# Characterization of Heat-Treated Synthetic Imogolite by $^{27}$Al MAS and $^{27}$Al MQMAS Solid-State NMR

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The structure of imogolite treated at 623, 773, and 973 K was characterized by $^{27}$Al MAS and $^{27}$Al multiple-quantum magic-angle-spinning (MQMAS) NMR. For comparison, $^{27}$Al NMR spectra of imogolites, allophanes, and kaolinite heated at 623, 773, and 973 K were acquired to investigate the structural change of these clay minerals. From these spectra, the structural change of imogolite has been observed at 623 K as well as in the case of allophane, while that of kaolinite has been demonstrated at a higher temperature of 773 K. The formation of five-coordinated Al from the original six-coordinated Al in imogolite after heat-treatment was confirmed as well as in the case of kaolinite and allophane. Furthermore it is found that the peaks for five- and four-coordinated Al of imogolite shifted to lower field and that their quadrupolar products ($P_Q$) increased with treated temperature. It can be concluded that the five- and four-coordinated Al species are generated from the decomposition of six-coordinated Al. The chemical shifts of all peaks above 623 K indicate the increase of the structural strain in the heat-treated imogolite and the formation of amorphous phases by the decomposition of the original tubular structure.

Imogolite, a type of clay mineral, is often found in volcanic ashes and weathered basalts.

This clay mineral is a fibrous aggregation where parallel thin tubes accumulate. Its chemical composition has been reported to be $SiO_2 \cdot Al_2O_3 \cdot 2H_2O$.[1–3] The outer surface of imogolite consists of gibbsite sheet with Al–OH groups, while its inner wall consists of tetrahedral Si which shares three oxygen atoms with Al and has an apex OH. However, in contrast to kaolinite and montmorillonite, the tetrahedral Si units are not connected to each other, meaning that no Si–O–Si linkage occurs. Recent progress in synthetic methods allows the application of imogolite as a highly functional catalyst in industry.[4] Heat-treatment of imogolite is believed to increase its catalytic activity. For several kinds of aluminosilicates, the generation of five-coordinated Al during heat-treatment has been suggested in some literature.[5–7] However the experimental evidence for its generation in the case of imogolite remains vague. In addition, atomic-level (local) structural changes of imogolite during heat-treatment have not been sufficiently understood although structural information on an atomic level may be critical to catalytic activity.

Therefore, the aim of this study is to investigate the local structural change around Al, a major element, using magic angle spinning (MAS) and high-resolution multiple quantum magic angle spinning (MQMAS) NMR.

## Experimental

Imogolite was synthesized from concentrated solution using the method of Suzuki.[8]

The application of heat to imogolite was performed using a thermal container.

Temperature was raised at 6 K min$^{-1}$ and kept at a desired temperature for one hour. With respect to imogolite samples prepared at several temperatures, the $^{27}$Al NMR spectra were acquired using a superconducting magnet (14.1 T, JEOL ECA-600) with $^{27}$Al resonance frequency of 156.32 MHz. The sample rotor of zirconia (4 mm$\varphi$) was spun at the spinning frequency of 15 kHz. The measurement of NMR spectra was performed using single-pulse method (non-decoupling) with a small flip angle of 30 degrees estimated from the 90 degree pulse width for $AlCl_3$ aqueous solution, and a pulse delay of 1 to 3 s. Chemical shifts were referenced to 1.0 M aqueous $AlCl_3$ as external standard (−0.1 ppm).

$^{27}$Al MQMAS NMR spectra were recorded using a pulse sequence including a z-filter scheme.[9–11]

## Results and Discussion

**$^{27}$Al MAS NMR of Imogolite.** $^{27}$Al MAS NMR spectra of imogolite are shown in Figure 1. For the R.T. (unheated) sample, two peaks were observed at 6 and 60 ppm, which are assigned to six- and four-coordinated Al, respectively.[7,12] On the other hand, the heated imogolite (623, 773, and 973 K) showed an increasing ratio of four-coordinated Al and a new peak (around 30 ppm). MacKenzie[6] has reported that a new species, which is not a six-coordinated Al, was observed in $^{27}$Al MAS spectra of imogolite treated at 623 K. In the case of allophane, which has structure similar to imogolite, the formation of five-coordinated Al has been reported.[13] It is well-known from the analysis of the crystalline substances including five-coordinated Al that the chemical shift of five-coordinated Al ranges from 31 to 41 ppm.[13]

