Clays and Clay Minerals, Vol. 45, No. 5, 724–732, 1997.

NMR STUDY OF DYNAMICS AND EVOLUTION OF GUEST MOLECULES IN KAOLINITE/DIMETHYL SULFOXIDE INTERCALATION COMPOUND

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Abstract—Motion of the guest molecules in kaolinite/dimethyl sulfoxide (DMSO) intercalation compounds $Al_2Si_2O_5(OH)_4 \cdot (CH_3)_2SO$ has been studied by means of solid-state nuclear magnetic resonance (NMR) in the temperature range between 300 and 380 K, which is just below the evolution temperature. The ^{13}C magic angle spinning (MAS) NMR spectra show 2 inequivalent methyl carbons: 1 methyl carbon is keyed in the ditrigonal hole of the silicate sheet, while the other is located parallel to the sheet. Above 320 K, the 2 peaks have different intensities, suggesting that the keyed methyl groups from some of the DMSO molecules are released from the hole. The ^2H NMR spectra have been measured for kaolinite/DMSO-d_6 intercalate. The methyl group of the interlayer DMSO molecule undergoes free rotation around its C_3 axis over the temperature range studied. The axis of rotation is fixed at the low temperature (about 160 K), and the methyl group initiates a wobbling motion whose amplitude increases with temperature. The wobbling angles have an anisotropy, estimated from theoretical analysis of the ^2H spectral line shapes. The DMSO molecules released from the silicate layer undergo anisotropic rotation of the whole molecule.

Key Words—^2H NMR, ^{13}C NMR, Dimethyl Sulfoxide, Intercalation Compound, Kaolinite, Layered Silicate.

INTRODUCTION

Kaolinite, $Al_2Si_2O_5(OH)_4$, is a layered aluminosilicate with a dioctahedral 1:1 layer structure consisting of an octahedral aluminum hydroxide sheet and a tetrahedral silicate sheet (Adams 1983; Young and Hewat 1988; Bish and Von Dreele 1989; Bish 1993). The interlayer space of the kaolinite is 2-dimensional and asymmetric, with SiO_4 tetrahedra on 1 side and AlO_6 octahedra with hydroxyl groups on the other. Dimethyl sulfoxide can intercalate between kaolinite layers (Olejnik et al. 1968, 1970; Costanzo and Giese 1990). Thompson (1985) has found from the ^{13}C NMR study that there are 2 inequivalent methyl groups in the interlayer DMSO molecules. Thompson and Cuff (1985) and Raupach et al. (1987) have analyzed X-ray and neutron powder diffraction data of the intercalation compound. According to their studies, DMSO molecules are ordered in the interlayer space and their orientation is perpendicular to the layer plane, as indicated schematically by the A-type DMSO molecule in Figure 1. One methyl group is keyed into the ditrigonal hole in the silicate sheet (named "keyed methyl"), whereas the other is approximately parallel to the sheet ("parallel methyl"). The sulfonyl oxygen forms hydrogen bonds with the inner-surface hydroxyls of kaolinite.

Duer et al. (1992) and Duer and Rocha (1992) have studied molecular motions in kaolinite/deuterated DMSO (DMSO-d_6) by ^2H NMR, and proposed another structure model consisting of 2 kinds of interlayer DMSO sites. One DMSO molecule is keyed into the kaolinite lattice like the A-type in Figure 1, and the other is not keyed and oriented differently like the B-type in Figure 1. There is a large discrepancy between the 2 structure models proposed by the above 2 groups.

In our previous studies, we have verified the orientation of the guest molecule by use of cross polarization (CP) dynamics from ^1H in the host kaolinite to ^{13}C in the guest DMSO-d_6 (Hayashi and Akiba 1994). The 2 methyl carbons have ^{13}C chemical shifts different from one another; the high-frequency signal is ascribed to the keyed methyl carbon, while the low-frequency signal to the parallel methyl carbon. We have also studied the motion of the guest molecules in the kaolinite/DMSO compounds below 330 K, mainly by means of ^{13}C and ^2H NMR (Hayashi 1995). The results obtained demonstrate that the dominant motion of the interlayer DMSO molecules is rotation of methyl groups around their C_3 axis. Although there was indication of a wobbling motion with a small amplitude, we did not analyze the data theoretically.

Evolution of the guest DMSO molecules from the interlayer space begins at about 380 K. The guest molecules are expected to undergo some motion before they evolve. In the present work, we have studied the motion of the guest molecules in the temperature range between 300 and 380 K by means of ^{13}C and ^2H solid-state NMR, and have discussed this motion in relation to the evolution of the guest molecules.

EXPERIMENTAL

Materials

Two samples were used, which were the same as used previously (Hayashi and Akiba 1994; Hayashi

