^{29}Si and ^{1}H NMR of Expandable Mica Ion-exchanged by NH_4^+

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The ^{29}Si-NMR chemical shift of expandable mica ion-exchanged by NH_4^+ changes from –95 to –99.5 ppm after heat-treatment at 600 °C, which indicates a change from the mica to a talc structure. The ^{1}H static NMR spectrum of protons remaining in the structure after heating showed a sharp signal with a full width at half maximum of 0.8 kHz at 1.0 ppm, which suggests a rapid proton motion in the structure.

Expandable fluorine mica, which has similar properties with swellable clay, was synthesized from the mixture of talc and Na_2SiF_6 heated at 800 °C.[1] The expandable properties of the swellable clay changed with the ion-exchange treatments and calcination.[2,3] In the present report the structural change and the behavior of the protons in the NH_4^+-exchanged mica before and after heating were studied using NMR spectroscopy.

A 1.5 g sample of expandable fluorine mica (EM-A) was stirred for one day in 150 ml of 0.1 N NH_4NO_3 solution and centrifuged. The above treatment was repeated 7 times to exchange Na^+ with NH_4^+ ions in the interlayer sites of the expandable mica. The specimen was centrifuged 4 times with distilled water and air-dried at room temperature. The dried specimen (EM-B) was then heated at 600 °C for 3 h and the heated specimen (EM-C) was obtained. The properties of the three specimens were analyzed by XRD, IR and TG-DTA.

NMR spectra were recorded using a Bruker AC200 (4.7 T magnetic field). ^{29}Si high power decoupling (HD-MAS) spectra were obtained using a $\pi/2$ pulse (4 μs) with a recycle time of 120 s and 360 pulses. ^{29}Si cross polarization (CP-MAS) spectra were obtained with a recycle time of 5 s, a contact time of 4 ms and 1024 pulses. ^{1}H NMR spectra were acquired using an ordinary single-pulse sequence with a $\pi/2$ pulse (2 μs), a recycle time of 5 s and 18 pulses under MAS and static conditions. All magic angle spinning (MAS) rates were 3250 Hz. A rotor was washed with hexane and dried using a dryer to remove away water and some organic contamination.[4]

The ^{29}Si HD-MAS and CP-MAS NMR spectra of each specimen are shown in Figure 1. The chemical shifts of EM-A and EM-B were close to each other at –95.0 and –95.3 ppm, respectively, while the line width of EM-B is ca 1.3 times as large as that of EM-A as shown in Figures 1 (A) and (B). The X-ray diffraction patterns indicated that EM-B had a mica structure, which suggests that NH_4^+ ions fit into the hexagonal holes of the upper and lower Si–O tetrahedral sheets. EM-C in Figure 1 (C) has a main signal at –99.5 ppm with a shoulder peak at –96 ppm. The chemical shift, –99.5 ppm, is near the –98 ppm of talc in Figure 1 (D). Tennakoon et al.[5] observed a ^{29}Si resonance shift from –93.5 to –95.5 ppm for the NH_4^+-exchanged montmorillonite heated at 500 °C, and suggested that this change was related to the structural change from montmorillonite to pyrophyllite (neutral analogue of montmorillonite). Therefore, the change in the chemical shift is considered to be the change from a mica to a talc (neutral analogue of expandable mica). The chemical shift of talc showed a higher frequency shift than that of EM-C. This difference may be caused by the F ions in the structure of EM-C because the infrared absorption spectrum of EM-C is almost same as that of the fluoride-substituted talc.[6] The shoulder peak at –96 ppm is assigned to Q^3, which shows the mica structure caused by the remaining Na^+ ions, because the chemical analysis of EM-C shows that it includes 20% Na^+ ions per unit cell.

