Journal of the European Ceramic Society 16 (1996) 1299–1308
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0955-2219/96/$15.00
PII: S0955-2219(96)00062-3

Structural Evolution in Gel-Derived Mullite Precursors

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(Received 19 December 1995; revised version received 27 February 1996; accepted 14 March 1996)

Abstract

The evolution of mullite from organo-metal gel precursors above 700°C is found to be strongly influenced in both gel pieces and powdered samples by the thermal pretreatment at lower temperatures. Under the present conditions, the optimum preheating temperature was found to be 350°C, at which temperature an anomalously high concentration was found of an Al species with a characteristic ^{27}Al magic-angle spinning NMR resonance at about 30 ppm. Such Al sites are often described as pentacoordinated, but an alternative assignment is considered. The optimum temperature for the formation of this Al site is also optimal for the catalytic formation of aromatic molecules from the residual organic fragments and/or solvent present. Mass spectrometry shows that under the present reaction conditions, these aromatics are thermally stable up to at least 900°C in air, and the prolonged presence of their decomposition products (CO and water) could facilitate the transformation of the gel to crystalline mullite. The ^{29}Si NMR spectra indicate at least three different Si environments, including one which may arise from the formation of silicon oxycarbide glasses in these gels. © 1996 Elsevier Science Limited

1 Introduction

Because of its increasing importance as a high-technology ceramic, considerable interest is being shown in the production by sol–gel synthesis routes of high-purity mullite with reproducible particulate characteristics. Since the mechanism by which mullite evolves when these gel precursors are heated depends strongly on the homogeneity of the gels, considerable effort has been put into understanding how the degree of mixing of the silica and alumina components is influenced by the various possible different starting reagents and reaction conditions, as reviewed in two recent papers.[1,2] Taylor and Holland[1] have suggested that in very homogeneous gels, the Al is largely incorporated into the tetrahedral silica network, and mullite is the major phase appearing after recrystallization at about 980°C. By contrast, less homogeneous gels contain extensive Al- and Si-rich regions, the former being characterized by octahedral Al; this type of gel transforms to an Al-rich spinel, which forms mullite only on further heating.[1] These conclusions are largely supported by the observations of Selvaraj *et al.*[2] on gels produced using different hydrolysis conditions.

Schneider *et al.*[3] have investigated mullite precursors derived from tetraethoxysilane (TEOS) or $SiCl_4$ and aluminium sec-butoxide by both slow and rapid hydrolysis, which they designate type I and type III precursors, respectively. They observed, as did previous authors,[1,2] resonances in the ^{27}Al magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectra at about 30 ppm, variously attributed to 5-coordinated Al[1,2,4,5] or very strongly distorted tetrahedra.[6] In other structures containing well-defined 5-coordinate Al, the isotropic chemical shift is 35–36 ppm.[7] The Al in this coordination state, which has been suggested by Taylor and Holland to occur in the interfacial material between the silica-rich and alumina-rich domains,[1] appears to be implicated in the reaction which occurs at 980°C, since the 30 ppm resonance disappears abruptly at about this temperature.[1–3] Schneider *et al.*[3] reported that type I precursors are extremely homogeneous, containing a random assortment of 4-, '5'- and 6-coordinate Al which, although X-ray amorphous below about 900°C, crystallize above this temperature to mullite. Type III precursors differ, in forming an Al-rich spinel above 900°C.

During preliminary experiments in which thermally induced changes in type I mullite precursors were monitored by MAS NMR, it was observed that the reaction route to mullite (i.e. whether directly or via the spinel phase) was strongly influenced by the lower temperature pre-calcination conditions.

The aim of the present work was to investigate in greater detail the effect of thermal pretreatments at various temperatures on the structural evolution in type I precursors, using thermal analysis, X-ray diffraction and ^{27}Al and ^{29}Si MAS NMR.

2 Experimental

The type I precursors were synthesized to mullite stoichiometry (72 wt% Al_2O_3, 28 wt% SiO_2) by diluting TEOS and Al sec-butylate with isopropyl alcohol, mixing and slowly hydrolysing in a humidity chamber at 40% relative humidity for 14 days. The subsequent heating experiments were carried out on two types of sample, viz. gel pieces resulting directly from the synthesis and powders prepared by grinding the gel pieces. After drying at 150°C, one portion of the precursor phase was heated directly to various temperatures up to 650°C and held at temperature for 15 h before cooling. Another sub-set of these preheated samples was further heat-treated at 700°C for 15 h. All the heated samples were ground if necessary, and examined by X-ray powder diffraction (Siemens D500 computer-controlled powder diffractometer with Cu K_α radiation), and by ^{27}Al and ^{29}Si MAS NMR. The solid-state MAS NMR spectra were obtained at 11·7 T using a Varian Unity 500 spectrometer and 5 mm Doty probe spun at up to 12 kHz. The ^{27}Al spectra were acquired at 130·3 MHz with a 15° pulse of 1 μs and a recycle time of 0·1 or 1s. The spectra were referenced to $Al(H_2O)_6^{3+}$. The 11·7 T ^{29}Si spectra were acquired at 99·3 MHz using a 90° pulse of 6 μs and recycle times up to 3000 s (but typically 100 s). The spectra were referenced to tetramethylsilane (TMS). ^{29}Si cross-polarization (CP) spectra were also obtained at 4·7 T for some of the samples using a 5 μs contact time and a 3 s delay between the pulses. Thermal analyses were carried out using a Netzsch DSC 404 at a heating rate of 10°C min^{-1} in air. Evolved gas analyses (EGA) were carried out by packing the sample into a silica capillary tube through which was passed a stream of air (3 cm^3 min^{-1}) while heating in a micro furnace at a linear heating rate of 20°C min^{-1} up to 900°C. The effluent gas was analyzed using a Dycor MA100M quadrupole mass spectrometer fitted with a Varian 301/s triode ion pump and a 60 μm silicone rubber membrane inlet.

