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Synthesis of Layered Polysilicic Acid-Acrylamide Intercalation Compounds and Polymerization in the Interlayer Spaces

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Layered polysilicic acid–acrylamide intercalation compounds were synthesized by the reaction of H-magadiite ($H_2Si_{14}O_{29}\cdot xH_2O$) and H-kenyaite ($H_2Si_{20}O_{41}\cdot xH_2O$) with acrylamide saturated aqueous solutions. The formation of the intercalation compounds were ascertained by X-ray powder diffraction, IR, ^{13}C-CP MAS NMR, DTA, and chemical analysis. However, when H-magadiite was used, a part of the intercalated acrylamide molecules was oligomerized during the intercalation. A heat treatment of the layered polysilicic acid–acrylamide intercalation compounds led to a polymerization of the acrylamide in the interlayer spaces.

Many types of intercalation compounds have been synthesized from layered inorganic compounds. For example, clay mineral–polymer intercalation compounds[1)] have been synthesized by a direct polymer intercalation or polymerization of monomer molecules in interlayer spaces. Synthesis of inorganic–organic polymer complexes by polymerization of monomers in the interlayer space has attracted much attention from the viewpoints of both intercalation chemistry and polymer science.

Layered polysilicates, such as Na-magadiite ($Na_2Si_{14}O_{29}\cdot xH_2O$) and K-kenyaite ($K_2Si_{20}O_{41}\cdot xH_2O$), consist of SiO_4 tetrahedra layers.[2,3)] Layered polysilicic acids, which are the acid type of layered polysilicates, also consist of SiO_4 tetrahedra layers, and have silanol groups on their surfaces. Because of the presence of silanol groups, the layered polysilicic acids act as a solid acid with high surface acidity.[4)] However, the detailed crystal structures of many layered polysilicates have not yet been defined. Similar to clay minerals, it has been known that layered polysilicates and layered polysilicic acids can intercalate various organic cations and molecules, such as alkylammonium ions and alkylamines.[2,3,5,6)] Rojo et al.[7)] investigated the adsorption of *N*-substituted amides into layered polysilicic acids and the interaction between amides and interlayer silanol groups. However, only a few polymer intercalated layered polysilicic acids have been synthesized; Sugahara et al.[8)] reported on the polymerization of acrylonitrile in the interlayer space of H-magadiite, and Lagaly et al.[9)] also mentioned that caprolactam and acrylamide were polymerized in the interlayer space of H-magadiite. However, in the latter work, the characterization of polymer intercalated H-magadiite was not described. No polymer intercalated H-kenyaite has been reported.

In our previous studies, acrylamide was intercalated into montmorillonite[10)] and kaolinite,[11)] and was polymerized in their interlayer spaces. Acrylamide is liable to be intercalated into layered materials and to be polymerized. In this study, acrylamide was intercalated to layered polysilicic acids, H-magadiite ($H_2Si_{14}O_{29}\cdot xH_2O$) and H-kenyaite ($H_2Si_{20}O_{41}\cdot xH_2O$), and was allowed to polymerize in their interlayer spaces. The results were compared with those of montmorillonite- and kaolinite–polyacrylamide intercalation compounds.

Experimental

Materials. H-magadiite and H-kenyaite were prepared by a method described by Lagaly et al.;[3,9)] 0.1 mol dm^{-3} HCl was added dropwisely to a suspension of Na-magadiite or K-kenyaite until the pH became 2. The suspensions were stirred for 24 h and the pH value was kept at 2 with 0.1 mol dm^{-3} HCl. The products were filtered, washed until no Cl^- ions were detected, and air-dried. Their formation was checked by X-ray powder diffraction; X-ray fluorescence analysis showed the absence of alkali metal ions. Acrylamide (Wako Pure Chemical Ind., extra pure) was recrystallized before use.

Layered Polysilicic Acid–Acrylamide Intercalation Compounds. About 10 ml of an acrylamide saturated aqueous solution was added to 1 g of the layered polysilicic acids, and the suspensions were stirred for 2 days at room temperature. After the products were separated from the solutions by centrifugation, they were washed with CCl_4 and air-dried. For interlayer polymerization, a part of the washed products was heat-treated at 200 °C for 30 min with a DTA apparatus.

