

# The Formation of Mullite from Kaolinite Under Various Reaction Atmospheres

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## Abstract

*In addition to its importance as a high-technology ceramic, mullite is also an intermediate phase in the formation of non-oxide ceramics (sialons) by carbothermal reduction of clay minerals. This reaction involved the formation of mullite under non-oxidizing atmospheres and in the presence of carbon. The effect of eight different reaction atmospheres on mullite formation from kaolinite in the presence and absence of carbon was studied by X-ray diffraction,  $^{27}\text{Al}$  and  $^{29}\text{Si}$  magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy. Generally, a greater amount of mullite is formed at 1200°C under vacuum and reducing atmospheres, which also produce mullites that are slightly more silica-rich (as deduced from X-ray lattice parameter measurements) but contain higher proportions of tetrahedral  $^{27}\text{Al}$  NMR resonance at  $\approx 46$  ppm, probably associated with  $\text{Al}^*$  sites. Reaction systems containing either nitrogen or ammonia in the presence of carbon show NMR evidence of previously unreported early stage formation of  $\text{Si-O-N}$  bonds. Thermodynamic calculations are presented which suggest that the formation of  $\text{SiO}$  is an important factor in the complex interactions between the various solid and gaseous reactants.*

## 1 Introduction

Mullite is an important high-technology ceramic in its own right, especially when prepared in high purity, by contrast with the product generally formed by heating clay minerals. However, the mullite resulting from the thermal reaction of clays plays an important role in the formation of sialons (silicon aluminium oxynitrides), another class of high-technology materials. The synthesis of sialon from natural aluminosilicates involves heating a clay such as kaolinite with carbon in a nitrogen atmosphere, but if other inert atmospheres such as argon are used, equally useful

carbide phases can be formed.<sup>1</sup> The practical importance of such synthesis reactions has led us to study the effect of a number of different reaction atmospheres on the formation of mullite from kaolinite, both in the presence and absence of carbon.

The aim of these studies was to measure the effect of eight different reaction atmospheres on:

- (1) the amount of mullite formed under standard conditions (2 h heating at 1200°C),
- (2) the composition of the mullite formed, and
- (3) the structure of the mullite formed.

The amount and composition of the product was measured by X-ray diffraction (XRD), from peak intensities and unit cell dimensions respectively, while aspects of the bonding and structure were studied by  $^{29}\text{Si}$  and  $^{27}\text{Al}$  solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy. A thermodynamic analysis was also made, to clarify some of the details of the complex interactions occurring in these reacting systems.

## 2 Experimental

Kaolinite of high purity and good crystallinity ('Light' grade, supplied by British Drug Houses) was ball milled with an excess (25 wt%) Degussa lampblack under hexane for 16 h, extruded into 2 mm diameter rods, dried and heated in an alumina boat in an electric tube furnace under various flowing gases (flow rate 150 ml min<sup>-1</sup>). The maximum temperature, at which the samples were held for 10 min, was 1200°C. A parallel set of experiments was also made omitting the carbon. After rapid cooling, maintaining the gas atmosphere, the samples were ground and examined by powder XRD (Philips PW1700 automatic diffractometer with  $\text{CoK}_\alpha$  radiation) and solid-state nuclear magnetic resonance spectroscopy (Varian Unity 500 spectrometer). All the NMR

spectra were acquired at 11.7 T using a 5 mm Doty magic angle probe spinning up to 12 kHz. The recycle delay time used for the  $^{29}\text{Si}$  spectra was 300 s, to allow for the possible presence of species with very long relaxation times.

The thermodynamic calculations were made using a computer program<sup>2</sup> which uses tabulated thermodynamic data to determine the concentration of the various gas and solid species in complex systems as a function of gas concentration and reaction temperature.

### 3 Results and Discussion

Figure 1 shows the amount of mullite formation from kaolinite at 1200°C under the various reaction atmospheres, estimated semi-quantitatively from the height of the major mullite XRD peak at 3.4 Å. In the absence of carbon, oxidizing atmospheres produce the least mullite, while reducing atmospheres, which include ammonia and  $\text{CO}_2$ , produce the greatest amount. Inert atmospheres are intermediate in their effect. In the presence of carbon the reaction atmosphere clearly changes, with inert gases producing the most mullite, but oxidizing gases still producing the least mullite, due to the fact that the carbon burns off very readily under these conditions.

