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Characterization of Metakaolinite with Multiple Quantum MAS NMR

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Abstract: Metakaolinite produced by thermal transformation from kaolinite was studied by ^{27}Al multiple quantum magic angle spinning (MQMAS) NMR technique in addition to 1-dimensional ^{27}Al and ^{29}Si MAS NMR. Our results confirm that 4-, 5-, 6-coordinated aluminum sites co-exit with some distribution of isotropic chemical shifts. This is consistent with amorphous character of metakaolinite observed with X-ray diffraction. In addition, characterization with MQMAS is briefly discussed in comparison with other NMR techniques to identify different aluminum sites especially when peaks are severely overlapped in 1-dimensional ^{27}Al MAS NMR spectra.

INTRODUCTION

Although there is still a dispute over the thermal transformation sequence of kaolinite to mullite, it is generally accepted that the transformation occurs through several stages.[1-6] Kaolinite and mullite are crystalline, but intermediate materials produced by heating the kaolinite sample at the temperature of 550 ~ 900°C are amorphous and show only broad halos in X-ray diffraction (XRD) data.[1-2] Initial stage of the transformation is known to involve dehydroxylation of kaolinite producing metakaolinite.[1-6] The microscopic structure of this metakaolinite phase is reported to be retained up to about 900°C[4-5] but it is hard to confirm it with XRD due to amorphous property. Fortunately, all these materials are composed of aluminum, silicon, oxygen, and hydrogen, of which aluminum and silicon are frequently employed to get structural information on solid state samples by NMR techniques.[7] In this report, the annealing temperature range, over which the metakaolinite phase exists in our samples, is confirmed from 1-dimensional ^{27}Al and ^{29}Si MAS NMR spectra. In the 1-dimensional ^{27}Al MAS NMR of metakaolinite peaks are severely overlapped, therefore,

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multiple quantum MAS (MQMAS)[8] NMR is applied to the metakaolinite samples for better identification of the aluminum sites. In addition, other NMR techniques[9-11] to distinguish aluminum sites are discussed in comparison with MQMAS in practical aspects.

EXPERIMENTAL

Materials

Kaolinite powder sample was obtained from the Kampaku mine. For the thermal transition study, the sample was heated with an electric furnace in air at the rate of 10°C/min. up to a certain temperature such as 630, 840, 900, 960, 1020, 1120, 1200 and 1240°C and held for 30 mins. at that temperature and then cooled down to room temperature in air by turning off the heater power. All NMR spectra of the sample were taken at room temperature.

NMR Spectroscopy

All the NMR experiments were carried out on a DSX 400 Instrument (Bruker Analytik GmbH, Germany) with a 9.4 Tesla wide-bore magnet except the MQMAS experiments at 11.7 Tesla. Solid state ^{27}Al and ^{29}Si NMR spectra were acquired with a CP-MAS probe equipped with 4 mm rotors. Typical sample spinning rate was 13 – 14.5 kHz and its stability was within ± 4 Hz. Solution 90° pulse length for ^{27}Al was 5 μs and 0.7 μs pulse length and 2 s repetition delay were used for obtaining ^{27}Al spectra. 1.2 μs pulse length and 20 s pulse repetition delay were employed for ^{29}Si NMR and the 90° pulse length for ^{29}Si was 4.5 μs.

For MQMAS 2D experiments, a spinning rate of 30 kHz with a 2.5 mm rotor were used on the DSX 500MHz instrument at the Bruker Analytische Messtechnik GmbH, Silberstreifen, Germany. The first and second pulse length in the two pulse sequence was 1.5 and 0.55 μs, respectively, and t1 was increased in step of 3 μs up to 99 μs with an initial value of 3 μs for MQMAS spectra. Spectral width was 500 and 30 kHz for F2 and F1 dimension, respectively. There are several pulse sequences which can be used for MQMAS experiments.[12,13] Among them we chose a simple two pulse sequence for the experiments at 400MHz and an additional zero quantum filter after the two pulses was applied to the experiments at 500MHz. MQMAS technique uses an indirect detection method which observes a forbidden transition indirectly.[12-15] Signals of higher order are smaller than those of lower order[12] so that all our MQMAS data were taken from triple quantum transition. Other transitions can be observed *via* different phase cycling.[12-13] In addition to ordinary double Fourier transformation for 2-dimensional data, shearing was applied to get the final 2-dimensional processed spectra.[12,13,15] This shearing amount is 19:12=F2:F1 for triple quantum transition for nuclei of $I = 5/2$.[15] Chemical shifts of ^{27}Al and ^{29}Si NMR were referenced to external 1 M aqueous solution of $AlCl_3$ and neat tetramethylsilane (TMS), respectively.

