

The Rehydration of Metakaolinite to Kaolinite: Evidence from Solid-State NMR and Cognate Techniques

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We have studied the process of rehydroxylation of metakaolinite to kaolinite by ^{27}Al and ^{29}Si MAS NMR in tandem with Fourier transform infrared spectroscopy, powder X-ray diffraction, thermogravimetric analysis, specific surface area measurement, atomic absorption spectrophotometry, and electron microscopy. The efficiency of the process strongly depends on temperature. The reaction is initiated at the edges of metakaolinite particles and is followed by diffusion of the water into their bulk. Regions of the metakaolinite structure, which locally retain the symmetry of kaolinite, act as nuclei for the reconstitution of kaolinite particles. The latter grow perpendicular to the c^* axis and their edges are parallel to those of metakaolinite, showing that rehydroxylation is a topotactic solid-state process. ^{27}Al and ^{29}Si MAS NMR reveal that metakaolinite is an ill-defined mixture of amorphous silica and alumina, and can be transformed into kaolinite by a correct choice of experimental conditions. NMR also shows that: (i) the 5-coordinated Al occupancy decreases with the reaction time faster than that of 4-coordinated Al, which supports the view that 5-coordinated Al in metakaolinite acts as a structural defect; and (ii) the 001 and 002 XRD reflections of kaolinite are only observed when the 5-coordinated ^{27}Al signal is faint. Further studies on the synthesis of kaolin (and indeed other clay minerals) are needed to assess the role of 5-coordinated Al in the process. © 1990 Academic Press, Inc.

Introduction

Kaolinite is a dioctahedral 1:1 layer silicate. The crystal chemical formula of the mineral is $\text{Si}_2\text{O}_5(\text{OH})_4\text{Al}_2$, which shows that the structure is anhydrous but contains hydroxyl groups. Upon thermal treatment kaolinite is transformed into metakaolinite which is semi-crystalline and very reactive. The question arises as to whether the reverse reaction is possible. Schachtschabel (1) reported that only a small amount of kaolinite was regenerated upon the cooling of metakaolinite. Barrett (2) suggested that in "clay bodies" fired at relatively low

temperatures, the clay minerals may be reformed by absorption of water with loss of durability of the product. Grim and Bradley (3) studied the rehydration of kaolin which had been heated at between 500 and 800°C for 1-3 hr and concluded that some water had been regained after the fired product had stood in air for 272 days. According to Comeforo *et al.* (4) the dehydroxylation of kaolinite "is not a normal equilibrium reaction and is not reversible." Later [(5) and Refs. therein], kaolinite and other clay minerals were calcined at temperatures between 500 and 1150°C and then rehydrated in saturated

steam. It was observed that rehydrated samples are "composed of clusters of rather smaller and irregular particles" than kaolinite or metakaolinite. The small size and irregular shape of the particles of rehydrated kaolinite could be caused by the breaking of the original particles along "lines of weakness between domains" (6). In a study of the thermal decomposition of kaolinite and halloysite Roy *et al.* (7) found that mild hydrothermal treatment of metakaolinite produced much smaller particles than the parent kaolinite and metakaolinite. They claimed that, although pseudomorphous with the original hexagonal plates, the particles of metakaolinite had "fine scale discontinuities." More recently, Kodama *et al.* (8) and Engelhardt and Roethe [cited in (9)] reported ^{27}Al and ^{29}Si magic-angle-spinning (MAS) NMR spectra of hydrated metakaolinite samples and found that some reconstitution of the parent kaolinite does take place. Unfortunately, both these papers studied only one hydrated sample each and gave no further analytical data.

Previous work on the synthesis of kaolinite minerals from different materials [e.g., (10)] suggested that, in order to understand the processes involved, it may be important to monitor the amounts of 4- and 6-coordinated Al. However, the conventional techniques of structural investigations are not sufficiently powerful to tackle the problem. By contrast, ^{27}Al and ^{29}Si MAS NMR, a newer technique, can directly monitor atomic environments in a variety of solids. In particular, the ^{27}Al MAS NMR allows the occupancy of Al in 4-, 5-, and 6-fold coordination to be followed as a function of reaction time.

We and others have recently studied (11–13) the process of dehydroxylation of kaolinite by ^{27}Al and ^{29}Si MAS NMR in tandem with other analytical techniques. The aim of this work is to examine the rehydration of metakaolinite using a combination of

several techniques, some of which (MAS NMR and FTIR) became available only recently.

Experimental

Samples. The highly crystalline [Hinkley index (14) 1.24] Cornish kaolinite contained 3 wt% mica and had analytical TiO_2 and Fe_2O_3 levels of 0.18 and 0.40 wt%, respectively. Circa 80% of the particles were smaller than $2\ \mu\text{m}$. The cation exchange capacity (ammonium acetate saturation) was 4.0 meq/100 g and the specific surface area (N_2) ca. $9.8\ \text{m}^2\ \text{g}^{-1}$. Metakaolinite was prepared by heating in air for 1 hr at 650°C , using bed depths of 6–7 mm. For hydrothermal treatment, 1.0-g samples of metakaolinite were mixed with $4\ \text{cm}^3$ of water and the suspensions stirred for 1–2 min before heating in an autoclave at 155°C for 1, 2, 7, or 14 days, at 200°C for 1 or 2 days, and at 250°C for 3 or 6 days. Some rehydrated samples were further calcined in air at different temperatures. In one experiment, 0.02 g of parent kaolinite was added as seeds to metakaolinite (1.0 g) and then rehydrated at 200°C for 2 days.

X-ray diffraction (XRD). Powder XRD patterns were acquired on a Philips automatic diffractometer fitted with a vertical goniometer using $\text{CuK}\alpha$ radiation selected by a graphite monochromator in the diffracted beam.

Fourier transform infrared (FTIR). Spectra in the region $4000\text{--}400\ \text{cm}^{-1}$ were recorded by using a Nicolet MX-1 Fourier Transform spectrometer and the conventional KBr technique. The pellets were outgassed at 160°C for 1 hr prior to obtaining spectra. The spectra were typically an average of 128 scans with 1-cm^{-1} resolution.

Atomic absorption spectrophotometry (AA). Silicon and aluminum absorption data were obtained with a Perkin-Elmer 2380 spectrophotometer.

Specific surface area (SSA). SSA (N_2)

(BET) were measured with a Micromeritics instrument.

Thermogravimetric analysis (TGA). TGA data were obtained with a Perkin-Elmer TGA 7 thermogravimetric analyzer equipped with a TAC 7/3 instrument controller and a 3700 data station. Samples were heated in nitrogen at a scanning rate of 5°C/min.