Figure 2 shows the alumina content of the mullites, estimated from the unit cell dimensions using the relationship of Cameron.<sup>3</sup> The unit cells were determined from careful measurements of at least 11 mullite XRD peaks, with angular corrections

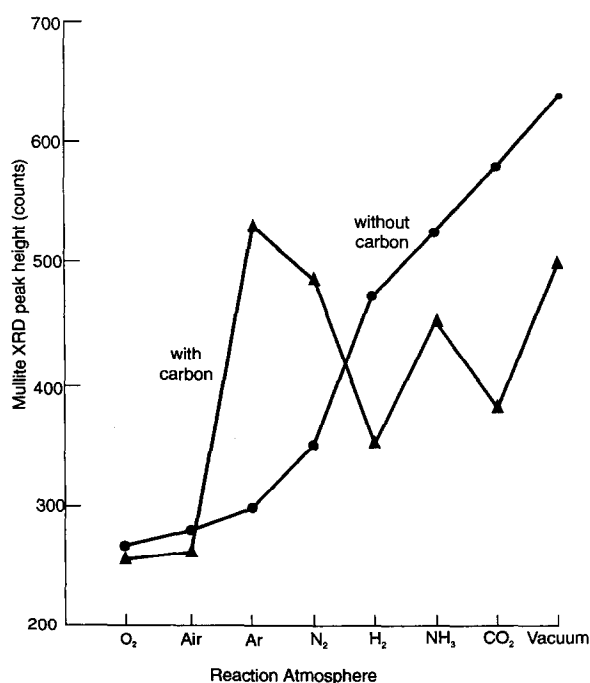


Fig. 1. Mullite formation in kaolinite (1200°C, 10 min) under various atmospheres, with and without carbon.

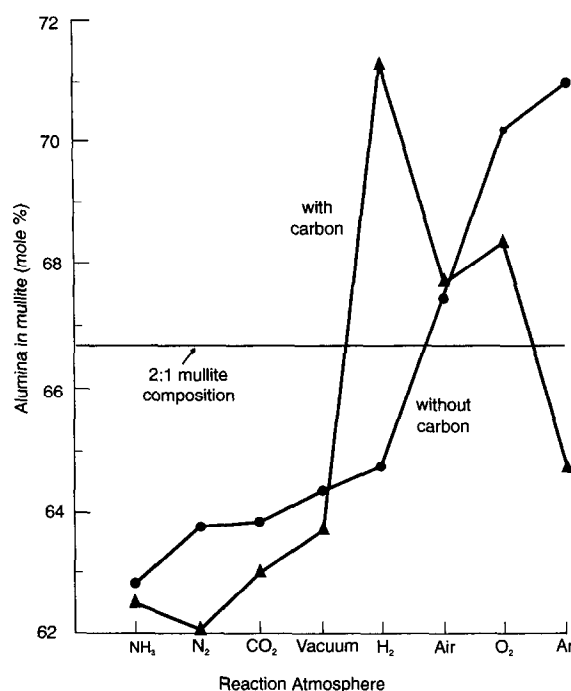


Fig. 2. Composition of mullites formed from kaolinite (1200°C, 10 min) under various atmospheres, with and without carbon.

made using an external silicon standard. In the absence of carbon, the alumina content of the mullite is highest under oxidizing conditions and argon, whereas under reducing conditions and vacuum, the composition is intermediate between 3:2 and 2:1 mullite. A similar situation occurs in the presence of carbon, except that hydrogen atmospheres now produce mullite with the highest alumina content.