3 Results and Discussion

The most obvious difference in all the samples was their colour, which ranged for the powder samples from pure white for the 150°C-dried sample, through ochre at 250°C to grey at 350–450°C and black at 550–650°C. The gel piece samples displayed very weak colour effects in samples preheated at 250–450°C only, the other preheated materials being transparent. After reheating at 700°C, all the powder samples appeared black, indicating the presence of either carbon or unoxidized organic residues, or structural defects which can also cause dark coloration. The reheated gel pieces were all transparent.

3.1 Differential thermal analysis (DTA)

The thermal analysis curve of mullite precursor type I dried at 150°C is as expected for a gel precursor, showing a large, low-temperature endotherm centred at about 150–250°C, caused by the removal of residual water and solvent. Other broad and weak endotherms at 550–700°C are probably related to the further removal of solvent and residual organics. A sharp exotherm at about 980°C, typical of monophase type I mullite precursors, is associated with the formation of Al_2O_3-rich mullite.

3.2 X-ray diffractometry (XRD)

X-ray powder diffraction showed both the preheated powder and gel piece samples to be amorphous, with two broad humps in the diffraction baseline centred at about 3·5 and 1·4 Å. The XRD patterns of the reheated samples are shown in Fig. 1, and indicate a complex temperature-dependent phase development. The reheated powder sample preheated at 250°C [Fig. 1(E)] contains a cubic spinel phase with a cell parameter similar to that of γ-Al_2O_3. The reheated powder samples preheated at 350°C and 450°C [Figs 1(D) and (C)] show evidence of crystalline mullite, whereas the reheated powder samples preheated at 550°C and 650°C [Figs 1(B) and (A)] are still amorphous. Reheated gel piece samples preheated at 200°C show weak Al-spinel reflections [Fig 1(K)] which become progressively weaker in samples preheated at 250°C and 350°C [Figs 1(J) and (I)], but become markedly stronger in the sample preheated at 450°C [Fig 1(H)]. Preheating the gel pieces at 550°C produces a lower Al-spinel content in the reheated sample, which also contains evidence of another transition alumina, θ-Al_2O_3 [Fig. 1(G)], typical of an Al-rich system which has progressed further in its high-temperature transformations. The reheated gel piece sample preheated at 650°C is amorphous [Fig. 1(F)]. These

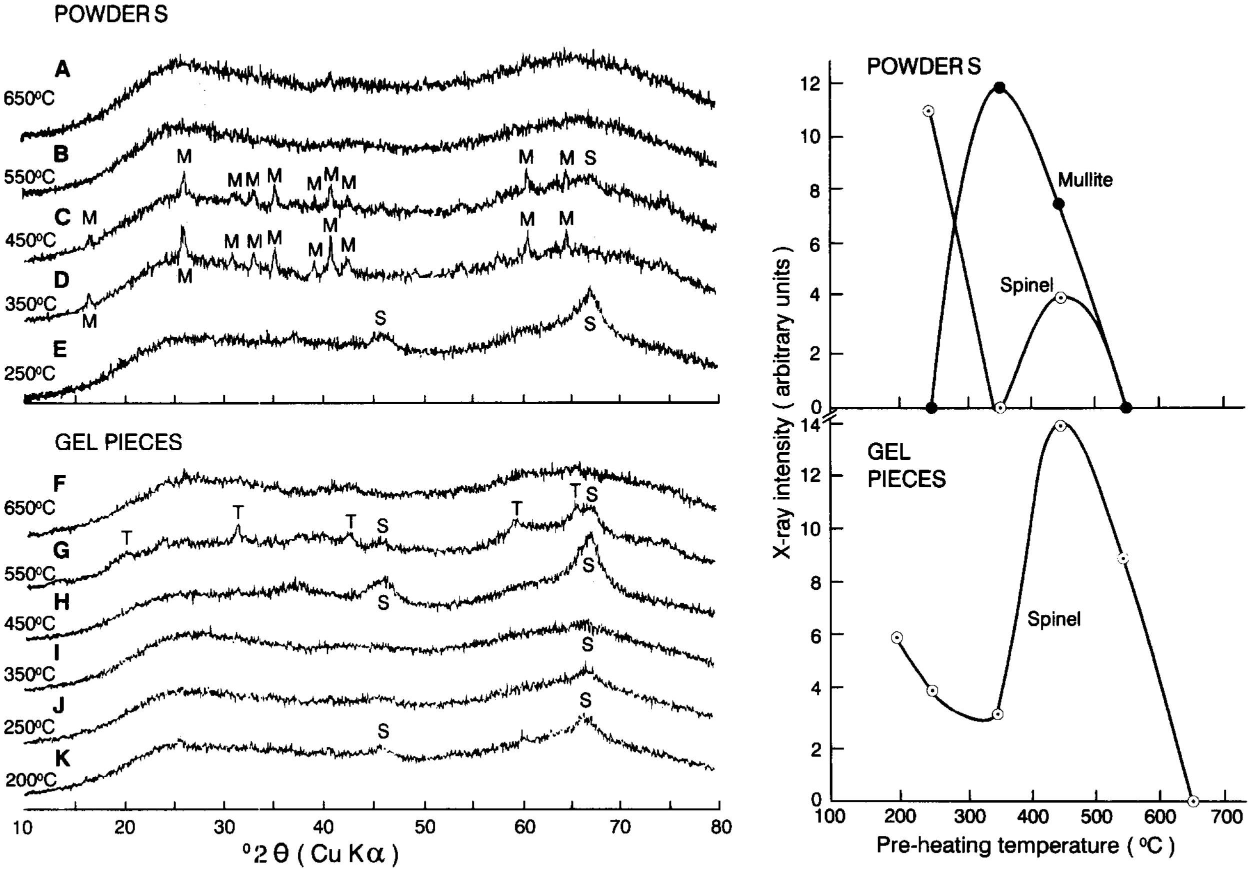


Fig. 1. XRD traces of mullite precursors preheated for 15 h at the marked temperatures, then reheated at 700°C for 15 h. (A)–(E) powdered samples, (F)–(K) gel piece samples. Right-hand diagram: semi-schematic representation of the variation in the XRD intensity of mullite and Al-spinel in reheated powder and gel samples, as a function of preheating temperature. Key: M = mullite, S = Al-spinel, T = θ-Al_2O_3.

changes in the mullite and spinel content are shown semi-schematically as a function of preheating temperature in Fig. 1, constructed from measurements of the 4 4 0 spinel peak areas and the 2 1 0 mullite peak heights.

