks</td>
</tr>
<tr>
<td>NEF(180)-Oct-cal</td>
<td>Decrease in the intensities of the peaks</td>
</tr>
</tbody>
</table>

⁴: Koike et al., 2017.
Effect of amide molecules on interlayer condensation of RUB-15

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The intensities of the peaks in the XRD pattern of the FA(180)-RUB (Figure 2(b)) are much lower than those of NMF(180rf)-RUB and DMF(155rf)-RUB, and the peaks at 14.3°, 20.1°, and 24.7° are assignable to the 110, 200, and 211 diffractions of the sodalite structure, respectively. The intensities of the corresponding XRD peaks of NEF(180)-RUB (Figure 2(e)) are further lowered and only the broad and weak peak at 20.1°, probably assignable to the 200 diffraction of the sodalite structure, is observed. In the NEF case, another peak at 11.7° arising from the slightly decreased basal spacing of Ac-RUB is also observed after the thermal treatment at 180°C. The latter two cases suggest incomplete/irregular interlayer condensation.

The 29Si MAS NMR spectrum of DMF(155rf)-RUB (Figure 3(d)) shows a Q4 signal at −114 ppm and a shoulder Q3 signal at −102 ppm, with a Q3/Q4 ratio of 0.4. The intensity of the Q3 signal is less than that of Ac-RUB, indicating condensation of the interlayer Si–OH groups between the layers. Though the XRD pattern clearly shows the formation of zeolite, the degree of condensation in DMF(155rf)-RUB is lower than that in NMF(180rf)-RUB (Figure 3(c), Koike et al., 2017). The 29Si MAS NMR spectra of FA(180)-RUB and NEF(180)-RUB (Figure 3(b) and (e), respectively) show that these Q3 signals and shoulder Q3 signals are broader than those of NMF(180rf)-RUB and DMF(155rf)-RUB. This result indicates incomplete/irregular interlayer condensation of the layers, which is consistent with the XRD results. In addition,

the TEM image of DMF(155rf)-RUB (Figure 4(a)) shows a plate-like morphology, and the bright spots of the electron diffraction (ED) patterns correspond to diffraction of the sodalite structure along the [110] direction, which is consistent with the stacking direction of pristine RUB-15 layers. All these results indicate that sodalite is obtained by refluxing in NMF and DMF, and incomplete/irregular condensation is observed for samples obtained by heating in FA and NEF. On the basis of simulated geometrical considerations (Figure 5), the molecular sizes of four amide molecules used in this study are smaller than that of the sodalite cage. Because FA is smaller than NMF, and NEF is larger than DMF, the size smaller than that of sodalite cage is not simply the condition for interlayer condensation. The molecular constraints of introduced amide molecules, influenced by interactions between the molecules and the silicate layers, should also be a condition for successful interlayer condensation, which is described below.

Fig. 4. TEM images of (a) DMF(155rf)-RUB and (b) DMF(155rf)-RUB-cal and the ED patterns of the selected areas of (a) and (b) (denoted by circles).

Fig. 5. Geometry optimized framework structures of sodalite with (a) FA, (b) NMF, (c) DMF, and (d) NEF encapsulated within the sodalite cage by using DFT calculations (CASTEP module).
Influences of the size of amide molecules on both the intercalation behaviors and defect formation in sodalite

The FT-IR spectrum of DMF(155rf)-RUB (Figure 6(d)) shows two absorption bands due to C=O stretching vibrations (ν(C=O)) at 1765 cm⁻¹ (carbonyl groups of acetic acid) and 1650 cm⁻¹ (amide I in DMF). The band at 1765 cm⁻¹, which is shifted to lower wavenumber than that found for monomeric acetic acid, is very similar to that found for NMF(180rf)-RUB (Figure 6(c)). The wavenumber of 1650 cm⁻¹ is also lower than that of the band due to amide I of DMF in toluene (Bormann et al., 2000), strongly suggesting that DMF can also be present inside the sodalite framework and that carbonyl groups interact with the silanol groups of the frameworks. In contrast, the distinctive sharp absorption band at 3450 cm⁻¹ for NMF(180rf)-RUB, arising from ν(N–H), suggests the interactions between N–H groups and the frameworks only in NMF(180rf)-RUB. Less DMF is present between the layers (please refer to the N/Si ratio in Table 2) than for NMF in NMF(180rf)-RUB, which may be related to the higher vaporization of DMF than NMF, because DMF interacts with the silicate layers using only C=O in a lesser degree. The TG curves of NMF(180rf)-RUB and DMF(155rf)-RUB (Figure 7(b) and 7(c)) show that two-step weight losses corresponding to adsorbed water and decomposition of the organic species within the frameworks. In particular, the decomposition of the species at higher temperature (around 400°C) than that of the same species intercalated in layered silicate magadiite (Mitamura et al., 2001; Asakura et al., 2015) suggests their confined states.