Magic-angle-spinning nuclear magnetic resonance. ^{29}Si MAS NMR spectra were measured at 79.5 MHz with a Bruker MSL-400 multinuclear spectrometer. An Andrew-Beams probehead was used with rotors spinning at 2.5–3 kHz with air as the driving gas. Radiofrequency pulses equivalent to 50° pulse angle were applied with a 30-sec recycle delay. ^{29}Si chemical shifts are quoted in ppm from external tetramethylsilane (TMS). ^{27}Al MAS NMR spectra were measured at 104.2 MHz with very short and powerful (0.6 μs , equivalent to 9° pulse angle) rf pulses and a 0.2-sec recycle delay. Rotors were spun in air at 4–5 kHz. Chemical shifts are quoted in ppm from the ^{27}Al resonance in external $\text{Al}(\text{NO}_3)_3$ (aq).

Transmission (TEM) and scanning (SEM) electron microscopy. TEM was performed with Hitachi H-7000 and Jeol JEM 200 CX electron microscopes at 75 and 200 kV, respectively, and SEM with a Jeol JSM-840 at 25 kV.

Results

FTIR and XRD. Two sensitive IR spectral regions may be used to monitor the transformation of metakaolinite into kaolinite (Fig. 1a and 1e): the OH stretching vibration (3800–3500 cm^{-1}) and the Si–O stretching and Si–O–Al combination bands (1300–400 cm^{-1}). The Al–O–H bending mode bands at 910 and 940 cm^{-1} are also useful. In comparison with the original kaolinite, the number of IR lattice vibration bands in metakaolinite (Figure 1a) is reduced and individual

bands are broadened. The characteristic Al–O₆ octahedron stretching band of kaolinite (540 cm^{-1}) is faint in metakaolinite and shifted to 560 cm^{-1} . Nevertheless, this reveals the presence in metakaolinite of some 6-coordinated Al and may be used to monitor the formation of the Al octahedral sheet of kaolinite upon rehydration.

The IR spectrum of the sample of metakaolinite treated hydrothermally at 155°C for 2 days (not shown) is very similar to that of metakaolinite. After 7 days under the same conditions (Figure 1b) the IR spectrum shows a new shoulder at ca. 890 cm^{-1} , a clearly more developed AlO₆ octahedron stretching and, in the OH stretching region, an increase in signal intensity. A sample treated at 200°C for 1 day gives a similar spectrum. Samples rehydrated at 155°C for 14 days display IR spectra (Fig. 1c) characteristic of kaolinite (Fig. 1e), although some bands are still either faint or unresolved and in the 3800–3500 cm^{-1} range only two signals (at 3690 and 3647 cm^{-1}) are present. These may be assigned to inner-surface hydroxyls and inner hydroxyls, respectively (15, 16). A band similar to that seen here at ca. 3430 cm^{-1} has been observed in silica gel powder samples (17) and assigned to hydrogen-bonded silanol groups. This band is also present in the IR spectra of synthetic kaolinite prepared from aluminosilicate gels (18). Samples treated at 250°C for 3 days or more give IR spectra (Fig. 1d) similar to the parent kaolinite. We note that the four OH stretching bands of kaolinite have reappeared and are completely resolved and unshifted. When the hydrothermally treated sample (155°C, 14 days) is recalcined in air at 400°C for 3 hr a broad band (not shown) in the OH stretching range is produced.

The XRD pattern of kaolinite given in Fig. 2g is characteristic of a highly crystalline kaolinite. XRD patterns of metakaolinite (Fig. 2a) exhibit only an intense broad background in the 2θ range of 18–28°. Samples

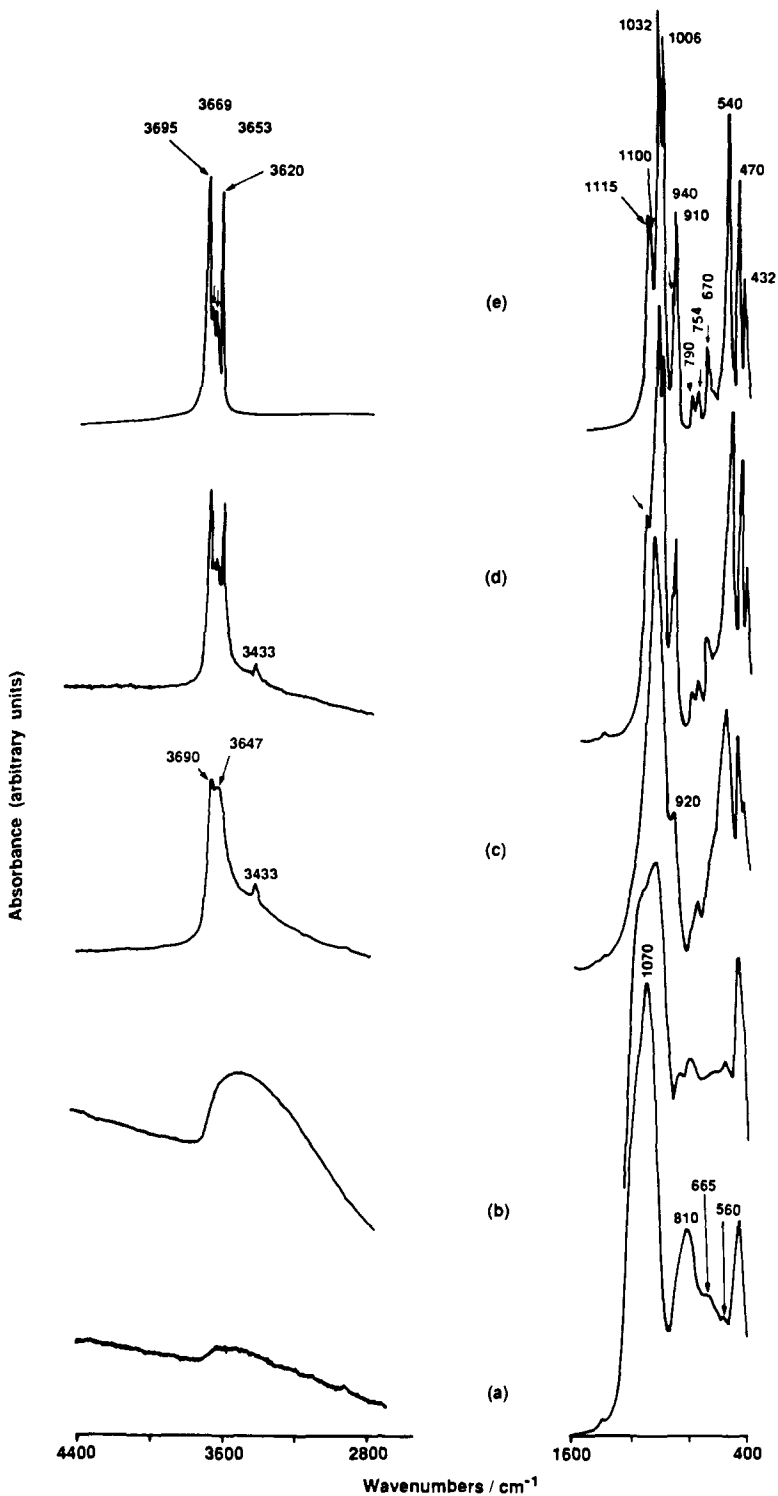


FIG. 1. FTIR spectra of (a) metakaolinite, (e) kaolinite, and samples treated hydrothermally (b) at 155°C for 7 days, (c) at 155°C for 14 days, and (d) at 250°C for 6 days, showing the lattice vibration region (right-hand side) and the OH stretching region (left-hand side); the sensitivity of the absorbance scale of the latter region is 1.3 times greater than that of the former.

