Journal of Thermal Analysis, Vol. 38 (1992) 2053-2065

FLASH CALCINATION OF KAOLINITE STUDIED BY DSC, TG AND MAS NMR

R. H. Meinhold, H. Atakul, T. W. Davies and R. C. T. Slade

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF EXETER, EXETER EX4 4QD,
UNITED KINGDOM

The structural changes occurring during the dehydroxylation of kaolinite have been followed using flash calcination to produce kinetically frozen calcines. The percentage of dehydroxylation was varied by changing the furnace residence time or temperature and/or heating speed. These calcination conditions affected the reaction kinetics, but the products depended only on the extent of dehydroxylation.

Changes in the position and enthalpy of the endothermic transformation to metakaolinite and the high temperature exothermic reaction of metakaolinite have been followed using Differential Scanning Calorimetry of the flash calcines and related to Thermogravimetry.

^{27}Al magic-angle-spinning NMR spectra, at high magnetic fields and spin rates, enabled the reaction of kaolinite to be monitored and provides new information on the nature of the species formed in the course of dehydration.

Keywords: calcination, high temperature reactions, kaolinite, kinetics

Introduction

The thermal transformations of clay minerals are of considerable economic importance in the manufacture of ceramics. The high temperature firing of kaolinite has been used in the fabrication of bricks and pots for thousands of years, though the nature of the reaction was not well understood [1]. In 1887 Le Chatelier [2] observed heat changes during the thermal treatment of clay, these endothermic and exothermic reactions showing that firing of clays involved more than simply drying them.

However, questions still remain as to the structures of the products [3]. The product of the initial endothermic dehydroxylation, metakaolinite, is X-ray amorphous and thus indirect methods of structure determination are needed. In 1985 the technique of magic-angle-spinning (MAS) nuclear magnetic resonance spectroscopy (NMR) was used to follow the changes in Al and Si environments at various points in the reactions and suggestions were made as to the nature of the species [4–6]. Subsequent workers [7–12] have been able to use higher magnetic fields now available to reduce the effects of quadrupolar interactions on the ^{27}Al spectra, but there is still disagreement on the species formed.

Most studies of kaolinite dehydroxylation have involved the slow raising of temperature, the industrial equivalent being 'soak calcination', and examination of the products at completion of the reaction. Calcination is a rate process and one can produce calcines kinetically frozen at different stages during the dehydroxylation by using the process of 'flash calcination'. In flash calcination [13] powdered clay is heated very rapidly (e.g. 10000 K s^{-1}) by plunging into a stream of hot flowing gas, maintained at the gas temperature for fractions of a second, and then quenched with cold gas. Thus time resolution of the reaction can be achieved by varying the residence time at the reaction temperature. We have previously reported [14–17] the effects of flash calcination variables, such as heating speed, furnace temperature, residence time and carrier gas, on physical properties such as specific gravity, voids (or blisters) and aluminium leachability, and have used medium field MAS NMR to probe the structural changes which occur [7, 8].

Here we report the use of differential scanning calorimetry (DSC) and thermogravimetry (TG) to follow the thermal transformations occuring in flash calcines. By using the highest commercially available magnetic fields combined with high MAS spinning speeds we have been able to follow the changes in Al environment as dehydroxylation proceeds.

Experimental

Differential Scanning Calorimetry measurements were made on a Stanton Redcroft DSC 1500. Temperatures were calibrated using barium carbonate and indium phase transitions, and enthalpy calibrated using melting of indium. Samples of about 16 mg were heated at 20 deg·min^{-1} in static air.

Thermogravimetry was carried out in a Stanton TG-750 instrument. Samples (ca. 10 mg) were heated from ambient temperature to 960°C at 20 deg·min^{-1} in flowing dry N_2 and soaked at 960°C to constant mass. The degree of dehydroxylation α is defined by $\alpha = (m/M)\times 100\%$ where the sample has lost m grams of the initial M grams of water present. The original water content (M) of the kaolinite used in this study (after drying at 105°C) was 12.2% by mass.

Magic angle spinning nuclear magnetic resonance spectra were obtained using Bruker MAS probes with spinning speeds of ca. 12.5 kHz. ^{27}Al spectra at frequencies of 156.3 and 130.3 mHz were acquired on Bruker AMX 600 and MSL 500 spectrometers. Shifts are reported relative to the aluminium hexaquo ion using yttrium aluminium garnet as a secondary standard. Short pulses of 0.6 μs were used with a 1 s delay between pulses.

