

High-Resolution Solid-State NMR Study of Microstructures in Layered Aluminosilicate

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1. INTRODUCTION

Kaolinite, $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$, is a layered aluminosilicate with a dioctahedral 1:1 layer structure consisting of an octahedral aluminum hydroxide sheet and a tetrahedral silica sheet. Figure 1 shows the structure of kaolinite. The crystal structure is not fully understood because of the absence of a large single crystal.

In the present paper, we have traced ^{29}Si , ^{27}Al , and ^1H NMR spectra of various kaolinities, using high-resolution solid-state techniques. Analyzing the spectra theoretically, correlations between the NMR data and the local structures are discussed quantitatively.

2. EXPERIMENTAL

Totally eight samples were used. Six samples were natural, which were Kanpaku kaolin (called N1; Hinckley index 1.4), API No.9 standard kaolinite specimen (N2; 1.4), Georgia kaolin (N3; 0.7), Hakone Owakudani kaolin (N4; 0.4), Kibushi clay (N5; 0.2), and Gairome clay (N6; 0.2). Two synthetic samples were used, which were synthesized at 290°C (S1; 0.9) and 220°C (S2; 0.8).

NMR spectra were traced at room temperature by a Bruker MSL400 (a static magnetic field of 9.4 T) and a JEOL GSH200 (4.7 T). The line shapes of the spectra were analyzed using computer programs written by ourselves.

3. RESULTS AND DISCUSSION

3.1. ^{29}Si spectra

Figure 2 shows ^{29}Si CP/MAS NMR spectra of the sample N1, which has the highest crystallinity and the lowest content of paramagnetic impurities

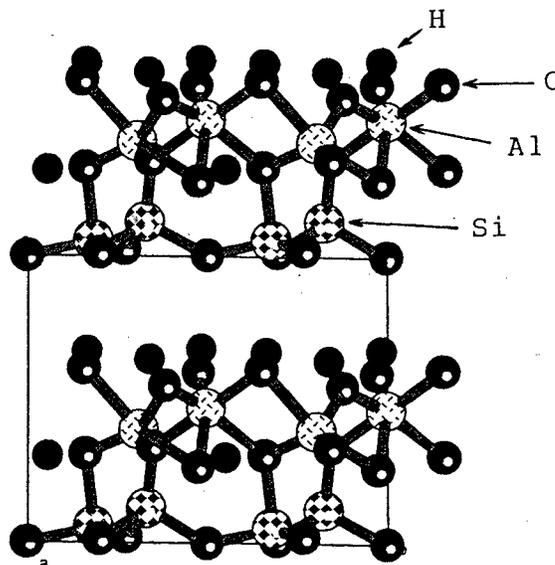


Fig. 1. Projection of the structure of kaolinite from the (100) direction.

among the eight samples studied. The spectra have two signals at -90.8 and -91.4 ppm from tetramethylsilane, being ascribed to $Q^3(0\text{Al})$. The line shapes do not depend on the contact time, and the two peaks have the same cross relaxation time between ^1H and ^{29}Si , which is 2.0 ms. Maximum intensities are obtained at the contact time of 8 ms. The field dependence experiments demonstrate clearly that two inequivalent Si sites are present.

The linewidth in the ^{29}Si CP/MAS spectra is originated from the dipole-dipole interaction with ^{27}Al , the chemical shift dispersion due to structural disorders, and the anisotropic magnetic susceptibility due to paramagnetic impurities.