3.3 MAS NMR

A selection of typical ^{27}Al MAS NMR spectra of powdered samples, both preheated and reheated to 700°C, is shown in Fig. 2, with the corresponding spectra for the gel piece samples shown in Fig. 3. All the ^{27}Al MAS NMR spectra contain three resolvable resonances at about 0, 30 and 55 ppm. The resonances near 0 and 55 ppm indicate 6-fold and 4-fold coordinated Al respectively, whereas the 30 ppm signal has been attributed to 5-coordinated Al.[1] Each of the spectra was fitted to three Gaussian peaks, from which the relative intensities were obtained by integration. The relative areas of the 0, 30 and 55 ppm spectral components are plotted in Fig. 4 as a function of the preheating temperature for the powder and gel piece samples, both preheated only [Fig. 4(A)] and reheated at 700°C after pre-heating [Fig. 4(B)].

Figure 4 indicates that in all the samples there is a general trend with increasing temperature towards greater concentrations of 30 ppm Al, at the expense of 4- and 6-coordinated Al. The samples preheated at 350–450°C are rather anomalous, showing a discontinuity in the amount of 30 ppm

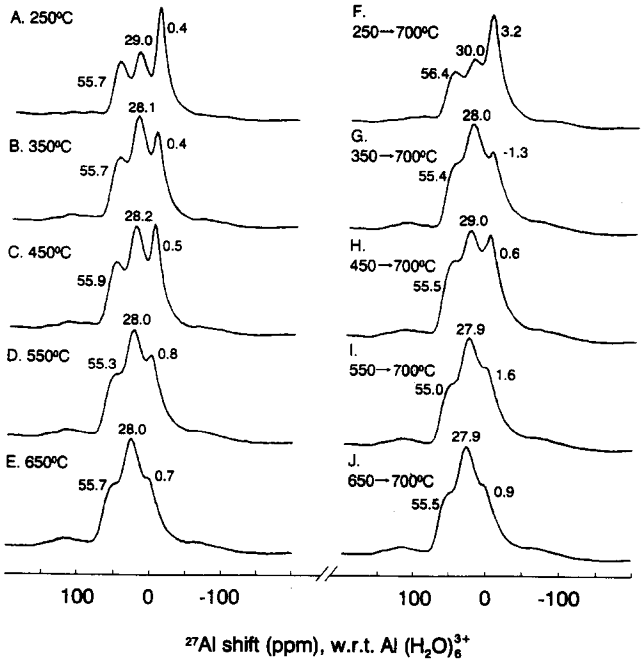


Fig. 2. 11·7 T ^{27}Al MAS NMR spectra of powdered mullite precursor gel: (A)–(E) preheated for 15 h at the indicated temperatures; (F)–(J) preheated for 15 h at the indicated temperatures, then reheated for 15 h at 700°C.

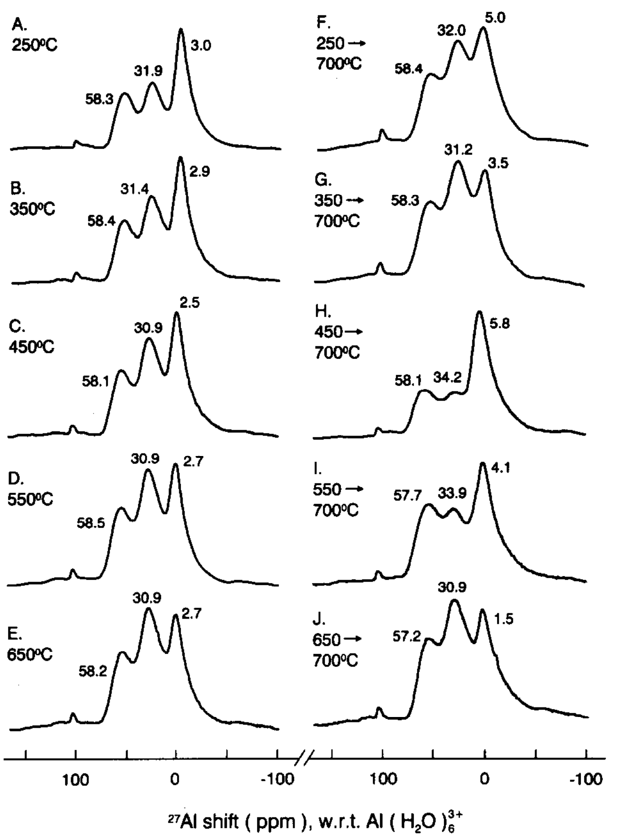


Fig. 3. 11·7 T ^{27}Al MAS NMR spectra of gel piece mullite precursors: (A)–(E) preheated for 15 h at the indicated temperatures; (F)–(J) preheated for 15 h at the indicated temperatures, then reheated for 15 h at 700°C.

