Solid-State NMR Studies on Pillar-Interlayered Naturally-Occurring Montmorillonite

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(Received June 21, 1985)

Synopsis. Solid-state MAS NMR spectroscopy on naturally occurring montmorillonite has revealed that the Fe(III), contained in the octahedral layer, exerts a greater influence on octahedral Al nuclei than on tetrahedral ones. The same trend is observed in a more pronounced manner with the material intercalated with $[AlO_4Al_{12}(OH)_{24}(OH_2)_{12}]^{7+}$ cations. Mechanisms of selective peak broadening in solid-state NMR spectra are discussed.

Pillar interlayered montmorillonite (abbreviated as PILM hereafter) has attracted considerable interest since its well-defined pore structure of molecular dimension suggests promising wide applications as adsorbents[1] and catalyst supports.[2] The layer distance of PILM (ca. 0.9 nm), as determined by X-ray diffraction, is consistent with the size of $[AlO_4Al_{12}OH)_{24}(OH_2)_{12}]^{7+}$ cation introduced.[3] Direct evidence for the Al_{13} structure present in the interlayer of clay minerals was given by Plee et al.[4] with solid-state MAS ^{27}Al NMR.

The Fe(III) constituent in naturally occurring montmorillonite may exert a paramagnetic influence on solid-state MAS NMR. In the present study, Kunipia-G montmorillonites with and without the Al_{13} pillar have been examined in order to elucidate the limitation in quantitative analysis.

Kunipia-G Na-montmorillonite (abbreviated as Na-Mont), supplied from Kunimine Ind. Co., Ltd., was intercalated with Al_{13} cations and dried in an oven overnight at 393 K as previously described.[5,6] Chemical analysis was carried out by atomic absorption spectroscopy. The basal spacing was enlarged to 1.80 nm by the pillar substance, as confirmed by X-ray diffraction. Solid-state MAS ^{27}Al NMR spectra were recorded at 70.28 MHz on a JEOL FX270 NMR spectrometer. The spinning frequency of rotor was 3—4 kHz. All measurements were carried out at room temperature with $[Al(H_2O)_6]^{3+}$ as an external standard. The peak intensity was calculated by integration of the principal peak and of its spinning side bands. In deconvolving overlapping peaks, it was assumed that both the tetrahedral and octahedral Al ions would give symmetrical NMR spectra.

The crystal unit of Na-Mont is formulated according to Brindley and Sempels[7] as

$$[Na_{0.38}Ca_{0.03}Mg_{0.01}][Al_{1.59}Fe^{3+}_{0.10}Mg_{0.31}][Si_{3.86}Al_{0.14}]\,O_{10}(OH)_2nH_2O, \qquad (1)$$

where these brackets are arranged in the order: the exchangeable cation sites, the octahedral layer ones, and the tetrahedral layer ones. As for PILM, the composition of the exchangeable cation sites is changed into

