A study on hydration behaviors of interlayer cations in montmorillonite by solid state NMR

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Abstract

Solid state $^{23}$Na NMR spectra of Na-montmorillonite under dry and hydrated conditions have been measured to study hydration structure of Na$^+$ in interlayer spaces. The $^{23}$Na triple quantum (3Q) MAS NMR experiments have been performed to determine the quadrupole coupling constants ($C_Q$) and the isotropic chemical shifts ($d_{\text{iso}}$). The $C_Q$ values were found to remarkably depend on water content, i.e. the $C_Q$ values increase with changing from dry condition to hydrated one (at around 12.5 wt% water content) and gradually decrease with an increase in the water content. Since the $C_Q$ value is a sensitive parameter to the local structure of the nucleus measured, the changes in $C_Q$ values with water content should correspond to those in the hydration structure of Na$^+$ in the interlayer spaces. Thus, it is considered that the increment of the $C_Q$ value in the water content of 12.5 wt% is due to the formation of hydrated Na$^+$ with planner structure, and that the decrease in $C_Q$ values with the water content is attributed to the formation of hydrated Na$^+$ with spherical symmetric structure.

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1. Introduction

Montmorillonite has been studied to probe layer structure and physicochemical properties. The structure of montmorillonite is composed of two Si tetrahedral sheets and one Al octahedral sheet, which form nano interlayer structure. The various cations are adsorbed onto montmorillonite to balance negative charge in the interlayer spaces. Such negative charges are caused by substitution of lower charge cation for more highly charged cation in the tetrahedral or octahedral sheets.

The high resolution solid state NMR spectroscopy has become important as one of the methods for investigating the layer structure and the dynamic behaviors of cations and water in clay minerals such as montmorillonite.

$^{29}$Si and $^{27}$Al magic angle spinning (MAS) NMR have been used for characterizing the bridged oxygen atoms in the tetrahedral sheet and for determining the coordination numbers of Al in the layer [1], respectively. However, solid state MAS NMR of quadrupolar nuclei ($I > 1/2$) such as $^{23}$Na show broad or split spectra. Thus, the interpretation of $^{23}$Na MAS NMR spectra involve uncertainty caused by larger electric field gradient (EFG), which depends on distributions of electronic charge around the nucleus. Hence, it is difficult to obtain the isotropic chemical shifts ($d_{\text{iso}}$).

The multi-quantum (MQ) MAS method [2], which was reported by Frydman et al. in 1995, makes it possible to average out second order quadrupolar interaction without carrying out complicated handling (e.g. extrapolation of the MAS line positions at different magnetic field strength), and can estimate the $d_{\text{iso}}$ and the quadrupole parameter of quadrupolar nuclei.

In this study, we have examined the hydration structures of Na$^+$ ions in the interlayer spaces of dry and hydrated Na-montmorillonites using high resolution MAS NMR and three quantum (3Q) MAS NMR methods.

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2. Experimental

Na-montmorillonite used in the present study is classified as dioctahedral smectite, and was supplied from the Japan Clay Science Society (JCSS-3101). The structural formula of Na-montmorillonite is as follows:

$$\text{Na}_{0.77}(\text{Al}_{3.35}\text{Fe}^{3+}_{0.06}\text{Fe}^{2+}_{0.09}\text{Mg}_{0.46})(\text{Si}_{7.61}\text{Al}_{0.39})\text{O}_{20}(\text{OH})_{4}.$$ 

The dry Na-montmorillonite (named as the dry sample) was prepared by heating at 150 °C for 24 h. It was confirmed by differential thermal analysis that the dehydration treatment under above conditions is useful for removing water in the interlayer space of Na-montmorillonite. The Na-montmorillonite containing water (named as the hydrated sample) was prepared by adding appropriate amounts of water to the original Na-montmorillonite.

The NMR measurements were carried out using Chemagnetics CMX-300 spectrometer with a static magnetic field strength of 7.05 T. The $^{23}$Na Larmor frequency was 79.49 MHz for CMX-300. $^{23}$Na 3QMAS NMR spectra were measured by doubly tuned MAS probe heads at spinning rate of 16 kHz. Chemical shifts were calibrated with respect to 1 M (M = mol dm$^{-3}$) NaCl solution.

All NMR spectra were measured at room temperature. Saturation of signals was avoided by taking into account the spin–lattice relaxation times, which were measured by the saturation recovery method.

In order to avoid drying of samples with spinning at high speed and purging dry air for suppressing a rise in temperature of sample tube accompanied by pulse radiation, the hydrated samples were wrapped by poly (vinylidene chloride) sheet. The dry sample was measured without wrapping, because of free from adsorption of water under purging with dry air. The effectiveness of such sample treatments was confirmed by the facts that NMR spectra and weight of samples measured after spinning at high speed with purging dry air for 24 h are consistent with those of initial samples.

3. Result and discussion

Fig. 1 shows $^{23}$Na MAS NMR spectra of Na-montmorillonites with various water content. As shown in Fig. 1, the line shape becomes sharp and chemical shifts move to lower magnetic field with increasing water content. In spite of the solid state nature of the samples, furthermore, $^{23}$Na MAS NMR spectra of the hydrated samples show narrow lines as observed in the $^{23}$Na NMR spectra for liquid samples containing Na$^+$. These results suggest that the Na$^+$ ions in the interlayer spaces of the hydrated samples are in the form of the hydrated ions with the symmetric structure as the Na$^+$ ions in aqueous solutions.
constants calculated from the $^{23}$Na 3QMAS NMR measurements vs. [water molecules]/[Na$^{+}$ ions].

