

NMR Study of Kaolinite Intercalation Compounds with Formamide and Its Derivatives. 1. Structure and Orientation of Guest Molecules

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Local structures and orientations of guest molecules in kaolinite intercalation compounds of kaolinite/formamide (FA), kaolinite/formamide-*N,N*- d_2 (FA- d_2), kaolinite/*N*-methylformamide (NMF), and kaolinite/*N,N*-dimethylformamide (DMF) have been studied by means of solid-state NMR. ^{29}Si magic-angle-spinning (MAS) NMR spectra identify the original kaolinite and the intercalates, while ^{13}C MAS NMR spectra distinguish interlayer and outersurface adsorbed guest molecules. Quantitative analyses of ^{29}Si and ^{13}C NMR spectra combined with thermogravimetric analysis result in a formula of one interlayer guest molecule per $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ host unit for all the intercalates. Intercalation causes high-frequency shift in the ^{13}C resonance of the guest molecules. Strength in the guest–host interaction as revealed by changes in the ^{13}C chemical shift of the carbonyl group upon intercalation is in the order of $\text{FA} > \text{NMF} \sim \text{DMF}$. The ^{13}C chemical shift of the methyl group confirms a *cis* conformation for NMF in the kaolinite interlayer space, and changes in the methyl chemical shift upon intercalation are $\text{DMF (trans)} > \text{NMF (cis)} > \text{DMF (cis)}$. The magnitude of the temperature dependence in the ^{13}C chemical shift is on the order of $\text{FA} < \text{NMF} < \text{DMF}$, and the ^{13}C line width is $\text{FA} > \text{NMF} > \text{DMF}$. These facts reveal that the mobility of the guest molecules is in the order of $\text{FA} < \text{NMF} < \text{DMF}$. Kaolinite/NMF shows a second methyl peak whose amount increases with decreasing temperature, demonstrating the presence of molecules with a different orientation. The ^1H chemical shifts confirm hydrogen-bonding interactions between the amide protons and the kaolinite host in kaolinite/FA and no such hydrogen-bonding interactions in kaolinite/NMF at room temperature. The chemical shift value of the hydroxyl groups in the host kaolinite structure is not affected by intercalation. The ^1H line widths of carbonyls are $\text{FA} > \text{NMF} > \text{DMF}$, and those of methyls are $\text{NMF} > \text{DMF}$, which confirms again that the mobility of the guest molecules is $\text{FA} < \text{NMF} < \text{DMF}$.

I. Introduction

Kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, is a layered aluminosilicate with a dioctahedral 1:1 layer structure consisting of an octahedral aluminum hydroxide sheet and a tetrahedral silica sheet.^{1–7} Polar organic molecules such as formamide (FA) and dimethyl sulfoxide (DMSO),^{8–10} alkali salts, such as alkali acetates and alkali halides,^{10,11} and even long-chain alkylamines,¹² can be intercalated into the kaolinite layers. In the present work the intercalations of kaolinite with formamide and its derivatives have been surveyed.

Crystal structures obtained by diffraction techniques can provide reliable structural information, if available. To our knowledge, no crystal structures have been reported for kaolinite intercalation compounds with formamides, but those of dickite/FA¹³ and dickite/NMF¹⁴ were already published, which were supposed to provide reliable references to the arrangements of the guest molecules in the corresponding kaolinite intercalates.¹⁵ Dickite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, is a two-layer monoclinic modification of kaolinite.¹⁶ The crystal structure of dickite/FA shows an ordered arrangement of the guest molecules in the interlayer with five hydrogen bonds; three formed between the formamide O and the OH groups of the AlO_6 octahedra, one between the amide N and one of these hydroxyls, and one between the amide NH and O of the adjacent silica sheet.¹³ The crystal structure of dickite/*N*-methylformamide (NMF) reveals an ordered layout of the guest molecules in the interlayer space, too.¹⁴ Unlike the FA intercalate where five hydrogen bonds link the host layers

together, only three hydrogen bonds are formed between the OH groups of the AlO_6 octahedra and the carbonyl O, without forming the hydrogen-bond link between the amide group and the adjacent silica sheet. The methyl group in NMF molecules retains a *cis* conformation. On the basis of these structural data, the fine structures of the kaolinite intercalation compounds were drawn,¹⁵ which are schematically depicted in Figure 1.

Besides the diffraction techniques, solid-state NMR provides a supplementary way for obtaining structural information. We have successfully studied structures of the intercalate and orientations of guest molecules in kaolinite/DMSO intercalation samples mainly by applying ^{13}C , ^{29}Si , and ^1H solid-state NMR techniques.^{17–19} Thompson^{20,21} has studied the short-range ordering and bonding in the structures of the kaolinite/FA intercalation compounds through the interpretation of chemical shifts and line widths in the ^{29}Si and ^{13}C solid-state magic-angle-spinning (MAS) NMR spectra; a single unresolved peak at -91.9 ppm was observed in ^{29}Si NMR spectra for the kaolinite/FA intercalate, and ^{13}C NMR spectra showed peaks at 166.7 and 168.2 ppm for outersurface and interlayer FA molecules, respectively.