Flash calcines were produced in a laminar flow furnace described elsewhere, with a range of process variables including heating rate, furnace temperature, residence time and furnace gas.

The kaolinite feedstock was commercial grade SPS clay (ECC International, St Austell, Cornwall). Chemical analyses and particle size distributions (90%<2 μm) have been described elsewhere [16, 17].

Results

The reaction of kaolinite to form metakaolinite gave rise to a broad endotherm in the DSC experiment (Fig. 1), with a peak maximum at 570°C and an area corresponding to an enthalpy of 175 cal·g^{-1} (381 kJ·mol^{-1} $Al_4Si_4O_{10}(OH)_8$). As the percentage of dehydroxylation (α) increased with calcination, the area of the endotherm in the calcine decreased – as expected since there is less kaolinite to undergo the endothermic reaction. The enthalpy decreased linearly with increasing α and extrapolated to zero enthalpy at $\alpha = 76\%$, though there was still a small residual endotherm up to the maximum dehydroxylation achieved of 91% (Fig. 2). Although the enthalpy of the dehydroxylation of the remaining kaolinite might decrease as calcination proceeds, the results are consistent with the enthalpy of the reaction being constant with the reaction involving only 75% of the hydroxyl groups; once 3/4 of the hydroxyl groups have been lost there is only a small residual endotherm, corresponding to a few percent kaolinite (possibly due to a small percentage of kaolinite trapped in large particles?).

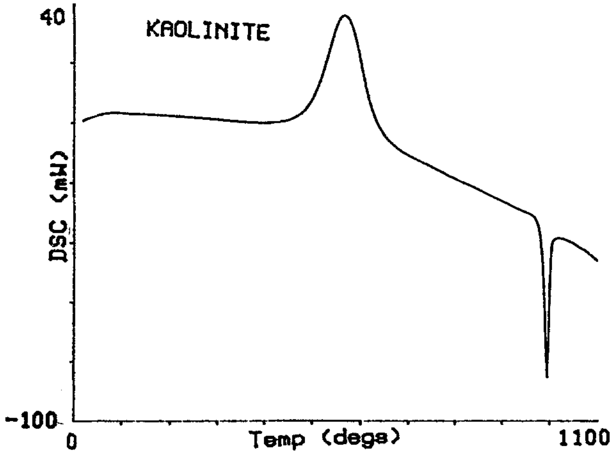

Fig. 1 Differential scanning calorimetry of kaolinite. Heat flux (mW) *vs.* °C

The peak temperature of the endotherm correlated with the onset temperature of the reaction as the peak width and shape remained constant. The temperature at the peak maximum, T_{end}, decreases slowly with increasing dehydroxylation, reaching 560°C at $\alpha = 75\%$, after which the temperature decreases rapidly to about 530°C at $\alpha = 90\%$. Thus increasing calcination appears to have only a slight effect on the position of the endotherm until about 3/4 of the hydroxyl groups have been removed, at which point there is only a very small endotherm.

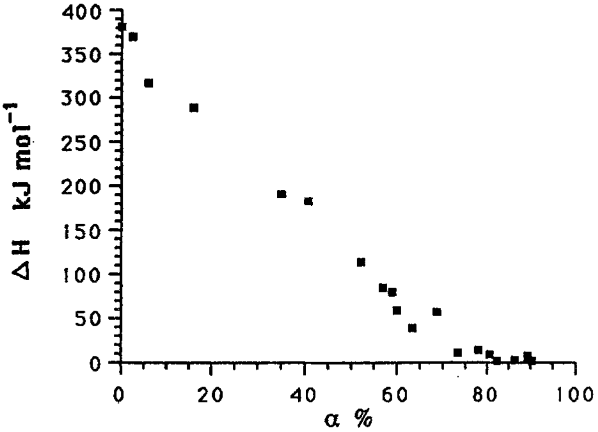

Fig. 2 Enthalpy of 570°C endotherm, ΔH_{end} kJ mol^{-1}, *vs.* α (%)