The ν(C=O) absorption bands in the spectrum of NEF(180)-RUB (Figure 6(e)) broaden and the intensity becomes weaker than those for NMF(180rf)-RUB and DMF(155rf)-RUB. The broadness of the band suggests inhomogeneous conformations of amide molecules in the frameworks, which may be related to reduced interactions of NEF with the layers of RUB-15, probably because of its molecular configuration. The broad band due to C=O shifts to a lower wavenumber than that of NEF in CCl₄ (Jones, 1967), suggesting the presence of NEF within the silicate layers and that carbonyl groups interact with the silanol groups of the silicate layers. The ν(N–H) band is not distinctly observed around 3700–3000 cm⁻¹ because of probable overlap with the OH vibrational bands; this result is quite different from that observed for NMF(180rf)-RUB, while the TG curve of NEF(180)-RUB (Figure 7(d)) was similar to those for the NMF and DMF cases mentioned above. The FT-IR spectrum of FA(180)-RUB (Figure 6(b)) shows a complex profile from 1770 to 1360 cm⁻¹, which is due to partial conversion of FA to unidentified substances. The first weight loss in the TG curve of the sample was larger than those of other three samples, which may be consistent with the formation of the unidentified substances. The second weight loss occurred at relatively lower temperature than those found for the other three samples, which also suggest the incomplete confinement within the layers.

The refluxed or heated samples were calcined to remove the interlayer organic species (NMF(180rf)-RUB-cal, FA(180)-RUB-cal, DMF(155rf)-RUB-cal, and NEF(180)-RUB-cal).

Table 2. Elemental analysis and the C/N and N/Si ratios of the samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C /mass%</th>
<th>H /mass%</th>
<th>N /mass%</th>
<th>C/N</th>
<th>N/Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA(180)-RUB</td>
<td>16.7</td>
<td>2.2</td>
<td>15.6</td>
<td>1.2</td>
<td>0.50</td>
</tr>
<tr>
<td>NMF(180rf)-RUB</td>
<td>7.5</td>
<td>1.3</td>
<td>3.6</td>
<td>2.4</td>
<td>0.19</td>
</tr>
<tr>
<td>DMF(155rf)-RUB</td>
<td>5.5</td>
<td>1.2</td>
<td>0.6</td>
<td>10.4</td>
<td>0.01</td>
</tr>
<tr>
<td>NEF(180)-RUB</td>
<td>5.5</td>
<td>1.1</td>
<td>1.6</td>
<td>4.1</td>
<td>0.04</td>
</tr>
<tr>
<td>FA(180)-RUB-cal</td>
<td>0.1</td>
<td>0.1</td>
<td>0.0</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>NMF(180rf)-RUB-cal</td>
<td>0.2</td>
<td>0.0</td>
<td>0.1</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>DMF(155rf)-RUB-cal</td>
<td>0.1</td>
<td>n.d.</td>
<td>0.1</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>NEF(180)-RUB-cal</td>
<td>0.1</td>
<td>0.0</td>
<td>0.0</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>FA-RUB</td>
<td>18.4</td>
<td>5.1</td>
<td>16.7</td>
<td>1.3</td>
<td>0.87</td>
</tr>
<tr>
<td>NMF-RUB</td>
<td>7.4</td>
<td>1.7</td>
<td>2.1</td>
<td>4.1</td>
<td>0.12</td>
</tr>
<tr>
<td>DMF-RUB</td>
<td>7.9</td>
<td>2.2</td>
<td>2.0</td>
<td>4.6</td>
<td>0.06</td>
</tr>
<tr>
<td>NEF-RUB</td>
<td>15.5</td>
<td>4.0</td>
<td>5.5</td>
<td>3.3</td>
<td>0.16</td>
</tr>
</tbody>
</table>

a: Koike et al., 2017. b: not detected. c: The amounts of Si were calculated from the residual amounts after TG up to 900°C, assuming that the residue is only SiO₂.
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Fig. 7. TG curves of (a) FA(180)-RUB, (b) NMF(180rf)-RUB, (c) DMF(155rf)-RUB, (d) NEF(180)-RUB, (e) FA-RUB, (f) NMF-RUB, (g) DMF-RUB, and (h) NEF-RUB.