In the present work, we have carried out for the first time a thorough NMR study on the local structures and orientations of the guest molecules in the intercalation compounds of kaolinite/FA, kaolinite/formamide-*N,N*- d_2 (FA- d_2), kaolinite/NMF and kaolinite/*N,N*-dimethylformamide (DMF). We analyzed ^{29}Si and ^{13}C NMR spectra quantitatively and determined

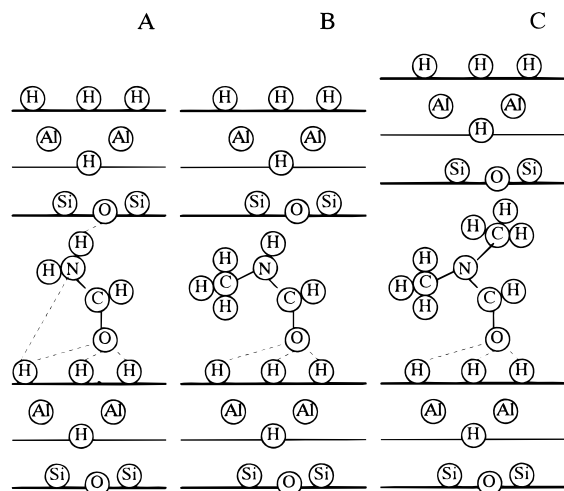


Figure 1. Schematics of the structure of kaolinite intercalation compounds with (A) FA, (B) NMF, and (C) DMF.

the concentrations of interlayer guest molecules. The ^{13}C and ^1H chemical shifts of the guest molecules provided us insight into the conformation of the guest molecules and hydrogen-bonding interactions between the guest and the host.

II. Experimental Section

Kaolinite used was Georgia kaolinite KGa-1 (named sample I) with a content of paramagnetic impurities of about 0.46 wt %. FA (HCONH_2), NMF (HCONHCH_3) and DMF ($\text{HCON}(\text{CH}_3)_2$) were obtained from Nacalai Tesque, Inc. (Kyoto, Japan). FA- d_2 (HCOND_2) was obtained from MSD Isotopes (Division of Merck Frosst Canada, Inc., Montreal, Canada). The kaolinite was dried at 373 K overnight before use. The intercalation for kaolinite/FA (sample II) was fulfilled by a two-step displacement method,⁹ with kaolinite/NMF as an intermediate. The kaolinite powder was mixed in NMF solvent with 9.0 vol % of H_2O ⁹ and stirred at 333 K for 5 days, followed by centrifugation of the mixture to produce the intermediate kaolinite/NMF. The intermediate was then mixed in FA solvent with 4.5 vol % of H_2O ⁹ and stirred at 333 K for another 5 days, followed by centrifugation and drying at 343 K for 3 days. Kaolinite/FA- d_2 (sample III) was prepared by a vaporizing method, in which the kaolinite powder was exposed to the solvent vapor at 343 K for 4 weeks, under nitrogen atmosphere, without further drying of the sample. Kaolinite/NMF (sample IV) was synthesized by the vaporizing method at 343 K for one week, without further drying of the sample. The intercalation for kaolinite/DMF (sample V) was accomplished by the two-step displacement method with kaolinite/NMF as an intermediate, where the intermediate synthesized by the same procedure as in sample II was mixed in pure DMF solvent and stirred at 333 K for 5 days, followed by centrifugation and drying at 343 K for 3 days. Intercalation of kaolinite with FA was also tried by a direct immersing method, where the kaolinite powder was mixed in FA solvent with 4.5 vol % of H_2O and stirred at 333 K for as long as 30 days, and the direct vaporizing method at 343 K for as long as 45 days. The obtained samples showed rather low intercalated fraction. Intercalation of kaolinite with NMF was also accomplished by the immersing method at 333 K for 5 days, and a sample similar to sample IV was obtained.

X-ray powder diffraction (XRD) data were collected by a Rigaku RAX-01 Geiger Flex diffractometer with $\text{Cu K}\alpha$ radiation. Thermogravimetric (TG) and differential thermal analyses (DTA) were performed by a Rigaku Thermoflex

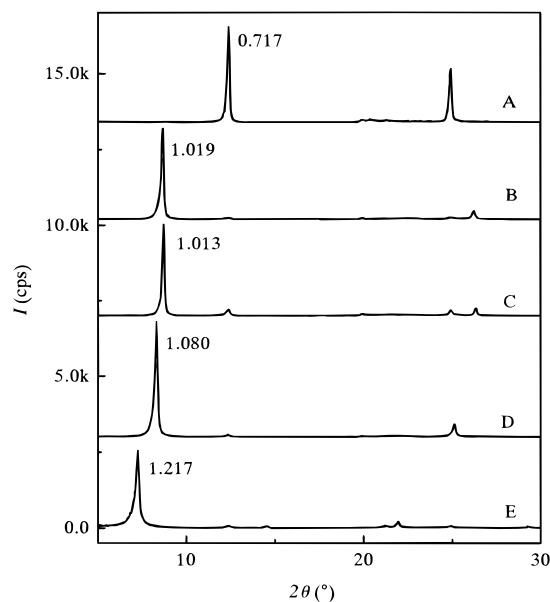


Figure 2. X-ray powder diffraction patterns of (A) kaolinite (sample I), (B) kaolinite/FA (sample II), (C) kaolinite/FA- d_2 (sample III), (D) kaolinite/NMF (sample IV), and (E) kaolinite/DMF (sample V). The numerical value attached to each peak is basal spacing in nanometers.