For Kanpaku kaolin, the chemical shift dispersion is 0.39 ppm, while the contributions of the dipolar interaction are 0.08 and 0.33 ppm for the fields of 9.4 and 4.7 T, respectively, being estimated from the field

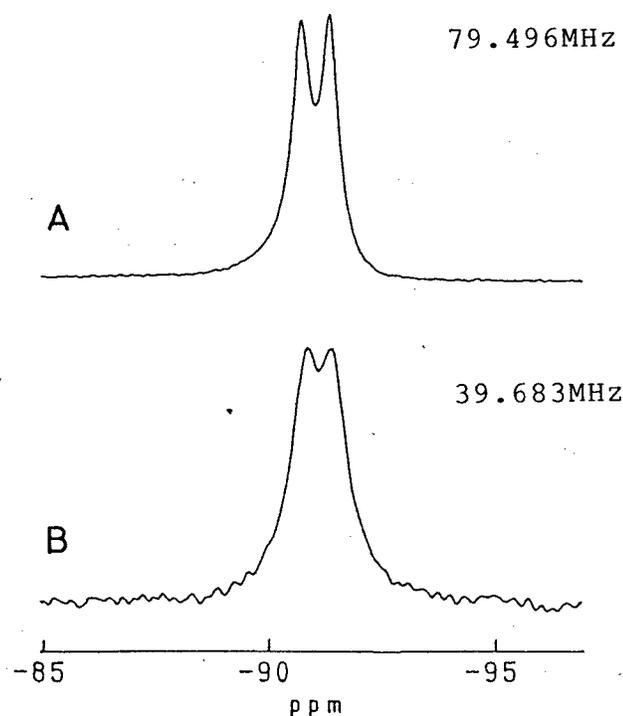


Fig. 2. ^{29}Si CP/MAS NMR spectra of the sample N1, measured at (A) 79.496 MHz and (B) 39.683 MHz. Chemical shifts are expressed with respect to tetramethylsilane.

dependence experiments. The effect of paramagnetic impurities is negligible. The contribution of the dipole-dipole interaction with ^{27}Al spins is calculated theoretically from the crystal structure. The estimated linewidths at 9.4 T are 0.14 and 0.09 ppm for Si(1) and Si(2), respectively, whereas those at 4.7 T are 0.55 and 0.35 ppm. These values are in excellent agreement with the values estimated experimentally.

Other kaolinites, with lower crystallinities and/or higher contents of paramagnetic impurities, have broader linewidths due to the structural disorders and the paramagnetic impurities.

3.2. ^{27}Al spectra

Figure 3 shows ^{27}Al DD/MAS NMR spectra of the sample N1, measured at different fields. The Al atom in the kaolinite structure is coordinated by six oxygen atoms, and they give a signal around 0 ppm with respect to 1M $\text{Al}(\text{NO}_3)_3$ aqueous solution. The spectrum at the lower field gives the broader signal at the lower frequency position, which suggests that the signal is the central transition, being broadened by the second-order quadrupole interaction. The

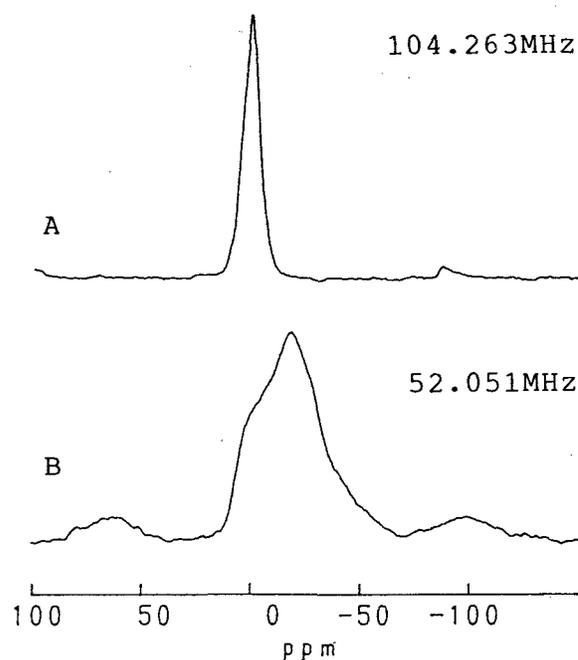


Fig. 3. ^{27}Al DD/MAS NMR spectra of the sample N1, measured at (A) 104.263 MHz and (B) 52.051 MHz. Chemical shifts are expressed with respect to 1 M $\text{Al}(\text{NO}_3)_3$ aqueous solution.

line shapes are simulated by our computer programs. The observed spectra cannot be simulated by one component, but can be simulated much better by two components with equal intensities. The obtained parameters for Al(1) are a chemical shift of 7.8 ppm, a quadrupole coupling constant of 3.36 MHz, and an asymmetry factor of the quadrupole interaction of 0.55, while they are 7.8 ppm, 2.88 MHz, and 1.00 for Al(2). The crystal structure indicates the presence of two inequivalent Al sites with a population ratio of 1:1.