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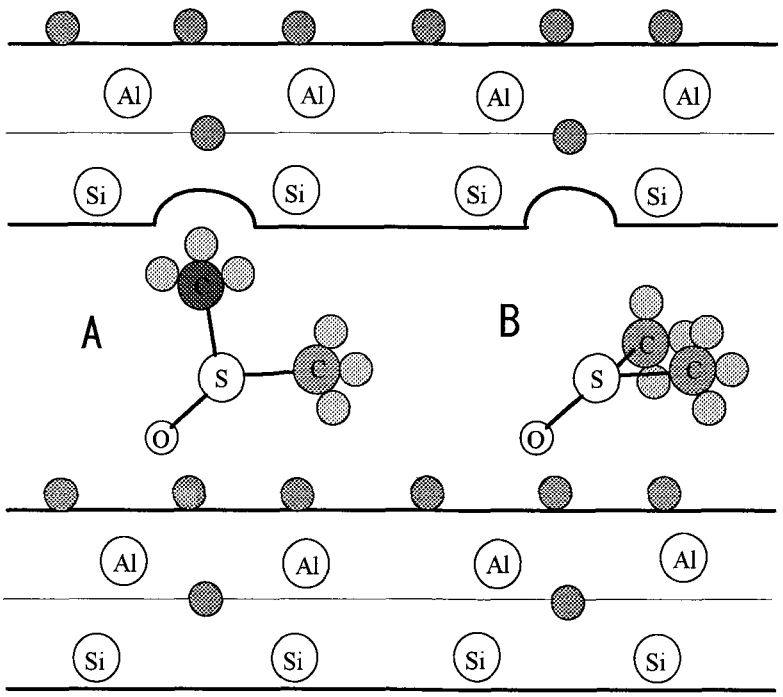


Figure 1. Schematics of the structure of the kaolinite/DMSO intercalation compound. The A-type DMSO molecule is keyed at 2 positions, and the B-type DMSO is keyed at the sulfonyl oxygen only.

1995). DMSO and DMSO-d_6 were intercalated, respectively, at room temperature for 2 mo, and then dried at 333 K for 2 d. X-ray powder diffraction patterns were presented previously (Hayashi 1995). The presence of some unintercalated kaolinite in these samples did not adversely affect the present work. The fraction of the intercalated kaolinite and the amount of surface-adsorbed DMSO were estimated in the previous work (Hayashi 1995). The intercalated kaolinite had the chemical formula $Si_2Al_2O_5(OH)_4 \cdot (CH_3)_2SO$. The interlayer DMSO began to evolve at 380 K and the evolution was finished at 460 K.

NMR Measurements

NMR measurements were carried out by Bruker MSL400 and ASX200 spectrometers with static magnetic field strengths of 9.4 and 4.7 T, respectively. The MSL400 was used for measurements of ^{13}C MAS spectra (Larmor frequency ν_0 of 100.61 MHz). The ASX200 was used for measurements of ^2H static spectra (30.72 MHz). The sample temperature was varied from 300 to 380 K.

The ^{13}C spectra were measured using CP and the single-pulse sequences with high-power ^1H decoupling (HD) under MAS conditions. In the CP sequence, the ^1H $\pi/2$ pulse of 6.1 μs length was applied. The contact time was set at 2 ms and the recycle delay at 4 s. The contact time used was optimized by a variable contact-time measurement. In the HD sequence, the ^{13}C $\pi/2$ pulse of 6.1 μs length was applied, and the recycle delay was 4 or 5 s, depending on the sample temperature. The ^2H spectra were obtained for static samples by Fourier transformation of the latter half of the echo signal obtained with quadrupole echo pulse sequences. The ^2H $\pi/2$ pulse width was 2.3 μs, and the recycle delay was set at 1 s. The recycle delays used were long enough compared to the spin-lattice relaxation times T_1 of ^{13}C and ^2H measured in our previous work (Hayashi 1995). Spectra were presented with the following signals at 0 ppm (0 Hz): neat tetramethylsilane for ^{13}C and D_2O for ^2H. The higher-frequency side of the spectra with respect to the standard signal was expressed as positive.

RESULTS AND DISCUSSION

^{13}C NMR

Figure 2 shows ^{13}C CP/MAS NMR spectra of the kaolinite/DMSO sample at several temperatures. At 300 K, 2 intense peaks with almost equal intensities are observed at 44.2 and 43.1 ppm, and a third broad peak is observed at 40.0 ppm. The third peak is assigned to DMSO molecules adsorbed on the outer surface, and the other 2 peaks are ascribed to the interlayer DMSO molecules (Thompson 1985; Hayashi 1995). From the previous work, the 44.2-ppm peak is ascribed to the keyed methyl group and the 43.1 ppm peak to the methyl group located parallel to the sheet (Hayashi and Akiba 1994).

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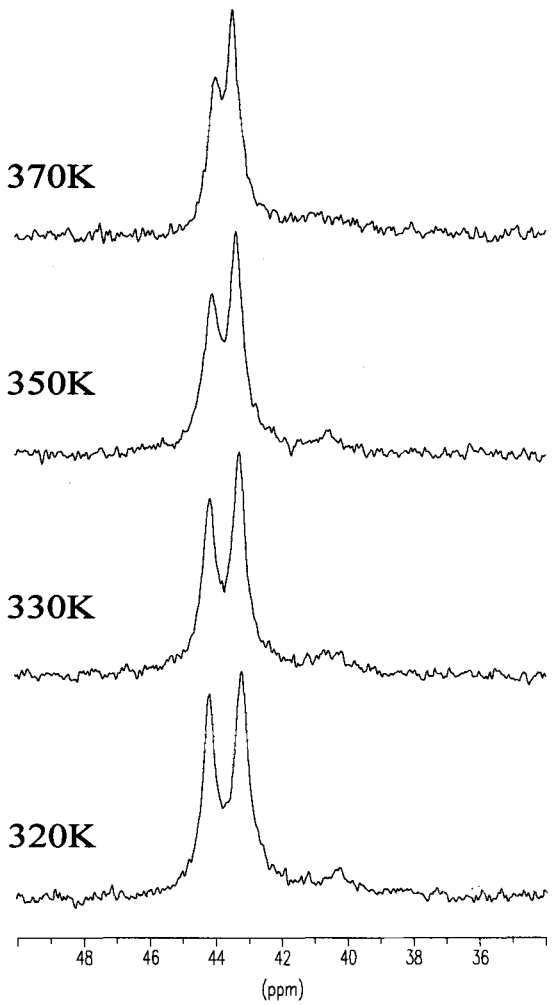


Figure 2. The ^{13}C CP/MAS NMR spectra of kaolinite/DMSO, measured at ν_0 = 100.61 MHz. The spinning rate was 3.0 kHz and the contact time was 2 ms.