hydrated at 155°C for 7 days still give meta-kaolinite-like patterns (Fig. 2b), but after 14 days at the same temperature the XRD trace is characteristic of poorly crystalline kaolinite and it is similar to that of halloysite (Fig. 2c). Hydrothermal treatment at 200°C for 2 days produces a specimen which gives the 001 and 002 kaolinite reflections at ca. 7.17 and 3.58 Å, respectively (Fig. 2d). There is also an intensity increase in the 2θ regions of 34–40° and 53–57°. Metakaolinite samples hydrated at 250°C for 3 or 6 days exhibit XRD traces (Fig. 2e) characteristic of a poorly crystalline kaolinite. The patterns clearly show that the rehydrated metakaolins are more disordered than the parent kaolinite from which they were derived. The (02, 11) (19–26° 2θ) kaolinite band of these samples displays the characteristic “sharp-rise–slow-fall” ascribed to layer stacking faults or to layer-to-layer shifting of the Al vacancies (see e.g., (19) and references therein). The band (20, 13) (34–40° 2θ), which has been associated with the presence of defects originated by random translation of layers, also lacks resolution. However, as the rehydration conditions become more severe (higher temperatures, longer times) the degree of crystal perfection increases.

Thermal data and specific surface area. The water content of samples hydrated at 155°C for different periods of time and at 250°C for 3 and 6 days was measured by TGA between 200 and 1000°C. The SSA of the same samples was also measured. Both sets of data are given in Table I. Metakaolinite and samples treated at 155°C for 2–14 days show an increase in water content and SSA with the reaction time. The parent kaolinite and the samples treated at 250°C for 3 or 6 days have a water content similar to the sample treated at 155°C for 14 days, but have lower SSA.

Electron microscopy. TEM and SEM suggest that hydrothermal transformation of metakaolinite into kaolinite occurs in, at least, four stages: (a) the changes are first

TABLE I
SSA AND WATER CONTENT, MEASURED IN TERMS OF WEIGHT LOSS, OF METAKAOLINITE, KAOLINITE, AND REHYDRATED KAOLINITE SAMPLES

Day (temperature/°C)	Surface area/m ² g ^{-1a}	Weight loss/% ^c
O (metakaolinite)	17	1.1
2 (155)	31	3.7
7 (155)	46	5.6
14 (155)	87	12.8
3 (250)	77	12.9
6 (250)	74	13.6
(kaolinite)	10 ^b	13.8

^a ± 4 m² g⁻¹.

^b ± 1 m² g⁻¹.

^c ± 0.1%.

noticeable after 2 days at 155°C, near the edges of the “metakaolinite” pseudo-hexagonal platelets, the general morphology remaining otherwise unchanged (Fig. 3a), while from Day 2 to Day 7 these changes spread across the sample; (b) after 7 days at 155°C treatment and even more so after 2 days at 200°C (Fig. 3b) very small (<90 nm) pseudo-hexagonal “particles” begin to emerge from the bulk of the “metakaolinite” plates (Fig. 3c); (c) between Day 7 and Day 14 these nuclei grow, reaching (Day 14) ca. 180 nm; (d) samples treated for 3 or 6 days at 250°C show that the nuclei continue to grow (<190–200 nm and >200 nm, respectively). SEM micrographs of metakaolinite and of a sample rehydrated at 155°C for 14 days (Figs. 4a and 4b, respectively) clearly show that the rehydrated metakaolinite particles (and aggregates) are much smaller than the parent metakaolinite ones. As shown in Figs. 3b and 3c, the hydrated kaolinite particles formed from metakaolinite grow perpendicular to the *c** axis and their edges are parallel to the parent kaolinite and metakaolinite. This indicates that rehydration is an *in situ* topotactic (solid-state) process.