TG8110. The sample temperature was raised at a rate of 10 K/min under a nitrogen gas flow for the deuterated sample and in air atmosphere for the others.

NMR measurements were carried out by Bruker ASX400, MSL400, and ASX200 spectrometers with static magnetic field strengths of 9.4, 9.4, and 4.7 T, respectively. ASX400 was used for the measurements of MAS spectra of ^{13}C (Larmor frequency of 100.61 MHz) and ^{29}Si (79.50 MHz), MSL400 for ^{13}C MAS spectra (400.14 MHz), and ASX200 for ^{13}C MAS (50.32 MHz) and ^1H CRAMPS (200.13 MHz) spectra. The ^{13}C spectra were measured using cross polarization (CP) and single-pulse sequence with ^1H high power decoupling (HD) under MAS. ^{29}Si spectra were recorded with CP/MAS. ^1H MAS spectra were obtained with the single pulse sequence using a Bruker high-speed-spinning type probehead with a rotor of 4 mm diameter. ^1H CRAMPS spectra were measured with BR24 multiple pulse sequence in a quadrature detection mode²² using a Bruker CRAMPS probehead. Chemical shifts were presented with respect to neat tetramethylsilane. The higher frequency side of the spectra with respect to the standard signal was expressed as positive.

^1H and ^{13}C MAS NMR measurements on pure liquid NMF were carried out by ASX200 using a Bruker MAS probehead with the 4 mm rotor. Details of such liquid/MAS measurements were described by Hayashi et al.²³ The magnetic field was carefully shimmed with liquid benzene to achieve a line width of less than 0.010 ppm at a MAS rate of 1.40 kHz. The ^1H spectra were obtained by a single-pulse sequence, and on-resonance ^1H high-power decoupling was carried out during the data acquisition for the ^{13}C measurements. Chemical shifts were determined by an external reference without resetting the probehead throughout all the measurements.

III. Results and Discussion

X-ray Powder Diffraction. Figure 2 shows the X-ray diffraction patterns of the original kaolinite and its intercalation compounds as well. The basal spacing of the original kaolinite (sample I) is 0.717 nm, while the spacings of kaolinite/FA (sample II), kaolinite/FA- d_2 (sample III), kaolinite/NMF (sample

TABLE 1: Quantitative Analyses of TG and ^{13}C and ^{29}Si NMR Data

sample no. (guest molecules)	II (FA)	III (FA- d_2)	IV (NMF)	V (DMF)
TG				
weight loss (wt %) (360~450 K)	13.6	7.5	14.0	15.0
R^a	0.90	0.44	0.75	0.73
^{29}Si NMR: fraction of intercalation compounds	0.81	0.25	0.74	0.76
^{13}C NMR: fraction of interlayer guest molecules summarized R^c	0.88 ^b	0.57	1.00	1.00
	0.98	1.00	1.01	0.96

^a The number of guest molecules per host unit $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, including outersurface adsorbed molecules. ^b Including NMF of 0.04.

^c The number of guest molecules per host unit $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, excluding outersurface adsorbed molecules.

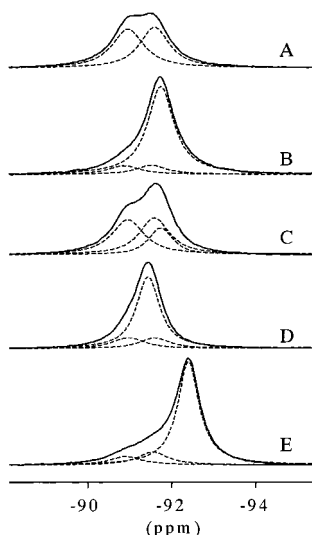


Figure 3. ^{29}Si CP/MAS NMR spectra of (A) kaolinite (sample I), (B) kaolinite/FA (sample II), (C) kaolinite/FA- d_2 (sample III), (D) kaolinite/NMF (sample IV), and (E) kaolinite/DMF (sample V), measured at $\nu_L = 79.50$ MHz and 298 K with a spinning rate of 3.5 kHz, a contact time of 8 ms and a recycle time of 15 s. The components indicated by dashed lines show the deconvolution results, in which a fixed line shape was assumed for the residual kaolinite.

IV), and kaolinite/DMF (sample V) are 1.019, 1.013, 1.080, and 1.217 nm, respectively. The intercalated samples contain residual of the original kaolinite. The diffraction pattern shows that the 002 peak intensity ratios of the original kaolinite to the intercalates are 2%, 7%, 2%, and 3% for samples II, III, IV, and V, respectively.

