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Thermal reactions of kaolinite studied by solid state 27-Al and 29-Si NMR

R. H. MEINHOLD, K. J. D. MacKENZIE, I. W. M. BROWN
Chemistry Division, DSIR, Private Bag, Petone, New Zealand

The development of high-resolution solid-state NMR techniques using magic-angle spinning (MAS) has provided a sensitive method for investigating atomic environments in various solids including minerals, for which 29-Si NMR is particularly appropriate. Studies of silicates and aluminosilicates show a correlation between the chemical shift δ of the silicon resonance and the coordination environment [1], bond angle and bond length of the Si–O group [2], or total cation–oxygen bond strength [3]. Furthermore, cross-polarization experiments with the 1-H nucleus provide information specifically about silicon atoms close to proton-bearing species such as in hydroxyl-containing minerals [4]. Although less well documented, high-resolution 27-Al NMR has proved useful for determining the coordination number (CN) of aluminium in various Al–O compounds [5].

These techniques seem particularly appropriate for studying the structure of the intermediate phases formed by heating kaolinite, $Al_4Si_4O_{10}(OH)_8$. This is the reaction of fundamental importance in the production of clay-based ceramics. At 650° C, most hydroxyl water is lost, forming metakaolinite, a disordered and defect phase which transforms to a cubic phase at ~ 980° C, eventually forming mullite, $Al_6Si_2O_{13}$ and crystobalite, SiO_2, at higher temperatures. Previous X-ray structural studies of these intermediate phases have been hampered by their lack of crystallinity, while attempts to measure changes in the CN of the aluminium by X-ray fluorescence spectroscopy are subject to difficulties in the choice of calibration standards [6]. As an independent method of studying the aluminium and silicon environments in these phases, high-resolution NMR of both 27-Al and 29-Si was carried out on natural kaolinite (BDH "light") which had been heated in air to various temperatures. The spectrometer was a Varian XL200, using spinning speeds up to 2600 r.p.s.

The 27-Al spectra are shown in Fig. 1. The principal resonance in unheated kaolinte (Fig. 1a) is in the expected position for octahedral aluminium coordinated to hydroxyl groups [7]; the splitting may be due to the presence of more than one silicon site, or to the effect of an electric field gradient (efg) at the quadrupolar aluminium nucleus. Heating the kaolinite to 490° C (just below dehydroxylation) produces no change in the 27-Al spectrum, but further heating to 540° C reduces the signal to 30% of its original intensity. After dehydroxylation at 650° C, the intensity of the aluminium signal is reduced to about 8% of its unheated intensity, and tetrahedral aluminium signals appear at 65 to 70 ppm, in addition to the octahedral resonance at 0 ppm (Fig. 1c). The relative proportions of tetrahedral and octahedral aluminium, estimated by cutting out and weighing the peaks, is about 1:1, somewhat higher in octahedral aluminium than previously found by XRF[6] (although the latter was measured on a sample heated at 800° C). While the chemical shift of the resonance at 65 to 70 ppm is characteristically tetrahedral, the shift of the second resonance at 35 ppm is smaller than any previously reported in tetrahedral aluminosilicates, although we have observed shifts of this order in tetrahedral aluminium phosphates (unpublished results) and in dehydroxylated pyrophyllite (to be published). The loss of ~ 90° of the total aluminium signal intensity is probably related to the number of defects in the dehydroxylated product and the occurrence of most of the aluminium in distorted sites which are neither truly octahedral nor tetrahedral and hence have an electric field gradient which broadens the signal from quadrupolar 27-Al beyond detection. On heating to higher temperatures, ~ 20% of the total aluminium becomes