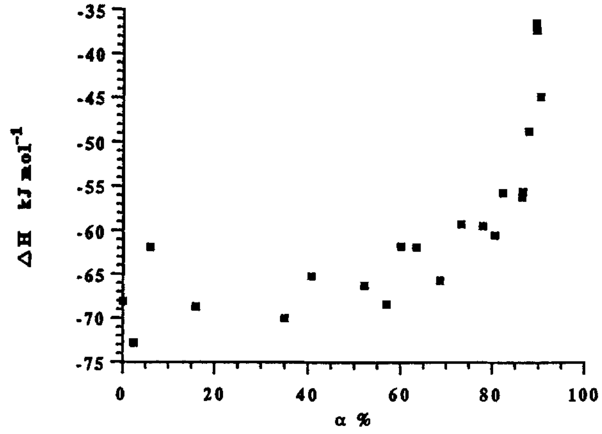

Fig. 3 Enthalpy of 994°C exotherma, ΔH_{exo} kJ·mol^{-1}, *vs.* α (%)

The exothermic peak had a peak maximum of 994±2°C and an average enthalpy of −66±4 kJ·mol^{-1} in the region α = 0–75%. At the higher levels of dehydroxylation, produced by very fast heating speeds at higher temperatures, there was a rapid drop in the enthalpy of the exotherm (Fig. 3); we ascribe this to partial completion of the exothermic reaction during the high temperature calcination. The change in area of the exotherm is shown in Fig. 4 as a function of the calcination temperature for calcination in

N_2 with a heating speed of 12000 deg·s^{-1} and residence time of 0.5 s. For flash calcination at temperatures above 1000°–1050°C the enthalpy decreases, with only 57±3% of the area remaining for calcination at 1200°C. Thus at calcination temperatures above ca. 1000°C some of the metakaolinite formed in the calcine may have undergone the subsequent exothermic reaction.

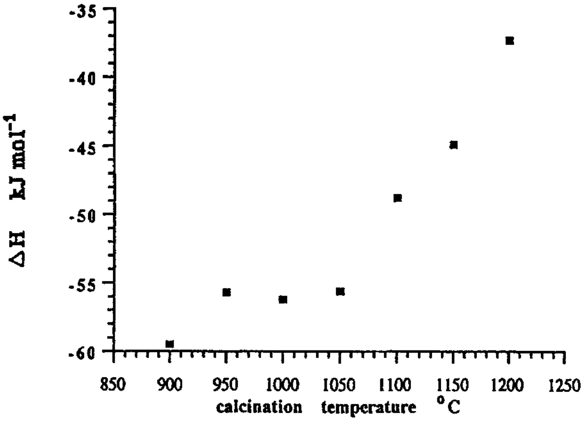

Fig. 4 Enthalpy of the exotherm as a function of calcination temperature for a heating speed of 12000 deg·s^{-1} and residence time of 0.5 s in N_2

A small endothermic peak was usually observed near 955°C, but no distinct peaks were observed which could be ascribed to the loss of the last 25% of hydroxyls, although a weak broad peak near 760°C could just be seen above the baseline. Most samples also showed a weak broad endotherm between 20° and ca. 300°C, which may be partly due to loss of adsorbed water.

Thermogravimetry of the calcines showed that as dehydroxylation increased there was an increase in the percentage weight loss occurring at lower temperatures. Figure 5 shows an example of percentage weight loss during TG for samples heated at 4700 deg·s^{-1}in N_2 to 1000°C with residence times of 0.3 s (similar TG to kaolinite) and 1.5 s.The low temperature weight loss for low α calcines is small and similar to kaolinite, but increases rapidly for calcines with high dehydroxylation. Percentage loss in weight which has occurred by 400°C in the TG of the calcine, f_{400}, as a function of the reciprocal of the fraction of remaining hydroxyls in the starting calcine has the linear relationship

$$f_{400}(1-\alpha/100) = 6.8(1-\alpha/100) + 6.1 \qquad (R = 0.963)$$

The first term is the actual weight loss of the sample up to 400°C and this is made up of a term which is 6.8% of the residual hydroxyls (1–α/100), and a term which is a constant weight loss of 6.1% independent of dehydroxylation. Thus as dehydroxylation proceeds, and few hydroxyls are left, the constant weight loss becomes the dominant contribution. This constant low temperature weight loss may perhaps be due to an impurity such as re-adsorbed water. It appears that the low temperature weight loss depends on the fraction of residual hydroxyls and not on the calcination conditions such as temperature, heating speed or furnace gas.