Therefore the new peak observed at 30 ppm (Figure 1) is considered to be five-coordinated Al. The presence of five-coordinated Al in imogolite was consistent with the results of MacKenzie[14] who proposed that the structural change of Al site

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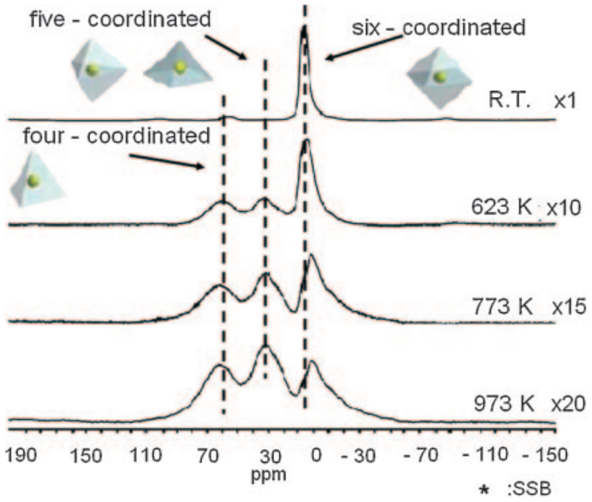

**Figure 1.** $^{27}$Al MAS NMR spectra of imogolite unheated (R.T.) and heated at higher temperatures (The longitudinal scale for each spectra is expanded by the times of values described at the right side).