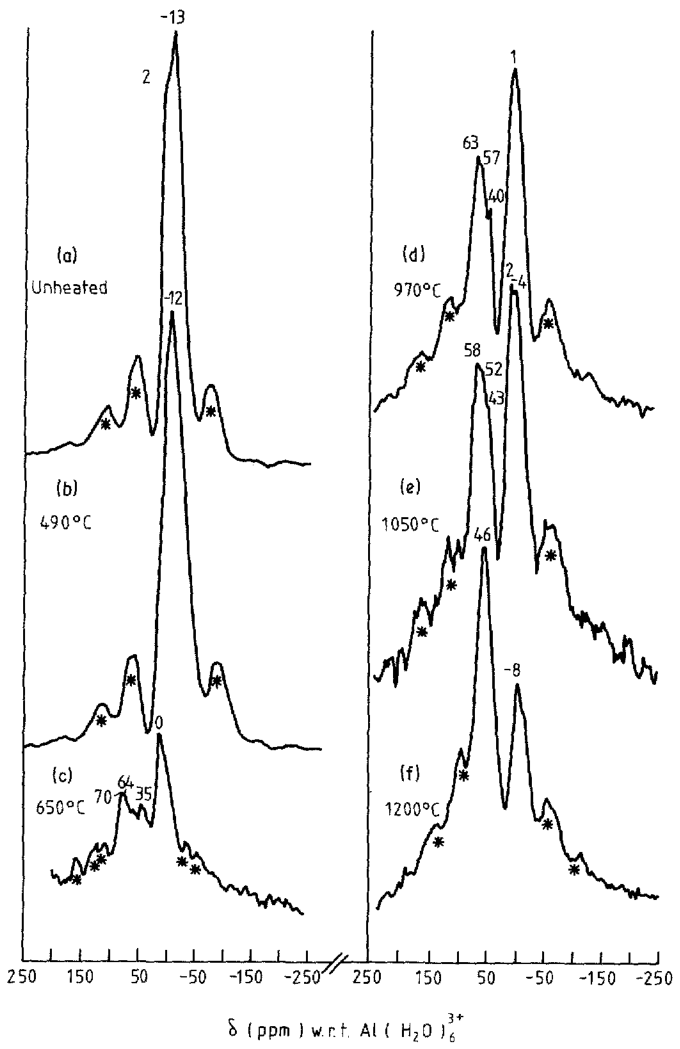

Figure 1 27-Al MAS NMR spectra of kaolinite heated to various temperatures. Peaks marked * are spinning side bands. Spectra are plotted on the same sensitivity scale except for (a) and (b) which are reduced 10X (variations in the number of transients averaged resulted in varying noise levels).

associated with a more symmetrical environment, and thus visible by NMR. The ratio of tetrahedral to octahedral aluminium increases from about 1:1 at 970 to 1050° C to 1.7:1 at 1200° C, in which sample well-crystallized mullite is found by X-ray diffraction. In the stability range of the cubic phase (970 to 1050° C), this ratio is consistent with previous XRF results [6], but the present result for well-crystallized mullite is higher in octahedral aluminium than previoulsy found [6]. The chemical shift of the major tetrahedral aluminium peak progresively decreases with increasing heating temperature, eventually attaining the value for well-developed mullite (46 to 48 ppm).

The corresponding 29-Si spectra are shown in Fig. 2. Unheated kaolinite shows a single sharp peak at -91.5 ppm relative to tetramethyl silane, in reasonably good agreement with previously-reported values for kaolinite, although the peak splitting reported by Barron *et al.* [8] was not resolved at the lower field strength available to us. A similar spectrum is found in samples heated to below the onset of dehydroxylation, but in samples heated to 650° C, the silicon resonance was broadened and shifted to ~ -100 ppm (Fig. 2c), consistent with the presence of a number of silicon sites of differing bond lengths, bond angles or cation–oxygen bond strengths. On heating to higher temperatures, the major silicon resonance progressively shifts upfield, reflecting a *decrease* in the number of aluminium groups bonded to the SiO_4 groups, i.e. silica is separating from the aluminosilicate phase. This process is essentially complete by 1050° C (Fig. 2e); the chemical shifts in this and higher-temperature

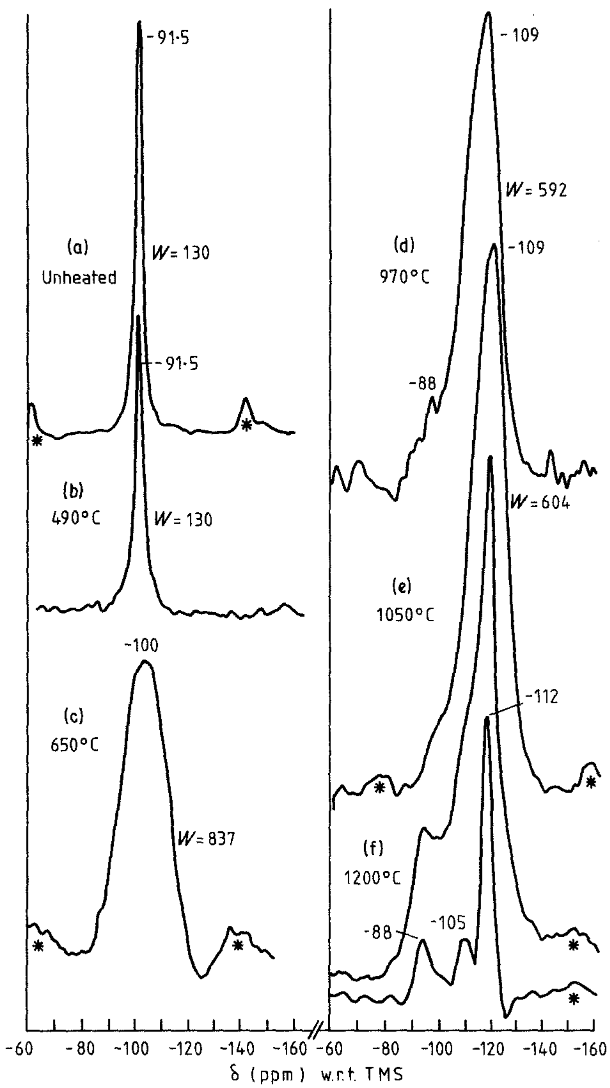

Figure 2 29-Si MAS NMR spectra of kaolinite heated to various temperatures. Peaks marked * are spinning side bands. Vertical scale of A and B 4X less sensitive. *W* denotes width at half height.