Examples of the more interesting  $^{29}\text{Si}$  and  $^{27}\text{Al}$  spectra are shown in Fig. 3. The  $^{29}\text{Si}$  MAS NMR spectra of all the mullites of this study are broad, but show the typical mullite peak at -87 ppm<sup>4</sup> and a higher-field peak at about -106 ppm due to the free silica which separates from the kaolinite during the reactions preceding mullite formation. However, differences were found in the  $^{29}\text{Si}$  spectra of samples heated with carbon in nitrogen (Fig. 3(A)) and heated without carbon in ammonia. In both these spectra there is evidence of broad spectral intensity downfield of the mullite peak. This is in the region of Si-N bonds, and in the spectral simulation of the sample heated in nitrogen (Fig. 3(B)) a peak centred at about -58 ppm could be fitted, the broadness of which suggests the presence of a continuum of nitride and oxynitride species. A similar situation was found in the  $^{29}\text{Si}$  spectrum of the sample heated in ammonia, in which two peaks were fitted in this region, their positions (-40 ppm and -68 ppm) consistent with silicon nitride and silicon oxynitride, respectively. Both these samples have experienced the combination of a reducing atmosphere

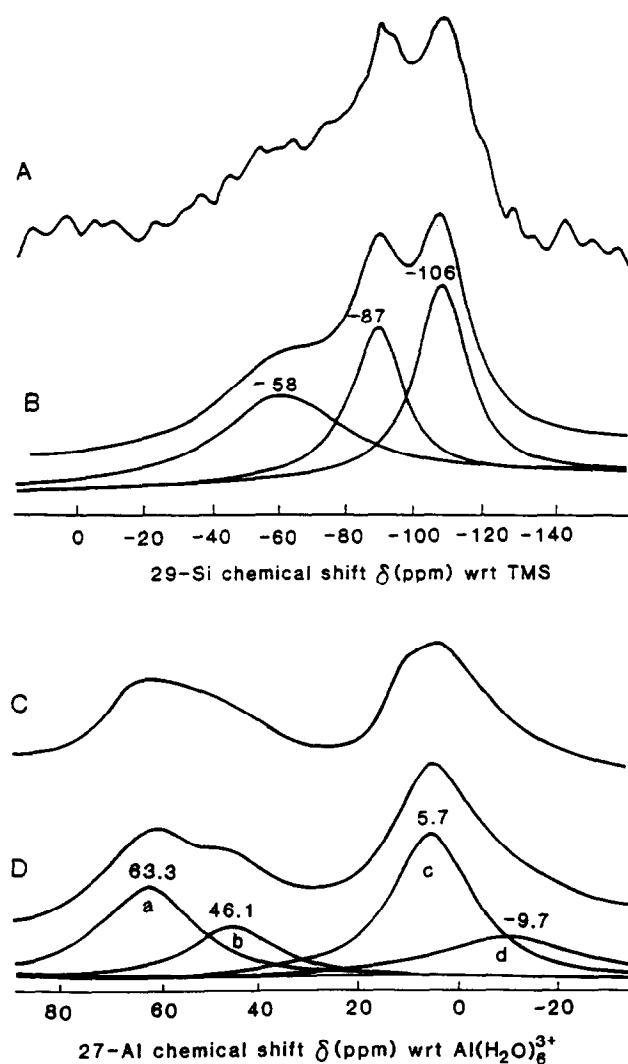


Fig. 3. Observed and simulated solid-state MAS NMR spectra of kaolinite reacted at 1200°C for 10 min: (A)  $^{29}\text{Si}$  spectrum of sample containing carbon, in  $\text{N}_2$ ; (B) simulation of A; (C)  $^{27}\text{Al}$  spectrum of sample containing carbon, in  $\text{H}_2$ ; (D) simulation of C.

and nitrogen, which seems to encourage the formation of Si-N bonding even at this low temperature.

The  $^{27}\text{Al}$  MAS NMR spectra (Fig. 3(C)) are typical for mullite, containing an octahedral resonance at 1–6 ppm and a tetrahedral resonance at about 59 ppm. The octahedral resonance shows a marked tail on the upfield side which in the simulation of (Fig. 3(D)) has been fitted to a small broad peak (d); this tailing is commonly found in association with octahedral resonances and does not indicate a second site, but arises from electric field gradient (EFG) effects. The tetrahedral resonance at about 59 ppm can also be resolved into two overlapping peaks in a number of the samples (Fig. 3(D)). Following the reasoning of Merwin *et al.*,<sup>4</sup> the tetrahedral peak at about 46 ppm may be due to the site associated with an oxygen defect. There is no readily discernible relationship between the area of this resonance and factors such as the amount of mullite formed or its total alumina content.

