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Thermal transformation of a kaolinite–poly(acrylamide) intercalation compound

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The thermal transformation of a kaolinite–poly(acrylamide) (PAAm) intercalation compound has been investigated. Acrylamide molecules were intercalated between the layers of kaolinite and were subsequently polymerized by heat treatment at 300 °C for 1 h. The kaolinite–PAAm intercalation compound was heated in the range 460–620 °C under a nitrogen atmosphere. XRD analysis revealed that carbonaceous materials remained between the layers in this temperature range. The ^{29}Si and ^{27}Al NMR spectra of the kaolinite–PAAm compounds heated above 500 °C showed that the structural change of aluminosilicate layers was relatively suppressed compared with that of kaolinite itself, indicating that the carbonaceous materials hindered the transformation of aluminosilicate layers. This new finding provides a method for controlling the skeletal transformation of inorganic layered materials upon thermal treatment.

Introduction

Kaolinite, $Al_2Si_2O_5(OH)_4$, is a layered aluminosilicate with a dioctahedral 1 : 1 layer structure consisting of tetrahedral silicate sheets and octahedral aluminium hydroxide sheets.[1] The clay mineral has widely been used as a raw material for ceramics, refractories, and paper. Thermal transformation of kaolinite has been studied for a long time from both practical and scientific standpoints. Upon heat treatment, kaolinite is transformed into anhydrous metakaolinite whose structure remains controversial because of its very poor crystalline nature. The structural characteristics of metakaolinite have been discussed for several decades using many techniques such as NMR, IR, TEM and XRD.[2–18]

Several papers on ^{29}Si NMR spectra of metakaolinites have clarified that the Q^3 signal in the spectrum of raw kaolinite is broadened and shifts toward the Q^4 region.[6–14] ^{27}Al NMR spectra of metakaolinites have shown coexistence of four-, five-, and six-coordinated Al atoms.[7–16] Based on these results, it has been suggested that segregation of both Si and Al takes place and the two-dimensional framework begins to transform into a three-dimensional one. On the other hand, TEM observations of metakaolinites have indicated the retention of a layer structure with a period of *ca.* 1.2 nm in place of kaolinite layers (0.7 nm) and electron diffraction spots have shown hexagonal symmetry.[17] Accordingly, it has been proposed that metakaolinite is not an amorphous material and that a two-dimensional periodicity in the *ab* plane is retained. Furthermore, Rocha *et al.* studied the process of rehydroxylation of metakaolinite to kaolinite and stated that it was a topotactic solid-state process.[18]

To elucidate the structural deformation of thermally treated aluminosilicate layers, a novel approach is required and the investigation of the thermal behavior of kaolinite–polymer intercalation compounds is such a technique. Kaolinite is known to form several intercalation compounds not only with isolated molecules[19] but also with polymers (Fig. 1).[20–24] The thermal behavior of kaolinite intercalation compounds with organic molecules such as *N*-methylformamide (NMF) and dimethyl sulfoxide shows that the guest molecules are easily deintercalated and that they only affected the dehydroxylation temperature of kaolinite.[25–28] On the other hand, intercalated polymers are expected to be preserved after heat treatment under a nitrogen atmosphere and hinder the interactions between adjacent aluminosilicate layers, if the selection of the polymers is appropriate. The synthesis of a kaolinite–PAAm intercalation compound was reported by us previously.[21] PAAm can be converted to carbonaceous materials if heated in an inert atmosphere. Consequently, the thermal transformation of a kaolinite–PAAm intercalation compound was investigated, and its thermal behavior compared with that of kaolinite itself.

Experimental

Materials

Kaolinite was an API clay standard No. 9, Mesa Alta, New Mexico and was used after grinding to pass a 100-mesh sieve. A small amount of quartz was detected as an impurity by X-ray powder diffraction ($2\theta = 26.7$ and 20.9°) and ^{29}Si MAS NMR (δ −107). Another kaolinite, KGa1 which was a well crystallized Georgia kaolinite obtained from the Source Clays

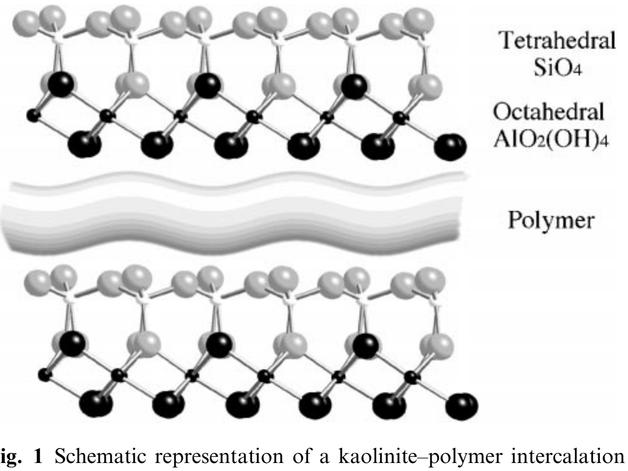

Fig. 1 Schematic representation of a kaolinite–polymer intercalation compound.