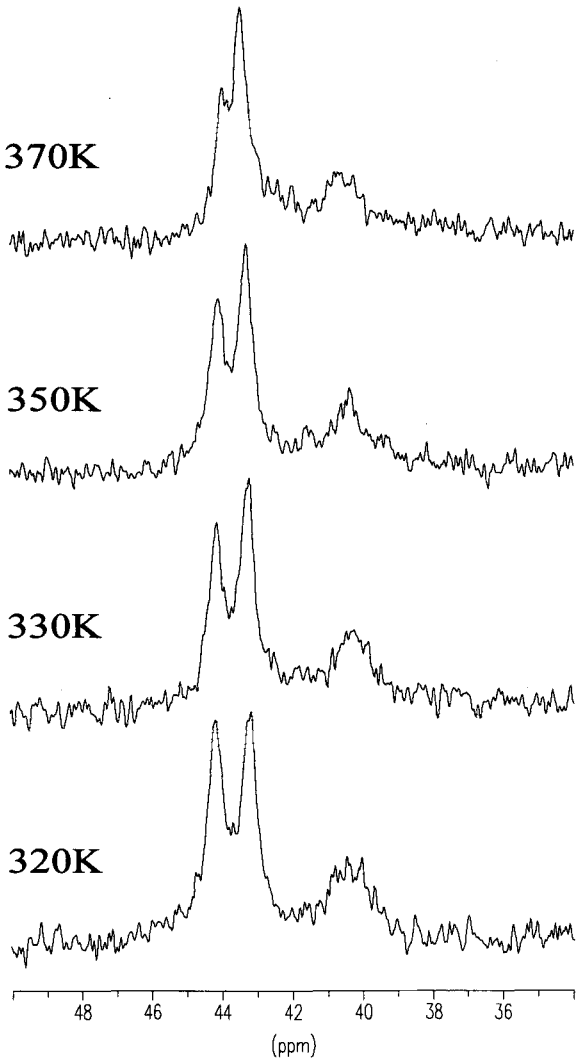


Figure 3. The ^{13}C HD/MAS NMR spectra of kaolinite/DMSO, measured at ν_0 = 100.61 MHz. The spinning rate was 3.0 kHz.

The signal intensities of the 2 methyl groups in the interlayer DMSO molecules are almost equal over the temperature range 170 to ~320 K (Hayashi 1995), demonstrating that no exchange between the 2 methyl sites takes place. Above 320 K, the 2 peaks have different intensities, as shown in Figure 2; the intensity of the higher-frequency peak decreases compared with the other peak. This suggests that the keyed methyl groups in some of the intercalate are no longer keyed. The B-type DMSO in Figure 1 shows the guest molecule released from the silicate sheet schematically. The 2 methyl groups in the B-type DMSO produce a signal at the same position as that of the parallel methyl group in the A-type DMSO. Even when the keyed methyl group is released, the DMSO molecule remains in the interlayer space, as the sulfonyl oxygen is bound to the host through hydrogen bonds. CP efficiency might affect the relative intensities of the 2 peaks. The rates of the polarization transfer from ^{1}H to ^{13}C were measured with a variable contact-time measurement, and it is confirmed that the 2 ^{13}C peaks have the same rate within the experimental error. To remove the effect of the CP efficiency on the relative signal intensities completely, we have measured ^{13}C HD/MAS NMR spectra as well, although the signal-to-noise ratio is somewhat lower than that in the CP/MAS NMR spectra. Figure 3 shows ^{13}C HD/MAS NMR spectra.

We have deconvoluted the spectra to estimate the fraction of each methyl group. The similar fractions are obtained from the CP and HD spectra. Assuming the coexistence of the 2 types of DMSO shown in Figure 1, the fraction of the DMSO molecules released from the silicate sheet (the B-type) is plotted in Figure 4. The B-type DMSO appears at about 320 K, and its

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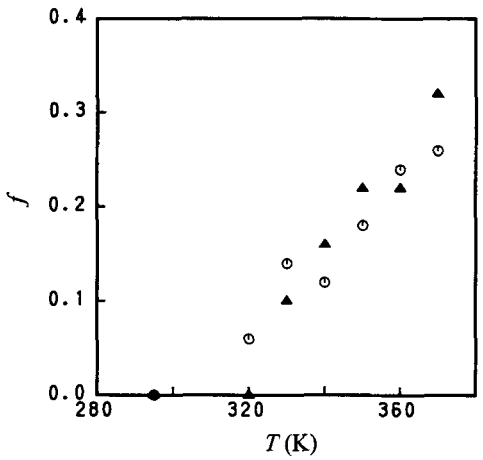


Figure 4. Fraction of DMSO molecules released from the silicate layer, estimated from ^{13}C CP/MAS (○) and HD/MAS (▲) NMR spectra.