### 3.1 Thermodynamic calculations for these systems

There is clearly some complex chemistry occurring between the aluminosilicate lattice and the gas atmosphere, which can be modified by the presence of the carbon. Thermodynamic calculations were made in an attempt to interpret the behaviour of the various systems. Although these thermodynamic calculations refer to equilibrium conditions, and the present experiments were conducted under dynamic conditions, it was thought that the calculations could provide an insight into the various processes occurring, provided the results are treated with caution.

For the purpose of the calculations, the system was assumed to be anhydrous, with the composition of kaolinite from which the structural water had been removed (metakaolinite). The thermodynamic calculations predicted that this decomposes to silica and  $\gamma$ -alumina in most cases, with the formation of mullite, which is also taken into account in the calculations. Vacuum conditions were approximated by extremely high concentrations of an inert gas such as Ar, in which the dilution effect mimics the removal of gas by pumping. In all other cases, an ample excess of reactant gas (100 moles) and carbon (10 moles) was assumed. A range of temperatures was calculated, but the greatest attention was paid to the calculations at 1200°C.

### 3.2 Reactions in the absence of carbon

Under these conditions at 1200°C, vacuum,  $\text{CO}_2$  and reducing atmospheres were found by experiment to be of most assistance to mullite formation. The conclusions of the thermodynamic calculations for these more beneficial atmospheres are summarized in Fig. 4.

The calculations predict that at 1200°C, vacuum conditions should facilitate the decomposition of the silica to  $\text{SiO}$  but the alumina component should remain intact. The calculations for the system containing  $\text{CO}_2$  indicate that the  $\text{CO}_2/\text{CO}$  equilibrium lies heavily to the left, although under the dynamic gas flow conditions of the experiment it may be shifted more to the right. The resulting  $\text{CO}$  would also favour the formation of  $\text{SiO}$ . At 1200°C, ammonia is completely dissociated into  $\text{H}_2$  and  $\text{N}_2$ ; the resulting hydrogen again facilitates  $\text{SiO}$  formation but does not form appreciable  $\text{Al}_2\text{O}$  at 1200°C (Fig. 4). Reaction between the silica component and the  $\text{N}_2$  in the presence of the dissociated  $\text{H}_2$  to form silicon nitride or silicon oxynitride is not predicted, but the formation of  $\text{AlN}$  from the alumina component is slightly favoured (although not observed experimentally here). Thus, the thermodynamic calculations for all the atmospheres which were found to assist mullite formation suggest that the silica phase is

**KAOLINITE WITHOUT CARBON**

Experimental order for mullite formation:  
 Vacuum > CO<sub>2</sub> > NH<sub>3</sub> > H<sub>2</sub>

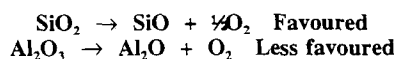
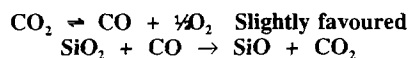
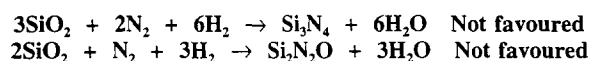
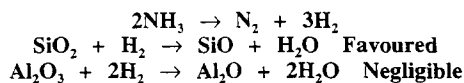
**A. Vacuum****B. Carbon Dioxide****C. Ammonia**

Fig. 4. Conclusions drawn from thermodynamic calculations for aluminosilicate systems reacted at 1200°C in the absence of carbon.

reacting with the gas in all cases, but the alumina component is much more stable.

**3.3 Reactions in the presence of carbon**

In the presence of carbon, the experimental results indicate that reducing conditions again exert a beneficial influence on the formation of mullite, but, by contrast with the results in the absence of carbon, the inert atmospheres Ar and N<sub>2</sub> now also strongly promote mullite formation. The primary action of the inert gases will be to maintain the carbon in its elemental form. The predictions of thermodynamic calculations at 1200°C for the inert and reducing gases in the presence of carbon are summarized in Fig. 5.