Repository of Clay Minerals Society (USA), was also used. Acrylamide was obtained from Wako Pure Chemical Industries Co. and used after recrystallization.

Preparation of the kaolinite–PAAm intercalation compound

The kaolinite–PAAm intercalation compound was prepared by the method reported by Sugahara *et al.*[21] First, a kaolinite–acrylamide intercalation compound was prepared by using a kaolinite–NMF intercalation compound as the intermediate. Intercalation was established by XRD, IR, ^{13}C MAS NMR, and C,H,N analysis.[21] Then, acrylamide was polymerized by heat treatment at 300 °C for 1 h under a nitrogen atmosphere. The formation of the kaolinite–PAAm intercalation compound was confirmed by XRD, IR, NMR and CHN analyses. The basal spacing of the product was 1.13 nm. Vinyl polymerization of acrylamide was verified by the disappearance of C=C bonds by ^{13}C CP MAS NMR and IR measurements. The carbon and nitrogen contents were 8.5 and 2.6 mass%, respectively, indicating an estimate of 0.73 PAAm units [$-CH_2CH(CONH_2)-$] per $Al_2Si_2O_5(OH)_4$ formula unit of kaolinite.

Thermal treatment

Kaolinite and the kaolinite–PAAm intercalation compound were heated to temperatures of 460, 500, 540, 580 or 620 °C at 4 °C min^{-1} before cooling. The samples were heated under a nitrogen flow in order to preserve carbonaceous materials in the interlayer space.

Analyses

XRD patterns were obtained by using a Mac Science MXP^3 diffractometer with monochromated Cu-Kα radiation. Thermogravimetric analysis (TG) was performed using a Shimadzu TGA-40 apparatus. The samples were heated to 900 °C under a dry air flow with a heating rate of 10 °C min^{-1}. The amount of organic material was determined by C,H,N analysis using a Perkin-Elmer PE-2400II apparatus. Solid state MAS NMR measurements were performed on a JEOL GSX-400 spectrometer with a spinning rate of 5 kHz. Larmor frequencies of ^{13}C, ^{29}Si and ^{27}Al were 100.40, 79.30 and 104.16 MHz, respectively. For ^{13}C NMR, the cross polarization (CP) technique was used. The recycle delays of ^{13}C, ^{29}Si and ^{27}Al were 5, 60 and 5 s, respectively. Chemical shifts were expressed relative to tetramethylsilane for ^{13}C and ^{29}Si, and $Al(H_2O)_6^{3+}$ (aq) for ^{27}Al. IR spectra were recorded on a Perkin-Elmer FT-IR 1640 spectrometer using the KBr-disk technique. The disks were heated at 180 °C before the measurements to avoid the effect of adsorbed water.

Results

The XRD patterns of the kaolinite–PAAm intercalation compound before and after heat treatment at different temperatures are shown in Fig. 2. Peaks due to the basal spacings were observed in all the patterns. At 460 °C, the basal spacing was *ca.* 1.27 nm, being increased from 1.13 nm for the intercalation compound before heat treatment. Because the layers of kaolinite do not change at this temperature, as described later, the increase in the basal spacing is probably due to the conversion of PAAm to carbonaceous materials despite some loss of organic material (Table 1). Broadening of the peak was also observed as a consequence of disordered stacking of the layers. The conversion of PAAm was confirmed by the ^{13}C NMR spectrum which showed no resolved peaks. Above 500 °C, broad XRD peaks due to the basal spacing were still observed. Moreover, the peaks were broadened toward lower diffraction angles, indicating a further disordering of the layers. This behavior is discussed later. On the other hand, a broad peak at $2\theta = 20°$ due to (020) planes was also observed, indicating preserved periodicity, to some extent, in the *ab* plane.