Analyses. X-Ray powder diffraction patterns were obtained with a Rigaku Rad-IB diffractometer using Ni-filtered Cu *Kα* radiation. Infrared spectra were recorded on a Perkin-Elmer FTIR 1640, using a KBr disk method. DTA curves were obtained with a Shimadzu thermal analyzer (DT-20B) with α-Al_2O_3 as the reference material. ^{13}C-CP MAS NMR spectra were obtained with a JEOL GSX-400 spectrometer at 100.54 MHz. The external standard was tetramethylsilane. The matched radiofrequency field amplitude was 39.7 kHz, with a 90° pulse of 6.3 µs. The CP contact time was 2 ms, and the pulse repetition time was 5 s.

Results and Discussion

Table 1 shows the values of the basal spacings of the starting materials, the reaction products, and the heat-treated products. After treatment with acrylamide saturated solutions, the product from H-magadiite indicated a basal spacing of 15.0 Å. The value of the product from H-kenyaite was 22.3 Å. The increments in H-magadiite were 3.8 Å and corresponded to the calculated thickness of an acrylamide molecule (3.7 Å),

Table 1. Basal Spacings of Layered Polysilicic Acids and Their Acrylamide Intercalated Compounds

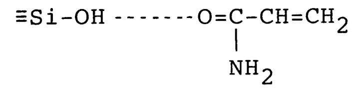
	H-magadiite/Å	H-kenyaite/Å
Original form	11.2	16.5
Acrylamide intercalated form	15.0	22.3
Heat-treated acrylamide intercalated form (200 °C)	14.0	21.7

Table 2. Infrared Assignments of Acrylamide and the Layered Polysilicic Acid–Acrylamide Intercalation Compounds

	Wavenumber/cm^{-1}		
	$\nu_{C=O}$	$\nu_{C=C}$	δ_{N-H}
Acrylamide[12]	1686	1647	1618, 1592
Montmorillonite–acrylamide intercalation compound (15 Å type)[10]	1676	1624	1602
Kaolinite–acrylamide intercalation compound[11]	1685	1621	1597
H-magadiite–acrylamide intercalation compound	1676	1624	1597
H-kenyaite–acrylamide intercalation compound	1671	1624	1588

which suggested that acrylamide molecules lay flat in the interlayer space. However, the increment in H-kenyaite (5.8 Å) was larger than the thickness of the acrylamide molecules. This value was close to that of the increment in the "15 Å basal spacing phase" of montmorillonite–acrylamide intercalation compound (5.4 Å),[10] in which it was thought that acrylamide molecules were probably adsorbed as a monomolecular arrangement with the molecular plane perpendicular to the silicate sheets. In the present kenyaite system, therefore, such an arrangement may be possible.

The infrared spectrum of the product from H-magadiite (Fig. 1b) indicated the appearance of new peaks at 1676 cm^{-1}, 1624 cm^{-1}, and 1597 cm^{-1}. By a comparison with the infrared spectrum of acrylamide in $CHCl_3$ solution,[12] these peaks were ascribable to $\nu_{C=O}$, $\nu_{C=C}$, and δ_{N-H}, respectively. The peak positions were in good agreement with those in montmorillonite–acrylamide and kaolinite–acrylamide intercalation compounds (Table 2). This fact means that the acrylamide molecules in the products have some interaction with SiO_4 tetrahedra layers, like that of montmorillonite- and kaolinite–acrylamide intercalation compounds. By a comparison with the IR results of H-magadiite–*N*-methylformamide and -*N*,*N*-dimethylformamide intercalation compounds,[7] it was reasonable to consider that this interaction between acrylamide and SiO_4 tetrahedra layers of layered polysilicic acid came about from hydrogen bonds between silanol groups and C=O groups in acrylamide molecules in the following way:



$$\equiv Si{-}OH \cdots\cdots O{=}\underset{\displaystyle NH_2}{\underset{|}{C}}{-}CH{=}CH_2 \qquad (1)$$

However, the shape of the ν_{O-H} peaks at 3500—3000 cm^{-1} of H-magadiite varied because of an overlapping of the ν_{N-H} peaks due to acrylamide. The IR spectrum of the product from kenyaite also showed peaks due to acrylamide, similar to that of the product from H-magadiite.