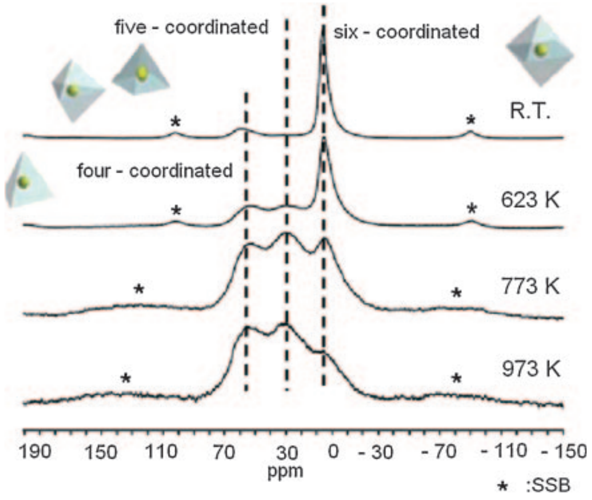

**Figure 2.** $^{27}$Al MAS NMR spectra of allophane unheated (R.T.) and heated at higher temperatures.

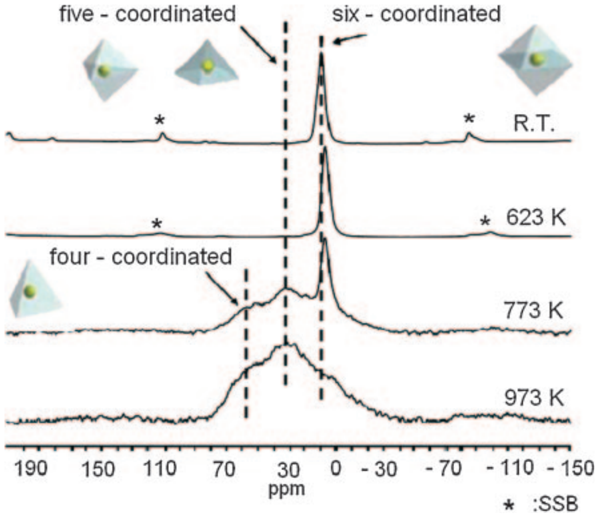

**Figure 3.** $^{27}$Al MAS NMR spectra of kaolinite unheated (R.T.) and heated at higher temperatures.

in imogolite depended on temperatures. Since the heat-treatment at high temperatures may eliminate the hydroxy group of six-coordinated structures, non-octahedral structures are generated by decomposition, and five- and four-coordinated Al are formed from six-coordinated Al. $^{27}$Al MAS NMR spectra of allophane and kaolinite (R.T., 623, 773, and 973 K) are also shown in Figures 2 and 3, respectively. Although the framework structure of allophane is similar to that of imogolite, it exists as a hollow sphere.[15] Kaolinite is a model substance of layered clay minerals. Imogolite (Figure 1) showed structural change at lower temperatures than kaolinite (Figure 3) at 623 K. The $^{27}$Al MAS NMR spectra of allophane that has similar structure to imogolite show two peaks at 6 and 60 ppm, similar to that for imogolite. The $^{27}$Al MAS NMR spectrum of the R.T. (unheated) kaolinite sample shows a peak at 2.5 ppm as shown in the cases of imogolite and allophane. The peak of kaolinite is positioned 3.5 ppm up field from those observed for imogolite and allophane. Despite the similarity in structure of imogolite and allophane, a clear difference in $^{27}$Al MAS spectra is recognized after heat-treatment (623, 773, and 973 K). Imogolite (Figure 1) shows a larger peak shift of six-coordinated Al at 6 ppm than kaolinte (Figure 3). Meanwhile allophane (Figure 2) has not demonstrated any significant peak shift. Therefore it is suggested that the framework structure of imogolite is easily influenced by heating. Heat-treatment of allophane (Figure 2) and kaolinite (Figure 3) at 773 and 973 K gave rise to a new peak at 30 ppm indicating the five-coordinated Al. Gilson[16] reported that a novel peak with chemical shift of about 40 ppm in the $^{27}$Al MAS spectra of kaolinite treated at 700–1033 K may be assigned to five-coordinated Al.

Rocha previously conducted 3QMAS of kaolinite treated at 823–873 K and revealed the structure of five-coordinated Al.[17]

**$^{27}$Al MQMAS NMR of Imogolite.** Since line shape of quadrupolar nuclei includes the broadening effect generated by second-order quadrupolar interaction, the accurate chemical shift cannot be estimated based on a MAS spectrum. To estimate quadrupolar products and accurate chemical shifts of all Al sites, MQMAS spectra were acquired for all samples. It is difficult to perform this estimation based on only MAS spectra, because the combination of high magnetic fields and fast spinning rates more than 30 kHz are necessary to clearly distinguish all Al sites.[17] The 3QMAS spectra of imogolite before and after are shown in Figure 4. The chemical shift $\delta_{\mathrm{ISO}}$ and quadrupolar products ($P_{\mathrm{Q}}$) estimated from center of gravity according to eq 1 are summarized in Table 1. In eq 1, $\delta_{\mathrm{ISO}}$ and $\delta_{\mathrm{MAS}}$ are positions (ppm) of the center of gravity of contour plots projected on ISO and MAS axis, respectively and $S$ is the quantum number.[9] As seen from Table 1, the $P_{\mathrm{Q}}$ values for all sites are almost constant until 623 K, but clearly increase at temperatures above 623 K. Furthermore the chemical shift also changes significantly at 623 K. These results indicate that structural strain in imogolite clearly increase over 623 K. With the increase of temperature of heat-treatment, the area ratios of four- and five-coordinated

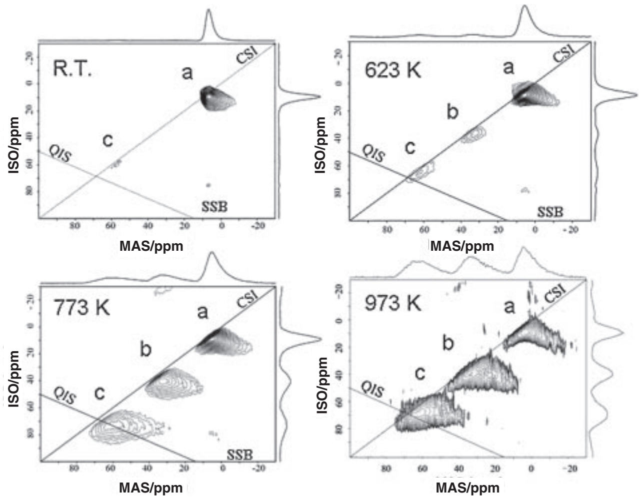

**Figure 4.** $^{27}$Al 3QMAS NMR spectra of imogolite unheated (R.T.) and heated at higher temperatures. QIS: quadruple induced shift. CSI: chemical shift. (a) Six-coordinate, (b) five-coordinate, and (c) four-coordinate.