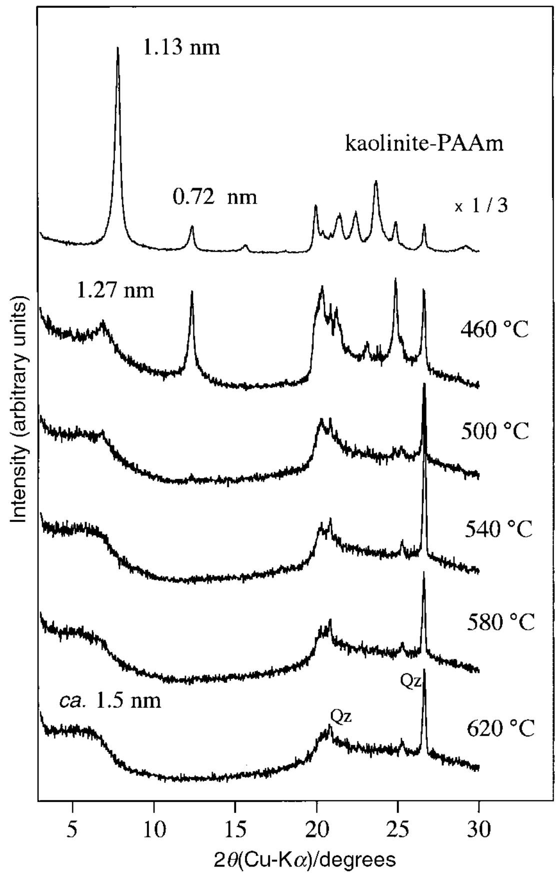

Fig. 2 XRD patterns of the kaolinite–PAAm intercalation compounds before and after heat treatment. 'Qz' denotes quartz.

Table 1 C,H,N contents (mass%) in the kaolinite–PAAm intercalation compounds before and after heat treatment at different temperatures

	C	H	N
Kaolinite-PAAm	8.5	2.0	2.6
460 °C	6.9	1.4	1.3
500 °C	6.9	0.7	1.3
540 °C	6.7	0.6	1.2
580 °C	6.4	0.5	1.1
620 °C	6.4	0.4	1.0

The XRD patterns of thermally treated raw kaolinite are shown in Fig. 3. The intensity of the peak due to the basal spacing at 0.72 nm decreased as the treatment temperature was increased and the peaks at *ca.* 20–22° also disappeared. This behavior is in line with previous reports which showed that the dehydroxylation reaction proceeded in the studied temperature range with loss of crystallinity.[9,16]

C,H,N analytical data for the kaolinite–PAAm intercalation compounds before and after heat treatment are listed in Table 1. In the heat-treated samples, the carbon and nitrogen contents were almost constant in the range of 6–7 and 1.3–1.0 mass%, respectively, although the calculated N/C ratio was far below 0.33 which is the calculated value for PAAm. These results indicate that carbonaceous materials were retained during the heat treatment although the structure of PAAm was changed. On the other hand, the hydrogen content decreased from 1.4 to 0.7 mass% 460 to 500 °C, which suggests that the dehydroxylation reaction of the aluminosilicate layers proceeded to some extent in this temperature range.

Table 2 shows the mass loss of the kaolinite–PAAm

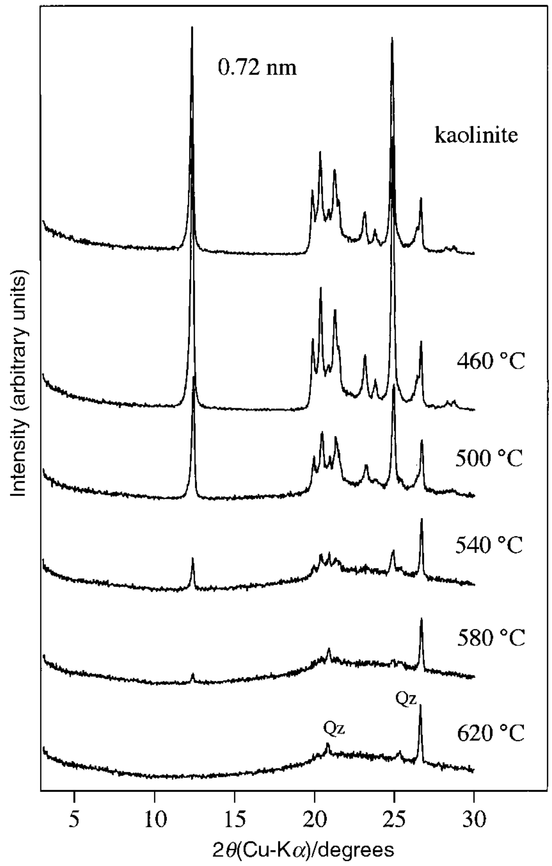

Fig. 3 XRD patterns of kaolinites before and after heat treatment. 'Qz' denotes quartz.