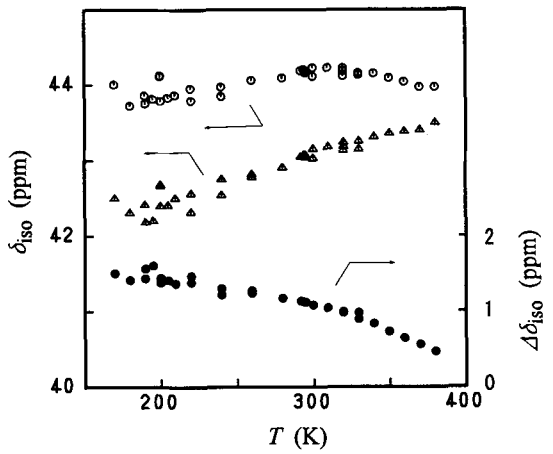


Figure 5. Temperature dependence of ^{13}C isotropic chemical shifts (○, △) and their difference (●) of kaolinite/DMSO, measured at ν_0 = 100.61 MHz. Data below 330 K were reported previously (Hayashi 1995).

fraction reaches about 30% at 370 K. The exchange between the A- and B-type DMSO molecules is negligible, since we can observe 2 inequivalent methyl groups even at 380 K. The DMSO molecules begin to evolve at about 380 K, at which temperature the hydrogen bonds between the sulfonyl group and the host begin to break.

Temperature dependence of the ^{13}C isotropic chemical shifts is plotted in Figure 5. The peak positions shift towards the higher-frequency side with increase in temperature up to 300 K. The magnitude of the frequency shift is larger for the low-frequency peak than for the high-frequency peak. Above 300 K, the shift in the peak position of the keyed methyl group changes direction, whereas the signal of the parallel methyl group continues to move to the higher frequency. The chemical shift of the keyed methyl group has a maximum value at about 300 K, which coincides well with the temperature of the appearance of DMSO released from the silicate sheet. The interval between the 2 peaks decreases gradually and monotonically.

The host-guest interaction is considered to cause the high-frequency shift, as has been discussed in our previous work (Hayashi 1995). The keyed methyl group has the strongest interaction at about 300 K. Above 300 K, the interaction slightly decreases, and some of the keyed methyl groups are released from the ditrigonal hole. The interaction for the parallel methyl groups increases monotonically with increasing temperature. These changes of the host–guest interaction presumably originate from the motion of the guest molecules.

^2H NMR

The technique of ^2H NMR spectroscopy is suitable for studying molecular motions whose rate is of the order of hundreds of kilohertz. In this work, we have measured ^2H NMR spectra of kaolinite/DMSO-d_6 in the temperature range between 300 and 380 K. Combining those with our previous results, we discuss the dynamics of the guest molecule. In contrast to the high-resolution solid-state ^{13}C NMR results described above, we cannot distinguish the 2 inequivalent methyl groups in the ^2H NMR spectra. Therefore, we discuss the average behavior of the 2 methyl groups in 1 molecule.

Figure 6 shows ^2H spectra at several temperatures. There is a marked change in the line shape, especially above 300 K. The guest molecules undergo a kind of motion other than the rotation of the methyl groups around the C_3 axis. Alternatively, the total signal intensity decreases gradually and monotonically with increase in temperature over the temperature range studied. The signal decrease agrees well with that estimated from Boltzmann distribution. Therefore, no intensity loss due to molecular motion was observed for the above temperature range. This fact strongly suggests that the motion of the guest molecule is fast enough compared to the quadrupole interaction; that is, at the fast motional limit.

We have measured dependence of the line shape on the time interval between the 2 pulses in the quadrupole echo pulse sequence by changing the pulse interval from 5 to 300 μs at all the temperatures studied, and no dependence was observed, except that the narrow central (NC) component decays faster than the other components. The NC component is due to surface-adsorbed species, and will be neglected in the following discussion.

We have deconvoluted the spectra into 2 or 3 components. Figure 7 shows the results of deconvolution at 300 K. The spectrum consists of 2 components: resolved doublet (RD) and NC components. Theoretical

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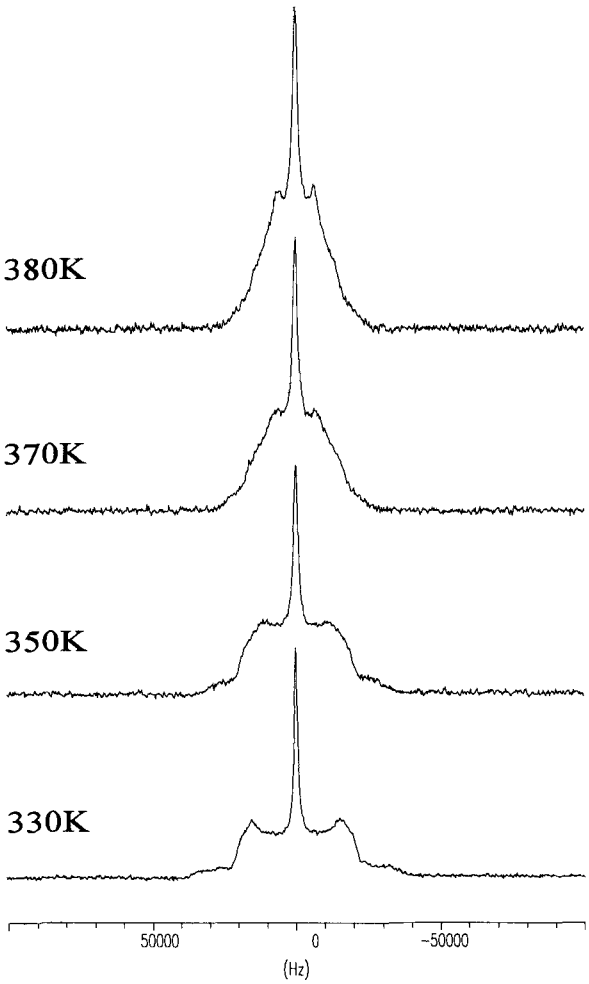