Thermogravimetric Analysis. The original kaolinite undergoes decomposition when heated. The decomposition, which corresponds to the dehydroxylation, starts at 733 K, is centered at 793 K, and ends at 873 K. The TG diagrams of the intercalated samples show an additional step (beginning at 360 K, centered at 420 K, and ending at 450 K), which means the collapse of the intercalation. The weight loss and the deduced molecular ratio of the guest molecules, both intercalated and outersurface adsorbed, per $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ unit are listed in Table 1.

^{29}Si NMR Spectra. The ^{29}Si CP/MAS spectra of kaolinite and its intercalates are depicted in Figure 3. The original kaolinite has two peaks at -90.97 and -91.59 ppm, which are ascribed to two inequivalent Si sites. The spectra of the intercalated samples show single unresolved peaks at -91.76 , -91.75 , -91.53 , and -92.42 ppm for kaolinite/FA (sample II),

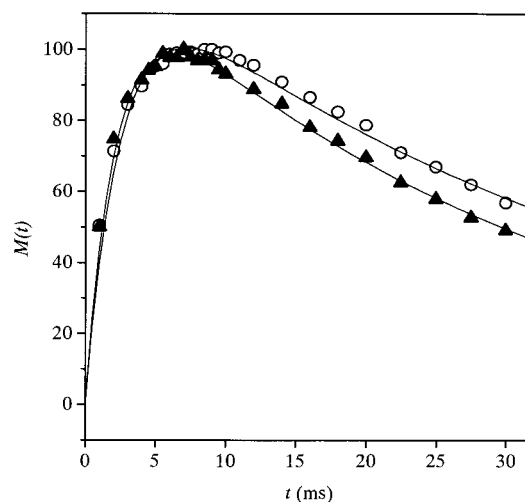


Figure 4. Contact time dependencies of signal intensities in ^{29}Si CP/MAS NMR spectra of kaolinite (O) and kaolinite/FA- d_2 (▲). The solid lines show theoretical fittings as described in the text. MAS spinning rate was 3.5 kHz.

kaolinite/FA- d_2 (sample III), kaolinite/NMF (sample IV), and kaolinite/DMF (sample V), respectively, in addition to peaks of the original kaolinite. The single unresolved peaks of the intercalates mean the degeneracy of the silicon environments after intercalation. The expansions of the basal spacing upon intercalation, i.e., the differences in the basal spacing between the intercalates and the original kaolinite, are 0.31, 0.37, and 0.51 nm for samples II, IV, and V, respectively, while the sizes of the corresponding guest molecules are estimated to be 0.47, 0.51, and 0.59 nm, respectively.⁹ The largest guest molecule DMF in sample V results in the most profound change in the Si environments, as revealed by the ^{29}Si chemical shift.

Kaolinite/DMSO, of which the ^{29}Si chemical shift is -92.6 ppm, has an expansion of the basal spacing of only 0.40 nm.¹⁸ The chemical shift value shows a severe distortion in the Si environment, which is due to the strong keying of one methyl group into the ditrigonal hole of the kaolinite host. Kaolinite/octylamine intercalation compound with an expansion of the basal spacing of 2.48 nm shows a chemical shift of -91.5 ppm,¹² which implies weak distortion in the Si environment most probably due to weak interaction between the guest octylamine molecules and the kaolinite host.

Variable contact time cross polarization experiments were carried out to check the cross polarization efficiency among the compounds. Figure 4 shows contact time dependence of the ^{29}Si signal intensity in kaolinite (sample I) and kaolinite/FA- d_2 (sample III). The curves are analyzed by using the following equation:¹⁷

$$M(t) = C \left[\exp\left(-\frac{t}{T_{1\rho}(\text{H})}\right) - \exp\left(-\frac{t}{T_{1\rho}(\text{Si})}\right) \right] \left(1 - \frac{T_{1\rho}(\text{Si})}{T_{1\rho}(\text{H})} \right)^{-1} \quad (1)$$

where $M(t)$ is the signal intensity, C is a constant of proportionality, $T_{1\rho}(\text{H})$ is the ^1H spin-lattice relaxation time in the rotating frame, and $T_{1\rho}(\text{Si})$ is the cross relaxation time between the I and S spins. Here the I spin is ^1H , and S spin is ^{29}Si . The experimental data have been fitted to eq 1. The cross relaxation time $T_{\text{H-Si}}$ obtained are 2.5 and 2.2 ms for sample I and sample III, respectively, which means a negligible difference in the cross relaxation between kaolinite and the intercalate. Our previous study¹⁷ showed that the $T_{\text{H-Si}}$ values of kaolinite/DMSO and its original kaolinite are 2.5 and 2.2 ms, respectively. For the