RESULTS AND DISCUSSION

In Fig. 1, representative ^{27}Al and ^{29}Si MAS NMR spectra of kaolinite, mullite and intermediate materials produced by heating kaolinite are shown. Our spectra are similar to previously reported spectra.[1,3-5] When kaolinite was heated at 630°C, ^{29}Si NMR peak was broadened and upfield shifted and ^{27}Al NMR peak was also broadened and seems to have three singularities. The ^{27}Al NMR spectra do not change much up to 900°C while ^{29}Si peak starts to split. According to previous NMR results,[1-6] all these results indicate that our samples are in metakaolinite phase between 630 and 900°C, which was produced by dehydroxylating kaolinite. Three singularities in ^{27}Al spectra were assigned to 4, 5, and 6 coordinated aluminum species[1,3] or 4 and 6 coordinated aluminum species[4] from chemical shift values in previous reports. Thus, it is not certain if they are from three different coordinated aluminum species or two sites with powder patterns broadened by the second order quadrupolar line-broadening interaction. To distinguish these two possibilities, MQMAS pulse technique was employed. The MQMAS spectrum of the metakaolinite sample prepared at 630°C is displayed in Fig. 2 which clearly manifests three peaks. The upper and left projection are the ordinary MAS spectrum and the second order quadrupole interaction broadening depleted spectrum, respectively. The broad peak widths of the left projection spectrum suggest distribution of chemical shifts for each peak, which is consistent with amorphous characters observed in the XRD results. The contour plot also indicates three singularities in the 1-dimensional spectrum are indeed from three different sites. If there are only two sites, the left projection spectrum would have only two peaks and the contour spectrum would have two contours elongated along F2 axis instead of three relatively rounded shapes. The observed gravity centers of three peaks versus the left projection axis are -5, -38, -70 ppm. On the other hand, those versus the upper projection axis are 0, 28, 53 ppm. From these values, isotropic chemical shifts, 2, 28, 51 ppm, were calculated according to reference 15. These values correspond to hexagonal, pentagonal, and tetragonal coordinated aluminum species, respectively. Our MQMAS results show that this technique is much better to distinguish aluminum sites unambiguously than 1-dimensional MAS. Another advantage is that isotropic chemical shifts, which do not vary with magnetic field strength, can be obtained without spectrum simulation. Information on structural distribution is also demonstrated as broadening of contour line along F1 axis. Ordinary MAS or CP/MAS probe can be used for MQMAS experiments; however, spinning rates should be faster than the maximum isotropic peak distance for good results. Our attempt to use the CP/MAS probe with maximum spinning rate of 15 kHz was not as good as that with 30kHz or higher spinning rate for metakaolinite sample. However, for the sample with smaller isotropic peak distances than

