

## The Rehydration of Metakaolinite to Kaolinite

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The dehydration of kaolinite to metakaolinite can be completely reversed; particles of rehydrated metakaolinite grow perpendicular to the  $c^*$  axis and their edges are parallel to those of parent metakaolinite and kaolinite, showing that the rehydration is a topotactic solid-state process.

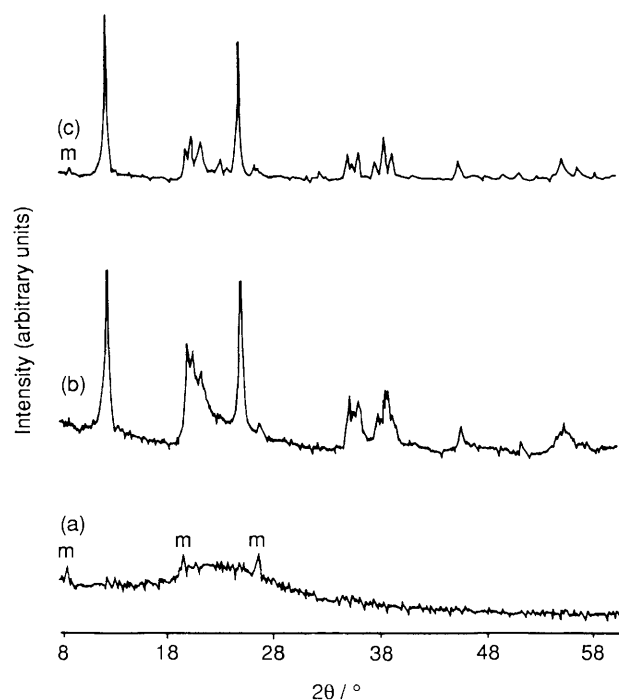
Kaolinite is a dioctahedral 1:1 layer silicate with the crystal chemical formula  $\text{Si}_2\text{O}_5(\text{OH})_4\text{Al}_2$ . The structure is thus anhydrous but contains hydroxy groups. Upon thermal treatment kaolinite is transformed into metakaolinite, a pseudo-amorphous material. The question arises as to whether the reverse reaction is possible. It has been suggested<sup>1-4</sup> that some reconstitution of the parent kaolinite does take place, although few experiments have been reported to substantiate this claim.

In order to understand the processes involved in the synthesis of kaolin minerals, it is important to quantify the different Al coordinations.<sup>5</sup> While the conventional techniques of structural investigation are not sufficiently powerful to tackle the problem,  $^{27}\text{Al}$  and  $^{29}\text{Si}$  magic-angle-spinning (MAS) NMR can directly monitor atomic environments in a variety of solids. We and others have recently studied the dehydration of kaolinite by  $^{27}\text{Al}$  and  $^{29}\text{Si}$  MAS NMR in tandem with other analytical techniques. We now report that the reaction can be readily reversed under mild hydrothermal conditions.

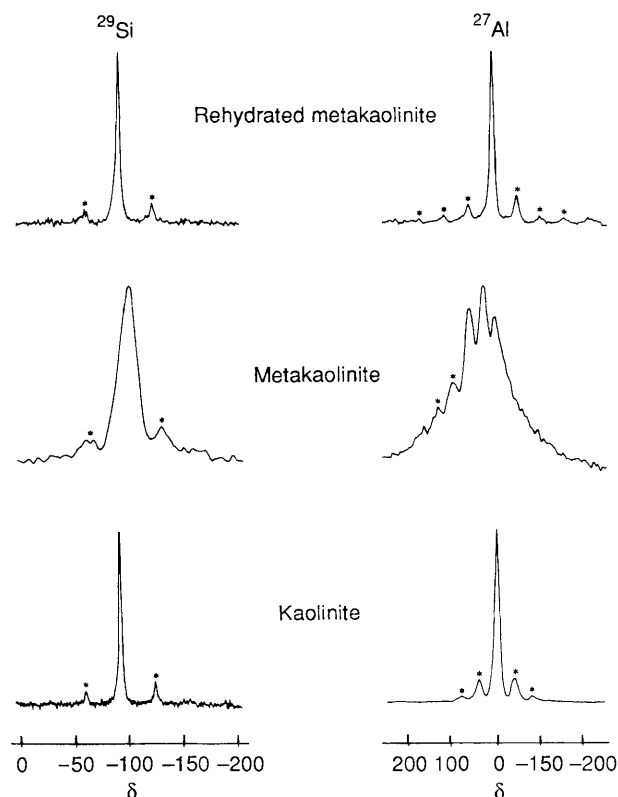
We have used a highly crystalline (Hinckley index<sup>9</sup> 1.24) Cornish kaolinite (sample 1) with 3 wt % mica and  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$  levels of 0.18 and 0.40 wt %, respectively. 1.0 g portions of metakaolinite were mixed with 4  $\text{cm}^3$  of water and the suspensions stirred for 1–2 min before being heated in an autoclave at temperatures between 155 and 250 °C for

different lengths of time. In one experiment, 1.0 g of metakaolinite was seeded with 0.02 g of parent kaolinite and then rehydrated at 200 °C for 2 days.