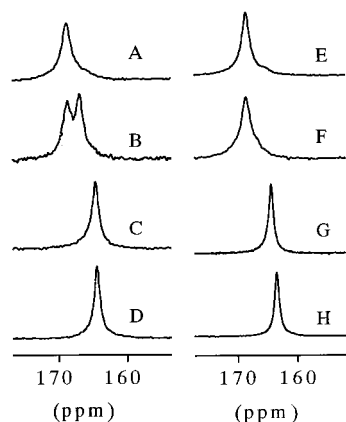


Figure 5. ^{13}C MAS NMR spectra of the carbonyl group in (A, E) kaolinite/FA (sample II), (B, F) kaolinite/FA- d_2 (sample III), (C, G) kaolinite/NMF (sample IV), and (D, H) kaolinite/DMF (sample V), measured at $\nu_L = 100.61$ MHz, 298 K and a spinning rate of 4.0 kHz. The pulse sequences were (A–D) HD and (E–H) CP with a contact time of 3.5 ms.

original kaolinite cross polarization to ^{29}Si takes place from both intralayer and interlayer protons, in which the intralayer contribution corresponds to $T_{\text{H-Si}} = 4.0$ ms.¹⁷ The value $T_{\text{H-Si}} = 2.5$ ms in kaolinite/DMSO indicates that the guest molecules contribute to the cross polarization as largely as the interlayer protons in the original kaolinite do. The guest molecule FA- d_2 in sample III also contribute to the cross polarization, suggesting that the proton in the $\text{CH}=\text{O}$ group is close to the silica sheet.

A contact time of 8 ms, which is supposed to be long enough to ignore the difference in cross polarization efficiency in the samples, was chosen for the measurements of the CP/MAS spectra used to estimate the amount of the reacted kaolinite. Deconvolution of the spectra as depicted in Figure 3 was carried out, and the results are listed in Table 1. The reacted fractions are 0.81, 0.25, 0.74, and 0.76 for samples II, III, IV, and V, respectively. Kaolinite/FA- d_2 (sample III) shows a small reacted fraction, which indicates difficulty in the direct intercalation of FA.

^{13}C NMR Spectra. Figure 5 shows ^{13}C HD/MAS and CP/MAS spectra for carbonyl groups in the intercalated samples. Kaolinite/FA- d_2 (sample III) shows a peak at 168.4 ppm for the intercalated molecules and another at 166.4 ppm which disappears in the CP/MAS measurement and is therefore assigned to outersurface molecules. Molecules loosely adsorbed on the outersurface of the kaolinite host have great mobility and produce negligible cross polarization efficiency. Kaolinite/FA (sample II) has a peak at 168.6 ppm for the intercalated molecules and another small one at 166.7 ppm for the outersurface molecules, the latter of which disappears in the CP/MAS measurement. Thompson²¹ has observed peaks at 168.2 and 166.6 ppm for intercalated and outersurface formamide molecules, respectively. Besides, sample II shows weak peaks at 165.2 and 27.3 ppm in both HD and CP spectra, which are due to signals of carbonyl and methyl groups in NMF not displaced by FA. Kaolinite/NMF (sample IV) has two peaks at 164.2 and 26.9 ppm, which are assigned to the carbonyl and methyl groups, respectively, of the interlayer guest molecules. The residual NMF in sample II has chemical shift values of 165.2 and 27.3 ppm which are different from the values of sample IV, probably because the residual NMF is surrounded by FA. Kaolinite/DMF (sample V) has peaks at 163.6 ppm for the carbonyl carbon and 38.8 and 32.7 ppm for the methyl groups for the intercalated molecules. Sample V shows no peaks for residual NMF. Chemical shifts of the neat liquid samples

are 166.5 ppm for FA, 163.5 and 24.6 ppm for NMF, and 162.9, 36.1, and 30.9 ppm for DMF.²³ Further comparison reveals that the outersurface species in samples II and III have chemical shifts very close to that of pure liquid FA, while samples IV and V show negligible outersurface species.

Deconvolution of the HD/MAS spectra produces the fraction of the interlayer guest molecules, which are listed in Table 1. For kaolinite/FA (sample II), 88% of the guest molecules (including 84% of FA and 4% of NMF) enter the kaolinite interlayer space. The content of NMF was estimated from the intensity of the methyl peak in the HD spectrum. The value is 57% for kaolinite/FA- d_2 (sample III). Kaolinite/NMF (sample IV) and kaolinite/DMF (sample V) show negligible outersurface guest molecules. Combined with the ^{29}Si NMR results which revealed the original residual kaolinite and the TG results, the molecular guest/host ratio of 1.0 ± 0.10 is obtained for all the intercalates. The ratio 1.0 means one guest molecule in every ditrigonal hole of the silica sheet.

Compared with the liquid-state values the intercalated samples show deshielded ^{13}C resonances. van der Waals shielding,²⁴ which is found to be negative,^{18,25,26} is supposed to be the main cause. Weak van der Waals interaction between the guest molecule and the kaolinite host produces an expansion of the electron cloud on the nuclei of the guest molecules and hence a reduction in the screening, which results in the deshielding of the resonance.²⁴ Among carbonyl groups FA shows the strongest guest–host interaction with the largest change in the chemical shift of 2.1 ppm, while the value is 0.7 ppm for both NMF and DMF sample. The strength in the guest–host interaction as revealed is in the order of FA > NMF \sim DMF. Kaolinite/NMF shows a ^{13}C NMR signal at 26.9 ppm for the cis methyl group. Accordingly, the 38.8 and 32.7 ppm peaks of kaolinite/DMF are ascribed to methyl groups at the trans and cis positions relative to the carbonyl oxygen, respectively. The trans position shows it possesses the stronger guest–host interaction than the cis position does, since the difference in the chemical shift compared with neat liquid is 2.7 ppm for the former and 1.8 ppm for the latter. The magnitude of the difference is in the order of DMF (trans) > NMF (cis) > DMF (cis).