²⁷Al and ²⁹Si MAS NMR. ²⁹Si MAS NMR

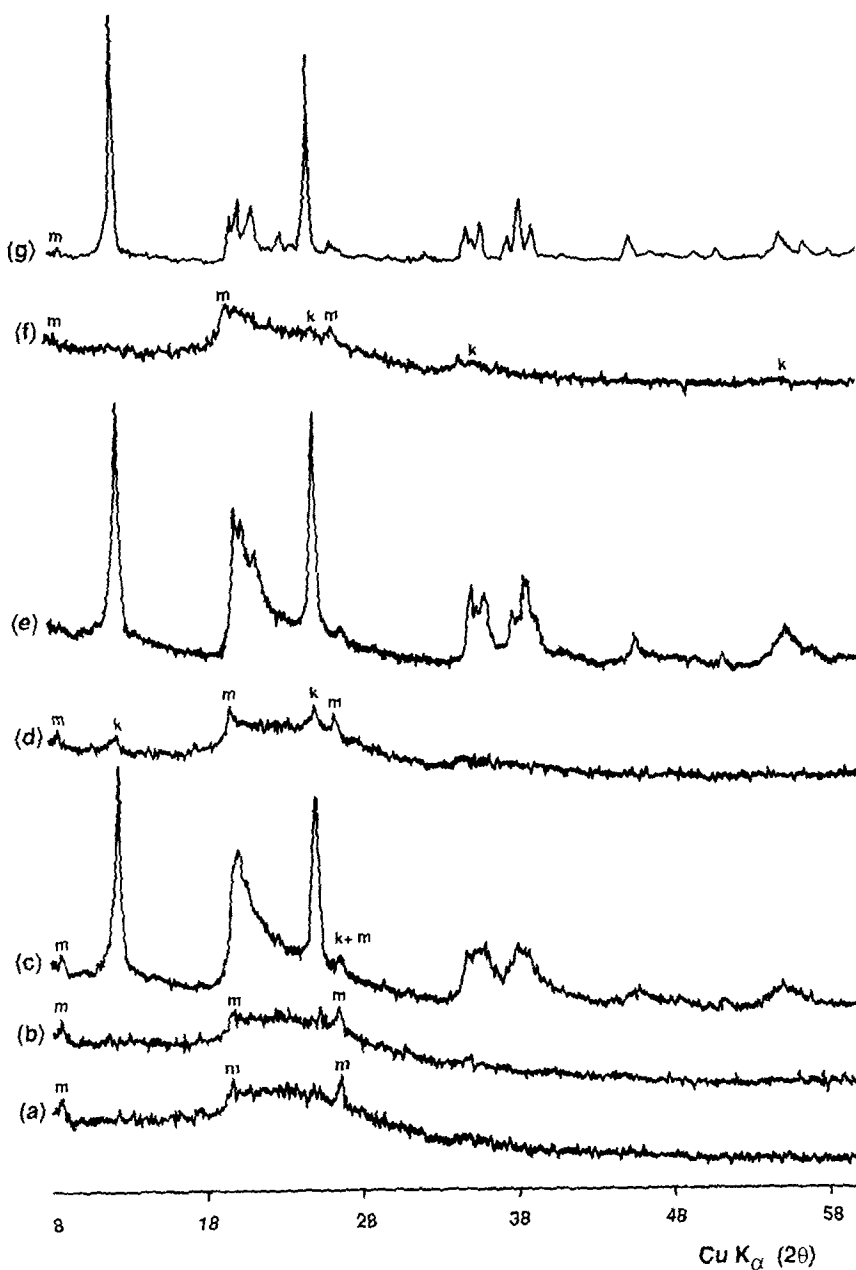
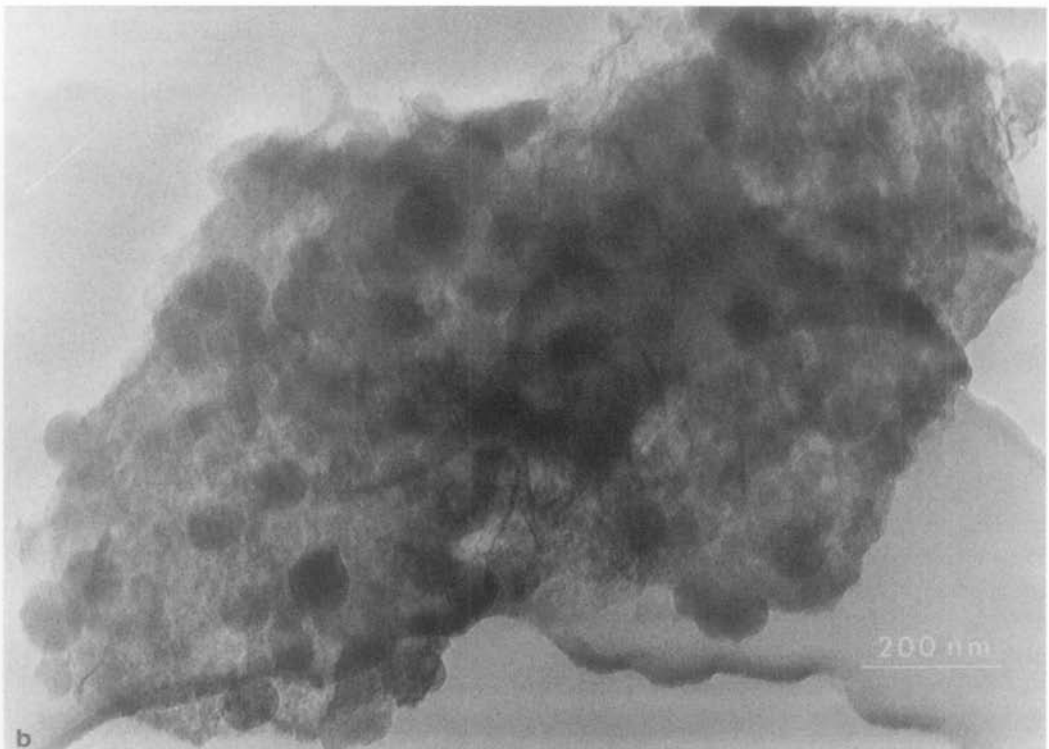
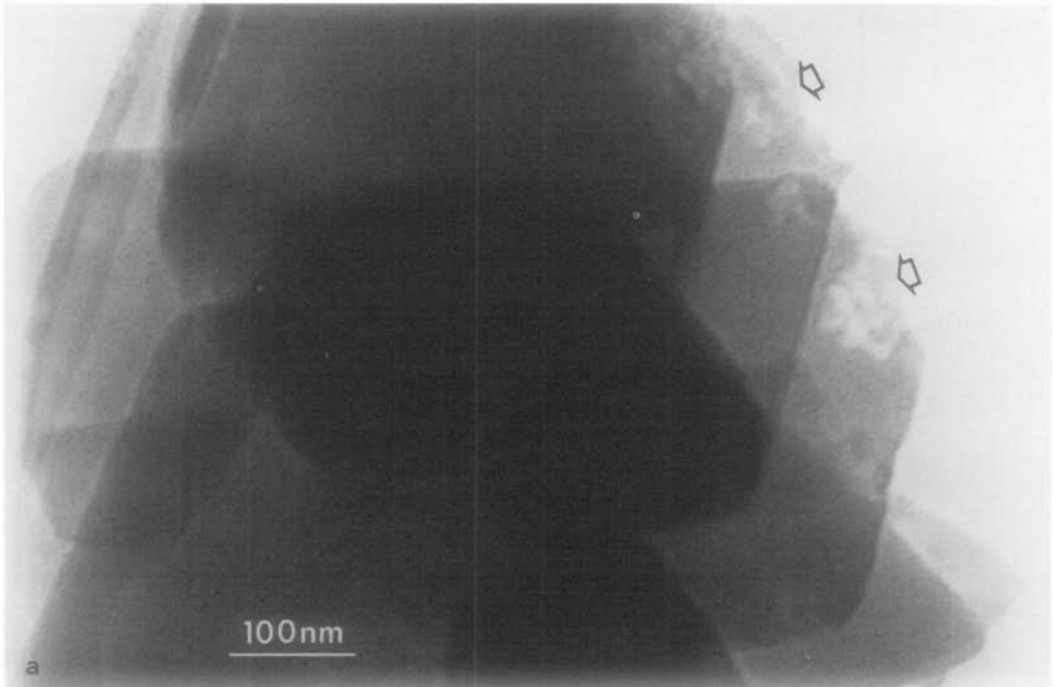


FIG. 2. XRD patterns ($\text{Cu K}\alpha$) of (a) metakaolinite, (g) kaolinite, and samples treated hydrothermally at 155°C for (b) 7 days, and (c) 14 days, (d) at 200°C for 2 days, and (e) at 250°C for 6 days, and (f) gives the XRD traces of a sample rehydrated at 155°C for 14 days and subsequently calcined in air at 500°C for 1 hr. The vertical scale in (g) is three times less sensitive than those in (a)–(f). The reflections given by the mica impurity and by kaolinite are labeled m and k, respectively.