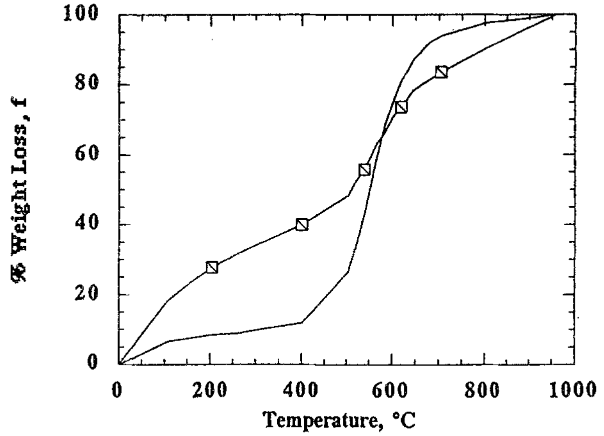

Fig. 5 Thermogravimetry of flash calcines prepared with a heating speed of 4700 deg·s^{-1} at 1000°C in N_2 with residence times of 0.3 s (—) and 1.5 s (-⊠-)

Other correlations can be found with the reciprocal of the fraction of residual hydroxyls, $(1-\alpha/100)$, although there is considerable scatter of the points, and other relationships which give a rapid change at high α values are possible. The temperature of the endotherm decreased linearly as $(1-\alpha/100)$ increased. Figure 6 shows that the enthalpy of the 994°C exotherm (reaction of metakaolinite to form spinel) decreased as $(1-\alpha/100)$ increased.

The 130 MHz ^{27}Al MAS NMR spectra showed a peak at 1.4 ppm due to the octahedral Al of kaolinite which decreased in size as calcination proceeded, with a concomitant increase in a tetrahedral peak at 55.6 ppm and a broad peak at 27 ppm (Fig. 7). A detailed analysis of the spectra and their field dependence will be published elsewhere [18]. The spectrum was divided into tetrahedral and octahedral regions with the balance being the broad peak at 27 ppm with its associated spinning sidebands and a tail due (in part) to distorted octahedral Al. The relative proportions of each type of Al are plotted in Fig. 8 as a function of the percentage dehydroxylation of the calcine. In the early stages of calcination the octahedral kaolinite peak dropped more rapidly than expected. Thus when the percentage of dehydroxylation was 17%, the octahedral peak was only 68% of the Al signal while the balance of Al was 8% tetrahedral plus 24% in the 27 ppm peak and an upfield tail due to distorted octahedral species. Thus the octahedral peak intensity shows that 32% of the kaolinite had reacted when only 17% of the hydroxyls had been lost and hence in the initial stages of calcination tetrahedral Al coordinated to hydroxyl groups is formed and possibly some distorted octahedral

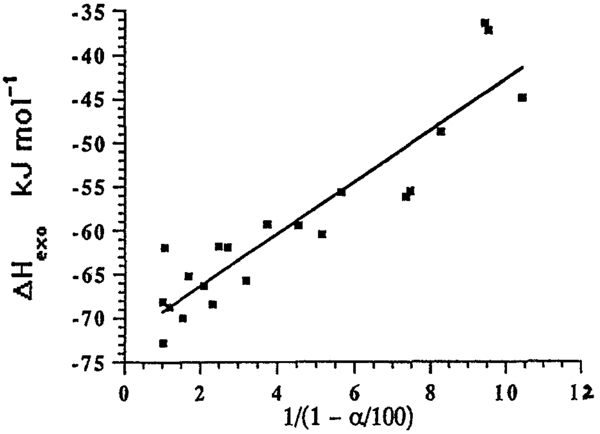

Fig. 6 Enthalpy of the 994°C exotherm *vs*. the reciprocal of the fraction of residual hydroxyls in the calcine