Fig. 8. SEM images of (a) FA(180)-RUB, (b) DMF(155rf)-RUB, (c) NEF(180)-RUB, (d) FA(180)-RUB-cal, (e) DMF(155rf)-RUB-cal, (f) NEF(180)-RUB-cal.
organic species are virtually removed by calcination. The retention of plate-like morphologies was confirmed by the SEM images (Figure 8 (a)–(f)). The powder XRD pattern of DMF(155rf)-RUB-cal (Figure 2(h)) shows peaks assignable to sodalite, and the ED patterns of DMF(155rf)-RUB-cal (Figure 4(b)) also show bright spots corresponding to diffraction along the [110] direction of sodalite, indicating retention of the sodalite framework. The results using DMF are similar to those using NMF (Figure 2(g)). The powder XRD patterns of calcined samples (FA(180)-RUB-cal and NEF(180)-RUB-cal, Figure 2(f) and (i), respectively) merely show small and broad peaks assignable to sodalite, and the $^{29}$Si MAS NMR spectra of FA(180)-RUB-cal and NEF(180)-RUB-cal (Figure 3(f) and (i)) also show broad Q3 and Q4 signals. The $^{29}$Si MAS NMR spectrum of DMF(155rf)-RUB-cal (Figure 3(h)) shows a slightly broadened Q4 signal at $-115$ ppm and a very broad Q3 signal at approximately $-102$ ppm. The intensity ratio of the Q3 signal over the Q4 signal decreases when compared with that of DMF(155rf)-RUB before calcination, which indicates further interlayer condensation between the layers. The remaining Q3 peak should be ascribed to defects of formed sodalite because the presence of non-condensed interlayer silanol groups is unlikely after calcination. The degree of condensation in DMF(155rf)-RUB-cal is lower than that of NMF (NMF(180rf)-RUB-cal, Figure 3(g)) but still higher than that using only acetic acid as an agent to control the layer stacking (Moteki et al., 2008).

Further experiments on the intercalation of FA, DMF, NEF, or NMF between Ac-RUB at room temperature were conducted in order to examine the amounts of the intercalated amides before refluxing or heating. The expansion of the interlayer spacing was confirmed for the samples using FA, DMF, or NEF on the basis of the XRD patterns (Figure 2(j), (l), and (m)), and the amounts of intercalated amides within the silicate layers were larger than those of the amides after refluxing or heating, as roughly estimated by the values of their N/Si ratio (Table 2). When NMF was used, the presence of NMF within the layers was also confirmed by the N/Si ratio (Table 2), while the distance of the layers did not change (Figure 2(k)), which suggests the specific interactions of NMF with the silicate framework. The TG curves of the samples containing NMF, DMF, or NEF (Figure 7(e)–(h)) showed the larger weight losses arising from desorption of adsorbed water and interlayer condensation. Then, gradual weight losses were found probably because of the decomposition of acetic acid. Finally the decomposition of the organics was found as the third weight losses. The TG curve of FA-RUB showed a quite different profile indicating only one weight loss at low temperature, suggesting both the desorption of adsorbed water and the decomposition of FA, which is reasonable because FA located in the interlayer of kaolinite also thermally decomposed at such a low temperature (Frost et al., 2001). Therefore, the effects of both the size of amides and their interactions with the silicate layers are worthy to be discussed from the viewpoint of the degree of sodalite formation because the amounts of amides between the layers are large enough for the comparison.

Interestingly, the structural simulation data indicate that the longest distances between atoms in amide molecules decrease from the gas state to the condensed state between the layers of RUB-15 (Figure 9(a)–(d)). The distance decreases from 0.26 to 0.22 nm (N and O) for FA, 0.30 to 0.27 nm (C and O) for NMF, 0.40 to 0.36 nm (C and O) for DMF, and 0.45 to 0.34 nm (C and O) for NEF. In the cases of the geometry optimized RUB-15 structures containing different amides, the distortion of the lattices was observed. The simulated XRD patterns were only partially consistent with the experimental data because the noncovalent bondings between the amides and layers such as hydrogen bonding were not fully reproduced in the calculation. Although the obtained numerals vary under the same criterion, the smallest decrease among the four amide molecules was observed for NMF, indicating that the distortion of NMF through interlayer condensation should be the smallest; further, the size of NMF matches that of the surface cavity of RUB-15.
Moreover, as shown in Figure 5, the decrease in the molecular distance is the least for the case of NMF (from 0.30 to 0.29 nm (C and O)), and also the distortion of sodalite framework is smallest. In fact, the angles between the axes of unit cell are closest to 90° in the case of cubic sodalite containing NMF among the four cases. These results indicate that the size of the amide molecules and their interactions with the RUB-15 layers are important factors during interlayer condensation of layered silicate RUB-15 through thermal treatment.

