

Single- and Triple-Quantum ^{27}Al MAS NMR Study of the Thermal Transformation of Kaolinite

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The kaolinite–mullite reaction process has been studied by single- and triple-quantum ^{27}Al magic-angle spinning (MAS) NMR. All materials have also been characterized by ^{29}Si MAS NMR and powder X-ray diffraction. It has been shown that in order to record reliable ^{27}Al MAS NMR spectra it is important to use very fast sample spinning rates (which at 9.4 T are in excess of 30 kHz). The conflicting values previously reported in the literature for the four-, five- and six-coordinated Al metakaolinite populations are, at least in part, due to the relatively modest and different MAS rates and magnetic fields used by the authors. Triple-quantum ^{27}Al MAS NMR provides hard evidence for the presence in metakolinite of distorted (and distributed) four-, five-, and six-coordinated Al local environments. It also suggests that kaolinite calcined at 950 °C is a mixture of amorphous material, poorly crystalline mullite, and γ -alumina and a small amount of unreacted metakaolinite.

Introduction

Kaolinite is a dioctahedral (1:1) layer silicate with chemical formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. The kaolinite layer can be regarded as the result of a fusion of the $(\text{Si}_2\text{O}_5)_n^{2-}$ sheet and the $\text{Al}(\text{OH})_3$ (gibbsite) sheet. Upon calcination at 550–600 °C kaolinite undergoes a phase transformation to a highly disordered material known as metakaolinite.^{1,2} At ca. 950 °C metakaolinite transforms to mullite and γ -alumina. The kaolinite–mullite reaction series, one of the most important processes in the entire field of ceramic technology,¹ has been the subject of intense study since the work of Le Chatelier in 1887.

The first comprehensive ^{27}Al and ^{29}Si solid-state NMR studies of the kaolinite–mullite reaction series were published over 10 years ago.^{2–7} In some cases, when recording the NMR spectra the authors did not use correct spectral parameters. This is particularly true for ^{27}Al , a quadrupolar ($I = 5/2$) half-integer nucleus.⁸ On the other hand, the sample spinning rates achievable those days with commercial MAS NMR probes were rather modest, often less than 5 kHz. Now, metakaolinite is a disordered material containing a large dispersion of distorted four-, five-, and six-coordinated aluminum local environments. Hence, the ^{27}Al MAS NMR resonances are severely broadened by the second-order quadrupole interaction, and the spectral resolution is poor.⁸ Some of the Al local environments in metakaolinite are so distorted that any narrowing of the resonances they give only occurs when very fast spinning rates, in excess of 30 kHz (at 9.4 T) or so, are used. This explains, at least in part, the conflicting values reported in the literature for the four-, five-, and six-coordinated Al metakolinite populations.^{2,6,7}

In this study we wish to report ^{27}Al MAS NMR studies on kaolinite, metakaolinite, and related materials. The spectra have been recorded using very fast (up to 32 kHz) sample spinning rates. Some selected samples have also been studied by ^{27}Al triple-quantum MAS NMR spectroscopy, a recently introduced technique which affords quadrupolar nuclei spectra with un-

precedented resolution.^{9,10} All materials have been characterized by other techniques such as powder X-ray diffraction, ^{29}Si MAS NMR and Fourier transform infrared spectroscopy. Since these results (obtained on the same samples) have already been reported,² here we shall not present them in detail.

Experimental Section

A highly crystalline (Hinckley index 1.24) Cornish kaolinite containing 3 wt % mica, 0.18 wt % TiO_2 , and 0.40 wt % Fe_2O_3 was used, with 80% of the particles being 2 μm . The cation exchange capacity (measured upon saturation with ammonium acetate) was 4.0 mEq/100 g and the specific surface area (N_2) was ca. 10 $\text{m}^2 \text{g}^{-1}$. Kaolinite was calcined in air for 1 h at temperatures up to 1000 °C.