In both argon and vacuum, reaction between the silica component and carbon to form SiC is predicted, although this product was not experimentally observed. Because of its ability to be removed in the gas stream, the formation of SiO is probably more significant than it would be under the equilibrium conditions of the thermodynamic calculations. In nitrogen, the formation of silicon oxynitride from the silica component is strongly favoured in the presence of carbon (Fig. 5), consistent with the <sup>29</sup>Si NMR spectrum of this sample (Fig. 3(A)), but the alumina component is predicted to remain unreacted. In ammonia, reaction between the dissociated H<sub>2</sub> and the carbon to form CH<sub>4</sub> is predicted at lower temperatures, but by 1200°C, the equilibrium has shifted back again to the left. Thus, ammonia in the presence of carbon is predicted to form silicon oxynitride, this reaction being confirmed by <sup>29</sup>Si NMR. In hydrogen

**KAOLINITE WITH CARBON**

Experimental order for mullite formation:  
 Ar > Vacuum > N<sub>2</sub> > NH<sub>3</sub> > H<sub>2</sub> > CO<sub>2</sub>

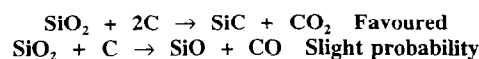
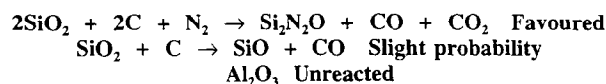
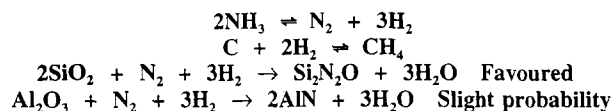
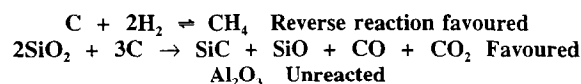
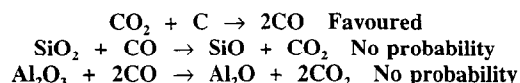
**A. Argon and Vacuum****B. Nitrogen****C. Ammonia****D. Hydrogen****E. Carbon Dioxide**

Fig. 5. Conclusions drawn from thermodynamic calculations for aluminosilicate systems reacted at 1200°C in the presence of carbon.

alone, the formation of SiC and SiO is predicted at 1200°C, but the alumina component of the reactant remains unreacted. As with Ar and vacuum atmospheres, the SiC is not experimentally observed. At 1200°C, CO<sub>2</sub> is predicted to react with carbon to form CO, but the thermodynamic probability of further reaction between CO and silica or alumina is low.

Thus, the thermodynamic calculations suggest that both in the presence and absence of carbon, the silica component is most affected by the various atmospheres, especially reducing atmospheres and those with the potential to become reducing. When the free silica in the reacting system has been consumed by the formation of SiO or Si<sub>2</sub>N<sub>2</sub>O, the silica component of the mullite present will be progressively decomposed by similar reactions (i.e. the formation of SiO, SiC or silicon oxynitrides). Removal of SiO in the gas stream will decrease the silicon concentration of the system unless it is retained by reacting with the alumina-rich components to form further mullite. A relationship between mullite formation and the tendency of the system to form SiO is illustrated in Fig. 6, in which the observed degree of mullite formation is plotted against the calculated SiO concentration for each system.

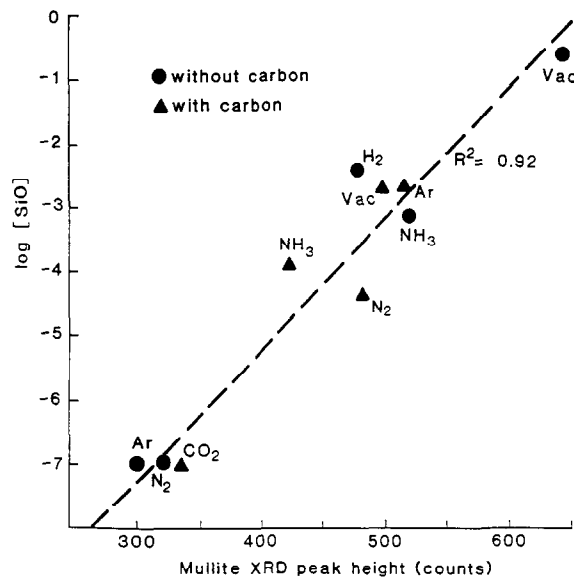


Fig. 6. Calculated SiO concentrations in systems of kaolinite composition, reacted in different atmospheres at 1200°C in the presence and absence of carbon, as a function of the experimentally determined mullite concentration.