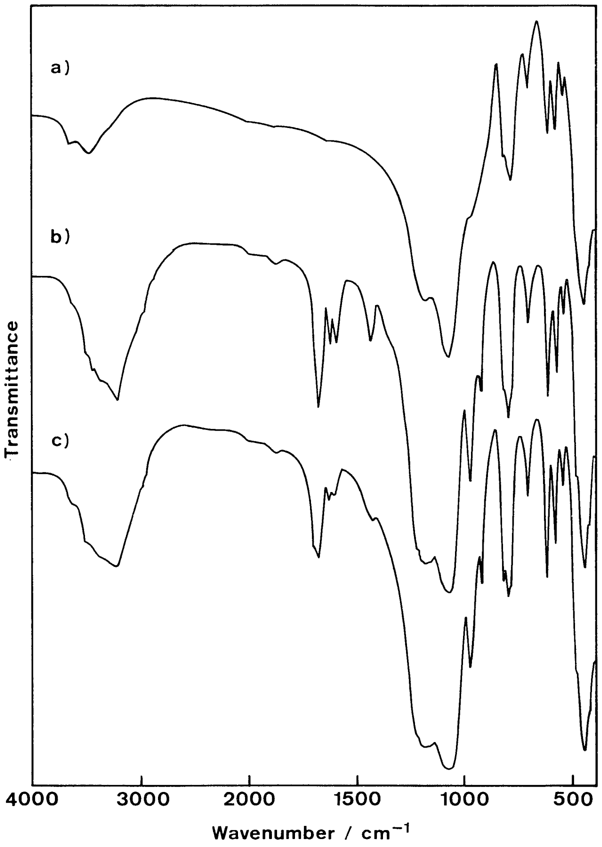


Fig. 1. IR spectra of a) H-magadiite, b) H-magadiite–acrylamide intercalation compound, and c) H-magadiite–polyacrylamide intercalation compound.

The ^{13}C-CP MAS NMR spectra of the products from H-magadiite and H-kenyaite (Figs. 2 and 3) indicated peaks at about 131 ppm and 172 ppm, which can be

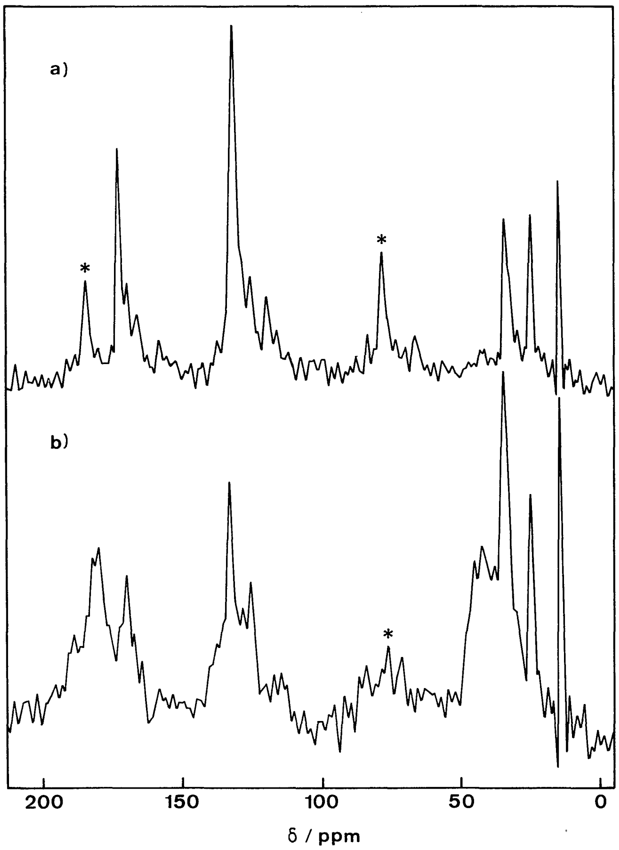


Fig. 2. ^{13}C-CP MAS NMR spectra of a) H-magadiite–acrylamide intercalation compound and b) H-magadiite–polyacrylamide intercalation compound. Spinning side bands are marked by asterisks.

