

Gel formation in mullite precursors obtained via tetraethylorthosilicate (TEOS) pre-hydrolysis

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Tetraethylorthosilicate (TEOS) and aluminium chloride were taken as sources of SiO_2 and Al_2O_3 to prepare precursors of mullite by pre-hydrolysis of TEOS under refluxing conditions. Gelation was carried out at different pH values and the effect of the pH of gelation on the subsequent temperature-induced phase transformations was characterized by differential thermal analysis, powder X-ray diffraction and ^{29}Si and ^{27}Al solid-state nuclear magnetic resonance spectroscopy. A pH-dependent exothermic peak was observed at $\sim 980^\circ\text{C}$. Strong acidic conditions ($\text{pH} = 1.5$) were found to be beneficial for improving the mixing scale of the Al–Si components, leading to a mullitization temperature of $\sim 1200^\circ\text{C}$ and a sharp 980°C exothermic peak. In strong basic conditions ($\text{pH} = 11.5$), no evident $\sim 980^\circ\text{C}$ exothermic peak was detected, and the mullitization temperature was as high as 1350°C , probably due to heterogeneity in the mixing scale of the Al–Si components in the precursor system. A gel formation process has been proposed.

1. Introduction

Synthesis of mullite precursors has continued to attract much attention owing to the wide application of mullite ceramics, namely as a structural and electronic material [1–3]. Many techniques have been developed to obtain mullite powders with high purity, high activity and narrow size distribution. Solution techniques are considered to be the most important because the aluminium- and silicon-containing precursors can be mixed in a very fine scale, allowing low mullitization temperatures to be achieved.

The mullitization temperature is now considered to be an important criterion to assess the mixing scale or the degree of aluminosilicate (–Si–O–Al–) bonds present in the precursor system. Sacks *et al.* [4] pointed out that temperatures in the range of 1600 – 1760°C are required to achieve complete mullitization when alumina and silica particles are mixed in the micrometre size range. For nanosized mixing, the mullitization temperatures are generally reduced to 1300 – 1450°C . If the mixing scale is at the molecular level, mullitization temperatures of 1000 – 1100°C can be achieved. For instance, Huling and Messing [5] obtained complete mullitization of their “SH” xerogel at $\sim 1000^\circ\text{C}$. Such low mullitization temperatures are indicative that all the aluminiums and silicons are

linked in the form of aluminosilicate bonds, eliminating the need for long-distance diffusion and bond rearrangement. However, when a cubic transition alumina was allowed to form, epitactic nucleation of spinel occurred at $\sim 1000^\circ\text{C}$ and higher temperatures were needed for the formation of mullite [5].

In this work, TEOS and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ were used as initial materials to prepare mullite by heat treatment of xerogels. The effects of the pH prevailing during gelation on the phase development during subsequent heat treatment of the xerogels has been studied to ascertain its influence on the mixing scale of the two silicon and aluminium components.

2. Experimental procedure

2.1. Synthesis of the mullite precursor

The colloidal Al_2O_3 – SiO_2 gel with the stoichiometry of 3:2 mullite was prepared by the following procedure: 13.2 g tetraethylorthosilicate ($\text{Si}(\text{OC}_2\text{H}_5)_4$, TEOS, Af products) was dissolved in a definite volume of absolute ethanol to obtain a 0.25 M TEOS solution. 0.5 M aluminium chloride hydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, BDH) aqueous solution was obtained by dissolving $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in 500 ml distilled water. Both solutions were then mixed in the proportions of stoichiometric

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mullite (200 ml TEOS ethanol solution and 300 ml AlCl_3 aqueous solution). After stirring for 2 h at room temperature, the transparent solution was heated and vigorously stirred at 70°C under reflux for 8 h. The hydrolysed mixture solution was then transferred to a beaker and stirring was continued at room temperature for 30 min. A dropwise dilute ammonia solution was added into the clear solution until pH 9 was achieved. The milky white coprecipitate was then washed with distilled water in a compressed air filter until no white precipitate occurred in the filtrate with the addition of a 3 N silver nitrate solution (AgNO_3). In order to investigate the effects of pH during gelation on the phase transformation in the xerogel, the obtained gel was divided into six equal portions. One was directly dried in an oven at 80°C for 72 h. This precursor was denoted M. The other five portions were adjusted to different pH values such as 1.5, 3.5, 5, 9, 11.5, by adding a suitable volume of 3 N nitric acid and ammonia solution. After being kept in air for 8 h, the gels were dried in an oven at 80°C for 72 h. These precursors were denoted M1, M3, M5, M9 and M11, respectively.

2.2. Characterization of the mullite precursors

In order to ascertain the phase transformation behaviour, the as-prepared xerogels were analysed by differential thermal analysis (DTA) at a heating rate of $10^\circ\text{C min}^{-1}$ up to 1100°C with $\alpha\text{-Al}_2\text{O}_3$ powder as reference material. The xerogels were calcined at 450, 950, 1100, 1200 and 1350°C for 1 h, and analysed by X-ray diffraction (XRD) analysis, using CuK_α radiation, voltage 40 kV, electric current 20 mA (Rigaku, Geigerflex, D/max-C).