Relationship between the characteristics of amide molecules and the surface structures of layered silicates (RUB-15 and layered octosilicate)

To investigate the relationships between amide molecules and the surface structures of layered silicates, layered octosilicate was also refluxed or heated in one of the four amides (FA, NMF, DMF, or NEF), and the obtained samples are denoted as FA(180)-Oct, NMF(180rf)-Oct, NEF(180)-Oct, and DMF(155rf)-Oct, respectively. The powder XRD pattern of NMF(180rf)-Oct (Figure 2(p)) shows diffraction peaks assignable to the RWR-type zeolite structure. The 29Si MAS NMR spectrum of NMF(180rf)-Oct (Figure 3(j)) shows only Q3 units with several environments, and the Q4 signal is not present, as reported (Asakura et al., 2014b). This result indicates that almost all the interlayer Si–OH groups are condensed between the layers. After calcination, the powder XRD pattern of the calcined sample (NMF(180rf)-Oct-cal, Figure 2(i)) shows peaks assignable to RWR-type zeolite and the 29Si MAS NMR spectrum of NMF(180rf)-Oct-cal (Figure 3(l)) shows sharp Q4 signals, indicating retention of RWR-type zeolite through interlayer condensation of H-Oct. However, the powder XRD patterns of the other three samples and their calcined samples (Figure 2(o), (q), (r), (s), (u), and (v)) do not show peaks assignable to the RWR-type zeolite.

The 29Si MAS NMR spectrum of DMF(155rf)-Oct (Figure 3(k)) shows broad Q3 and Q4 signals, and the 29Si MAS NMR spectrum of DMF(155rf)-Oct-cal (Figure 3(m)) shows very broad Q4 signals. The FT-IR spectrum of NMF(180rf)-Oct (Figure 6(g)) shows an absorption band at 1710 cm⁻¹ due to the stretching vibrations (amide I in NMF), but the FT-IR spectra of FA(180)-Oct, DMF(155rf)-Oct, and NEF(180)-Oct (Figure 6(f), (h), and (i), respectively) show very weak absorption bands due to C=O, indicating that only NMF interacts with the surface structure of the layered octosilicate and is located uniformly within the frameworks. These results indicate that NMF is the only amide molecule applicable to interlayer condensation of layered octosilicate. A comparison of the results of interlayer condensation of RUB-15 with those of layered octosilicate indicates the difference in the applicability of amide molecules to interlayer condensation. This difference should be caused by the surface structures of layered silicates, that is, cup-like surface cavities (RUB-15) and a one-dimensional surface nanogroove (layered octosilicate). On the basis of the geometrically optimized simulation data of amide molecules intercalated in layered octosilicate (Figure 9(i)–(l)), the decrease in the longest distance between atoms is smallest for NMF accommodation within the layered silicates (RUB-15 and layered octosilicate), though the slight distortion of the lattices was observed. The simulated XRD patterns are also only partially consistent with the experimental data. The cavity size of the surface structures of RUB-15 (the internal diameter of the cup-like cavity is approximately 0.58 nm) is larger than that of the layered octosilicate (the channel diameter of the nanogrooves is approximately 0.48 nm). Accordingly, amide molecules might be present in the larger spaces of RUB-15 than that in octosilicate. In contrast, only NMF could be retained between the layers of the layered octosilicate to control the stacking sequence of the layers.

CONCLUSIONS

Interlayer condensation of layered silicate RUB-15 was conducted through refluxing or heating in FA, DMF, NEF, and NMF. The sodalite framework was formed by interlayer condensation through refluxing in DMF with a lesser condensation degree than using NMF, and incomplete/irregular condensation was confirmed through heating in FA and NEF. Compared with interlayer condensation of layered octosilicate, differences in the applicable amide molecules were observed. Therefore, the geometrical matching, considering both the structure of layered silicates and molecular size of the amides, and the interactions between the layer surfaces and amide molecules are crucial factors for interlayer condensation of layered silicates. NMF is one of the most appropriate amide molecules because the size is small enough to be accommodated between the layers and the interactions of the molecule with the silicate layers are relatively strong for an ideal position between the layers, forming micropores, which results in successful interlayer condensation of layered silicates.

ACKNOWLEDGEMENTS

We gratefully acknowledge Dr. Takahiro Moteki (The University of Tokyo) for advice on the synthesis of RUB-15. This work was supported by a Grant-in-Aid for Strategic International Collaborative Research Program (SICORP), France-Japan Joint Project on “MOLECULAR TECHNOLOGY” from the Japan Science and Technology Agency (JST). We also acknowledge a Waseda University Grant for Special Research Projects. M. K. is thankful for support from the Clay Research Projects. M. K. is thankful for support from the Clay Research Projects.
The calculations were performed using the CASTEP module, which has been described following references. The kinetic energy cut-off and k-point mesh was adopted to ensure good convergence for computed structures and energies. The basis cut-off used is 10.0 eV. The energy tolerance is $2.0 \times 10^{-3}$ eV per atom, the force tolerance is 0.05 eV Å$^{-1}$, the maximum stress is 0.1 GPa, and the displacement tolerance is 0.002 Å.

The initial lattice parameters of sodalite containing amides are $a$, $b$, $c = 8.9096$ Å and $\alpha$, $\beta$, $\gamma = 90.00^\circ$. Calculated unit cell parameters are listed in Table 3.


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(Manuscript handled by Koichi Sato)