Figure 6. The ^{2}H NMR spectra of kaolinite/DMSO-d_6, measured at ν_0 = 30.72 MHz. Quadrupole echo pulse sequence was used with a pulse interval of 25 μs.

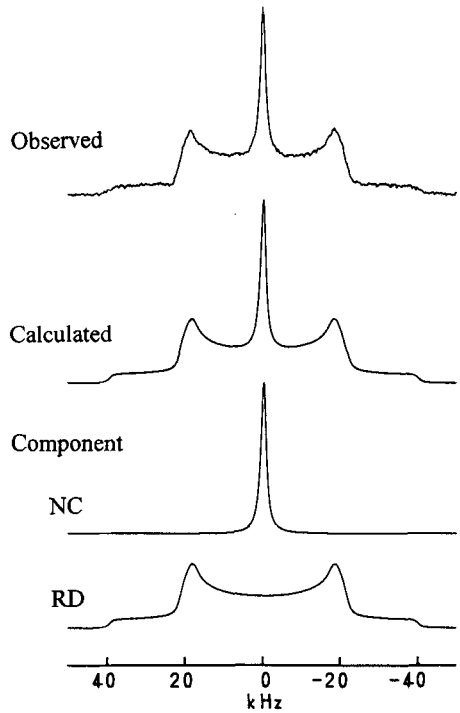


Figure 7. Simulation of ^{2}H NMR spectra of kaolinite/DMSO-d_6, measured at 300 K and at ν_0 = 30.72 MHz with a pulse interval of 25 μs.

powder line shapes for an I = 1 nucleus without motion are assumed for the RD component, since the motion is at the fast limit. A Lorentzian line shape is used for the NC component. Above 330 K, 1 additional component is necessary to simulate the spectra, as shown in Figure 8. This third component is a narrow resolved doublet (NRD) component, which has a quadrupole coupling constant (QCC = e^2Qq/h, where eQ is the nuclear quadrupole moment, eq is the electric field gradient and h is the Planck constant) of 19 kHz and an asymmetry factor (η_Q) of 0 for all the temperatures. Duer et al. (1992) have reported the presence of this component above 415 K.

We discuss motion of the DMSO molecules corresponding to the RD component using the derived quadrupole interaction parameters. Figure 9 shows the QCC and the asymmetry factor. At 160 K, QCC = 59 kHz and η_Q = 0. This means that the methyl groups rotate only around their C_3 axis and that the fluctuation of the C_3 axis is negligible. With increase in temperature, QCC decreases gradually up to 300 K and rapidly above 300 K. The asymmetry factor is zero below 250 K, and increases above 250 K. At 380 K, QCC = 30 kHz and η_Q = 0.40. These large changes demonstrate that the RD component undergoes other types of motion than the C_3-axis rotation of the methyl group, and that those motions are fast enough not to give patterns in the intermediate motional regime; that is, they should be much faster than 100 kHz. The most probable motion is a wobbling motion within a potential barrier. The amplitude of the motion increases with temperature. Although 1 of the methyl group is keyed in the silicate layer, the keyed methyl group can move. Exactly speaking, the C_3 axis of the methyl group, or S-C bond, wobbles. The keyed methyl group does not form a chemical bond with the silicate sheet, and the direction of the S-C bond for the keyed methyl group can be changed. Although there are 2 inequivalent methyl groups, we discuss the average behavior of the 2 methyl groups in 1 molecule.

We discuss the nature of the wobbling motion theoretically. Figure 10 shows the relation between QCC and η_Q. The QCC value decreases linearly with increase in η_Q. If the C_3 axis of the methyl group undergoes 2-site jump with the angle of $2\theta_1$:

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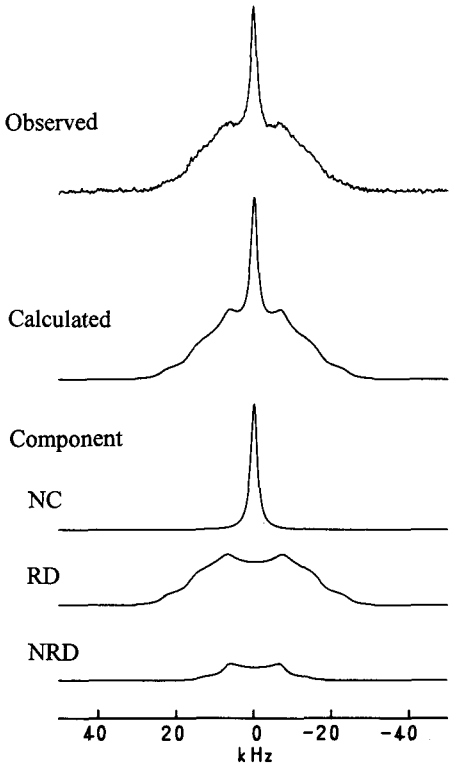