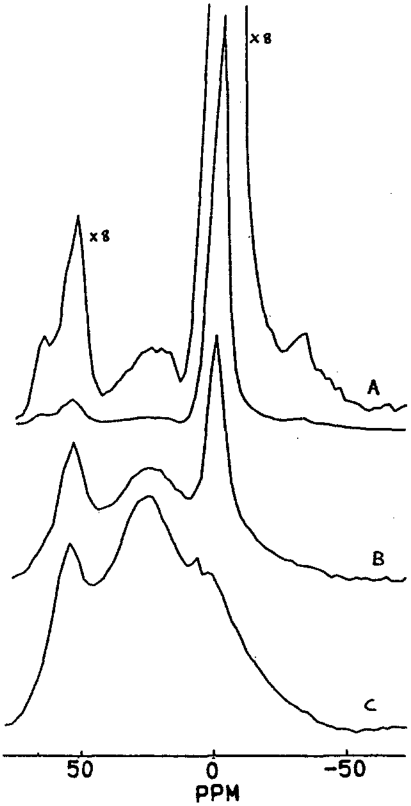

Fig. 7 ^{27}Al NMR spectra of flash calcines (A and B) in N_2 with heating speed 4700 deg·s^{-1} and residence times of (A) 0.3 s (α = 17%) and (B) 1.5 s (α = 80%) (C) is a soak calcine at 800°C for 30 min

species also containing hydroxyl groups. After about 20% dehydroxylation the octahedral intensity decreased linearly with α until ca. 75–80% weight loss when it started to increase as the high temperature exothermic reaction commenced. Up to ca. α = 80% there was a linear increase in the percentage of the 27 ppm peak but at high calcination temperatures there was a decrease due to the formation of some octahedral Al and a small amount of tetrahedral Al. After the initial rapid formation of tetrahedral Al there was a slower increase until about 60–80% dehydroxylation where it remained approximately constant.

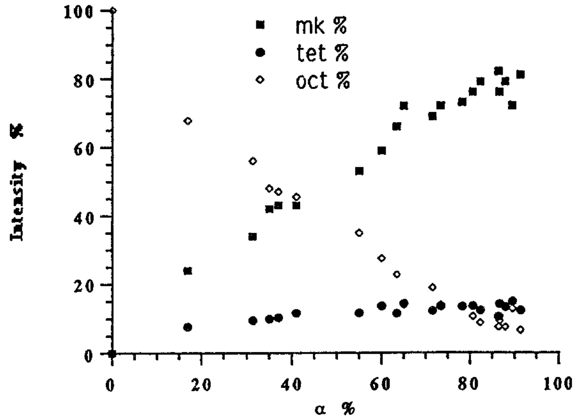

Fig. 8 Percentages of total Al signal in tetrahedral peaks (●), octahedral peaks (◇), and the 27 ppm peak (■), as a function of α (%)

The amount of tetrahedral Al appeared to increase as the octahedral decreased until ca. 12% octahedral (at 75% dehydroxylation) when a sharp decrease in tetrahedral intensity occurred.

In kaolinite soak calcined at 800°C both the tetrahedral and octahedral peaks were only visible as shoulders on the 27 ppm metakaolinite peak.

Instead of plotting the enthalpy of the metakaolinite endotherm against α as in Fig. 1 one can plot ΔH against the percentage of octahedral Al, which shows the endotherm vanishing when about 12% octahedral remains (at 75% dehydroxylation). Similarly there is a linear decrease in ΔH as the 27 ppm peak grows and the endotherm is predicted to disappear when the 27 ppm peak reaches 75% of the Al intensity.

Discussion

The properties of the calcines, determined by DSC, TGA and NMR, depend on the extent of dehydroxylation and are independent of the flash calcination conditions used to produce the dehydroxylation. As expected, dehydroxylation increased with furnace temperature and residence time, but also with heating speed. Rapid heating, particularly in a He atmosphere, leads to the formation of bubbles or voids (seen by SEM) and a decrease in specific gravity greater than predicted from the weight loss [14–16]. The increase in dehydroxylation with heating speed might be due to structural disruption (and hence easier loss of water); build up of steam within the particles, at a rate greater than it can escape by diffusion, may lead to an 'explosive' loss of water and formation of additional channels for subsequent water egress. Rapid heating might also result in formation of a crustal layer of metakaolinite (or spinel above 1000°C) which causes water pressure to rise to explosive levels. The furnace gas has a small effect with He giving slower dehydroxylation than N_2. The presence of water vapour in the flash calciner has previously been shown [7] to effect Al and Si NMR spectra, with greater conversion to metakaolinite at higher water pressures.