For these reasons, we measured $^{23}$Na 3QMAS spectra of Na-montmorillonites with various water content. The typical results are shown in Fig. 2, in which contours represent 15, 25, 35, 45, 55, 65, 75, 85 and 95% of the maximum intensity in each spectrum. The $^{23}$Na 3QMAS NMR spectrum of dry sample is found to distribute widely along CS axis. This suggests that the Na$^{+}$ ions in dry sample exist in the sites with slightly different structures in the interlayer spaces, which are supposed to be the hexagonal cavities of Na-montmorillonite [4].

On the other hand, in the hydrated sample, the line shapes of $^{23}$Na 3QMAS NMR spectra became sharp as typically shown in Fig. 2. This suggests that the structural distribution of Na$^{+}$ ions in the interlayer spaces of hydrated samples becomes homogeneous with an increase in water content.

The NMR parameters of $\delta_{\text{iso}}$ and $C_{Q}$ were estimated from the centers of gravities in F1 and F2 axes of the $^{23}$Na 3QMAS NMR lines, and are plotted against the mole ratios of water molecules to Na$^{+}$ ions, [water molecules]/[Na$^{+}$ ions], (see Fig. 3). As seen in Fig. 3, the $\delta_{\text{iso}}$ values are approximately constant in all samples except the dry one. The difference in $\delta_{\text{iso}}$ between the dry and hydrated samples clearly indicates that the interlayer Na$^{+}$ ions of the dry sample have the structure different from those of the hydrated ones. As one of the reasons of such a difference, we propose that the Na$^{+}$ ions located in the hexagonal cavities of the dry sample are migrated to the interlayer space with an increase in water content.

Fig. 3 also shows the dependence of $C_{Q}$ value on water content. As seen there, the $C_{Q}$ value increases up to 12.5 wt%, which corresponds to [water molecules]/[Na$^{+}$ ions]=5, and decrease with a further increase in water content. In general, the $C_{Q}$ value depends on both the number of coordinated ligands and the structures in the first nearest neighbor of metal ions of interest, because influence of second and further outer coordination spheres decreases abruptly due to the $r^{-3}$ dependence of the EFG ($r$ is the distance between metal ions and the coordinated atoms) [5]. Hence, the $C_{Q}$ values of $^{23}$Na should become small with an increase in the symmetry of the nearest neighbor coordination sphere of hydrated Na$^{+}$ ions. However, the $C_{Q}$ values in hydrated samples of 12.5 and 17.2 wt% are larger than that of the dry sample as shown in Fig. 3. As one of the reasons for this phenomenon, we propose that the structures of hydrated Na$^{+}$ ions corresponding to [water molecules]/[Na$^{+}$ ions]=5 and 7 are less symmetric than those of the dry and other hydrated samples.

Koller et al. calculated the $C_{Q}$ values by using point charge model for coordination structure of Na and oxygen, and concluded that the $C_{Q}$ value, which is zero for regular tetrahedral or octahedral coordinations, has moderate values for trigonal bipyramidal or quadratic pyramidal structure, and show much larger value for planner structures with four or six oxygens around Na [6]. Hence, it is considered that the Na$^{+}$ ions are located in the hexagonal cavities in the dry sample, and with increasing water content the Na$^{+}$ ions are hydrated and their hydration structures are changed from planner to octahedral.

4. Conclusion

The hydration behaviors of the interlayer Na$^{+}$ ions of Na-montmorillonites with various water content (0, 12.4, 17.2, 26.1, and 34.6 wt%) have been studied using the solid state $^{23}$Na NMR methods. The results are summarized as follows:

1. The $\delta_{\text{iso}}$ values are approximately identical in all the samples except the dry one.
2. The $C_{Q}$ value is 1.5 MHz for the dry sample, which increases in the hydrated sample with increasing water content up to 12.5 wt% (3.8 MHz), then decreases and approaches to zero in the hydrated sample of 34.6 wt%.

From these results, we proposed that the Na$^{+}$ ions are located in the hexagonal cavities in the dry sample, and with the increase in water content the Na$^{+}$ ions are hydrated and their structures are changed from planner to octahedral ones.

References

[1] T. Ohkubo, K. Kanehashi, K. Saito, Y. Ikeda, Observation of two 4-coordinated Al in montmorillonite using high magnetic field strength $^{27}$Al MQMAS NMR, Clays Clay Miner. 51 (2003) 513–518.
[2] L. Frydman, J.S. Harwood, Isotropic spectra of half-integer quadrupolar spins from bidimensional magic-angle-spinning NMR, J. Am. Chem. Soc. 17 (1995) 5367–5368.
[3] J.W. Akitt, Multinuclear studies of aluminum compounds, Progr. NMR Spectrosc. 21 (1989) 1–149.
[4] J.T. Kloprogge, J.B.H. Jansen, R.D. Schuiling, J.W. Geus, The interlayer collapse during dehydration of synthetic Na$_{0.7}$-beidellite: a $^{23}$Na solid-state magic-angle spinning NMR study, Clays Clay Miner. 40 (1992) 561–566.
[5] G. Engelhardt, D. Michel, High-Resolution Solid-State NMR of Silicates and Zeolites, Wiley, New York, 1988.
[6] H. Koller, G. Engelhardt, A.P.M. Kentgens, J. Sauer. $^{23}$Na NMR spectroscopy of solids: interpretation of quadrupole interaction parameters and chemical shifts, J. Phys. Chem. 98 (1994) 1544–1551.