$$[(Al_{1.16}O_{0.55})^{+0.38}Ca_{0.01}Mg_{0.02}], \qquad (2)$$

where the interlayered alumina is represented as

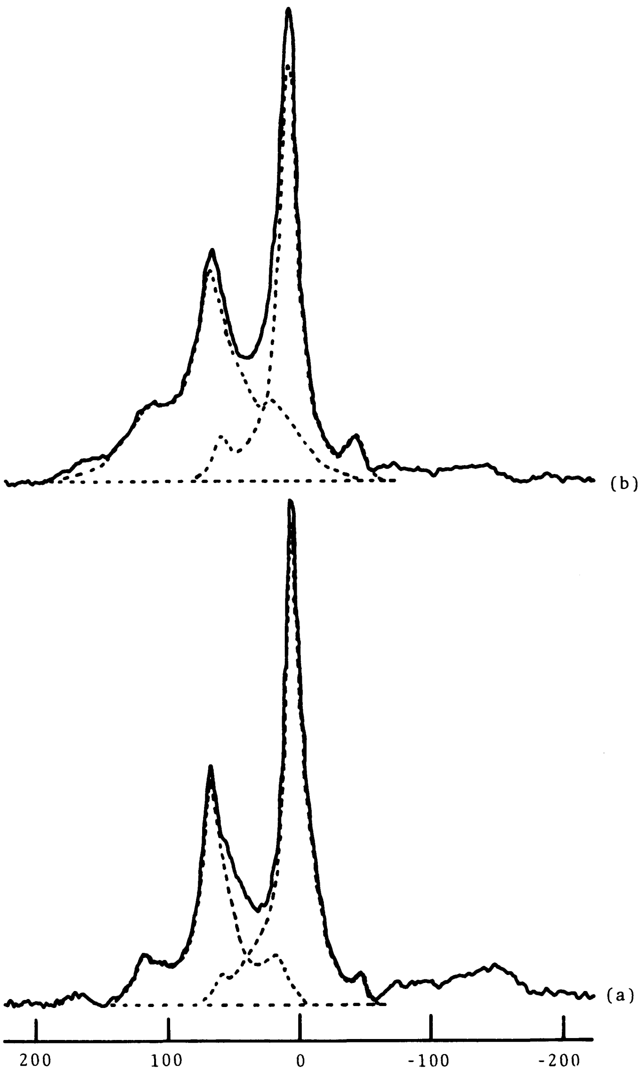

Fig. 1. Solid-state MAS ^{27}Al NMR spectra of Na-Mont (a) and PILM (b). The observed spectra are the full lines. The dotted lines are the deconvolved patterns. Resonance frequency: 70.28 MHz. Standard for δ: $[Al(H_2O)_6]^{3+}$.

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$(Al_{1.16}O_{0.55})^{+0.38}$.

The solid-state MAS ^{27}Al NMR spectra of Na-Mont and PILM are shown in Fig. 1 with deconvolved patterns indicated by the dotted lines. The chemical shift assignments already made for the octahedral and tetrahedral Al ions[8] are aptly applied to the peaks of 5.4 (Na-Mont) and 7.4 (PILM) ppm and of 67.0 (Na-Mont) and 66.0 (PILM) ppm, respectively.

The numbers of Al nuclei in the tetrahedral and octahedral coordinations per unit structure of Na-Mont, (Al_{tet}) and (Al_{oct}), respectively, are given from formula 1 as

$$(Al_{tet}) = 0.14, \tag{3}$$

$$(Al_{oct}) = 1.59. \tag{4}$$

The peak intensity ratio of Al_{tet}/Al_{oct} for Na-Mont should be obtained as

$$\alpha(Al_{tet})/\beta(Al_{oct}) = 0.50, \tag{5}$$

where α and β are positive coefficients which become unity when the Al nuclei involved are all detected by NMR spectroscopy. From Fig. 1, the value of β/α is obtained as 0.18. This magnitude far less than unity has certainly resulted from a rather difficult NMR detection for octahedral Al nuclei.

It is to be noted that the paramagnetic Fe(III) constituent of the naturally occurring montmorillonite is concentrated in the octahedral layer,[7] and that Al atoms are contained in the tetrahedral layer only in a small amount. Selective peak broadening due to electron-spin relaxation[9] would therefore be operative more efficiently for Al_{oct} in the same layer than for diluted Al_{tet} in a different layer.

The numbers of interlayered Al nuclei in the tetrahedral and octahedral coordinations, $\langle Al_{tet}\rangle$ and $\langle Al_{oct}\rangle$, respectively, are given from formula 2 as

$$\langle Al_{tet}\rangle + \langle Al_{oct}\rangle = 1.16. \tag{6}$$

The intensity ratio of the peak at 66.0 ppm (Al_{tet}) to that at 7.4 ppm (Al_{oct}) in Fig. 1 leads to the relationship

$$[\alpha(Al_{tet}) + \gamma\langle Al_{tet}\rangle]/[\beta(Al_{oct}) + \delta\langle Al_{oct}\rangle] = 1.3, \tag{7}$$

where γ and δ are positive coefficients not greater than unity.

The ratio of $\langle Al_{tet}\rangle/\langle Al_{oct}\rangle$ of the Al_{13} cation itself is equal to 1/12. By substituting Eqs. 3—6 in Eq. 7 we obtain

$$[\alpha(0.14) + \gamma(1/13)(1.16)]/ \\ [\alpha(0.14)(1/0.50) + \delta(12/13)(1.16)] = 1.3, \tag{8}$$

which is simplified to

$$\delta/\gamma = 0.07 - 0.17\alpha/\gamma. \tag{9}$$

Apparently, δ/γ should be smaller than 0.07, whatever the values of α and γ may be.

Since supporting evidence for the Al_{13} structure has been obtained by solid-state NMR spectroscopy for interlayered hectorite,[4] the small magnitude of 0.07 ought to be understood in terms of the paramagnetic influence due to Fe(III) centers on the close octahedral Al nuclei of the pillar. In addition to this, the distortion factor, which has been pointed out for interlayered hectorite as becoming dominant on calcination,[4] must be taken into consideration. Moreover, any structural transformations, leading to increasing the tetrahedral sites, might occur in the pillar species partially.

Quantitative analysis of naturally occurring clay minerals by solid-state NMR spectroscopy should be undertaken with precaution against these intrinsic factors.

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