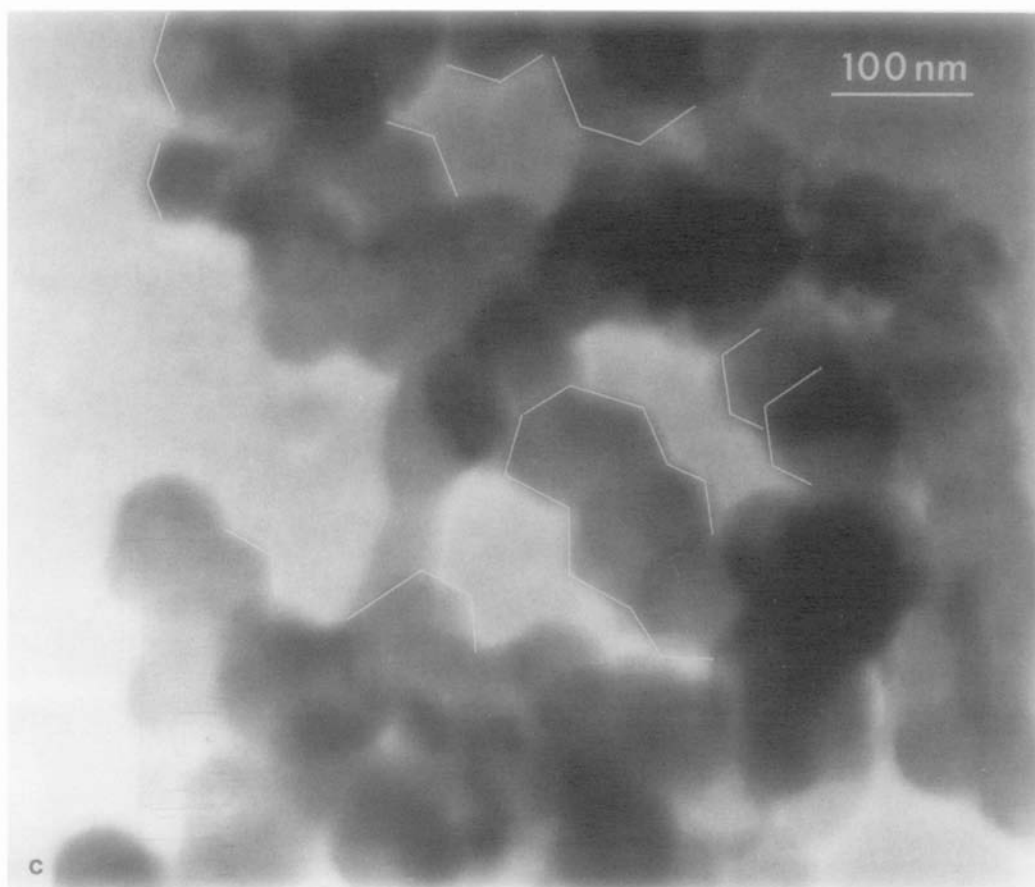


FIG. 3. TEM photographs of metakaolinite samples hydrothermally treated (a) at 155°C for 2 days and (b), (c) at 200°C for 2 days; adjacent tracings of photograph (c) highlight the features which show that rehydroxylation is a topotactic solid-state reaction.

spectra of the parent kaolinite, metakaolinite, and hydrated samples are given in Fig. 5. The spectrum of kaolinite (Fig. 5a) consists of a single resonance at -91.5 ppm with a full-width-at-half-maximum (FWHM) of 2.5 ppm, characteristic of layered silicates and assigned to a Q^3 Si environment (Si linked via oxygens to three other Si atoms). Metakaolinite displays a ^{29}Si signal centered at ca. -101 ppm with a FWHM of 20–21 ppm (Fig. 5b), indicating that the material is amorphous or pseudo-

amorphous (11–13). Hydrothermal treatment of metakaolinite at 155°C for 2–7 days causes no major changes in the ^{29}Si spectra, but similar treatment at 200°C for 2 days produces a spectrum (not shown), intermediate between those given in Figs. 5b and 5c, which displays an asymmetric signal with the center of gravity shifted toward -95 ppm and FWHM of 20–21 ppm. After 14 days of treatment at 155°C the ^{29}Si spectrum shows that important structural changes have occurred. A relatively sharp resonance