Table 2 lists temperature dependences of the ^{13}C isotropic chemical shifts in CP/MAS spectra recorded at $\nu_L = 100.61$ MHz for samples II, IV, and V. The isotropic chemical shift of the carbonyl group has very weak temperature dependence in kaolinite/FA, and the magnitude of the temperature dependence is on the order of FA < NMF < DMF. The magnitude of the temperature dependence for the methyl group is in the following order: NMF (cis) \sim DMF (trans) < DMF (cis). All the shifts are along the high-frequency direction toward high temperature, which means the increase in the guest–host interaction is caused by molecular motions. These orders in the temperature dependence agree with those in the frequency shift reflecting the guest–host interaction.

Line widths decrease with increasing temperature, as shown in Table 2. To survey mechanisms of line broadening, line widths were measured at a lower resonance frequency of $\nu_L = 50.32$ MHz and at room temperature (298 K). Full widths at half-maximum (fwhm) at room temperature changed from 1.5 to 3.1 ppm for HCO in kaolinite/FA (sample II), from 1.3 to 2.2 ppm for HCO and from 0.6 to 1.4 ppm for CH_3 in kaolinite/NMF (sample IV), from 0.8 to 1.4 ppm for HCO, and from 0.6 to 1.1 ppm for both of the CH_3 groups in kaolinite/DMF (sample V), when the static field changed from 9.4 to 4.7 T. No splitting due to the residual dipolar interaction with ^{14}N was observed

TABLE 2: Variable Temperature ^{13}C CP/MAS NMR Results^a

T (K)	FA (sample II) shift/fwhm ^b (ppm)	NMF (sample IV)			DMF (sample V)		
		shift/fwhm ^b (ppm)	shift (ratio) ^c (ppm)	shift/fwhm ^b (ppm)	shift/fwhm ^b (ppm)	shift/fwhm ^b (ppm)	shift/fwhm ^b (ppm)
200	168.5/2.1	163.7/1.9	27.8 (14%)	26.4/1.3	162.8/1.2	38.3/0.9	31.8/0.8
230	168.5/2.1	163.9/1.8	27.9 (14%)	26.6/1.1	163.0/1.0	38.5/0.7	32.0/0.6
260	168.6/1.8	164.1/1.6	27.8 (10%)	26.8/1.0	163.3/0.9	38.7/0.5	32.3/0.6
298	168.6/1.5	164.2/1.3	27.8 (4%)	26.9/0.6	163.6/0.8	38.8/0.6	32.7/0.6
330	168.6/1.5	164.4/1.0		27.0/0.5	163.8/0.8	38.9/0.5	32.9/0.6
liquid ^d	166.5	163.5		24.6	162.9	36.1	30.9

^a Measured at 100.61 MHz with MAS rate of 4.0 kHz. ^b Full width at half-maximum. ^c Values in parentheses present ratios of this component to another methyl component. ^d Isotropic chemical shifts of pure liquids obtained by the liquid/MAS method at 298 K in this work for NMF and ref 23 for the others.

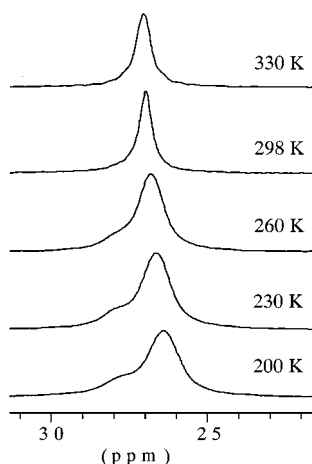


Figure 6. Temperature dependence of ^{13}C CP/MAS NMR spectra of the methyl carbon in kaolinite/NMF (sample IV), measured at $\nu_L = 100.61$ MHz. The spinning rates were 4.0 kHz at 298 and 330 K and 2.5 kHz at the other temperatures. The contact time was 3.5 ms.

even at the low field. Self-decoupling due to fast ^{14}N relaxation might take place, which is presumably caused by the motion of the guest molecules. The observed line widths are independent of the field if expressed in Hz units, which demonstrates that the line widths are of dipolar origin. Dipolar interactions with ^1H and ^{14}N cause the broadening, and they decrease with the temperature increase due to the molecular motion. The carbonyl line widths are in the order of FA > NMF > DMF, and the methyl line widths are NMF > DMF below 298 K. These trends suggest that the order of mobilities of the guest molecules in the interlayer space is FA < NMF < DMF, which reflects at the same time the strength of the guest–host interaction: FA > NMF > DMF.