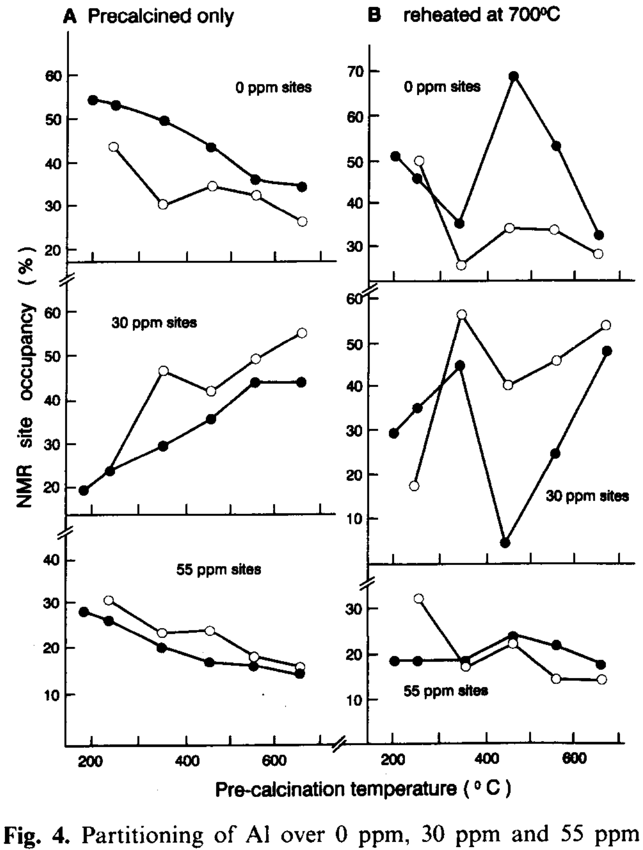


Fig. 4. Partitioning of Al over 0 ppm, 30 ppm and 55 ppm NMR sites in mullite precursor gel powders (open circles) and gel pieces (filled circles) as a function of preheating temperature. (A) Samples preheated for 15 h; (B) samples preheated for 15 h then reheated for 15 h at 700°C.

Al at these temperatures, especially in the powdered samples. A similar but even stronger effect is observed in both the powder and gel piece samples reheated at 700°C; both the powders and gel piece samples display a similar evolution of polyhedra, with reciprocal dependences between the 30 ppm Al and 6-fold coordinated Al. The high proportion of Al(6) and low proportion of 30 ppm Al in the reheated gel piece samples preheated at 450°C and 550°C [Fig. 4(B)] is typical of materials containing Al-spinel, and is consistent with the XRD results for these samples (Fig. 1). By contrast, the higher proportions of 30 ppm Al and decreased Al(6) observed in both powders and gels preheated at 350°C is more typical of a mullite-forming system, and has frequently been described in alumina-rich gels and glasses in the alumina–silica system,[1–3] the evolution of 30 ppm Al reaching a maximum in both gels and glasses just prior to mullite crystallization. Taylor and Holland[1] have related the Al coordination in aluminosilicate gels to their homogeneity, suggesting that Al(4) sites exist in regions of high homogeneity, and reflect efficient incorporation of Al into the tetrahedral silicate network. By contrast, less homogeneous regions, containing discrete alumina-rich and silica-rich domains, are suggested to be characterized by Al(6) sites. Taylor and Holland assign the 30 ppm Al sites to pentacoordinated Al in the interfacial regions between the homogeneous and inhomogeneous domains.[1] On this basis, the present starting material dried at 150°C would be fairly inhomogeneous, but as the sample is progressively preheated to higher temperatures, the number of interfacial 30 ppm Al sites increases, reflecting a progressive improvement in homogeneity with a decrease in the size of the domains and their improved distribution throughout the sample volume. Thus, the crystallization product of the most highly homogeneous systems is predicted to be mullite, as is found to be the case for the sample preheated at 350°C. However, although the NMR and XRD are self-consistent, they do not explain how the degree of homogeneity — which seems to be determined by thermal treatments at relatively low temperatures — is preserved throughout subsequent high-temperature reactions.

An alternative interpretation of the origin of the 30 ppm Al NMR resonance has recently been suggested.[8] This suggestion, which is supported by spectroscopic data and analysis of X-ray pair correlation functions for mullite gel precursors, is that the 30 ppm Al resonance does not arise from pentacoordinated Al but from distorted tetrahedral environments associated with Al triclusters sharing one common oxygen. Such Al sites occur in crystalline mullite, in which they lead to a ^{27}Al resonance at about 43 ppm.[9] In non-crystalline mullite precursors, the elongated bond lengths between the tricluster common oxygens and their adjacent aluminiums are more readily accommodated, permitting increased distortion from tetrahedral symmetry and an associated increase in electric field gradients (EFGs), reflected in an increased upfield chemical shift towards 30 ppm.[8] Since these triclusters are an essential element of the mullite structure, it is suggested that their increased concentration in the gel precursors, reflected by the strength of the 30 ppm Al signal, will lead to increased mullite formation on reheating by the principle of structural continuity.

However, the question remains as to why the concentration of 30 ppm Al sites, whether arising from pentahedral interfacial sites or distorted tetrahedral triclusters, should be so increased by thermal pretreatment at 350°C. The processes involved in the formation of both phase-separated microdomains and oxygen-deficient Al triclusters involve breaking and re-forming of bonds, the kinetics of which seems likely to be influenced by the presence of hydroxyls and organic functional groups. Both types of species are present in the gel precursors, and it will be shown below that the nature and thermal stability of the latter vary with thermal pretreatment.