Figure 8. Simulation of ^2H NMR spectra of kaolinite/DMSO-d_6, measured at 370 K and at ν_0 = 30.72 MHz with a pulse interval of 25 μs.

$$QCC = QCC_0 \frac{1 + 3\cos 2\theta_1}{4} \quad [1]$$

$$\eta_Q = \frac{3(1 - \cos 2\theta_1)}{1 + 3\cos 2\theta_1} \quad [2]$$

for $0 \leq \theta_1 \leq \theta_m$ ($\cos 2\theta_m = 1/3$). QCC_0 is a quadrupole coupling constant in the rigid lattice, which is assumed to be 59 kHz. (See "Addendum" section for the derivation of the equations.) The correlation between QCC and η_Q for the 2-site jump is plotted in Figure 10 by a solid line. The observed results do not deviate very much only when the angle of the motion is very small. When the angle is large, the deviation is clear. Wobbling motion within the angle of $2\theta_1$ gives the same correlation between QCC and η_Q as the 2-site jump does.

If the methyl axis rotates around the axis tilted by θ_1, the asymmetry factor is always zero, and QCC is expressed by Equation [1]. If the wobbling takes places inside the bottom surface of a cone, the asymmetry factor is again zero, and QCC is expressed by Equation [1]. These motions can be applied below 250 K.

The experimental results lie between the solid line corresponding to the 2-site jump and the line of η_Q = 0, as shown in Figure 10. The space where the guest molecule can move is surrounded by 2 layers, which

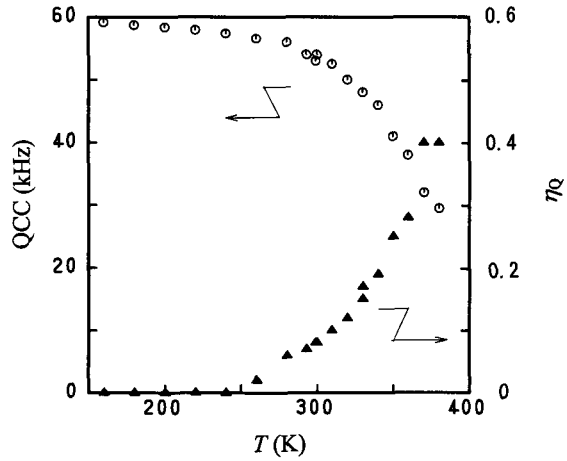


Figure 9. Temperature dependence of the QCC (○) and the asymmetry factor (▲) of the RD component in kaolinite/DMSO-d_6. Data below 330 K were reported previously (Hayashi 1995).

is markedly anisotropic. The wobbling motion may be largely anisotropic. Therefore, we assume that the methyl axis wobbles on an ellipsoid surface shown in Figure 11, where $-\theta_L \leq \theta_x \leq \theta_L$ and $-\theta_S \leq \theta_y \leq \theta_S$. The angles θ and φ are described as:

$$\tan\theta = \sqrt{\tan^2\theta_y + \tan^2\theta_x} \quad [3]$$

$$\tan\phi = \frac{\tan\theta_y}{\tan\theta_x} \quad [4]$$

QCC and η_Q are expressed by the following equations:

$$QCC = QCC_0 \frac{1 + 3\cos 2\theta}{4} \quad [5]$$

$$\eta_Q = \frac{3(1 - \cos 2\theta)\cos 2\phi}{1 + 3\cos 2\theta} \quad [6]$$

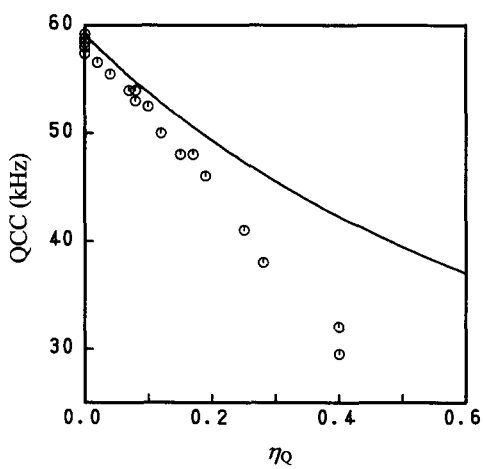


Figure 10. Correlation between the QCC and the asymmetry factor. The solid line shows the correlation calculated for the 2-site jump motion.

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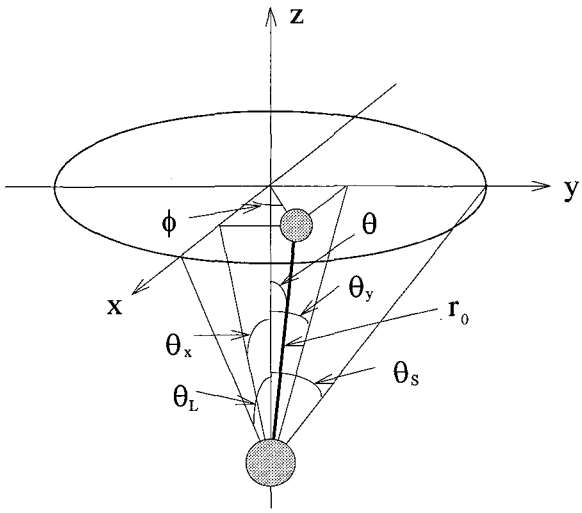


Figure 11. Illustration of the wobbling motion on an ellipsoid surface. Although the illustrated surface is flat, the real surface should be curved, satisfying the constant r_0 value. The description in the text is based on the curved surface.