**Table 1.** Isotropic Chemical Shift ($\delta_{\rm ISO}$) and Quadrupolar Products ($P_{\rm Q}$) for $^{[6]}$Al, $^{[5]}$Al, $^{[4]}$Al in Imogolite[a)]

| $T$/K | $^{[6]}$Al | | $^{[5]}$Al | | $^{[4]}$Al | |
|---|---|---|---|---|---|---|
| | $\delta_{\rm ISO}$ | $P_{\rm Q}$ | $\delta_{\rm ISO}$ | $P_{\rm Q}$ | $\delta_{\rm ISO}$ | $P_{\rm Q}$ |
| R.T. | 8.4 | 2.8 | — | | 59.0 | 2.7 |
| 623 | 8.0 | 2.7 | 36.0 | 3.3 | 63.7 | 2.6 |
| 773 | 7.4 | 3.6 | 36.7 | 3.9 | 65.8 | 3.8 |
| 973 | 7.2 | 3.7 | 38.0 | 4.3 | 66.7 | 4.1 |

a) $^{[6]}$Al, $^{[5]}$Al, and $^{[4]}$Al are six-, five-, and four-coordinated Al, respectively.

$$\delta_{\rm ISO} = \frac{17}{27}\delta_{\rm ISO} + \frac{10}{27}\delta_{\rm MAS} \tag{1}$$

$$P_{\rm Q} = \sqrt{\frac{170}{81}\frac{(4S(2S-1))^2}{(4S(4S+1)-3)}(\delta_{\rm ISO}-\delta_{\rm MAS})\frac{\nu_0{}^3}{10}} \tag{2}$$

Al peaks increase while that of six-coordinated Al peak decreases (Figure 1). These results show that the heat-treatment decompose the tubular structure of imogolite to generate amorphous phases with unsaturated coordinated Al (five-coordinated Al). MacKenzie has suggested that dehydroxylation induced by single-tube fracture mechanism occurs during thermal decomposition of imogolite and the five-coordinated Al is predominantly generated.[14] In the MQMAS measurement, projection to the ISO axis became a high-resolution spectrum due to the narrowing caused by removal of second nuclear quadrupole interactions. The spectrum peak of projected MAS axis is observed as an asymmetric line, resulting from the second nuclear quadrupole interactions. However, in the spectrum projected ISO axis it was a symmetric line, as shown in Figure 4. From this MQMAS spectrum, values of the quadrupolar products ($P_{\rm Q}$) and the isotropic chemistry shift ($\delta_{\rm ISO}$) can be calculated (Table 1).

The spectrum obtained with MQMAS is distributed in the CSI and the QIS axes when the values of $\delta_{\rm ISO}$ and $P_{\rm Q}$ have a distribution as seen for the amorphous substances. It is observed in Figure 4 that the peaks of $^{27}$Al MQMAS spectra of heat-treated (623, 773, and 973 K) imogolite show the distribution along direction of the CSI axis. Furthermore, the distribution along the direction of QIS or MAS axis was added at high temperatures such as 773 and 973 K. The value of $P_{\rm Q}$ is related to the electric field gradient tensor which depends on the kinds of atoms around $^{27}$Al. It seems that the value of the electric field gradient tensor was greatly influenced by the temperature. From the MQMAS spectrum of this heat-treated imogolite (623, 773, and 973 K), each $^{27}$Al site became randomly distorted and non-uniform indicating the change to an amorphous structure.

The present study certainly proves the formation of five-coordinated Al during heat-treatment. Based on the upper field shift of six-coordinated Al, the tubular structure of imogolite would be completely decomposed at around 773 K. According to the above results, we speculate the decomposition mechanisms in the following manner. The original thin layer wall of imogolite is composed of Al and Si based monolayers. After heat-treatment, the thin layer of imogolite is decomposed to form separate Al and Si thin layers. Thus Al-based thin layers contain mainly four- and five-coordinated Al as we observed by $^{27}$Al NMR measurement. Such a structural change probably affects the acidity of imogolite. It can be expected that improvement of the catalytic activity in imogolite by heating is related to the formation of five-coordinated Al species.[5]

## Conclusion

In this study, we have acquired $^{27}$Al MAS and 3QMAS spectra of imogolite and also $^{27}$Al MAS NMR spectra of allophane and kaolinite for comparison to investigate local structural changes of imogolite during heat-treatment. Since imogolite showed a larger peak shift of six-coordinated Al unlike allophone, it can be concluded that the imogolite structure may be readily affected by heat-treatment. The 3QMAS spectra provide clear evidence for the formation of a five- and four-coordinated Al, produced by the decomposition of six-coordinated Al. The chemical shifts of all peaks after heating above 623 K were observed for imogolite and these results indicate the formation of the amorphous structure by the decomposition of the tubular structure.

## Supporting Information

$^{29}$Si MAS NMR spectra and XRD patterns for as-prepared or heat-treated imogolite catalysts. This material is available free of charge on the Web at: http://www.csj.jp/journals/bcsj/.

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