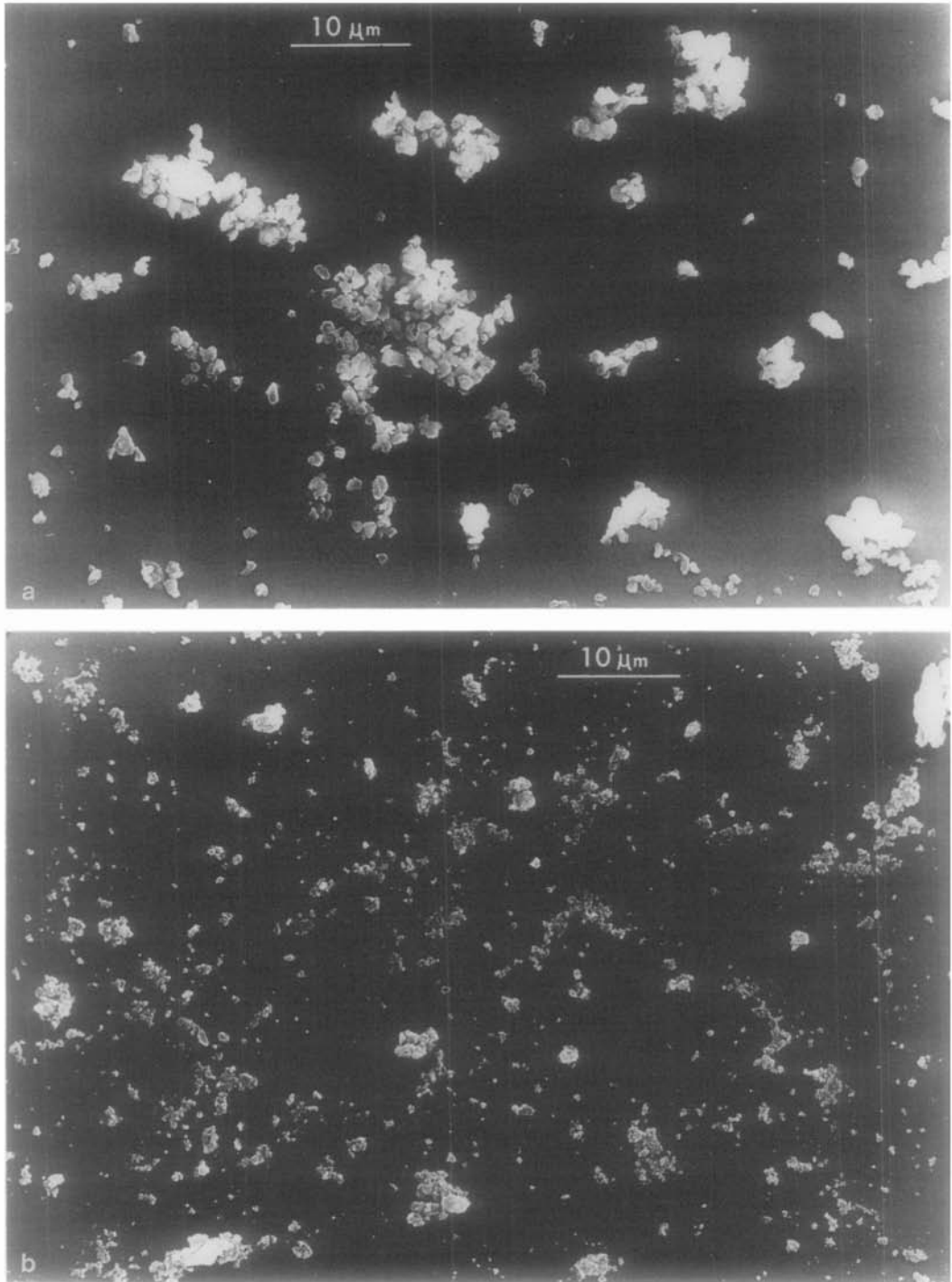


FIG. 4. SEM photographs of (a) metakaolinite and (b) sample rehydrated at 155°C for 14 days.

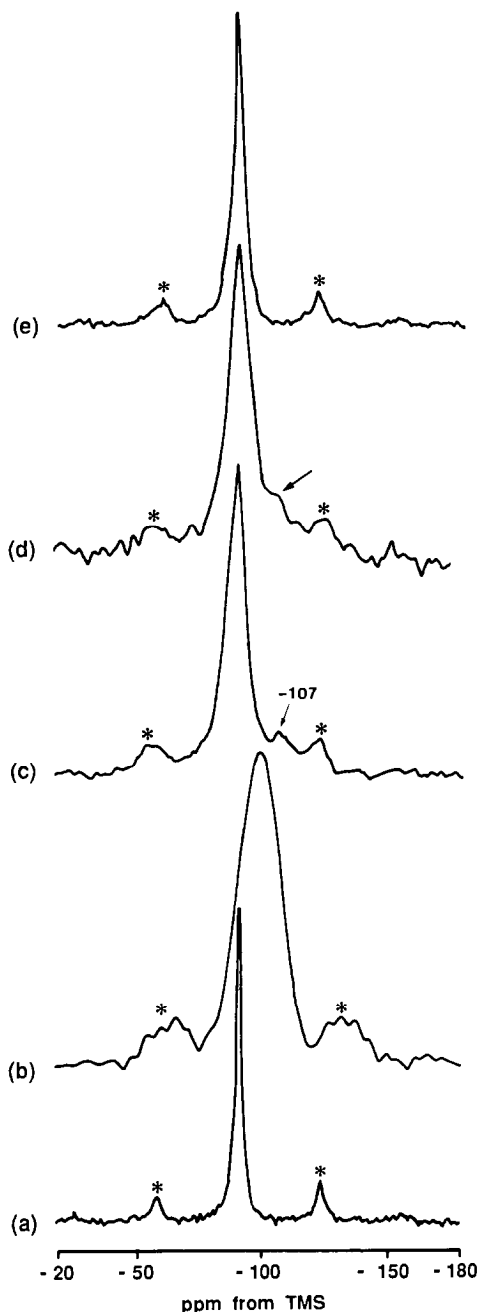


FIG. 5. ^{29}Si MAS NMR spectra of (a) kaolinite, (b) metakaolinite, and samples rehydrated (c) at 155°C for 14 days and (e) at 250°C for 6 days (3 days is very similar); (d) shows the spectrum of a sample rehydrated at 155°C for 14 days and subsequently calcined in air at 500°C for 1 hr. Asterisks denote spinning sidebands.

(FWHM ca. 8 ppm), centered at -92 ppm is accompanied by a much less intense resonance at ca. -107 ppm (Fig. 5c). The latter is typical of a Q^4 Si site and suggests the presence of ca. 5% silica in the hydrated material. When the same sample is recalcined in air at 400°C for 3 hr, the intensity of the -107 ppm resonance substantially increases (Fig. 5d) and the two resonances begin to coalesce. Samples hydrated at 250°C for 3 days do not display the -108 ppm resonance (Fig. 5e). Since no significant amounts (<1 mol %) of silicon and aluminum were found by atomic absorption in the filtered water after the hydrothermal reactions under these experimental conditions, most of this amorphous silica must have been transformed to kaolinite. At the same time, the resonance centered at -92 ppm narrows to ca. 5 ppm, which shows that the local order of the ^{29}Si sites approaches that observed in the parent kaolinite.

The ^{27}Al MAS NMR spectrum of kaolinite (Fig. 6a) contains one peak at ca. 0 ppm (FWHM = 12 ppm) assigned to 6-coordinated Al. Metakaolinite exhibits two other resonances (Fig. 6b), one at ca. 28 ppm, assigned to 5-coordinated Al (11–13, 20, 21), and the other at ca. 57 ppm, due to 4-coordinated Al. Hydrothermal treatment of metakaolinite at 155°C for 2–14 days converts 4- and 5-coordinated Al into 6-coordinated Al (Figs. 6c–6e), thus restoring kaolinite symmetry to the Al metakaolinite matrix. The plot given in Fig. 7 shows the dependence of the Al occupancy on the reaction time. The signal from 5-coordinated ^{27}Al decreases faster than the 4-coordinated one, and after 14 days the former signal is no longer present. The ^{27}Al spectra of samples treated at 200°C for 2 days (Figs. 8b and 8c) and 250°C for 3 days (Fig. 8d) confirm this trend. Although the transformation of 5- into 6-coordinated Al is statistically more favorable than the reaction of 4- to 6-coordinated Al, some 4-coordinated sites should also react to produce 5-coordinated Al. The trend