Rapid heating may result in increased dehydroxylation for a given residence time, due to faster kinetics arising from easier water loss after disruption of the structure, but the properties of the calcine depend only on the extent of dehydroxylation.

Dehydroxylation, in flash calcination, appears to proceed in several stages:

I. $\alpha = 0–75\%$

(a) The area of the endotherm decreases linearly to near zero, while the temperature of the endotherm drops slightly (from 570° to 560°C).

(b) The exothermic reaction (to form spinel) is unaffected by the preceding flash calcination.

(c) The NMR spectra show a greater loss of octahedral kaolinite Al than expected from the weight loss. At low dehydroxylation ($\alpha = 17\%$) about half the octahedral kaolinite peak was lost by dehydroxylation of the kaolinite, with the other half being converted to 2 tetrahedral species and a distorted octahedral species without loss of hydroxyls. As α increases after the initial dehydroxylation there is a linear decrease in octahedral (kaolinite) Al and a slow increase in tetrahedral Al (to $14.5\pm0.5\%$); the major metakaolinite peak, at 27 ppm, increases linearly.

II. $75 < \alpha < 90\%$

(a) The area of the endotherm is only about 1% of the initial enthalpy for kaolinite dehydroxylation. The temperature of the endotherm decreases rapidly as dehydroxylation increases, reaching about 530°C at $\alpha = 90\%$. No specific DSC peaks were observed for the loss of the remaining (up to 25%) hydroxyls – possibly indicating a low enthalpy, spread over a large temperature range.

(b) The enthalpy of the 994°C exothermic reaction (to spinel) decreases at high levels of dehydroxylation, implying some reaction of the metakaolinite during the high temperature flash calcination, and/or a reduction in the enthalpy of the reaction. This effect could be due to temperatures >1000°C being required to produce high levels of dehydroxylation in the short furnace residence times.

(c) ^{27}Al NMR spectra show a minimum octahedral peak of ca. 9% for $\alpha = 75–80\%$, with the tetrahedral and 27 ppm peaks reaching their maximum percentages of 15 and 75% respectively. Rapid heating at 1200°C produced 89.5% dehydroxylation, with a decrease in the fraction at 27 ppm, a slight increase in tetrahedral and a greater increase in octahedral peak proportions, with the exothermic enthalpy only 56% of the kaolinite value. The decrease in the 27 ppm peak is much less than expected from the decrease in the enthalpy of the metakaolinite reaction, thus the phase formed in the 994°C exothermic reaction contains Al in similar environments to metakaolinite (though with a higher proportion of octahedral Al), and/or the enthalpy of the reaction is lowered by high temperature flash calcination.

A sample soak calcined at 800°C for 30 minutes showed only traces of octahedral Al (i.e. very little residual kaolinite or newly formed alumina/mullite), with ca. 7% tetrahedral and the remainder in the broad 27 ppm peak.

The model of the metakaolinite structure proposed by Mackenzie *et al.* [3–6], taking into account NMR data and the structural consequences of reacting pairs of hydroxyl groups, contains both residual tetrahedral and octahedral Al with attached hydroxyl groups in agreement with our results, but does not contain 5-coordinate Al. The peak near 27 ppm has previously been assigned [11] to 5-coordinate Al by analogy with 5-coordinate Al in andalusite and calcined pyrophylite. However, based on variable field NMR studies we consider that the alternative explanation of 4-coordinate Al with elongated Al–O bonds is also possible. This agrees with radial electron density distribution (RED) measurements [19]. Recent EXAFS and XANES results [20] on flash calcines are consistent with 4-coordinate Al with Al–O bond lengths of 1.81 Å.

At first sight the several distinct stages in the dehydroxylation of kaolinite appear to coincide with the proportions of different hydroxyl groups in kaolinite. Three of the four hydroxyl groups associated with the alumina sheets of edge-shared AlO_6 octahedra are adjacent to the interlamellar space between successive pairs of alumina and silica sheets; the fourth hydroxyl is intralamellar, lying in the plane of oxygens between the Si and Al layers. The interlamellar space provides a pathway for easy diffusion out of the structure of water formed by reaction of pairs of hydroxyls in the layer adjacent to this space. The remaining 25% of hydroxyls, located in the centre of the sheet between the Si and Al layers, may be more difficult to remove. Pampuch *et al.* [21] showed that 1/3 of the hydroxyl groups in the interlamellar sheet have short H-bonds and are thought to be the first groups to be lost.