The ^{27}Al MAS NMR spectra were recorded at 104.3 MHz on a (9.4 T) Bruker MSL 400P spectrometer. Single-quantum (“conventional”) ^{27}Al MAS NMR spectra were measured using short and powerful radio frequency (rf) pulses (0.6 μs , equivalent to 10° pulse angle), spinning rates of 5–32 kHz, and a recycle delay of 1 s. Chemical shifts are quoted in ppm from $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$. The triple-quantum (3Q) ^{27}Al MAS NMR spectra were recorded with rf magnetic field amplitudes of ca. 150 and 280 kHz on, respectively, 4 (MAS at 15 kHz) and 2.5 mm (MAS at 30 kHz) Bruker double-bearing probes with a 2.5 s recycle delay. Because in kaolinite the ^1H – ^{27}Al dipolar coupling is strong, the single and the triple-quantum spectra were recorded with high-power proton decoupling. For the 3Q spectra, 128 or 256 data points were acquired in the t_1 dimension in increments of 8 (kaolinite) and 4 μs (calcined materials). To produce pure absorption line shapes in the 3Q MAS spectra, the optimum conditions for excitation and transfer of the ($\pm 3\text{Q}$) coherences using a simple two-pulse sequence¹⁰ were optimized on the very samples studied. The phase cycling was composed of six phases for the selection of 3Q coherences. This phase cycling was combined with a classic overall four-phase cycle in order to minimize phase and amplitude missettings of the receiver. The ppm scale was referenced to ν_0 frequency in the ν_2 domain and to 3 ν_0 in the ν_1 domain (reference $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$).

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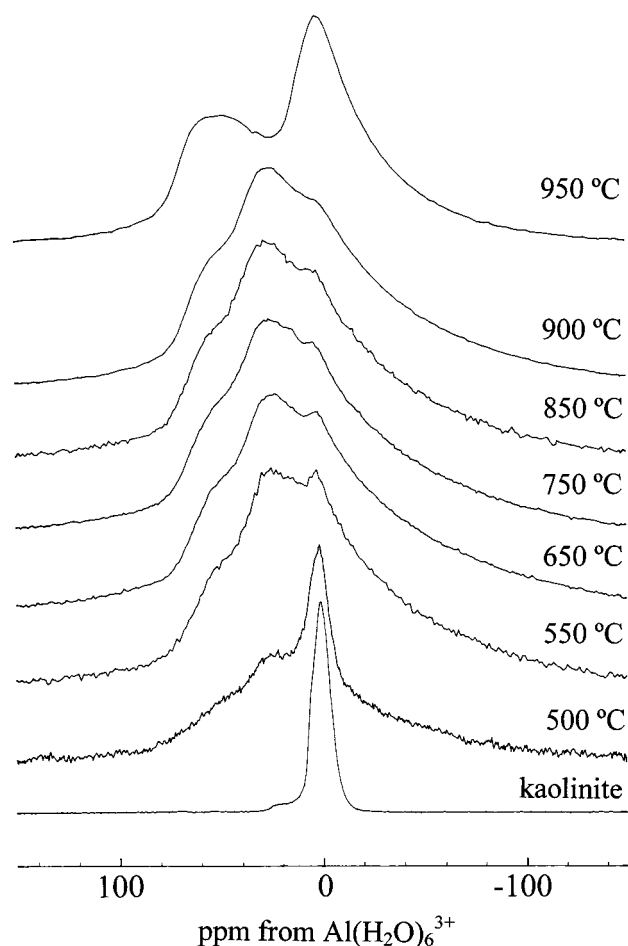


Figure 1. Single-quantum ("conventional") ^{27}Al MAS NMR spectra of kaolinite and kaolinite materials calcined at the temperatures indicated.

Results and Discussion

Figure 1 shows central-transition ("conventional") ^{27}Al MAS NMR spectra of kaolinite and kaolinite samples calcined at temperatures in the range 550–950 °C. Kaolinite gives a single peak centered at about 1 ppm. The structure of kaolinite calls for the presence of two crystallographically inequivalent Si sites and Al sites.¹¹ In accord, the ^1H - ^{29}Si MAS NMR spectrum of highly crystalline and pure kaolinite specimens (including the one studied here) give two resonances.¹² Moreover, although not entirely conclusive, a previous ^{27}Al satellite transition MAS (SATRAS) NMR¹³ study found some evidence for the presence of two Al species in kaolinite.¹⁴ We have reexamined this problem by ^{27}Al 3Q MAS NMR, using fast (32 kHz) sample spinning, high-power proton decoupling, and a very strong (ca. 280 kHz) B_1 rf field. The spectrum in Figure 2 contains a single peak, suggesting the presence of a single slightly distributed six-coordinated Al site with an average quadrupole coupling constant estimated to be¹⁵ in excess of 3 MHz. This distribution precludes the observation of the two distinct kaolinite six-coordinated Al species.