^{29}Si and ^{27}Al magic angle spinning nuclear magnetic resonance (MAS NMR) spectra of the M1 and M11 precursors were recorded on a Bruker MSL 400P(9.4T) NMR spectrometer. ZrO_2 rotors were used. ^{29}Si MAS NMR spectra were recorded at 79.49 MHz, using 50° pulses, 30 s recycle delays and 4–5 kHz spinning rates. Chemical shifts are quoted in parts per million (p.p.m) from external TMS (tetramethylsilane). ^{27}Al MAS NMR spectra were recorded at 104.26 MHz, using short ($0.6\ \mu\text{s}$, equivalent to 10°) and powerful radio frequency pulses, 0.4 s recycle delays and 15 kHz spinning rate. Chemical shifts are quoted in p.p.m. for external $\text{Al}(\text{H}_2\text{O})_6^{3+}$.

3. Results and discussion

3.1. Structural evolution upon heating

The DTA curves (from $600\text{--}1100^\circ\text{C}$) for all samples with a different gelation pH are shown in Fig. 1. The differences at $960\text{--}980^\circ\text{C}$ are evident. In acidic conditions, the DTA curves show strong exothermic peaks in that region. At pH = 7, a weak exothermic peak is observed and in the basic region, no exothermic peak is observed.

The XRD patterns for M1 (strong acidic conditions) heat-treated samples are shown in Fig. 2. The xerogel is amorphous. At 450°C , no evident crystalline phase

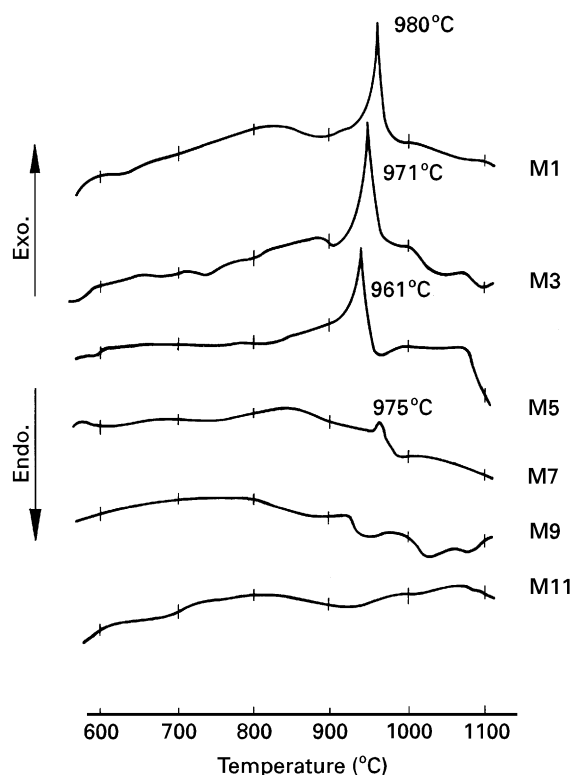


Figure 1 DTA curves of mullite precursors obtained under different pH gelation conditions, at a heating rate of $10^\circ\text{C min}^{-1}$ in air.

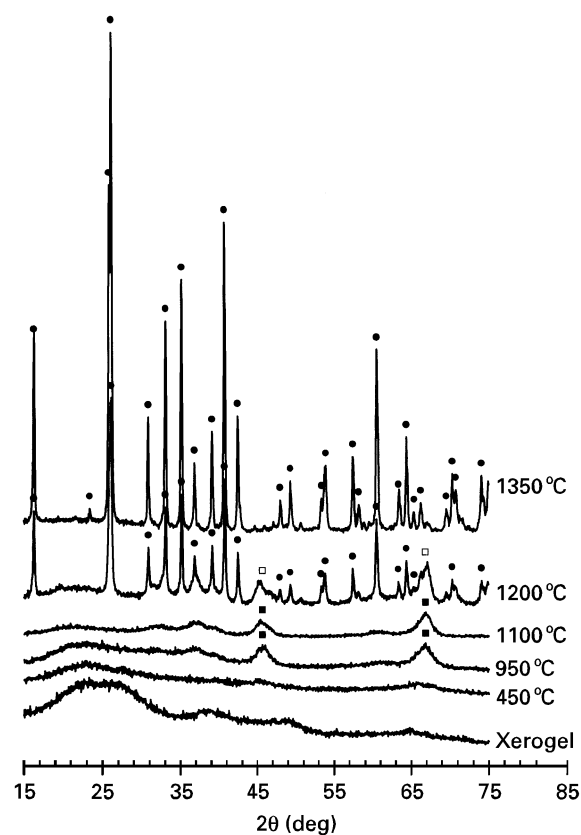


Figure 2 XRD patterns for the M1 xerogel and the powders heated at various temperatures for 1 h. (■) $\gamma\text{-Al}_2\text{O}_3$, (□) $\theta\text{-Al}_2\text{O}_3$, (●) mullite.