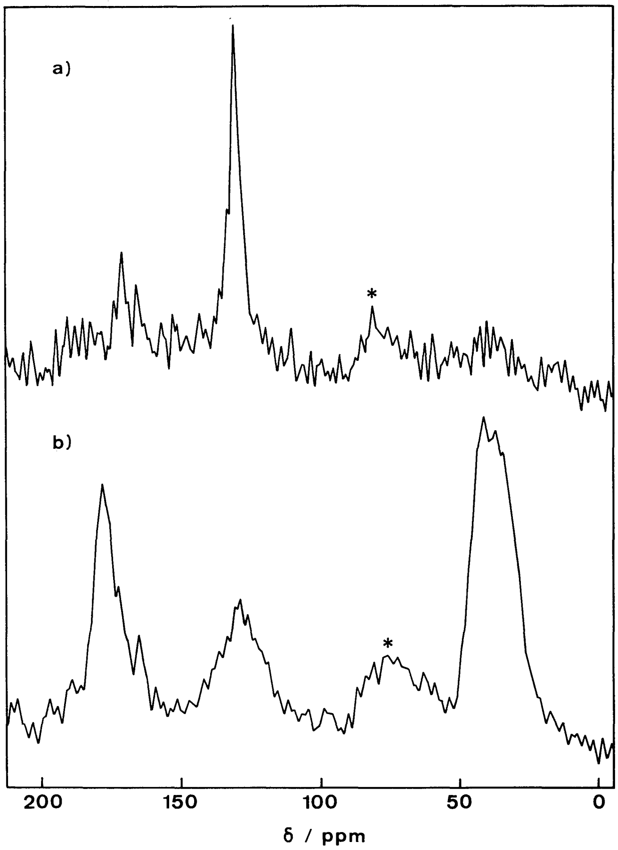


Fig. 3. ^{13}C-CP MAS NMR spectra of a) H-kenyaite–acrylamide intercalation compound and b) H-kenyaite–polyacrylamide intercalation compound. Spinning side bands are marked by asterisks.

attributed to the carbon atoms in the $-\underline{C}H=\underline{C}H_2$ and $-\underline{C}O-NH_2$ groups, respectively.[13]

From all of these results, it was confirmed that acrylamide molecules were intercalated into the interlayer regions of the layered polysilicic acids, H-magadiite and H-kenyaite.

However, the ^{13}C-CP MAS NMR spectrum of the H-magadiite–acrylamide intercalation compound indicated additional peaks at 14.1 ppm, 24.3 ppm, and 33.6 ppm (Fig. 2a). These were attributable to single-bonded C atoms arising from a polymerized product. In particular, the peak at 14.1 ppm, which can be assigned to the terminal $-CH_3$ group in alkyl chain, appeared to be strong, even after taking into account an enhancement of the peak due to $-CH_3$ groups by the CP technique. This means that some of the acrylamide molecules in the interlayer spaces were oligomerized simultaneously with the intercalation. On the other hand, the NMR spectrum of the product from H-kenyaite (Fig. 3a) did not show any peaks due to the oligomerized product. It has been reported that H-magadiite is a solid acid with $H_0=-5$—-3 of surface acidity.[4] Consequently, it is reasonable to consider that the Si–OH groups on the surface of SiO_4 tetrahedra layers in H-magadiite acted as a catalyst for the oligomerization of acrylamide. The acidity of H-kenyaite has been reported to be $H_0=-3$—$+1.5$. This difference in the acidity may explain the oligomerization of acrylamide only regarding the H-magadiite.

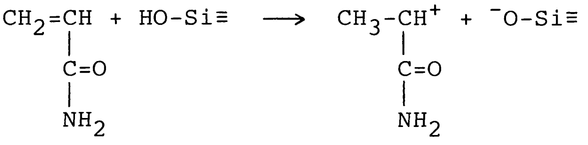
The results of chemical analyses of the layered polysilicic acid–acrylamide intercalation compounds were as follows: $H_2Si_{14}O_{29}:CH_2CHCONH_2=1:1.61$ and $H_2Si_{20}O_{41}:CH_2CHCONH_2=1:2.81$. This difference in the contents of acrylamide was possibly ascribable to the different structures, including the interlayer spaces of H-magadiite and H-kenyaite, although they have not yet been clarified.[14] This difference agreed with the fact that the increment in the basal spacing of the H-magadiite–acrylamide intercalation compound was smaller than that of H-kenyaite–acrylamide intercalation compound.