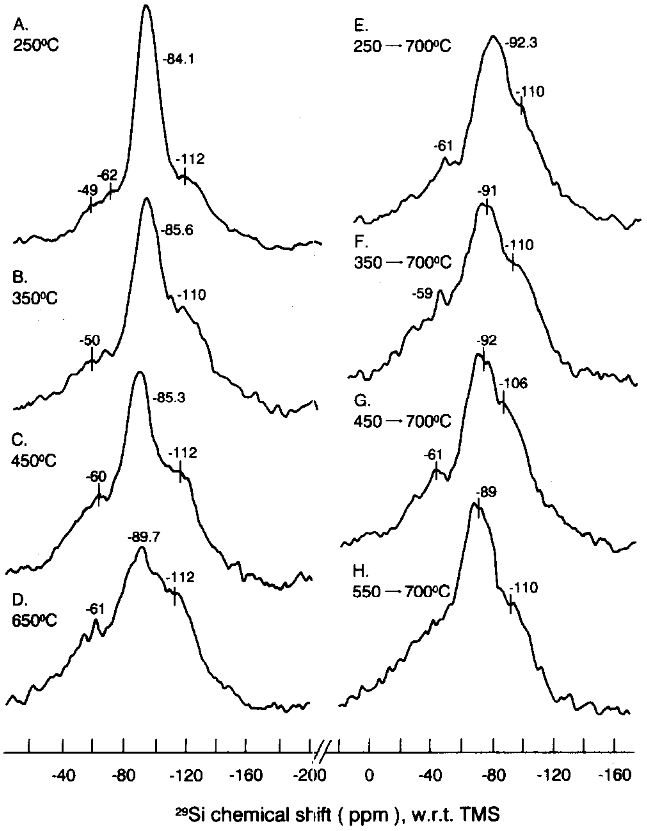


Fig. 5. Typical 11·7 T ^{29}Si MAS NMR spectra of powdered mullite precursor gel: (A)–(D) preheated for 15 h at the indicated temperatures; (E)–(H) preheated for 15 h at the indicated temperatures, then reheated for 15 h at 700°C.

Figures 5 and 6 show a selection of typical ^{29}Si MAS NMR spectra for powdered and gel piece samples, respectively, both after preheating and reheating at 700°C. All the ^{29}Si NMR spectra of the powder samples contain a main region of intensity at about –88 ppm, with two broad but distinguishable shoulders at about –55 and –113 ppm; the gel piece sample spectra (Fig. 6) are more symmetrical. All the powder sample spectra can be fitted by three peaks (Fig. 7), with positions that are essentially independent of the heating conditions.

The peak of maximum intensity shifts slightly from about –85 ppm in the powder and gel piece samples preheated at 250°C, to about –91 ppm in the gel piece sample preheated at 650°C. This spectral region is associated with aluminosilicates such as mullite.[6] The small but significant upfield trend observed in the position of this peak with increasing preheating temperature may reflect an increase in the number of –Si–O–Si– bonds with respect to –Si–O–Al– bonds, caused by the gradual disappearance of unbridged –Si–O–H or –Si–O–R (R = organic residual) structural units.

The broad shoulder at about –110 to –117 ppm, particularly noticeable in the spectra of the powder samples (Fig. 5), indicates the presence of varying amounts of uncombined X-ray amorphous SiO_2 in these samples, which has been cited as evidence for gel inhomogeneity.[2] The formation of –Si–O–Si– domains in the powder precursor

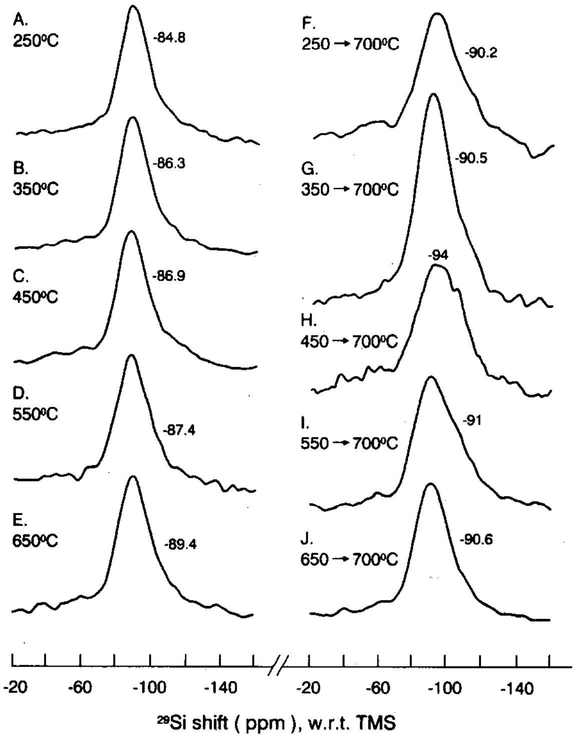


Fig 6. Typical 11·7 T ^{29}Si MAS NMR spectra of mullite precursor gel pieces: (A)–(E) preheated for 15 h at the indicated temperatures; (F)–(J) preheated for 15 h at the indicated temperatures, then reheated for 15 h at 700°C.

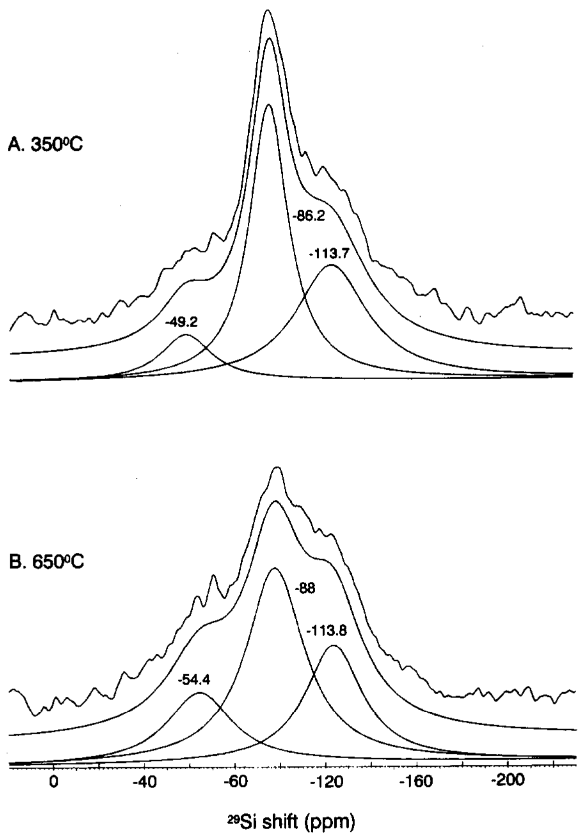
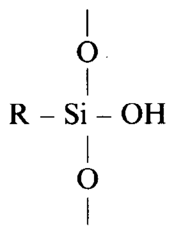


Fig. 7. Typical fits of three Gaussian peaks to ^{29}MAS NMR spectra of mullite precursor gel preheated as indicated.