The decomposition of kaolinite to metakaolinite begins at about 500 °C (Figure 1). This is also confirmed by ^{29}Si MAS NMR and powder XRD (not shown).² At 550–600 °C, only traces of kaolinite are present in the samples. In the range 650–900 °C the ^{27}Al MAS NMR are very similar, containing three main peaks at ca. 4, 25, and 53 ppm assigned to six-, five-, and four-coordinated Al, and displaying a broad, low-frequency tail extending down to ca. 200 ppm. The ^{27}Al MAS NMR spectrum

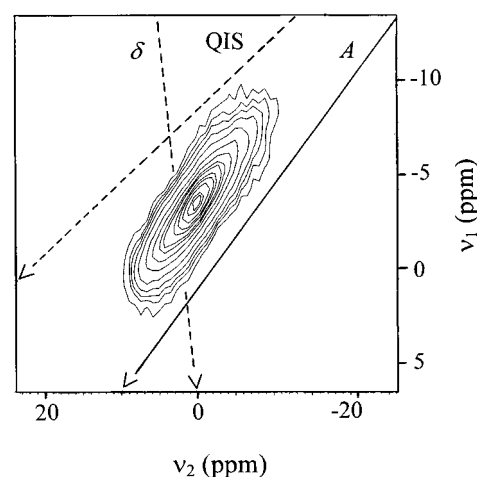


Figure 2. ^{27}Al 3Q MAS NMR spectrum of kaolinite recorded with a 30 kHz spinning rate and high-power proton decoupling. A depicts the anisotropic axis while QIS and δ denote, respectively, the quadrupole induced shift axis and the isotropic shift axis.

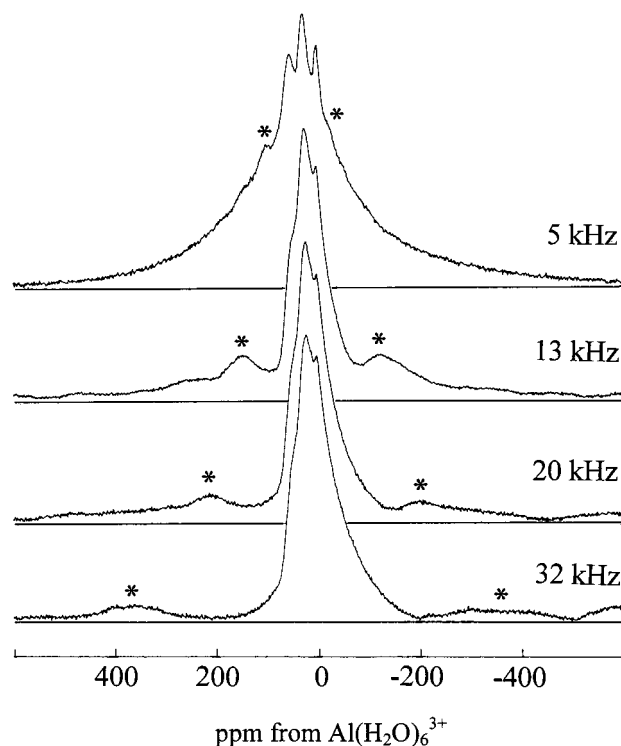


Figure 3. Single-quantum ("conventional") ^{27}Al MAS NMR spectra of metakaolinite (kaolinite calcined at 650 °C) recorded at the spinning rates indicated. Asterisks depict spinning side bands.

of metakaolinite changes considerably when the spinning rate increases (Figure 3). For example, comparing the 13 and 32 kHz spectra (Figure 4) we see that the intensity of the low-frequency tail increases considerably. In addition, the spectra baseline is clearly raised even with MAS at 20 kHz but is almost flat at 32 kHz. This is probably due to insufficient averaging of the second-order quadrupole couplings at slow spinning for some of the sites in the sample (similar effects have been observed on alumina samples by Kraus et al.,¹⁶ and here we follow closely their discussion). These sites with large quadrupole couplings contribute weakly to the center line because their MAS center band and spinning side bands are not well separated. Thus, their intensity is smeared out substantially. With increasing spinning rate, more and more of these sites are narrowed to their residual MAS line width, thus contributing