The DTA curves of the layered polysilicic acid–acrylamide intercalation compounds showed exothermic peaks which started at about 100 °C. Therefore, the compounds were heat-treated at 200 °C for 30 min, and the products were analyzed.

After the heat treatment, the basal spacings of the layered polysilicic acid–acrylamide intercalation compounds decreased from 15.0 Å to 14.0 Å for H-magadiite, and from 22.3 Å to 21.7 Å for H-kenyaite. However, even after the heat treatment, these values were larger than those of the starting layered polysilicic acids (Table 1).

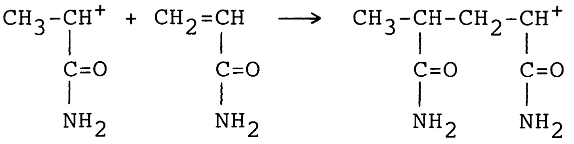
The infrared spectrum of the heat-treated product from the H-magadiite–acrylamide intercalation compound (Fig. 1c) showed that the peak at 1624 $\mathrm{cm^{-1}}$ ($\nu_{C=C}$) decreased remarkably. In the infrared spectrum of the heat-treated product from the H-kenyaite–acrylamide intercalation compound, no significant peak appeared at about 1620 $\mathrm{cm^{-1}}$. In the ^{13}C-CP MAS NMR sectra of the heat-treated products, a new broadened peak appeared at 35—40 ppm, which was assignable to the C–C single bonds in polymers, although weakened peaks due to the C=C double bond still remained. (Figs. 2 and 3). The fact that acrylamide molecules partly remained in the heat-treated intercalation compounds may result from their specific arrangements in the interlayer space. The DTA curves of the heat-treated products indicated the disappearance of an exothermic peak starting from about 100 °C.

These facts mean that the exothermic peak starting from about 100 °C in the DTA curve was attributable to a polymerization of acrylamide in these intercalation compounds. Therefore, from these results, it was confirmed that acrylamide molecules in the interlayer spaces of layered polysilicic acid were polymerized by a heat treatment at 200 °C. This polymerization of intercalated acrylamide without an initiator was attributable to the high surface acidities of the layered polysilicic acids.[3,4] Namely, as described above, Si–OH groups on the surface of SiO_4 tetrahedra layers in the layered polysilicic acids acted as catalysis for cationic polymerization, according to the following equations:



$$\mathrm{CH_2{=}CH(C{=}O)NH_2 + HO{-}Si{\equiv} \longrightarrow CH_3{-}CH^+(C{=}O)NH_2 + {}^-O{-}Si{\equiv}} \qquad (2)$$

and



$$\mathrm{CH_3{-}CH^+(C{=}O)NH_2 + CH_2{=}CH(C{=}O)NH_2 \longrightarrow CH_3{-}CH(C{=}O)NH_2{-}CH_2{-}CH^+(C{=}O)NH_2} \qquad (3)$$

Since montmorillonite and kaolinite have no silanol groups on their layer structures, it was difficult to polymerize acrylamide in their interlayer spaces in the process expressed in Eqs. 2 and 3.

The organic contents of the layered polysilicic acid–polyacrylamide intercalation compounds were as follows: $H_2Si_{14}O_{29}:CH_2CHCONH_2=1:1.25$ in the H-magadiite–polyacrylamide intercalation compound, and $H_2Si_{20}O_{41}:CH_2CHCONH_2=1:2.62$ in the H-kenyaite–polyacrylamide intercalation compound. These values were smaller than those of the layered polysilicic acid–acrylamide intercalation compounds. This fact suggested that some of the acrylamide molecules in the interlayer spaces were eliminated during the heat treatment.

In conclusion, both H-magadiite and H-kenyaite, which are the layered polysilicic acids, intercalated acrylamide into their interlayer spaces by a treatment with acrylamide saturated aqueous solutions. However, in the case of the H-magadiite–acrylamide intercalation compound, a part of acrylamide molecules in the interlayer surfaces was oligomerized because of the high surface acidity of H-magadiite.

By a heat treatment of these layered polysilicic acid–acrylamide intercalation compounds, acrylamide was polymerized in the interlayer spaces. However, a part of acrylamide was eliminated during the heat treatment.

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