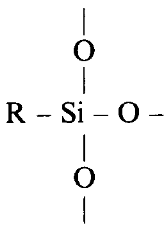
may be due to weak phase separation which is necessary for the formation of alumina-rich mullite plus silica above about 980°C. This phase separation must be much weaker than in type III mullite precursors,[3] which at about 980°C form Al-spinel plus non-crystalline silica. Phase separation into alumina-rich and silica-rich phases prior to recrystallization is less evident in the gel piece samples, possibly due to slower diffusion processes in the gel pieces by comparison with the higher surface area powder samples.

The origin of the lower-field ^{29}Si intensity present in all these spectra at about –55 ppm is more difficult to explain, since this shift is low for Si–O resonances. The olivine minerals $(Mg,Fe)_2SiO_4$, with ^{29}Si chemical shifts of about –62 ppm,[10] represent one of the few entities resonating in this region, but the absence of divalent cations in the present system militates against this explanation for the observed spectra. Another possibility, consistent with the dark colours of the present gels and the persistence of organic residues up to at least 700°C (see below), is the presence of stable amorphous oxycarbide ('black glass'). The $SiCO_3$ unit, one of the species present in gel-derived silicon oxycarbide, has a broad ^{29}Si resonance centred at about –67 ppm, with another unit, SiC_2O_2, giving rise to a peak at about –30 to –40 ppm.[11] These oxycarbide glasses also contain a major SiO_4 resonance at about –110 ppm,[11] consistent with the present spectra. Although such entities may well occur in the samples reheated at 700°C, they are unlikely to be present in the samples which had been only preheated at lower temperatures. In these, the origin of the lower-field NMR resonances is more likely to be precursor organosilicon species such as:



$$\begin{array}{ccc} & | & \\ & \mathrm{O} & \\ & | & \\ \mathrm{R}- & \mathrm{Si} & -\mathrm{OH} \\ & | & \\ & \mathrm{O} & \\ & | & \end{array}$$

and



$$\begin{array}{ccc} & | & \\ & \mathrm{O} & \\ & | & \\ \mathrm{R}- & \mathrm{Si} & -\mathrm{O}- \\ & | & \\ & \mathrm{O} & \\ & | & \end{array}$$

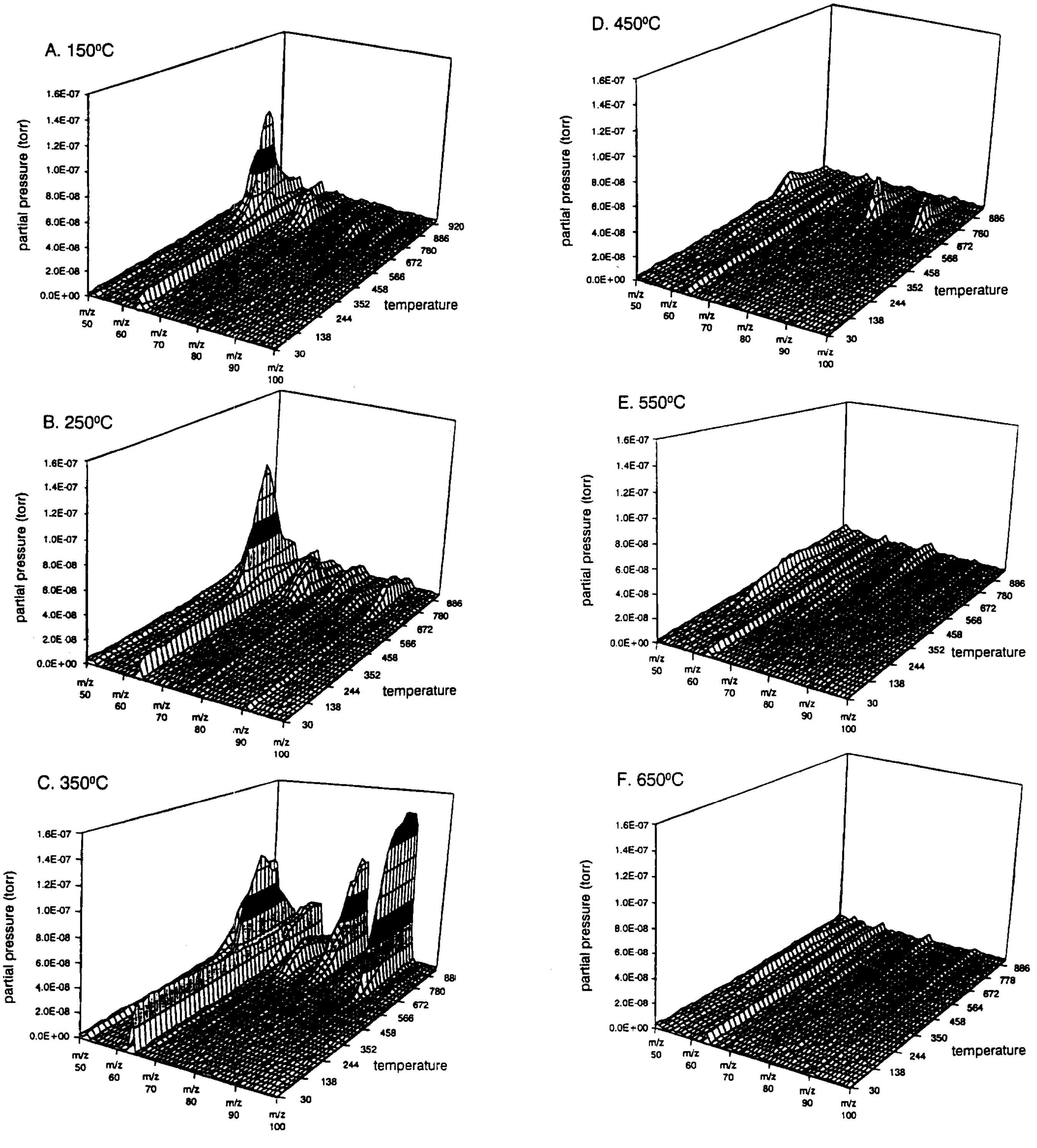
which have been reported[12] as having ^{29}Si resonances at about –56 and –66 ppm, respectively.