However, the division of flash calcination into stages corresponding to the loss of the different types of hydroxyl groups may not be entirely correct, as kinetic and other studies have shown a wide variation in the dependence of parameters on α. Brindley and Nakahira [22] postulated that dehydroxylation occurs layer-by-layer throughout the whole volume of the crystal. Wide-line ^{1}H NMR studies [23, 24] support this in the region $\alpha = 0–70\%$, where the average H–H distance remained constant. Above $\alpha = 70\%$

the remaining ^{1}Hs were said to be in 2 ensembles, P' and P''. P' may be linked to octahedral Al while P'' contains isolated protons which increase at the expense of P' as α increases.

Kinetic studies have been used to investigate the dehydroxylation mechanism. There are 2 stages to intraframework dehydroxylation as discussed by Stoch [25]:

(1) formation of water from hydroxyl groups, which depends on location and mobility of the reacting species.

(2) Removal of water molecules from the structure. Diffusion of water out of the structure may determine the kinetics. Collapse of the kaolinite interlayer space may lead to slow removal of the remaining hydroxyl water.

Although kinetics have been shown to change above certain levels of dehydroxylation the effect is related to the degree of ordering of the kaolinite and the particle size [26]. The highest rate of removal of water occurs at $\alpha = 50\%$ for coarse crystals but at $\alpha = 70\%$ for fine crystals. For fine or disordered crystals a greater amount of water can be evolved before structural collapse blocks egress channels and thus these crystals show [25]:

(1) dehydroxylation starts at lower temperatures
(2) the activation energy to overcome diffusion resistance is lower
(3) the heat of reaction is lower
(4) residual hydroxyl groups combine and are removed more rapidly

Clearly the kinetics of kaolinite dehydroxylation are dependent on the size and degree of disorder of kaolinite crystals. However, although flash calcination kinetics are influenced by heating speed, temperature and furnace gas, the physical properties of flash calcines determined by DSC and NMR are dependent only on the extent of dehydroxylation achieved.

Conclusions

Flash calcination can be used to produce a series of calcines kinetically frozen at various levels of dehydroxylation. The properties of the calcines depend only on the extent of dehydroxylation. Flash calcination conditions effect only the kinetics of the reaction, with high heating speeds giving faster kinetics, possibly due to disruption of the structure allowing faster water diffusion out of the crystal.

The metakaolinite endotherm at 570°C appears to be associated with the loss of the first 75% of hydroxyl groups, but it is not certain that this corresponds to loss of all the interlayer hydroxyls (leaving only the intralayer hydroxyls, and restricted water diffusion paths due to loss of the interlamellar space). The design of the flash calcination furnace used allows only short residence times, and hence to obtain completion of slow reactions high temperatures must be used. The dehydroxylation of kaolinite is slower for $\alpha > 70\%$ and hence at temperatures above ca. 1000°C some of the metakaolinite may be converted to the spinel phase before complete dehydroxylation has occurred.

NMR studies show that in the initial stages of calcination some of the octahedral kaolinite Al is converted to tetrahedral Al and some distorted octahedral Al without substantial loss of hydroxyls, while the loss of hydroxyls corresponds to formation of the broad 27 ppm peak. As calcination proceeds the tetrahedral peak grows slowly and the 27 ppm peak grows as the octahedral decreases. The assignment of the 27 ppm peak is uncertain, but it could be due to 4-coordinate Al with long Al–O bond-lengths and a range of chemical shifts and electric field gradients. The assignment to 4-coordinate rather than 5-coordinate Al is in agreement with other (non-conclusive) evidence. The presence of several tetrahedral Al species, a distorted 4-coordinate species, and a distorted octahedral species is in accord with the structural model for metakaolinite proposed by Mackenzie *et al.* [3–6].

* * *

We thank the Science and Engineering Council for supporting our studies of mineral transformations and. R. Meinhold thanks N.Z. D.S.I.R. chemistry, and H Atakul thanks Istanbul Technical University, for leave to undertake these studies. We thank Bruker Analytische for access to NMR spectrometers in their Karlsruhe laboratory.