samples (− 110.5 ppm) correspond to those reported for cristobalite [1, 2]. At about 970° C, a smaller peak appears at − 88 ppm; by 1200° C this can be resolved into at least two resonances, at − 88 and − 105 ppm (Fig. 2f), corresponding to silicon associated with the mullite phase, which is shown by XRD to be present even at 970° C. Thomas *et al.* [9] reported a single peak at − 86.0 ppm in crystalline mullite formed from a xerogel.

Cross-polarization 29-Si spectra are shown in Fig. 3. Comparison of the areas of these spectra with the corresponding spectra of Fig. 2, after making 1-H and 29-Si spin relaxation rate corrections (to be detailed elsewhere), indicates that up to 490° C, all the silicon atoms are in sufficient proximity to hydroxyl groups to contribute to the CP spectra, which also show identical chemical shifts (Fig. 3a). The corrected area of the CP spectrum of dehydroxylated kaolinite (Fig. 3b) is decreased to only about 6% of the value for unheated kaolinite, reflecting the persistence in the metakaolinite structure of 11 to 12% of residual structural water (estimated from weight-loss measurements). With resolution enhancement (Fig. 3c), the broad 650° C CP spectrum appears to contain resonances at − 93, − 97 and − 103 ppm, suggesting that the remaining hydroxyls are associated with both kaolinite-like and metakaolinite-like structure. By 1050° C, the CP spectra indicate the presence of less than 1% residual hydroxyls.

To summarize, these results lead to the following conclusions regarding the kaolinite–mullite

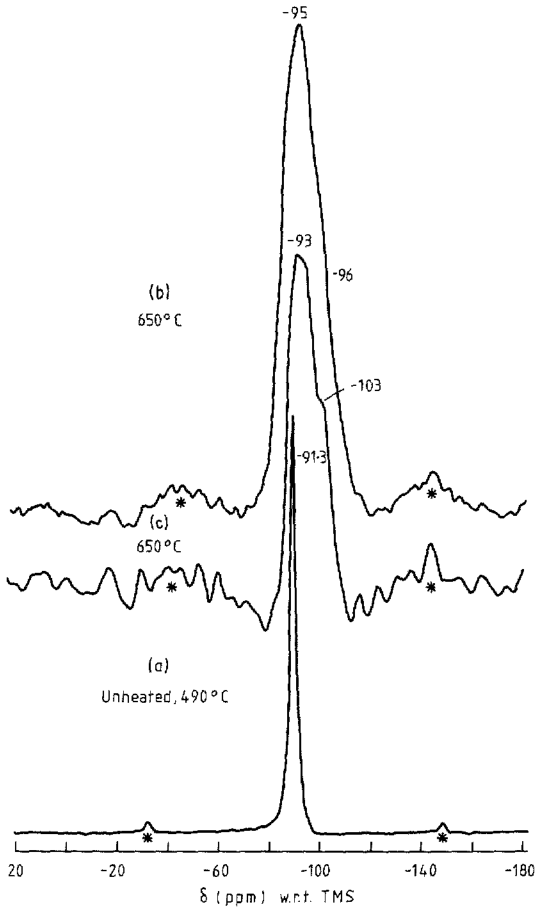

Figure 3 Cross-polarization 29-Si spectra of kaolinite heated to various temperatures. Peaks marked * are spinning side bands. Vertical scale of A 62.5× less sensititve.

reaction:

(a) Metakaolinite contains 11 to 12% of the original kaolinitic structural water, probably associated with the ~ 8% of aluminium atoms which remain in undistorted sites. Approximately one-half of these well-defined aluminium sites are octahedral, one-quarter are tetrahedral, and the remainder are either tetrahedral, or some other regular site with a chemcial shift intermediate between tetrahedral and octahedral. The silicon atoms in the fully dehydroxylated regions of the structure occur in a range of distorted environments; the aluminium atoms in these regions are also too distorted to be detected by MAS NMR.

(b) On further heating, metakaolinite progressively loses the remaining hydroxyls, the latter stages of this process (at ~ 970° C) being accompanied by the separation of free silica (i.e. silica not in intimate association with aluminium). At the same time, there is an increase in the number of well-defined aluminium sites, of which the tetrahedral site population progressively increases at the expense of the octahedral. However, even in very well crystallized mullite, about 80% of the aluminium sites are too distorted to be detected by MAS NMR.

More detailed structural implications of these results, and details of the nuclear spin relaxation rate measurements, will be presented elsewhere, and discussed in the light of an NMR investigation of the thermal reactions of pyrophyllite, with which it shows strong similarities.

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