To investigate the relationship of protons to the Si atoms, and their possible retention during the thermal treatments, ^{29}Si cross-polarized (CP) spectra were obtained for several samples. The Si atoms detected in this way are those in proximity to protons, and produced spectra which were similar to those run at the same field strength without cross-polarization, suggesting that the protons are distributed throughout the sample and not localized at one particular type of Si site. Although the sample weights within the coil volume were somewhat variable, making the analysis only semi-quantitative, the CP intensity was approximately constant up to 450°C, decreasing as expected to about 39% of its original value after heating at 650°C, with a further decrease to about 31% after reheating at 700°C. These results indicate that thermal treatment removes the silanol protons more or less uniformly, but since some of these remain in the structure up to recrystallization temperatures, their presence could influence mullite formation. However, the CP results give no indication that abnormal proton activity might be implicated in the enhanced transformation to mullite of the sample preheated at 350°C.

3.4 Evolution of organic species during heating

Mass spectra were continuously recorded of the effluent gas streams from the preheated and reheated gel samples as they were heated in flowing air up to 900°C. A selection of three-dimensional mass spectra plotted as a function of heating temperatures is shown in Fig. 8 for the samples which had been preheated to various temperatures as marked.

The spectra of samples preheated at 150 and 250°C [Figs 8(A) and (B)] are characterized by the evolution of a series of fragments of mass 56–58, which begin to appear at about 600°C, reaching their maximum concentration in the gas stream at



A. 150°C

B. 250°C

C. 350°C

D. 450°C

E. 550°C

F. 650°C

Fig. 8. Mass spectra of gases evolved during heating of mullite precursor gels in air at 20°C min^{-1}. Prior to this experiment, the gels were preheated for 15 h at the indicated temperatures.

about 800°C and disappearing by about 900°C [Fig. 9(A)]. A maximum in the mass signal for CO_2 at 800°C suggests that these species are rather resistant to oxidation up to this temperature, after which their disappearance is related to their oxidation. The unambiguous identification of these organic species is complicated by the possible presence of a mixture of compounds, but the complete mass spectra including the lower-intensity cracking fragments are consistent with organic species such as hexane, heptane or their cyclic forms, or cyclohexanone. These compounds apparently originate from the organic by-products of gel formation, perhaps with residual traces of solvent, but their considerable thermal stability, which extends into the temperature region of gel crystallization, is unexpected.

Even less expected is the mass spectrum from the sample preheated at 350°C [Fig. 8(C)] which shows, in addition to the group of masses at

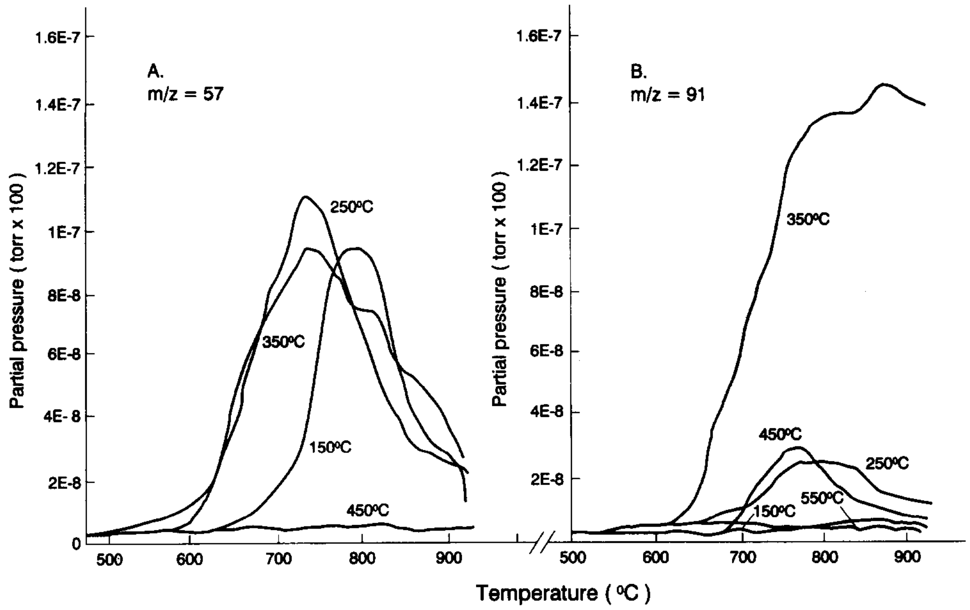


Fig. 9. Temperature dependence of the thermal evolution of two representative organic species from mullite precursor gels preheated for 15 h at the temperatures indicated on each curve: (A) species of mass 57, (B) species of mass 91.

56–58, significant concentrations of masses 76–79, 90–93 and 103–106. These species are even more thermally stable, beginning to be evolved at about 700°C and continuing to increase in concentration up to 900°C [Fig. 9(B)]. Based on their cracking patterns, these species represent mixtures of aromatic-containing benzene and ethyl- and methyl-substituted benzenes. Their formation in the sample preheated at 350°C for a long period (15 h) appears to be related both to the catalytic activity known to be associated with alumina gels containing high proportions of Al$^{'5'}$ (the so-called 'high-5' gels[13] and the preheating temperature, which is sufficient to promote the catalytic reactions of the residual organic species but not sufficiently high to cause oxidation. The effect of the preheating temperature is clearly shown in Fig. 10, in which are plotted the maximum ion signals for masses 57 and 91 as a function of the preheating temperature. Figure 10 shows a marked increased in the aromatic masses in the sample heated in 350°C, whereas at > 350°C the amounts of all organics rapidly decrease, having apparently been carbonized, consistent with the increasingly darker colours of these samples. Mass spectra resembling Figs 8(E) and (F) were obtained from all the preheated samples which had been subsequently reheated at 700°C for 15 h; the reheating conditions were apparently sufficient to remove most of the organic species formed during the preheating stage.