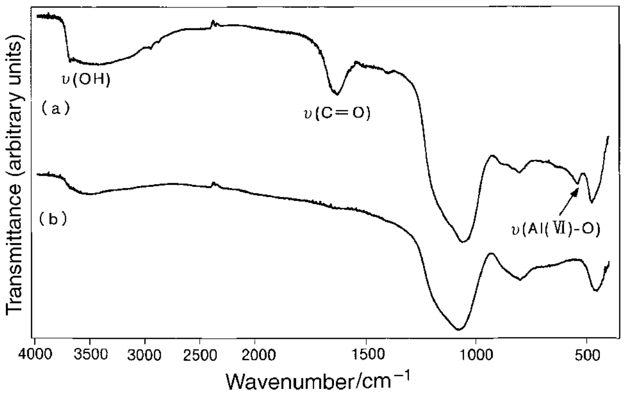

Fig. 4 IR spectra of (a) the kaolinite–PAAm intercalation compound and (b) kaolinite after heat treatment up to 620 °C.

intercalation compound and kaolinite before and after heat treatment as calculated from the TG curves. For the kaolinite–PAAm intercalation compounds, the mass losses were due to the combustion of organics and dehydroxylation; a clear mass loss between 460 and 500 °C is evident. Since the carbon and the nitrogen contents did not change between the two samples, the difference should correspond to the degree of the dehydroxylation as suggested by the decrease in the hydrogen content (Table 1). On heating above 500 °C, the mass loss for the intercalation compound was almost constant, indicating that the dehydroxylation reaction ceased. For kaolinite itself, the dehydroxylation reaction proceeded gradually as the temperature was increased and was virtually complete at 620 °C.

Fig. 4 shows the IR spectra of the kaolinite–PAAm intercalation compound and of kaolinite heated to 620 °C. In the spectrum of the heated compound, the broad band in the OH stretching region was still observed whereas the band was much weaker in the spectrum of heated kaolinite. The presence of unreacted hydroxy groups in the intercalation compound at 620 °C implies a cessation of the dehydroxylation reaction between 500 and 620 °C. On the other hand, the band at 1650 cm^{-1} arising from C=O stretching showed the preservation of the carbonyl group. In the framework region, a weak characteristic band at 540 cm^{-1} assigned to Al(VI)–O stretching still appeared, indicating six-coordinated Al remained in the heated samples to some extent while this peak was not clearly detected in kaolinite heated at 620 °C, though the ^{27}Al MAS NMR spectrum of the heated kaolinite showed the presence of Al(VI).

The transformation behavior for the Si environments is revealed by ^{29}Si NMR spectra as shown in Fig. 5. In the spectrum of the kaolinite–PAAm intercalation compound heated to 460 °C, a sharp peak at δ −91 assignable to a Q^3 environment was observed. At 500 °C the Q^3 signal shifted to δ −94 and was broadened. These changes may be caused by various distortions of silicate sheets. Above 540 °C, however, the peak position and the profile were unchanged, indicating no further structural change of the aluminosilicate sheets. By contrast, the ^{29}Si MAS NMR spectra of heated kaolinites showed a considerable change of the Si environments, in accord with the literature.[6–14] As the temperature was increased, the intensity of the Q^3 signal at δ −91 decreased and a new broad signal at δ *ca.* −95 appeared and shifted towards the Q^4 region, indicating transformation of the silicate sheets.

The ^{27}Al MAS NMR spectra in Fig. 6 reveal the thermal evolution of the Al environments. In the spectrum of the intercalation compound treated up to 460 °C, a peak at δ *ca.* 0 assigned to six-coordinated Al was observed. A small peak at δ 50 is not so clear because of its overlapping with a spinning sideband. At 500 °C, small peaks at δ *ca.* 50 and *ca.* 30 were clearly detected, and were assigned to four- and five-coordinated Al, respectively. Above 540 °C, the peak positions and the profiles remained unchanged. Thus even at such high temperatures, a relatively large signal due to Al(VI) was present and the peak intensities of Al(IV) and Al(V) were small even at 620 °C. On the other hand, in the ^{27}Al MAS NMR spectra of the unmodified kaolinites at 460 and 500 °C, one signal at δ *ca.* 0 was observed. However, above 540 °C, the intensity of the

Table 2 Mass loss of kaolinite–PAAm intercalation compounds and kaolinites before and after heat treatment at different temperatures

	Kaolinite–PAAm Mass loss[a](%)	Kaolinite	
		Mass loss[a] (%)	Degree of dehydroxylation[b]
Before heat treatment	27.0	13.5	0
460 °C	19.1	12.6	0.07
500 °C	14.8	6.7	0.50
540 °C	14.4	2.2	0.84
580 °C	12.4	1.0	0.93
620 °C	12.2	0.5	0.96

[a] Mass loss was measured from room temperature to 900 °C under air atmosphere. [b] The degree of dehydroxylation for kaolinite was calculated from the mass loss.