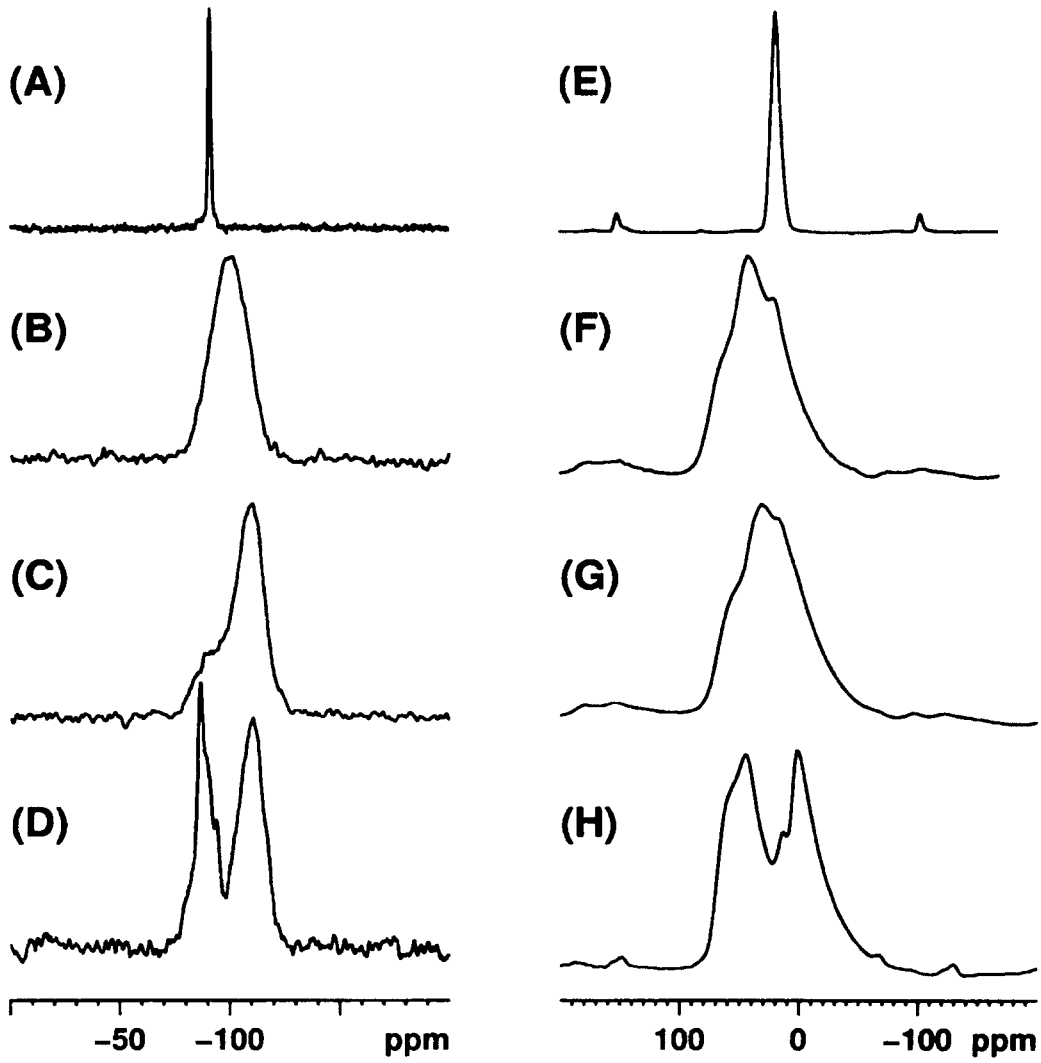

Fig. 1. ^{29}Si MAS spectra of (A) kaolinite, (B) intermediate sample (metakaolinite) prepared by heating kaolinite at 630°C, (C) intermediate sample (metakaolinite) prepared by heating kaolinite at 900°C, (D) mullite sample prepared by heating kaolinite at 1200°C. ^{27}Al MAS spectra of (E) kaolinite, (F) intermediate sample (metakaolinite) prepared by heating kaolinite at 630°C, (G) intermediate sample (metakaolinite) prepared by heating kaolinite at 900°C, (H) mullite sample prepared by heating kaolinite at 1200°C.