Figure 6 shows temperature dependence of the spectra corresponding to the methyl group of kaolinite/NMF (sample IV). Besides changes in the chemical shift and the line width, a second peak appears on the high-frequency side of the main peak when the temperature is reduced to be lower than room temperature (298 K). The ratio of the second peak to the main one increases from 4% at 298 K to 14% at 200 K. In our previous study on kaolinite/DMSO intercalate,¹⁸ even at room temperature two peaks of an equal intensity were found at 44.2 and 43.1 ppm, which was due to the existence of two different methyl carbons in the interlayer DMSO molecules, where the one at 44.2 ppm was ascribed to the methyl group keyed into the host silicate layer and another to the methyl group located in parallel to the sheet. A group which is keyed into the ditrigonal hole of the host layer is expected to have its signal on the high-frequency side. However, for NMF molecules in the interlayer a cis conformation has been confirmed by the

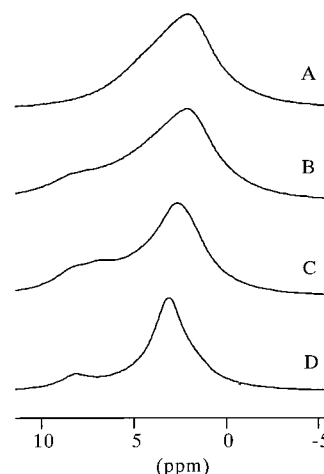


Figure 7. ^1H MAS NMR spectra of (A) kaolinite (sample I), (B) kaolinite/FA (sample II), (C) kaolinite/NMF (sample IV), and (D) kaolinite/DMF (sample V), measured at $\nu_L = 400.14$ MHz, 294 K and a spinning rate of 15.0 kHz.

TABLE 3: ^1H NMR Results

no. of sample	guest	solvent ^a shift (ppm)	HS-MAS ^b		CRAMPS	
			shift (ppm)	fwhm ^c (ppm)	shift (ppm)	fwhm ^c (ppm)
I			2.0	3.5	3.0	1.0
II	FA		2.0	3.5	2.6	1.2
		7.35, 7.60				
		8.063, 8.097	8.0	4.5	7.9	0.4
IV	NMF	2.669, 2.693	2.5	3.0	2.5	0.4
		7.87, 7.65	6.7	2.5		
		8.098	8.1	2.5	7.7	0.3
V	DMF	2.761, 2.929	2.9	2.0	2.8	0.4
		8.000	8.0	2.0	7.6	0.3

^a This work for NMF and ref 23 for the others. ^b With a MAS spinning rate of 15.0 kHz. ^c Full width at half-maximum.

^{13}C chemical shift and was also supported by the crystal structure consideration, where no keyed methyl group would be allowed by the steric restriction. In kaolinite/DMF no second peaks were observed. One tentative explanation is formation of a hydrogen bond between amide NH and O in the adjacent silica sheet at lower temperatures.

^1H NMR Spectra. Figure 7 shows ^1H MAS NMR spectra at 400.13 MHz and a spinning rate of 15 kHz. High-speed (HS) MAS reduces the line width tremendously, although spinning sidebands have considerable intensities. Table 3 lists the corresponding results, together with isotropic chemical shifts of the solvents in pure liquid state as a better reference. Kaolinite (sample I) has an intense peak at 2.0 ppm, which comes from the host hydroxyl protons; kaolinite/FA (sample II) shows a similar central peak at 2.0 ppm with one more shoulder at 8.0

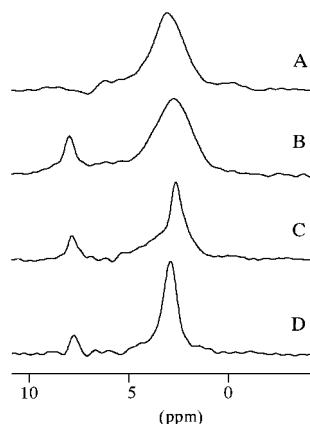


Figure 8. ^1H CRAMPS spectra of (A) kaolinite (sample I), (B) kaolinite/FA (sample II), (C) kaolinite/NMF (sample IV), and (D) kaolinite/DMF (sample V), measured at $\nu_L = 200.13$ MHz and 298 K with BR24 pulse sequence in the quadrature detection mode under a spinning rate of 1.8 kHz. The $\pi/2$ pulse width was 1.55 μs , the cycle time for 12 pulses was 72 μs , totally 600 data points were acquired for the two receiver channels, and the repetition time was 10 s. Chemical shift was calibrated by the signal position of silicone rubber which is 0.12 ppm from tetramethylsilane.²⁷ Noise appeared at about 6 ppm, which was set to be the central point of the spectra.

ppm, which is ascribed to the carbonyl and amide protons of the guest FA molecules; kaolinite/NMF (sample IV) has a sharper central peak at 2.5 ppm contributed by the methyl protons, and two more shoulders at 6.7 and 8.1 ppm for the NH and HCO protons of the guest NMF molecules, respectively; and kaolinite/DMF (sample V) has a peak at 2.9 ppm for the methyl protons and a shoulder at 8.0 ppm for the HCO proton of the guest DMF molecules.