The ^{27}Al spectra are also recorded for the other kaolinites. The same quadrupole coupling parameters as those in the sample N1 can well explain the line shapes of the other kaolinites.

A small fraction of tetrahedral Al is observed at about 70 ppm for several samples, which might be ascribed to impurities.

3.3. ^1H static spectra

Figure 4A shows an ^1H static NMR spectrum of the sample N1. The spectrum consists of two components with different line shapes; a narrow Lorentzian line with a width of 1.4 kHz and a broad Gaussian with a 28.9 kHz width.

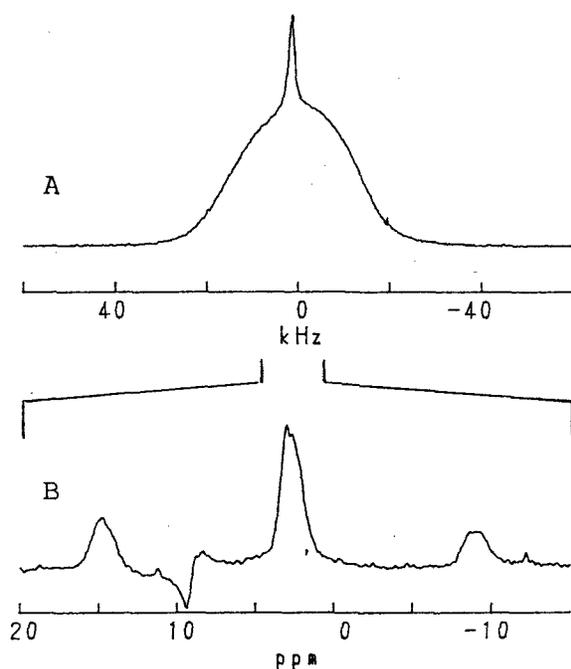


Fig. 4. ^1H NMR spectra of the sample N1, measured at 400.136 MHz. (A) The ordinary single-pulse sequence is used for the static sample. (B) The CRAMPS spectrum measured with the BR24 pulse sequence in the quadrature phase detection mode. Chemical shifts are expressed with respect to tetramethylsilane.

The narrow component can be ascribed to water molecules adsorbed on the outer surface. This component is easily diminished by evacuation, and they grow up gradually in the air atmosphere.

On the other hand, the broad component can be ascribed to the hydroxyl groups in the kaolinite structure, whose second moment is 105 kHz^2 . The second moment estimated from the crystal structure is 92 kHz^2 , in which $^1\text{H}\text{-}^1\text{H}$ and $^1\text{H}\text{-}^{27}\text{Al}$ contributions are 67 and 25 kHz^2 , respectively. The calculated second moment agrees with the experimental value. These results demonstrate that the hydrogen atoms in the CH group is in a rigid lattice state at room temperature.

The ^1H static NMR spectra of other kaolinites also consist of the two components.

3.4. ^1H CRAMPS

The CRAMPS technique is successfully applied to the kaolinite samples. Figure 4B shows ^1H CRAMPS

spectra of the sample N1. The BR24 pulse sequence is used in the quadrature phase detection mode. Considerably large spinning sidebands are observed on both sides of the central peak, which are caused by the strong dipole-dipole interaction between ^1H and ^{27}Al spins. The linewidth in the static state, 29 kHz, is reduced to about 600 Hz by the use of the CRAMPS technique, where the reduction factor is about 50. The chemical shift is 2.8 ppm from tetramethylsilane.

The chemical shift of the hydroxyl groups in the kaolinites changes slightly depending on the sample, which might reflect the strength of the hydrogen bonding or the acidity of the hydrogen.

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