Figures 1 (E), (F) and (G) show the ^{29}Si CP-MAS NMR spectra of EM-A, EM-B and EM-C. EM-A has no signal and EM-C shows a weak broad signal at –97 ppm, while EM-B shows a highly sensitive signal. These results indicate that the protons of the interlayer water of EM-A rapidly rotate[4] but the protons of the NH_4^+ ions do not rotate as rapidly and the rotational speed of the NH_4^+ ions in the hexagonal holes may be reduced because NH_4^+ ions form the hydrogen bonds –N–H···O–Si– on the oxygen surface of the tetrahedral sheets. In the case of EM-C, the number of protons was reduced to 1/4 because of NH_3 evaporation from the interlayer site by heat-treatment. However, the signal intensity of EM-C was extremely weak compared with the concentration of protons, which suggests a rapid motion of the protons in the structure. In the case of talc in Figure 1 (H), the sharp signal is recognized because the protons of OH in the octahedral sheet are placed at a fixed site near the

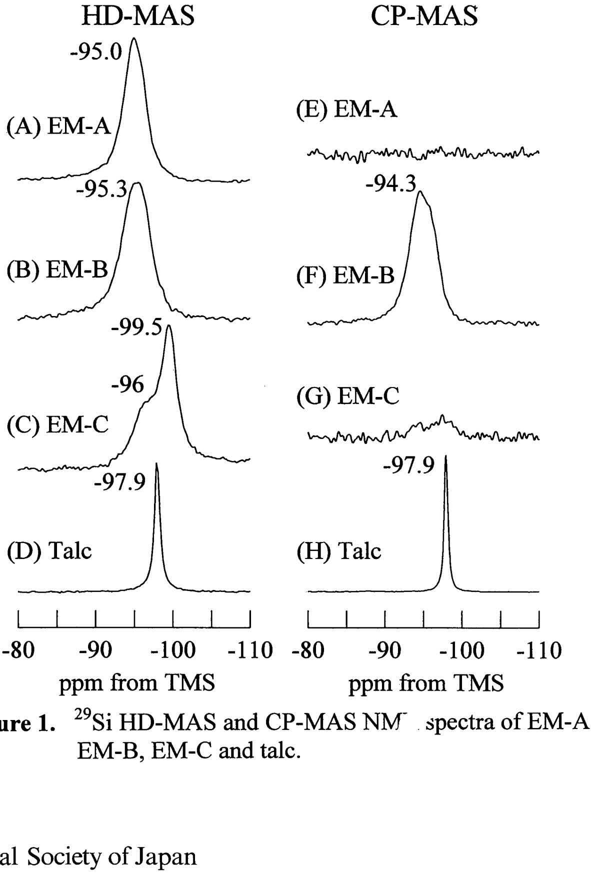

Figure 1. ^{29}Si HD-MAS and CP-MAS NMR spectra of EM-A, EM-B, EM-C and talc.