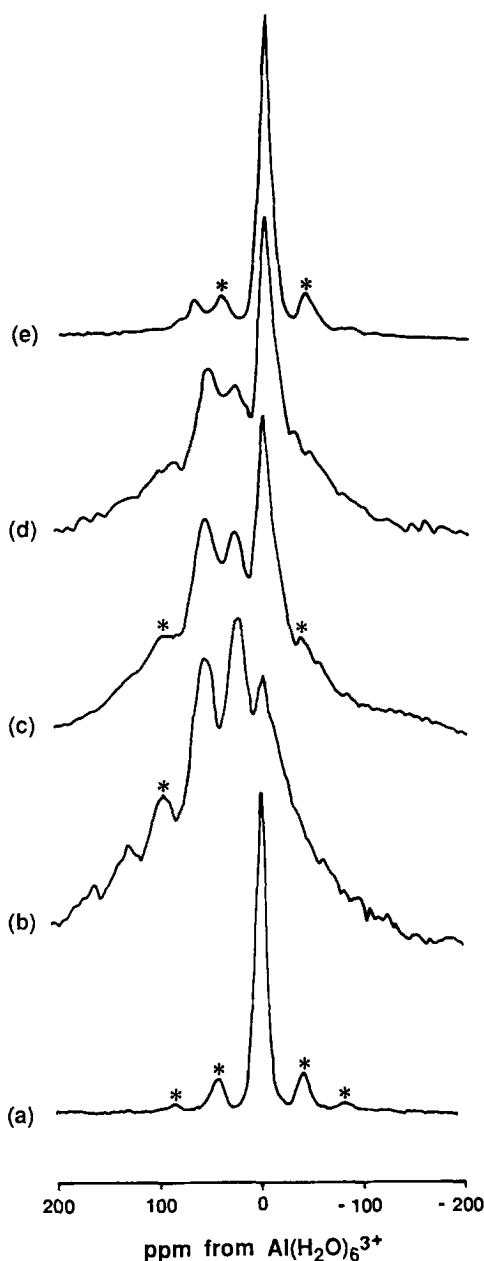


FIG. 6. ^{27}Al MAS NMR spectra of (a) kaolinite, (b) metakaolinite, and samples rehydrated at 155°C for (c) 2 days, (d) 7 days, and (e) 14 days. Asterisks denote spinning sidebands.

shown in Fig. 7 suggests that at least some 4-coordinated Al sites are less reactive than the 5-coordinated ones. This conclusion is

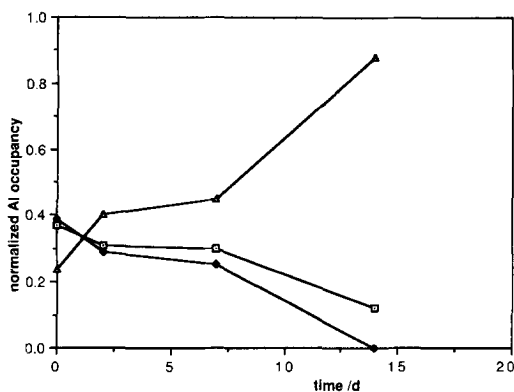


FIG. 7. The change of the 4- (squares), 5- (diamonds) and 6-coordinated (triangles) ^{27}Al populations as a function of the time of rehydration for a sample treated at 155°C . Deconvolutions were carried out with quasi-Gaussian lines (5–10% of Lorentzian character) over the range 120 to -60 ppm; the spinning sidebands were included in the simulations [further details of the deconvolution procedures are given in (11)].

supported by the careful examination of the ^{27}Al spectra. The 4-coordinated ^{27}Al resonance of specimens treated at 155°C for 14 days (Fig. 6e) and at 250°C for 3 days (Fig. 8d) is shifted from ca. 57 ppm (metakaolinite and other hydrothermally treated samples) to ca. 68 ppm. However, after treatment for 6 days at 250°C this signal is almost completely lost. The 6-coordinated Al signal is also slightly shifted from 0–1 to ca. 2 ppm. These facts are consistent with the presence of some amorphous alumina in partially hydrated samples. For comparison, the ^{27}Al spectrum of γ -alumina is given in Fig. 8e. There are two resonances at ca. 7 ppm and ca. 69 ppm. We have earlier suggested the presence of an amorphous alumina phase in metakaolinite (11, 12). Note that the shift of the 4-coordinated ^{27}Al resonance from ca. 57 to ca. 68 ppm could in principle also be due simply to the stabilization of much less distorted tetrahedral Al sites. However, this does not seem to be the case. Figure 9 shows the ^{27}Al MAS NMR spectra of samples treated at 155°C for 14 days and the recalculated in air at various temperatures. There

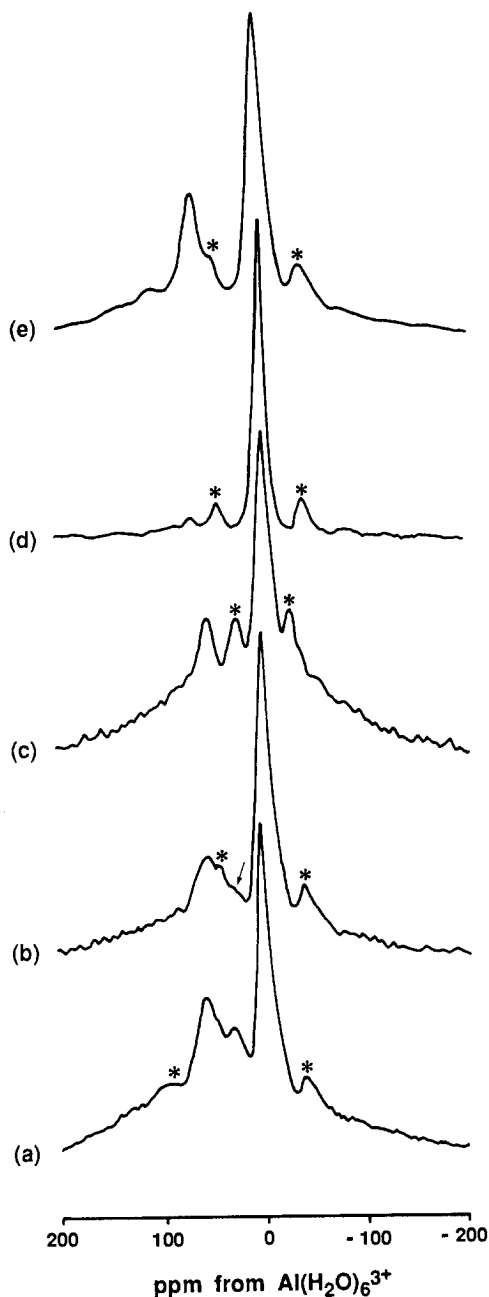


FIG. 8. ^{27}Al MAS NMR spectra of samples rehydrated at 200°C for (a) 1 day, (b), (c) 2 day, spinning rates of 4.5 and 2.8 kHz, respectively, and (d) at 250°C for 3 days. For comparison (e) shows the spectrum of γ -alumina. Asterisks denote spinning sidebands.

are two important differences between these spectra and the spectra of parent kaolinites (poorly and highly crystalline) calcined at the same temperatures (11): (a) the 5- (and 4-) coordinated Al appears much earlier in the recalced hydrated samples ($400/480^\circ\text{C}$), which is probably due, at least partially, to the smaller size of rehydrated metakaolinite particles and (b) hydrated samples recalced at $400\text{--}650^\circ\text{C}$ are much poorer in 5-coordinated Al and richer in 4- and in 6-coordinated Al. This further supports the presence of amorphous alumina in hydrothermally treated samples and, by implication, in metakaolinite. ^{27}Al MAS NMR shows that only hydrated samples which have little or no 5-coordinated Al (Figs. 6e, 8b, 8d, and 9b) exhibit the 001 and 002 kaolinite XRD reflection (Figs. 2c–2f).