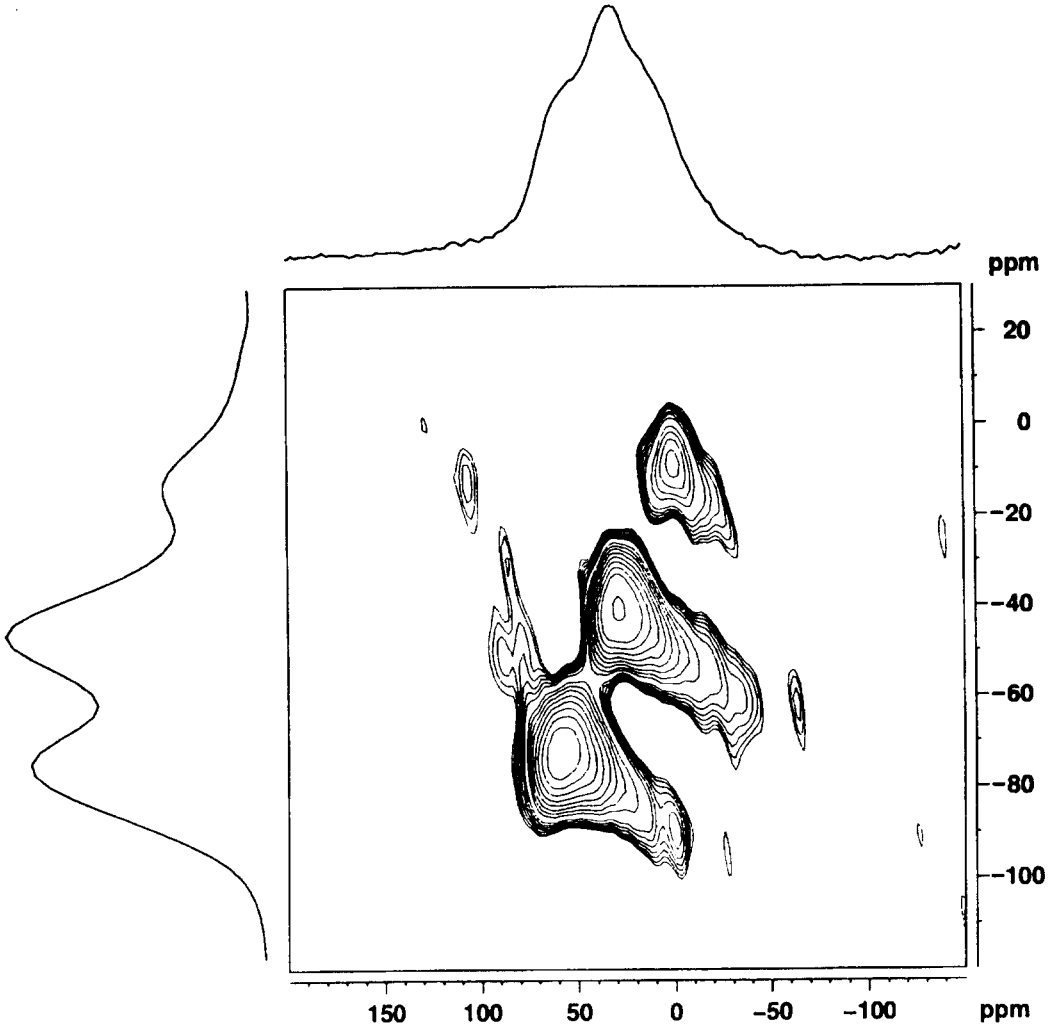

Fig. 2. 27Al MQMAS spectrum of the intermediate sample (metakaolinite) prepared by heating kaolinite at 630°C obtained at 11.7 T and sample spinning rate of 30 kHz.

8kHz, the CP/MAS probe with 15kHz maximum spinning rate was good enough. When the sample spinning faster than 15 kHz is recommended, only the sample with high sensitivity would work since a rotor size is smaller for faster spinning. Therefore, in general, it is more

economic to employ MQMAS than VAS (Variable Angle Spinning),[9] DOR (Double Rotation)[10] or DAS (Dynamic Angle Spinning)[10] techniques each of which requires a special probe specifically designed for it. Moreover, MQMAS experiments do not require computer simulation to find out isotropic chemical shifts or the number of peaks so that the data interpretation is simplified in comparison with nutation[11] and magnetic field dependence study with 1D MAS experiments. However, MQMAS requires higher RF power than ordinary MAS experiments to achieve reasonable results and works better for the sites with small quadrupole coupling constants than those with large second order quadrupole interaction.

In summary, MQMAS technique was applied to metakaolinite to probe the number of different aluminum sites. The results demonstrate that 4-, 5-, 6-coordinated aluminum sites are present in the sample and each site has some structural inhomogeniety. Advantages and disadvantages of MQMAS technique have also been discussed.

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