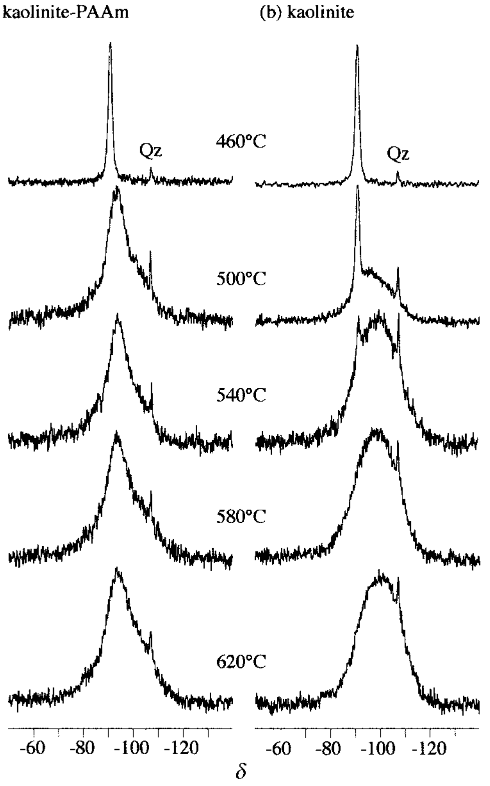

Fig. 5 ^{29}Si MAS NMR spectra of (a) kaolinite–PAAm intercalation compounds and (b) kaolinites after heat treatment. 'Qz' denotes quartz.

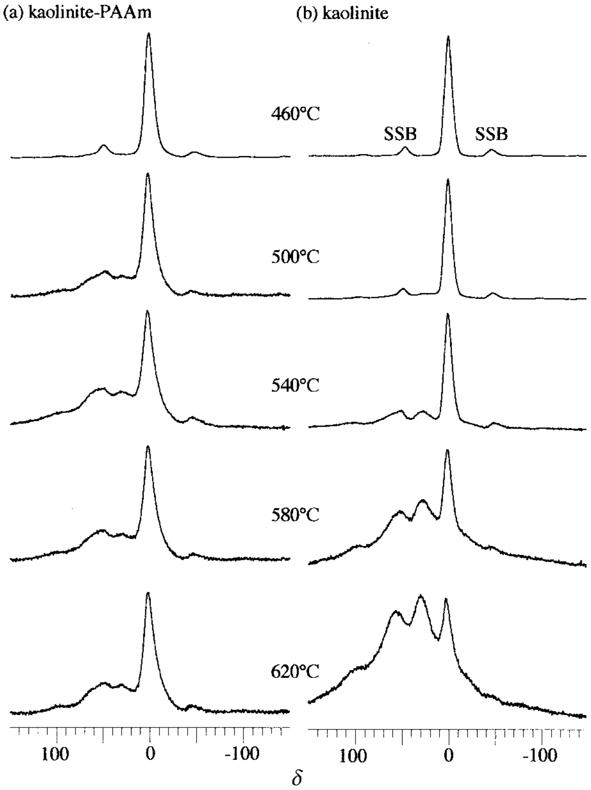

Fig. 6 ^{27}Al MAS NMR spectra of (a) kaolinite–PAAm intercalation compounds and (b) kaolinites after heat treatment. Spinning sidebands (SSB) are shown only in the spectrum of kaolinite (460 °C).

signal due to six-coordinated Al decreased, while the peak intensities of four- and five-coordinated Al increased, indicating gradual transformation of the octahedral Al sheets as the temperature increased.

The transformation of the second kaolinite sample (KGa1) was also investigated and very similar results were obtained for the dehydroxylation and transformation behavior of the kaolinite–PAAm intercalation compound. This implies that the thermal transformation of the intercalation compound was independent of the kaolinite source sample.