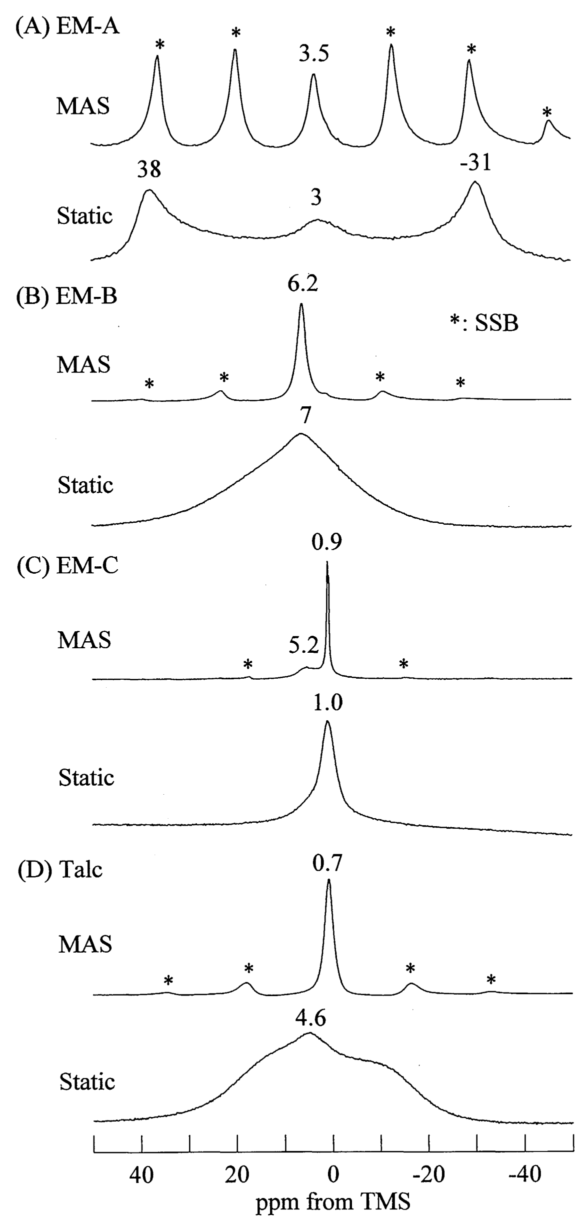

Figure 2. ^1H MAS and static NMR spectra of EM-A, EM-B, EM-C and talc.

Si atoms in the tetrahedral sheet.

The ^1H MAS and static NMR spectra of EM-A are shown in Figure 2 (A). The MAS spectrum shows a central signal of 3.5 ppm with large spinning side bands as indicated by the asterisks, which is characteristic of molecular water in the crystals.[4] The chemical shift, 3.5 ppm, is close to that of the water of analcite.[4] Therefore, the central signal is assigned to the protons of the water coordinating to Na^+ ions in the interlayer. The wideline spectrum of the ^1H static NMR of EM-A shows the typical "Pake Doublet" of molecular water.[7] Figure 2 (B) shows MAS and static spectra of EM-B. The chemical shift of the MAS spectrum is 6.2 ppm which is near the chemical shift of general ammonium salts,[8] and suggests the signal is assigned to the protons of the NH_4^+ ions. The static spectrum with a line width (full width at half maximum, 4.6 kHz) shows a narrower signal than the bell-shaped wideline of NH_4^+ ions in NH_4Cl with a line width (100 kHz) measured at 95 K because of crystal rigidity.[9] The rotational movement of NH_4^+ is not rigid in the structure. Figure 2 (C) shows MAS and static spectra of EM-C. The MAS spectrum shows a sharp signal at 0.9 ppm with a shoulder at 5.2 ppm. The sharp signal is assigned to the protons remaining in the structure because the organic contaminants in EM-C were completely removed by heat treatment at 600 °C and the background signal was negligible. The static spectrum shows that a very sharp signal with a line width (0.8 kHz) is noticeable. For example, the static ^1H-NMR of talc shows a bell-shaped wideline with a line width (6.8 kHz) in Figure 2 (D). The MAS spectrum of talc also shows a wider line than that of EM-C. The line width of the signal is affected by the concentration of protons in the structure. The concentration of protons in EM-C is estimated to be 0.36 versus that in talc due to TG loss upon evaporation of NH_3. Hayashi[10] obtained that the dipolar line width of talc is 5.6 kHz by the correction of magnetic susceptibility broadening and demonstrated that the inter-atomic distance between neighboring protons calculated from this line width is a reasonable value in view of the crystal structure, using Van Vleck formula[11] and the assumption of a simple cubic lattice arrangement of the protons. Using his assumption, the line width is proportional to the concentration of protons, therefore, the line width of the signal of EM-C must be more than 2.0 kHz, if the protons are fixed in the crystal structure. Moreover EM-C contains F ions at the sites corresponding to the OH sites of talc. The heteronuclear dipolar interaction between H and F should make the line width still broader than the calculated value (2.0 kHz). The discrepancy between the calculated line width (2.0 kHz) and the obtained one (0.8 kHz) strongly suggests that the protons rapidly move in the structure, which is also supported by the weakness of the CP-MAS spectrum of EM-C.

If the H^+ can diffuse in the negative vacant sites in EM-C after heat treatment via the hexagonal cavities in the tetrahedral sheet, the protons may mainly move in the vacant octahedral sites where the negative charges concentrate. The migration of the protons causes the neutralization of the layer charge. Increasing silicone net charges causes lower frequency shifts according to Engelhardt,[12] therefore this assumption explains the lower frequency shift of the ^{29}Si signal from EM-B to EM-C.

References and Notes

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