Discussion

Our results show that the rehydration of metakaolinite to kaolinite is at least quasireversible. The EM and SSA measurements support the findings of Roy *et al.* (7). Hydrothermally treated samples have much larger SSA and smaller particle size than the parent kaolinite and metakaolinite from which they were derived. Recalcination of the rehydroxylated samples would produce a metakaolinite material which is likely to be more reactive than the metakaolinite from which it originates.

The changing particle morphology sheds light on the mechanism of hydrothermal transformation of metakaolinite into kaolinite and shows this to be a topotactic solid-state reaction. Three possible mechanisms can be envisaged for the rehydration process: (a) dissolution of metakaolinite particles followed by subsequent crystallization; (b) local dissolution of microregions of the metakaolinite particles followed by crystallization of small kaolinitic nuclei which then increase in size; (c) a purely solid-state process whereby chemical bonds are re-arranged; the structural transformations in

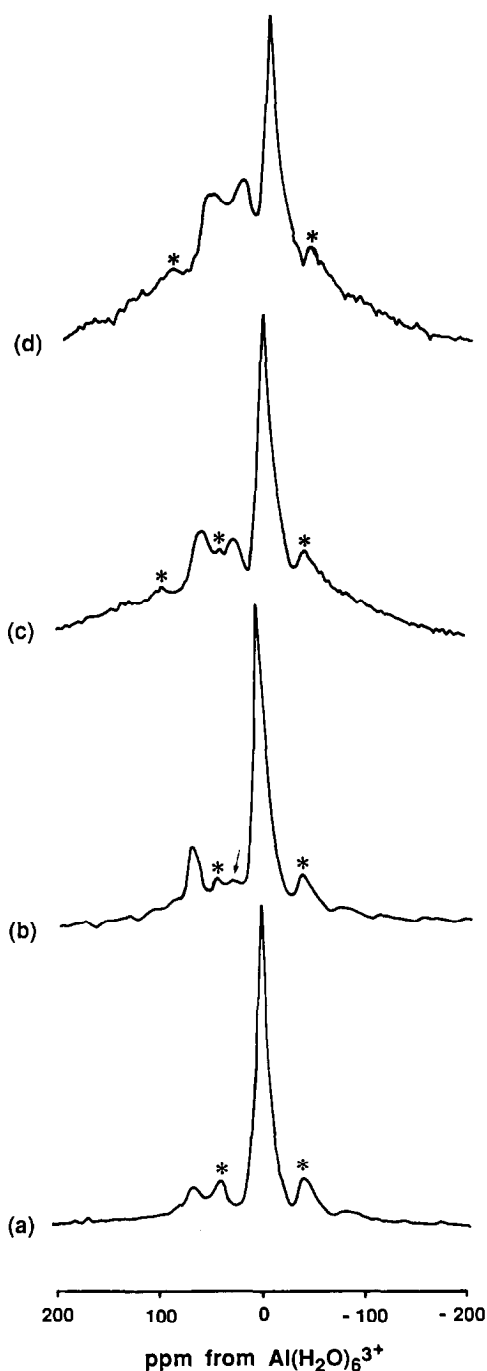


FIG. 9. ^{27}Al MAS NMR spectra of samples rehydrated at (a) 155°C for 14 days and calcined in air, (b) 400°C for 3 hr, (c) 500°C for 1 hr, and (d) 650°C for 1 hr. Asterisks denote spinning sidebands.

this case would probably occur first in regions of the metakaolinite *structure* that preserved the kaolinite symmetry (see below) and can act as germs for the nucleation process.

Chemical analysis of the reaction liquor prompts one to discard mechanism (a) since little or no Si or Al is found. TEM supports hypothesis (c): the small kaolinite crystals grow perpendicular to the c^* axis and their edges are parallel to the edges of the parent kaolinite and metakaolinite particles. This means that the symmetry along the a - b plane is similar: exactly what one would expect from a solid-state process.

The rehydroxylation mechanism we suggest in this paper bears some similarity to the proposed mechanism for *dehydroxylation* of kaolinite. Previous studies (22-24), suggested that dehydroxylation of kaolinite proceeds from the edges of the grains inward parallel to the (001) planes. Nonetheless, the presence of kaolinite germs in metakaolin will be responsible for differences between the rehydroxylation and dehydroxylation processes. Isothermal thermogravimetric studies (23) of the rehydroxylated material should provide a deeper understanding of the rehydroxylation process.

Earlier MAS NMR work on the structure and reactivity of metakaolinite (11-13) found some evidence for the presence of 5-10% amorphous silica and alumina in metakaolinite just above the onset of dehydroxylation. The present study provides further evidence for such segregation. We also suggested the presence in metakaolinite of structural regions preserving the symmetry of kaolinite. These could act as germs for the reconstitution of the parent kaolinite. When some of the latter was added to metakaolinite as seed, no improvement of rehydration was observed at 200°C after 2 days, which clearly shows that the regions of metakaolinite with kaolinite-like symmetry are a *structural* rather than a *separated* unreacted kaolinite phase.

It is interesting to consider the possible role of 5-coordinated Al in the rehydration process. In the first place, the NMR signal from 5-coordinated Al decreases more rapidly than the 4-coordinated Al signal. This is due not only to the statistical aspects of the rehydroxylation reaction but also to the presence of amorphous alumina. Nevertheless, there is another possible reason for this behavior. We have suggested (11, 12) that in metakaolinite 5-coordinated Al sites may act as structural defects and should be considered when discussing the reactivity of metakaolinite. Thus, we suggest that 5-coordinated Al sites in metakaolinite are more reactive than the 4-coordinated ones (not associated with the alumina phase). We note in passing that the 001 and 002 XRD reflections appear when the 6-coordinated Al signal is already well developed and the 5-coordinated Al signal is faint.

The importance of 6-coordinated Al in the starting material (not necessarily seed of kaolin itself) for the synthesis of kaolin minerals at low temperatures, and the strong dependence of the kinetics on the reaction temperature, has been emphasized in the literature [see, e.g., (10) and references therein]. It was suggested that the first step of the transformation is the "hydration" of the Al tetrahedra and their transformation into Al octahedra. Our work supports these early findings but also stresses that future studies on the synthesis of kaolin (and other clay minerals) should address the possible role of 5-coordinated Al. In conclusion, the rehydroxylation of metakaolinite to kaolinite bears remarkable similarities to reactions in which kaolinite is synthesized from gibbsite, pre-gibbsite gels, and bayerite (25), zeolites (10), montmorillonite (26, 27), and amorphous aluminosilicate gels (18).

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