Discussion

Effects of carbonaceous materials on the transformation behavior of the intercalation compound

The above experiments verified that carbonaceous materials were retained in the temperature range investigated (up to 620 °C). In the XRD patterns, the peaks due to the basal spacings of the products did not disappear (Fig. 2) and the amount of organic material was almost constant (Table 1). Furthermore, the IR spectrum of the product treated at 620 °C revealed the presence of carbonyl groups (Fig. 4). These results indicate that carbonaceous materials containing carbonyl groups are present in the interlayer space.

The carbonaceous materials hindered the thermal transformation of the silicate sheets. The presence of a broad peak at 2θ *ca.* 20° (Fig. 2) showed that two dimensional periodicity did not vanish completely. Additionally, a Q^3 signal at δ *ca.* -94 in the ^{29}Si NMR spectra (Fig. 5) was observed in heated sample. These results indicate that the fundamental structure of the silicate sheet was retained. The slight shift of the Q^3 signal to lower frequency from the original chemical shift at δ -91 can be interpreted as arising from a change in the flattened conformation of the silicate sheets.[6]

The dehydroxylation reaction started below 500 °C, which is lower than found for kaolinite itself. The decrease in the dehydroxylation temperature is in accord with reports of the thermal behavior of kaolinite intercalation compounds with small organic molecules.[25–28] The reason for this behavior was mainly considered as due to a disordered stacking of the layers. On the other hand, dehydroxylation was retarded between 500 and 620 °C; almost no changes were observed in the NMR spectra, indicating the cessation of transformation of the host layers. Although the dehydroxylation reaction proceeded to some extent below 500 °C, the hydroxy groups were retained even after heat treatment at 620 °C as established by IR spectroscopy (Fig. 4). We propose that the hydroxy groups, even though they are still hydrogen-bonded, are retained owing to the restriction of the transformation of the host layers.

The ^{27}Al NMR and the IR spectra show retention of a fraction of six-coordinated Al which would be related to the presence of hydroxy groups. In addition to six-coordinated Al, there were small signals due to four- and five-coordinated Al. In comparison to heated kaolinite, the generation of five-coordinated Al has been reduced. This implies that interactions with adjacent layers are essential for the occurrence of five-coordinated Al. On the other hand, the basal spacing slightly increased as a consequence of the dehydroxylation reaction (Fig. 2). This result suggests an increased layer thickness rather than a further conversion of carbonaceous materials and is probably due to the inversion of some tetrahedra of the silicate sheets towards the interlayer direction during thermal treatment.[29]

Structural change of kaolinite

In the NMR spectra of the thermally treated kaolinites, the signal due to five-coordinated Al was prominent (Fig. 6) and the Q^3 signal of the Si environment in the kaolinites was broadened and shifted to the Q^4 region (Fig. 5). These results are different from those for the polymer-intercalated compound in which carbonaceous materials are present in the interlayer space, indicating that the interactions of adjacent layers are essential for the structural change of kaolinite, especially for the occurrence of five-coordinated Al. If the silicate sheets in local regions are retained as suggested by TEM results,[17] Al(V) atoms in metakaolinite are coordinated by the oxygen atoms not only in the same layer but also in adjacent layers as has been suggested by Sanz *et al.*[10] Even if the signal at δ 30 is assigned to Al(IV) with elongated Al–O bonds,[15,30] the same mechanism can be applied; essentially, the Al atoms are coordinated by oxygen atoms in the same and adjacent layers.

In addition to Al(V), the presence of Al(IV) and Al(VI) has been observed in the ^{27}Al NMR spectra of metakaolinite in this study. Furthermore, a broad signal in the ^{29}Si NMR spectra indicates the various Si environments. Consequently, we infer that several local regions are present in metakaolinite as has been proposed in ref. 13. Some Al(IV) and Al(VI) atoms are possibly distributed suitably with Al(V) atoms to reduce distortion of the structure.

Conclusion

The thermal transformation of the kaolinite–PAAm intercalation compound was totally different from that of kaolinite. The carbonaceous materials in the interlayer space contributed to the retention of the two-dimensional network of the silicate sheets and suppressed both the appearance of five-coordinated Al and the dehydroxylation reaction. Consequently, the formation of five-coordinated Al in the structure of metakaolinite is associated with the silicate sheets not only in the same layer but also in adjacent layers. This study also implies that intercalated polymer guests affect the thermal properties of layered host materials. Thus, investigation of the thermal behavior of polymer-intercalated layered materials is an effective approach to elucidate the thermal characteristics of layer structures.

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