QCC and η_Q are numerically integrated over the ellipsoid surface: $-\theta_L \leq \theta_x \leq \theta_L$ and $-\theta_{SM} \leq \theta_y \leq \theta_{SM}$, where:

$$\left(\frac{\theta_x}{\theta_L}\right)^2 + \left(\frac{\theta_{SM}}{\theta_S}\right)^2 = 1 \qquad [7]$$

Figure 12 shows the angles θ_L and θ_S estimated from the experimentally obtained quadrupole interaction parameters. Below 250 K, we cannot distinguish the difference between the angles θ_L and θ_S due to the experimental error. Above 250 K, the anisotropic nature of the wobbling motion is clearly observed. This behavior is considered to be characteristic of the layered structure. The larger angle corresponds to the direction parallel to the sheet; the smaller one, to the direction perpendicular to the sheet.

For the NRD component, QCC = 19 kHz and η_Q = 0. The fraction of this component increases with increase in temperature, as shown in Figure 13. This component is considered to come from the interlayer DMSO molecules released from the silicate layer which is observed by ^{13}C NMR. These molecules undergo rotation around the axis inclined at about 42° to the C_3 axis of the methyl group.

Duer et al. (1992) and Duer and Rocha (1992) have carried out detailed analysis of ^2H spectral line shapes. They presented several motional models without addressing other structural data. In their analysis they ignored the contribution of surface-adsorbed DMSO molecules and did not consider the possibility of wobbling motion described above.

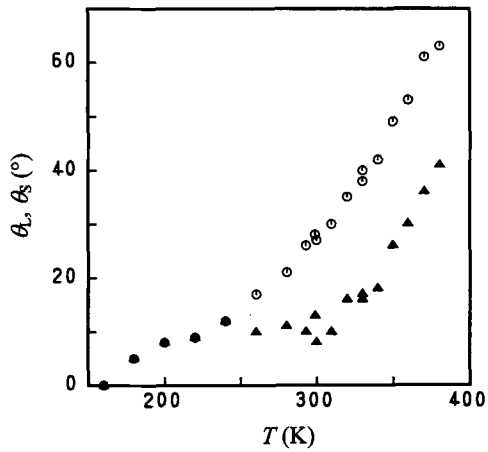


Figure 12. The angles of the anisotropic wobbling motion for the A-type DMSO molecule.

Motion and Evolution of The Guest Molecules

The evolution of the DMSO molecules takes place in the temperature range from 380 to 460 K, which was observed by thermogravimetric analysis.

Types of motion of the guest molecules are shown schematically in Figure 14. Below 300 K, all of the DMSO molecules in the interlayer space are keyed at 2 positions: a sulfonyl oxygen and 1 of the 2 methyl groups. At 160 K, only the rotation of the methyl group around its C_3 axis is observed. With increase in temperature, the guest DMSO molecules initiate a wobbling motion which is anisotropic in nature. Above 320 K, the wobbling motion becomes too violent, and then some of the keyed methyl groups are released from the ditrigonal holes of the silicate sheet. The molecules released from the silicate sheet are still fixed to the sulfonyl oxygen by hydrogen bonding, and undergo a rotation of the whole molecule. The fraction

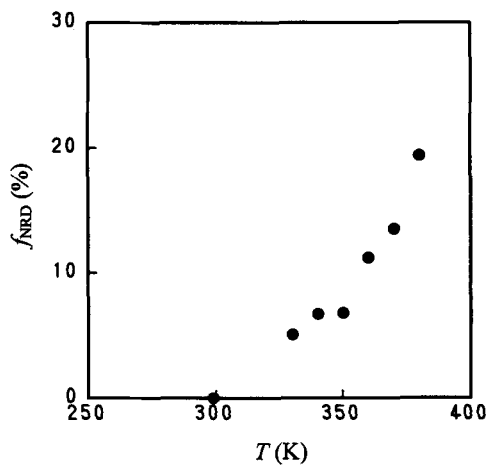


Figure 13. Temperature dependence of the fraction of the NRD component.

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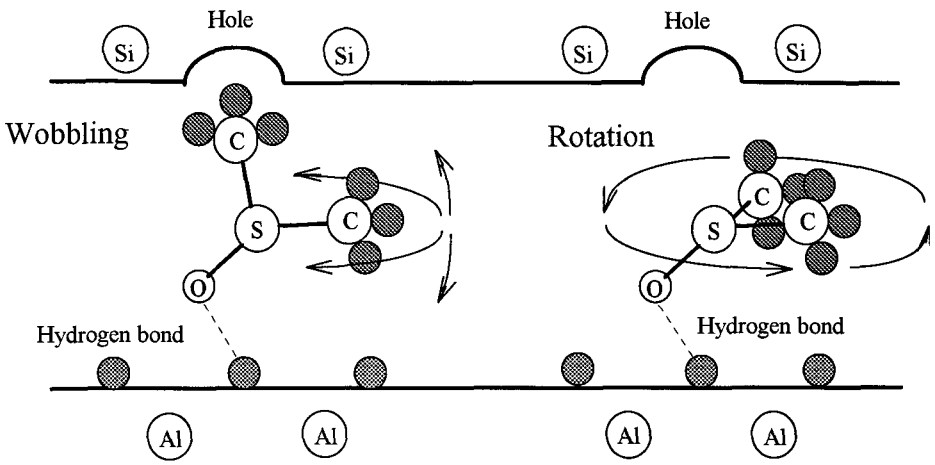


Figure 14. Motion of guest molecules in kaolinite/DMSO.

of the released molecules increases with temperature, and reaches 20 to 30% at 380 K. Above 380 K, the guest molecules begin to evolve due to breaking of the hydrogen bonds.