The CRAMPS technique is applied to obtain spectra with higher resolution, and Figure 8 shows the CRAMPS spectra of samples I, II, IV, and V, measured at 200.13 MHz. Kaolinite (sample I) has a peak at 3.0 ppm, being ascribed to the host hydroxyl groups. Kaolinite/FA (sample II) has peaks at 2.6 ppm for the kaolinite hydroxyl groups and 7.9 ppm for the carbonyl proton of the guest molecules. Kaolinite/NMF (sample IV) shows signals at 2.5 and 7.7 ppm for methyl and carbonyl protons of the guest molecules, respectively. No amide proton signals are detected probably due to the residual dipolar broadening caused by ^{14}N . The MAS spinning rate of 1.8 kHz applied for the measurements with BR-24 pulse sequence is insufficient to average out the ^1H – ^{14}N dipolar interaction. This was also noticed by Naito et al. in their ^1H CRAMPS studies on protons bonded to ^{14}N in solid amino acids²⁸ and by Chu et al. in their studies on *N*-benzoyl-L-phenylalanine by ^1H CRAMPS.²⁹ The methyl and carbonyl protons of the guest molecules in kaolinite/DMF (sample V) appears at 2.8 and 7.6 ppm, respectively.

^1H isotropic chemical shift values may serve as a practical tool in analyzing hydrogen bonds, in which hydrogen bonds cause a high-frequency shift in the ^1H resonance.^{29–31} In the study of hydrogen environments in calcium phosphates Yesinowski et al. observed ^1H chemical shifts in the range of 0 ~ 16 ppm, depending linearly on the O–H...O distances in the range of 0.307 ~ 0.247 nm.³¹ The amide protons have chemical shift values of 7.35 and 7.60 ppm for pure formamide in liquid state, while the corresponding value for the formamide intercalate (sample II) is around 8.0 ppm. The values in the intercalate and in liquid-state agree, considering the experimental errors (with an fwhm of 4.5 ppm). In the liquid state the intra- and intermolecular N–H...O=C type hydrogen bonds exist.³²

Therefore, the above agreement confirms formation of hydrogen bonds between the amide protons and the silica sheets of the kaolinite host in the intercalate, as suggested by the crystal structure data. The chemical shifts for the amide proton in neat NMF liquid are 7.87 and 7.65 ppm, whereas the corresponding value in kaolinite/NMF is 6.7 ppm. The obvious decrease in the chemical shift upon intercalation demonstrates disappearance of the hydrogen bond between the amide proton and the adjacent silica sheet of the kaolinite host at room temperature, as also suggested by the crystal structure data. The fact that kaolinite/FA has a spectrum with the central peak similar to that of the original kaolinite means that the state of the hydroxyl groups is not changed by intercalation, which was also found in our previous study on the kaolinite/DMSO intercalation compound.¹⁸

The carbonyl ^1H line widths in the MAS spectra are in the order of FA > NMF > DMF, and the methyl ^1H line widths are NMF > DMF. These trends agree with those in the ^{13}C spectra. The line broadening in ^1H spectra is mainly due to dipole–dipole interaction between protons, and such broadening is modified by molecular motions.

IV. Conclusions

We have measured NMR spectra of ^{13}C , ^{29}Si , and ^1H for kaolinite and its intercalation compounds with FA, FA- d_2 , NMF, and DMF and arrived at the following conclusions. (1) The ^{13}C MAS NMR spectra distinguish interlayer and outersurface adsorbed guest molecules, while those of ^{29}Si identify the original kaolinite and the intercalates. Combination of the NMR results with the TG data reveals a molecular guest/host ratio of 1.0 for all the intercalates. (2) Intercalation causes high-frequency shift in the ^{13}C resonance of the guest molecule, whose magnitude reflects strength of the guest–host interaction. The magnitudes of the high-frequency shift in the carbonyl group are in the following order: FA > NMF ~ DMF. Those for the methyl groups are DMF (trans) > NMF (cis) > DMF (cis). The cis conformation of the guest molecules is maintained in kaolinite/NMF. (3) The magnitudes of the temperature dependence in the ^{13}C chemical shift are in the following order: FA < NMF < DMF, for the carbonyl group, and NMF (cis) ~ DMF (trans) < DMF (cis), for the methyl group. All the shifts are along the high-frequency direction toward high temperature. The ^{13}C line widths are FA > NMF > DMF. These facts reveal that the mobility of the guest molecules is in the order of FA < NMF < DMF. Kaolinite/NMF shows a second methyl peak whose relative intensity increases with decreasing temperature, demonstrating the presence of molecules with a different orientation. (4) The ^1H chemical shifts confirm the existence of hydrogen-bonding interactions between the amide protons and the kaolinite host in kaolinite/FA and that no such hydrogen-bonding interactions in kaolinite/NMF at room temperature exist. The chemical shift value of the hydroxyl groups in the host kaolinite structure is not affected by intercalation. The ^1H line widths of carbonyls are FA > NMF > DMF, and those of methyls are NMF > DMF, which confirms again that the mobility of the guest molecules is FA < NMF < DMF.

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