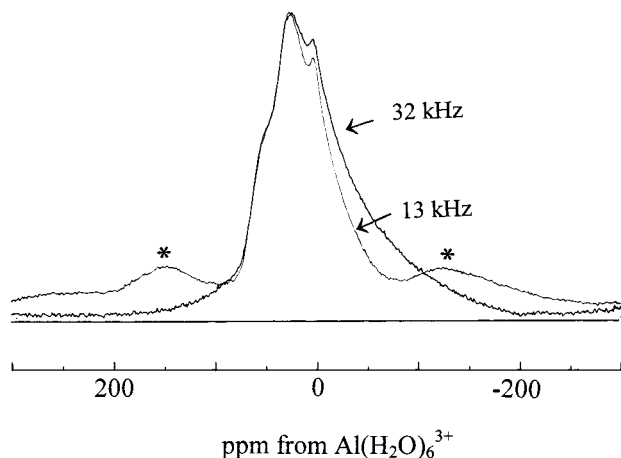


Figure 4. Single-quantum ("conventional") ^{27}Al MAS NMR spectra of meta-kaolinite (kaolinite calcined at 650°C) recorded with MAS at 13 and 32 kHz. Asterisks depict spinning side bands.

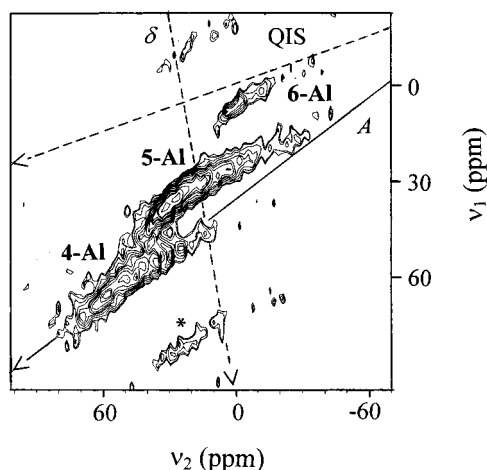


Figure 5. ^{27}Al 3Q MAS NMR spectrum of meta-kaolinite (kaolinite calcined at 750°C) recorded with a 15 kHz spinning rate. The asterisk depicts an F1 spinning side band given by five-coordinated Al.

to the observed center line, making it effectively broader. This process continues until the MAS rate exceeds the line width of the peak given by the site with the largest quadrupole coupling constant in the distribution.¹⁶ The conclusion is that very fast spinning rates are essential in order to obtain reliable ^{27}Al MAS NMR spectra of meta-kaolinite samples.

The ^{27}Al 3Q MAS NMR spectra of calcined kaolinite materials have been recorded with a spinning rate of 15 kHz and B_1 150 kHz. Although spectra have also been acquired with MAS at 30 kHz and B_1 280 kHz, they were of poor quality due to the small amount of sample (rotor volume about 12 mL) available on the 2.5 mm probe. The 3Q spectrum of meta-kaolinite (Figure 5) displays three peaks given by four-, five-, and six-coordinated Al. This is solid evidence for the presence in meta-kaolinite of such Al species. A previous ^{27}Al SATRAS¹³ study by Massiot et al.⁷ also provided some evidence that meta-kaolinite contains these three kinds of Al species. The 3Q NMR lines run approximately parallel to the anisotropic axis A. However, they are broadened along both the quadrupole induced shift axis (QIS) and the isotropic shift axis (δ), indicating a distribution in quadrupole interactions and chemical shifts. The average isotropic chemical shifts, d_{iso} , and quadrupole coupling constants, C_Q [in fact $C_Q(1 + \eta^2/3)^{1/2}$, where η is the asymmetry parameter] may be estimated from the F1 and F2 centers of gravity of the 3Q NMR lines.¹⁵ For four- and five-coordinated Al, respectively, the following values are obtained