The relationship shown in Fig. 6 is better than expected in view of the equilibrium assumptions of the thermodynamic calculations, which are very different from the present experimental conditions. Since the formation of mullite in these systems appears to be closely associated with their tendency to form SiO, the temperature dependence of SiO formation is also of interest (Fig. 7).

Although the calculated thermodynamic predictions of Fig. 7 must again be treated with caution, they indicate very different temperature dependences in the various atmospheres with and without carbon. In all but the two hydrogen-containing systems ( $H_2$  and  $NH_3$ ), the presence of carbon lowers the onset temperature for SiO formation, and in the case of Ar and  $N_2$ , increases the eventual SiO concentration. These results suggest that the relative behaviour in the various reaction systems (and also the effect on mullite formation) may change markedly with reaction temperature.

The mechanism of mullite formation under reactive atmospheres which decompose the siliceous component to form SiO probably depends on the enhanced reactivity of the gas-phase SiO species for the more alumina-rich components. Alternatively, if discrete SiO is not directly formed, the increased lability of the Si–O bonds in the solid silica or aluminosilicate phases may be sufficient to promote further reaction and an increase in the silica content of the mullite.

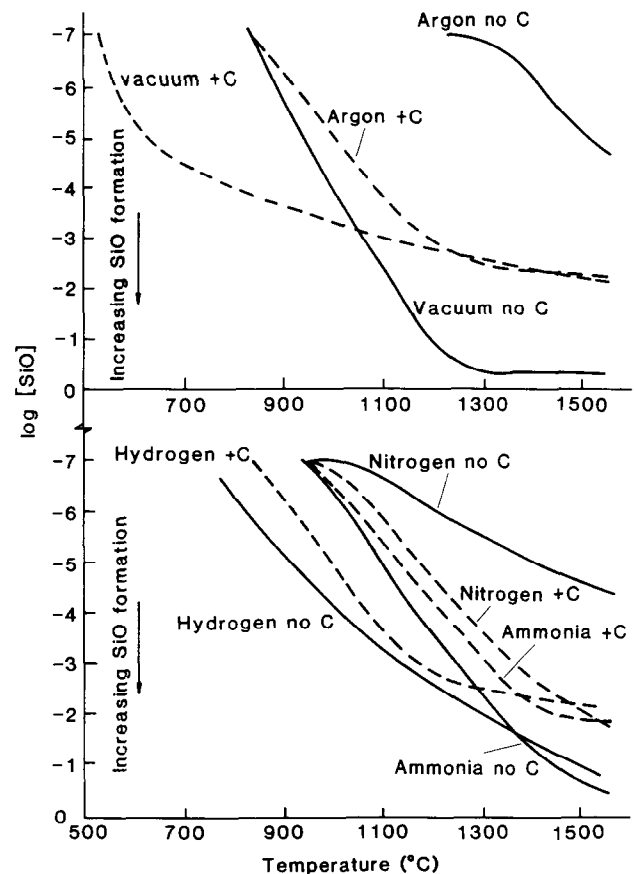


Fig. 7. Temperature dependence of calculated SiO formation in systems of kaolinite composition, under different atmospheres in the presence and absence of carbon.

Although the thermodynamic predictions must be applied with caution to the results of dynamic experiments, they shed interesting light on the relative importance of the various competing reactions occurring in complex gas–solid systems such as mullite-forming systems under various atmospheres.

## References

- MacKenzie, K. J. D., Meinhold, R. H., White, G. V., Sheppard, C. M. & Sherriff, B. L., Carbothermal formation of  $\beta'$ -sialon from kaolinite and halloysite studied by  $^{29}\text{Si}$  and  $^{27}\text{Al}$  solid state MAS NMR. *J. Mater. Sci.*, **29** (1994) 2611–19.
- Turnbull, A. G. & Wadsley, M. W., CSIRO Thermochemistry System, Version 5.1, 1988.
- Cameron, W. E., Composition and cell dimensions of mullite. *Am. Ceram. Soc. Bull.*, **56** (1977) 1003–11.
- Merwin, L. H., Sebal, A., Rager, H. & Schneider, H.,  $^{29}\text{Si}$  and  $^{27}\text{Al}$  MAS NMR spectroscopy of mullite. *Phys. Chem. Minerals*, **18** (1991) 47–52.