CONCLUSIONS

Molecular motions in kaolinite/DMSO intercalation compounds $Al_2Si_2O_5(OH)_4{\cdot}(CH_3)_2SO$ have been studied by means of ^{13}C and ^2H solid-state NMR. The following conclusions were obtained.

1) One methyl carbon of all of the interlayer DMSO molecules is keyed in the ditrigonal hole of the silicate sheet below 300 K. Above 320 K, the keyed methyl group in some of interlayer DMSO molecules is released from the trapped hole.
2) The methyl group of the interlayer DMSO molecule undergoes free rotation around its C_3 axis over the temperature range studied. The axis of rotation is fixed at low temperature (about 160 K), but above this temperature the methyl group initiates a wobbling motion whose amplitude increases with temperature. The wobbling angle is anisotropic. The DMSO molecules released from the silicate layer undergo an anisotropic rotation of the whole molecule.

ADDENDUM

The line shape of ^2H NMR spectra at the fast motional limit is well described by Barnes (1974). However, there are some mistypesettings, and therefore we describe the theory of the line shape briefly. Tensor of the quadrupole interaction is transformed from the principal axis system of the quadrupole interaction to Zeeman axis system with 2 angles, θ and ϕ. For a rigid lattice, $QCC_0 = e^2Qq_0/h$ and $\eta_Q = 0$. The components of the field gradient tensor are:

$$q_{11} = \frac{q_0}{2}(3\sin^2\theta\cos^2\theta - 1) \quad [8]$$

$$q_{22} = \frac{q_0}{2}(3\sin^2\theta\sin^2\phi - 1) \quad [9]$$

$$q_{33} = \frac{q_0}{2}(3\cos^2\theta - 1) = \frac{q_0}{4}(1 + 3\cos 2\theta) \quad [10]$$

$$q_{12} = \frac{3}{4}q_0\sin^2\theta\sin 2\phi \quad [11]$$

$$q_{23} = \frac{3}{4}q_0\sin 2\theta\sin\phi \quad [12]$$

$$q_{13} = \frac{3}{4}q_0\sin 2\theta\cos\phi \quad [13]$$

If $|q_{33}| > |q_{22}| > |q_{11}|$, the effective QCC and the effective asymmetry factor are:

$$QCC = e^2Qq_{33}/h \quad [14]$$

$$\eta_Q = \frac{q_{11} - q_{22}}{q_{33}} \quad [15]$$

We describe below about 4 kinds of motion:

1) Two-site jump: $\phi = 0$ and $\theta = +\theta_1$ and $-\theta_1$.

$$q_{11} = \frac{q_0}{4}(1 - 3\cos 2\theta_1) \quad [16]$$

$$q_{22} = -\frac{q_0}{2} \quad [17]$$

$$q_{33} = \frac{q_0}{4}(1 + 3\cos 2\theta_1) \quad [18]$$

and $q_{12} = q_{23} = q_{13} = 0$. For $0 \le \theta_1 \le \theta_m$ ($\cos 2\theta_m = 1/3$):

$$QCC = QCC_0\frac{1 + 3\cos 2\theta_1}{4} \quad [19]$$

$$\eta_Q = \frac{3(1 - \cos 2\theta_1)}{1 + 3\cos 2\theta_1} \quad [20]$$

2) Wobbling in one direction: $\phi = 0$, and θ is varied between $+\theta_1$ and $-\theta_1$ continuously. Integration from $-\theta_1$ and $+\theta_1$ is performed. For $0 \le \theta_1 \le \theta_m$ ($\sin 2\theta_m/2\theta_m = 1/3$):

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$$QCC = QCC_0 \frac{1 + 3 \sin 2\theta_1/2\theta_1}{4} \quad [21]$$

$$\eta_Q = \frac{3(1 - \sin 2\theta_1/2\theta_1)}{1 + 3 \sin 2\theta_1/2\theta_1} \quad [22]$$

3) Rotation around an axis inclined at θ_1: $\phi = 0$ to 2π and $\theta = \theta_1$:

$$QCC = QCC_0 \frac{3 \cos^2 \theta_1 - 1}{2} = QCC_0 \frac{1 + 3 \cos 2\theta_1}{4} \quad [23]$$

Asymmetry factor η_Q is always zero.

4) Wobbling in the bottom surface of a cone: $\phi = 0$ to 2π and $\theta = 0$ to θ_1:

$$QCC = QCC_0 \frac{1 + 3 \sin 2\theta_1/2\theta_1}{4} \quad [24]$$

Asymmetry factor η_Q is zero.

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(*Received 1 July 1996; accepted 7 January 1997; Ms. 2784*)

https://doi.org/10.1346/CCMN.1997.0450511 Published online by Cambridge University Press