References

1 K. J. D. Mackenzie, Chemistry in N.Z., 1978, March, 8.
2 H. Le Chatelier, Bull. Soc. Franc. Mineral, 10 (1887) 204.
3 K. J. D. Mackenzie, Chemistry in N.Z. 55 (1991) 30.
4 R. H. Meinhold, K. J. D. Mackenzie and I. W. M. Brown, J. Mater. Sci. Letts, 4 (1985) 163.
5 K. J. D. Mackenzie, I. W. M. Brown, R. H. Meinhold and M. E. Bowden, J. Amer. Ceram. Soc., 68 (1985) 293.
6 I. W. M. Brown, K. J. D. Mackenzie, M. E. Bowden and R. H. Meinhold, J. Amer. Ceram. Soc., 68 (1985) 298.
7 R. C. T. Slade and T. W. Davies, Colloids and Surfaces, 36 (1989) 119.
8 R. C. T. Slade and T. W. Davies, J. Mater. Chem., 1 (1991) 361.
9 J. P. Gilson, C. Edwards, A. Peters, R. Koppuswamy, R. F. Wormsbecher, T. G. Roberie, M. P. Shatlock, J. Chem. Soc. Chem. Commun., 91 (1987).
10 T. Watanabe, H. J. Shimizu, K. Nagasawa, A. Masuda, H. Saito, Clay Mineral., 22 (1987) 37.
11 J. F. Lambert, W. S. Millman and J. J. Fripiat, J. Am. Chem. Soc., 111 (1989) 3517.
12 J. Rocha and J. Klinowski, Phys. Chem. Minerals, 17 (1990) 179.
13 T. W. Davies, High Temp. Technology, 2 (1984) 141.
14 T. W. Davies and R. M. Hooper, J. Mater. Sci. Letts, 4 (1985) 39.
15 D. Bridson, T. W. Davies and D. P. Harrison, Clays Clay Minerals, 33 (1985) 258.
16 R. C. T. Slade, T. W. Davies, H. Atakul, R. M. Hooper and D. J. Jones, J. Mater. Sci., 27 (1992) 2490.
17 R. C. T. Slade, T. W. Davies and H. Atakul, J. Mater. Chem., 1 (1991) 751.
18 R. H. Meinhold, Appl. Magn. Reson., in press.
19 A. J. Leonard, J. Amer. Ceram. Soc., 60 (1977) 37.
20 K. J. Roberts, Personal communication.

21 R. Pampuch, M. Kawalska and M. Ptak, Ceramic Papers, Pol. Acad. Sci, Cracow Filial, 17 (1971) 63.
22 G. W. Brindley and M. Nakahira, J. Amer. Ceram. Soc., 42 (1958) 311.
23 M. C. Gastuche, F. Toussaint, J. J. Fripiat, P. Touilleaux and M. van Meersche, Clay Minerals Bull., 5 (1963) 227.
24 C. Otero-Arean, M. Letellier, B. C. Gerstein and J. J. Fripiat, Int. Clay Conf., 1981, Elsevier, 1982, p. 73.
25 L. Stoch, J. Thermal Anal., 29 (1984) 919.
26 A. R. Carthew, Amer. Mineral., 40 (1955) 107.

Zusammenfassung — Strukturelle Veränderungen bei der Dehydroxylierung von Kaolinit wurden durch die Anwendung einer Blitz-Kalzination untersucht, um kinetisch eingefrorene Kalzinationsprodukte zu erhalten. Der Prozentsatz der Dehydroxylierung wurde durch Veränderung der Verweilzeit im Ofen, durch Ofentemperatur und/oder Heizgeschwindigkeit modifiziert. Diese Kalzinationsbedingungen beeinflußten zwar die Reaktionskinetik, aber die Produkte hingen nur vom Ausmaß der Dehydroxylierung ab.

Abweichungen bei Lage und Enthalpie der endothermen Umwandlung zu Metakaolinit und die exotherme Hochtemperaturreaktion von Metakaolinit wurden mittels DSC der Blitz-Kalzinationsprodukte verfolgt und in Beziehung zur Thermogravimetrie gebracht.

^{27}Al Magic-Angle-Spinning NMR Spektren bei hohen magnetischen Feldstärken und Drehgeschwindigkeiten erlauben es, die Reaktion von Kaolinit zu verfolgen und liefern neue Informationen über die Natur der bei der Dehydroxylierung gebildeten Substanzen.