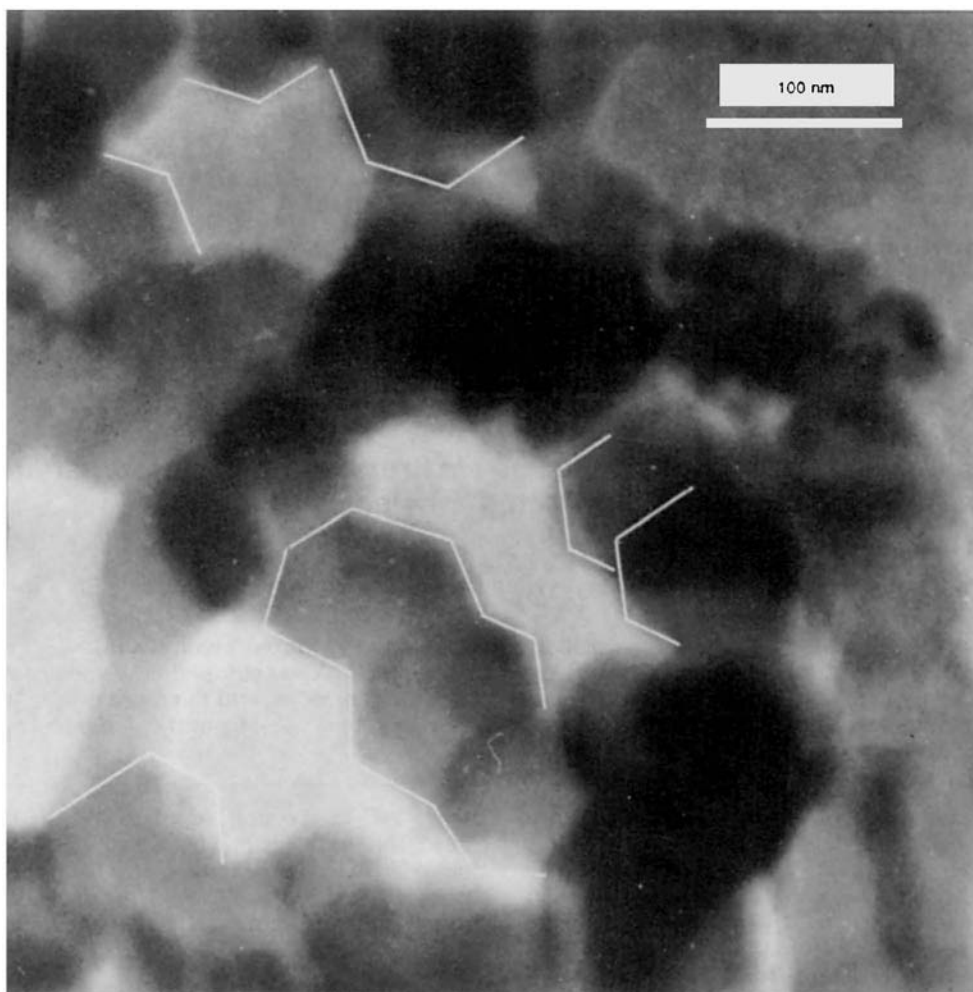
The X-ray diffraction (XRD) pattern of sample 1 shown in Fig. 1 is characteristic of a highly crystalline kaolinite, while metakaolinite (sample 2) gives only an intense broad background in the  $2\theta$  range of 18–28°. The XRD pattern of metakaolinite treated hydrothermally at 250 °C for 6 days (sample 3) shows that the rehydrated product is more disordered than the parent kaolinite: the (02,11) band at 19–26°  $2\theta$  exhibits the characteristic 'sharp-rise-slow-fall' shape ascribed to layer stacking faults or to layer-to-layer shifting of the Al vacancies.<sup>10</sup> The (20,13) band at 34–40°  $2\theta$ , associated with the defects caused by a random translation of layers, is also poorly resolved. The FT IR spectra (not shown) of samples 1 and 3 are very similar. In particular, the four OH stretching bands of kaolinite reappear completely resolved and unshifted. The water contents (measured by thermogravimetric analysis, TGA) of samples 1 and 3 are very similar (13.8 and 13.6 ± 0.1 wt %, respectively). The specific surface area (SSA,  $\text{N}_2$ , Brunauer–Emmett–Teller, BET) of sample 3 is about seven times larger than that of sample 1 (74 and 10 ± 1  $\text{m}^2 \text{g}^{-1}$ , respectively). Scanning electron microscopy



**Fig. 1** XRD patterns ( $\text{Cu-K}\alpha$  radiation) of (a) metakaolinite, prepared by heating kaolinite in air for 1 h at 650 °C (sample 2); (b) metakaolinite rehydrated at 250 °C for 6 days (sample 3); and (c) parent kaolinite (sample 1). The vertical scale in (c) is three times less sensitive than in (a) and (b). **m** denotes the reflections from the mica impurity.