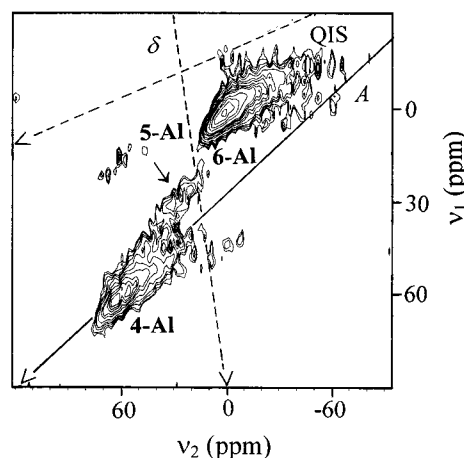


Figure 6. ^{27}Al 3Q MAS NMR spectrum of kaolinite calcined at 950°C and recorded with a 15 kHz spinning rate. The faint five-coordinated Al peak is probably given by a small amount of unreacted meta-kaolinite.

for d_{iso} and C_Q (assuming, for simplicity, $\eta = 0$): 63, 5.4, and 37 ppm, 5.0 MHz. In particular, an average isotropic chemical shift of 37 ppm is typical of five-coordinated Al. Along the F2 axis, the four-coordinated ^{27}Al 3Q MAS NMR resonance extends from ca. 80 to 5 ppm, while the five-coordinated Al signal covers the range ca. 50 to -35 ppm. The measured six-coordinated Al resonance ranges from ca. 10 to -20 ppm, F2. This spectrum indicates that in the single-quantum ("conventional") ^{27}Al MAS NMR spectrum the resonances given by the three distinct Al species overlap considerably. This is one of the reasons why the quantification of the three Al populations based on single-quantum ^{27}Al MAS NMR is a difficult task. ^{27}Al 3Q MAS NMR could, *in principle*, provide this information. However, the intensity of the resonances is not representative of the actual concentrations of the species because the excitation of the multiple-quantum coherences is strongly dependent on the NMR quadrupole frequency.¹⁵ In general, the detailed simulation of the 3Q MAS NMR spectra affords the correct signal intensities. However meta-kaolinite is a disordered material and the quantitative determination of the isotropic chemical shift and quadrupole parameter distributions can only be done using a nontrivial procedure devised by Fernandez, Amoureux, and co-workers.¹⁷ The strategy uses a leapfrog method to compute the evolution of the density matrix under the rf power and spinning conditions in the experiment, and it leads to the canonical representation shown in Figure 2 of ref 17. This corresponds to a direct inversion of the MQ MAS spectrum which may be achieved using a linear regularization method such as described by Zwaniger.¹⁸ In addition to this problem, in meta-kaolinite some of the local Al environments are so distorted that the strongest (<300 kHz) rf fields presently available on state-of-the-art MAS probes may not allow their excitation. For these reasons, here we do not offer any estimates of the different meta-kaolinite Al populations.

Powder XRD and ^{29}Si MAS NMR indicate that at ca. 950 to 1000°C meta-kaolinite transforms to a mixture of amorphous material, poorly crystalline mullite, and some γ -alumina.² The ^{27}Al MAS NMR spectra of kaolinite materials calcined in this temperature range (Figure 1) are very similar and display two broad peaks centered at ca. 3 and 48 ppm. This is to be expected in view of the samples composition.^{7,16} The ^{27}Al 3Q MAS NMR spectrum of a sample calcined at 950°C is shown in Figure 6. It contains broad peaks given by four- and six-coordinated Al. Important distributions of quadrupole parameters and isotropic chemical shifts are present for both resonances. The spectrum

contains also a small amount of five-coordinated Al, perhaps due to the presence of some unreacted metakolinite.

In conclusion, recording reliable ^{27}Al MAS NMR spectra of disordered materials with distorted local Al environments requires the use of very fast MAS. For metakaolinite in a 9.4 T magnetic field we have found that spinning rates in excess of 30 kHz should be used. Ideally, fast MAS should be combined with the highest magnetic field available. Triple-quantum ^{27}Al MAS NMR provides solid evidence for the presence in metakolinite of distorted (and distributed) four-, five-, and six-coordinated Al local environments.

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