These results suggest that catalytic reactions of the residual organic species are optimized at 350°C with respect to the formation of aromatic compounds that have a high degree of stability towards further heating in air. It was suggested earlier in this paper that the presence of residual organic species could facilitate the formation of the 30 ppm Al sites which may be related to the incipient mullite structure; these Al sites may also be implicated in the catalytic rearrangement of the organic residues during prolonged preheating at lower temperatures. The question remains, however, as to whether these relatively stable organic compounds might also influence the gel crystallization at higher temperatures. One possibility is

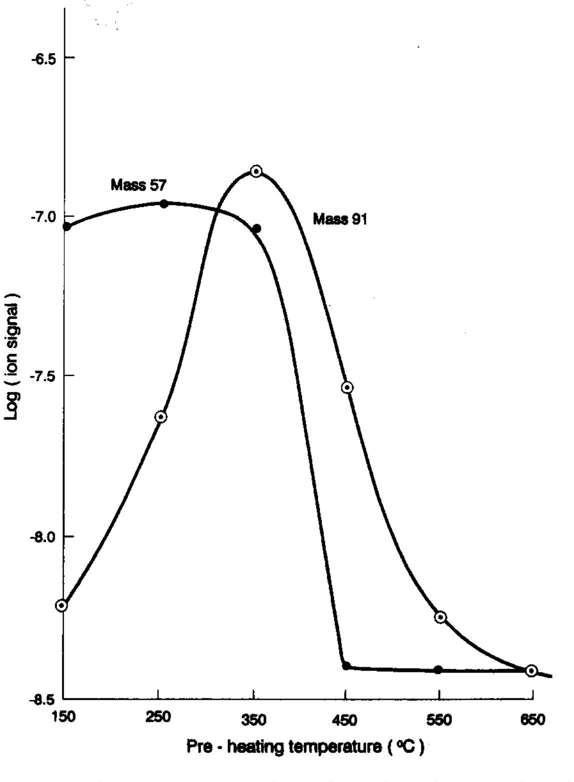


Fig. 10. Maximum concentration of species of mass 57 and 91 evolved from mullite precursor gels as a function of the gel preheating temperature.

that the presence of the thermal degradation products carbon and CO may influence the formation of mullite by providing a locally reducing atmosphere in intimate association with the incipient mullite grains. Although such an atmosphere effect has not previously been demonstrated for gel-derived mullites, it has been shown that the formation of mullite from kaolinite is assisted by reducing atmospheres in the presence of carbon.[14] Another interesting question arising from these results is whether the aromatic species formed at 350°C might somehow modify the catalytic sites in the gel by remaining tightly bound even at temperatures at which crystallization begins, and thereby influence the course of the high-temperature transformations. Further work is required to clarify these matters.

4 Conclusions

(1) The thermal evolution of mullite from organically derived gel precursors, in the form of both pieces and powders, is markedly influenced by thermal pretreatment at low temperatures (<450°C).

(2) Prolonged thermal pretreatment at the optimum temperature (OPT) (250–350°C in the present samples) produces an anomalously high concentration of Al species appearing in the ^{27}Al NMR spectra at ≈ 30 ppm. This situation is perpetuated when the preheated samples are reheated at higher temperatures, leading to the predominance of the 30 ppm Al signal immediately prior to mullite recrystallization.

(3) The 30 ppm Al signal is often attributed to pentacoordinated Al, which may be located in the mullite precursor gels at the interface between Si-rich and Al-rich microdomains. Alternatively, this Al signal could arise from the distorted tetrahedral Al environment in the region of an O-deficient tricluster which constitutes a distinctive element of the mullite structure on recrystallization. The enhanced formation of the 30 ppm Al sites during prolonged thermal treatment at the OPT may be related to the presence of residual hydroxyl groups or organic residues, which facilitate the atomic movements necessary for the formation of either microdomains or tricluster structures.

(4) The gels contain Si in at least three environments: (i) in an aluminosilicate, characterized by a ^{29}Si chemical shift of about −86 ppm, (ii) in uncombined silica (chemical shift of about −112 ppm) and (iii) in an environment which may be associated with residual carbon from the organic precursor (chemical shift of about −55 ppm). After heat treatment, the position of the aluminosilicate resonance moves upfield slightly, reflecting an increase in the number of Si–O–Si bonds resulting from phase separation or from the condensation of Si–OH or Si–OR groups.

(5) Thermal analysis and ^{29}Si cross-polarization experiments indicate the persistence of residual protons in the gels even above the OPT. These protons are not localized on any particular Si site, but may be implicated in the anomalous behaviour of the gels preheated at the OPT, by facilitating the atomic movements necessary for both phase separation and the formation of tricluster structures.

(6) The gels retain up to high temperatures residual organic species from the reactants and possibly traces of solvent. Below the OPT these are predominantly straight-chain or cyclic hydrocarbons, but prolonged heating at the OPT results in their conversion to aromatic species, possibly resulting from the enhanced catalytic properties of the high concentration of 'pentacoordinated' Al in these samples. Prolonged preheating above the OPT destroys the aromatic species, probably by oxidation; once formed, however, these species are thermally stable under dynamic heating conditions to at least 900°C. Their presence in the system at high temperatures could influence the structural evolution of the gel by providing a locally reducing and/or humid atmosphere which facilitates such transformations. Thus, the previously unreported influence of prolonged thermal preconditioning on the structural evolution of the gels under the present conditions appears to be related to the presence of organic residues, which may play an essential role in the formation of catalytically active Al sites characterized by the 30 ppm NMR resonance. These sites could influence subsequent mullite formation both because they form an essential element of the mullite structure, and by their catalytic conversion of the residual organic species to entities whose thermal stability at the recrystallization temperature allows them to participate in these transformations.

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