**Fig. 2**  $^{27}\text{Al}$  and  $^{29}\text{Si}$  MAS NMR spectra of samples 1–3 recorded at 104.23 and 79.5 MHz, respectively, with a Bruker MSL-400 multinuclear spectrometer, using  $\pi/20$  and  $\pi/4$  radio-frequency pulses and recycle delays of 0.2 and 30 s, respectively. [ $\delta$  in ppm from  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  and  $\text{SiMe}_4$ , respectively.] Asterisks denote spinning sidebands.



**Fig. 3** TEM photographs of metakaolinite samples hydrothermally treated at 200 °C for 2 days. Adjacent tracings of photograph (b) highlight the features which show that rehydration is a topotactic solid-state reaction.

(SEM) (pictures not shown) reveals that the particles of sample 3 ( $\leq 0.2 \mu\text{m}$ ) are much smaller than those of samples 1 and 2 ( $\leq 2 \mu\text{m}$ ). Recalcination of the rehydrated samples produces a material which is likely to be more reactive than metakaolinite and which may be a valuable precursor for the synthesis of zeolites, ceramics and other products of industrial interest.

The  $^{29}\text{Si}$  MAS NMR spectrum of sample 1 (Fig. 2) consists of a single narrow resonance at *ca.*  $-91.5$  ppm from  $\text{SiMe}_4$ , characteristic of layered silicates and assigned to a  $\text{Q}^3$  silicon environment (Si linked *via* oxygens to three other Si atoms). Sample 2 gives a broad  $^{29}\text{Si}$  signal centred at *ca.*  $-101$  ppm indicating that it is amorphous or pseudo-amorphous. The spectrum of sample 3 consists of a relatively narrow resonance centred at *ca.*  $-92$  ppm, showing that the local order of the  $^{29}\text{Si}$  sites approaches that observed in the parent kaolinite. The  $^{27}\text{Al}$  MAS NMR spectrum of sample 1 contains one peak at *ca.*  $0$  ppm from aqueous  $\text{Al}(\text{NO}_3)_3$ , assigned to 6-coordinated Al. NMR clearly shows that the rehydrated metakaolinite does not contain detectable amounts of metakaolinite, or of any other amorphous or pseudo-amorphous phase. Sample 2 exhibits two other resonances: at *ca.*  $28$  ppm, assigned to 5-coordinated Al,<sup>6</sup> and at *ca.*  $57$  ppm, due to 4-coordinated Al. Hydrothermal treatment of metakaolinite converts 4- and 5-coordinated Al into 6-coordinated Al, thus restoring kaolinite symmetry to the aluminous sheet.

Three possible mechanisms can be envisaged for the rehydration: (i) dissolution of metakaolinite particles followed by subsequent crystallization; (ii) local dissolution of micro-regions of the metakaolinite particles followed by crystallization of small kaolinitic nuclei which then increase in size; (iii) a purely solid-state process whereby chemical bonds are rearranged; the structural transformations in this case would probably occur first in regions of the metakaolinite structure which preserved the kaolinite symmetry and can act as seeds for the nucleation process. Results of the chemical analysis (by atomic absorption) of the reaction liquor prompts one to discard mechanism (i) since less than 1 mol % of either Si or Al is found. Transmission electron microscopy (TEM) shows that the transformations produced by rehydration start near the edges of the 'metakaolinite' pseudo-hexagonal platelets, the

general morphology remaining otherwise unchanged. Later, very small ( $< 90$  nm), pseudo-hexagonal, 'particles' emerge from the bulk of the 'metakaolinite' plates [Fig. 3(a)]; these nuclei grow, eventually reaching *ca.*  $200$  nm. It is clear [Fig. 3(b)] that the small kaolinite particles grow perpendicular to the  $c^*$  axis of kaolinite and metakaolinite and their edges are parallel to these parent materials. This means that the symmetry along the  $ab$  plane is similar exactly what one would expect from an *in situ* topotactic solid-state process [mechanism (iii)]. We have previously found evidence for the presence in metakaolinite of structural regions preserving the symmetry of kaolinite.<sup>6,7</sup> These could act as nuclei for the reconstitution. No enhancement of rehydration was observed when  $0.02$  g of parent kaolinite was added to  $1.0$  g of metakaolinite as seed, which shows that the regions of metakaolinite with kaolinite-like symmetry are a *structural* rather than a *separated* unreacted kaolinite phase.

We are grateful to the University of Aveiro for support.

Received, 27th December 1990; Com. 0105779G

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