is detected. At 950°C , $\gamma\text{-Al}_2\text{O}_3$ is observed. The distinction between $\gamma\text{-Al}_2\text{O}_3$ and Al–Si spinel is still open to controversy [6, 7]. Although it has been reported recently that a $\sim 12\ \text{mol}\%$ SiO_2 could be

incorporated into $\gamma\text{-Al}_2\text{O}_3$ in some precursors [8], in this paper the term $\gamma\text{-Al}_2\text{O}_3$ will be used. For the powder heated up to 1100°C , no big difference is observed except an increase in the intensity of the $\gamma\text{-Al}_2\text{O}_3$ peak. When the temperature is increased to 1200°C , mullite becomes the major phase with a trace of $\theta\text{-Al}_2\text{O}_3$. However, the pattern shows a low crystallinity because the (120) and (210) crystal faces of mullite are still hard to distinguish. During this heat-treatment, the SiO_2 component continues to be amorphous. At 1350°C , the powder only contains mullite.

The process of phase development in the M11 xerogel, however, shows some differences, as observed in Fig. 3. The M11 xerogel exhibits four phases: bayerite, gibbsite, boehmite and amorphous silica. This demonstrates that the segregation of alumina and silica has taken place in the precursor. After 1 h at 450°C , the bayerite, gibbsite and boehmite are decomposed and $\gamma\text{-Al}_2\text{O}_3$ is formed and maintained until 1100°C . When the temperature is increased to 1200°C , $\gamma\text{-Al}_2\text{O}_3$ transforms into $\theta\text{-Al}_2\text{O}_3$. At 1350°C , only mullite is observed.

The ^{29}Si MAS NMR spectra of M1 and M11 precursors are depicted in Fig. 4. The M1 precursor heated at 450°C and the M11 precursor heated at 450 and 950°C display two main resonances centred at -81 and -108 p.p.m. The latter peak exhibits a shoulder at about -100 p.p.m. The resonances at -81 and -108 p.p.m. are assigned to silicon atoms connected to four aluminium atoms via oxygens [$\text{Q}^0(4\text{Al})$ sites] and to $\text{Q}^4(0\text{Al})$ sites, respectively [9]. The shoulder at -100 p.p.m. may be given by $\text{Q}^4(1\text{Al})$ environments. When the temperature of M11 precursor is increased to 950°C the low-frequency line becomes more intense and shifts slightly, from -81 p.p.m. to -83 p.p.m. The spectrum given by the 950°C M11 precursor is rather different, displaying a broad line, probably due to the overlap of signals

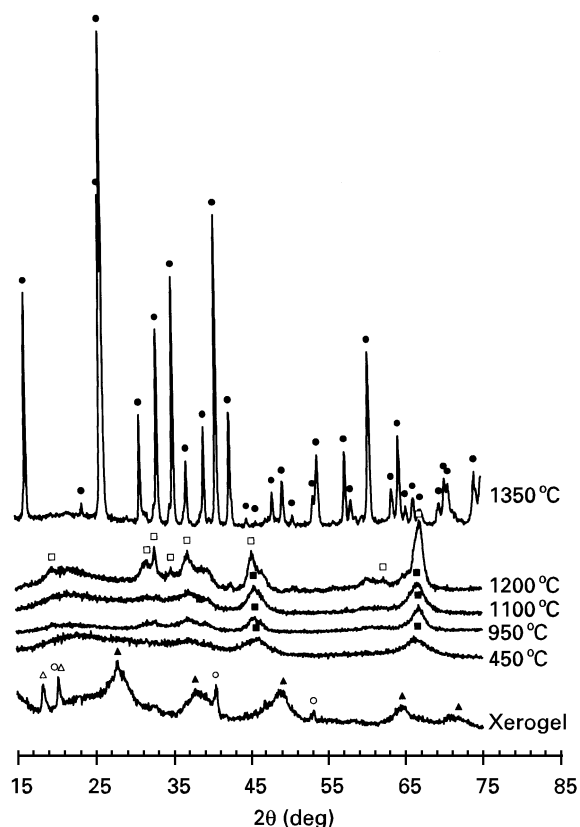


Figure 3 XRD patterns for the M11 xerogel and the powders heated at various temperatures for 1 h. (Δ) gibbsite, (\blacktriangle) boehmite, (\circ) bayerite, (\blacksquare) $\gamma\text{-Al}_2\text{O}_3$, (\square) $\theta\text{-Al}_2\text{O}_3$, (\bullet) mullite.

given by different $\text{Q}^n(m\text{Al})$ sites. At 1100°C the spectrum M11 clearly displays three signals at -91 , -101 and -109 p.p.m., while the deconvolution (not shown) of the M1 spectrum suggests that at least three similar signals are also present.

The ^{27}Al MAS NMR spectra of M1 and M11 precursors are depicted in Fig. 5. The spectrum of the M1

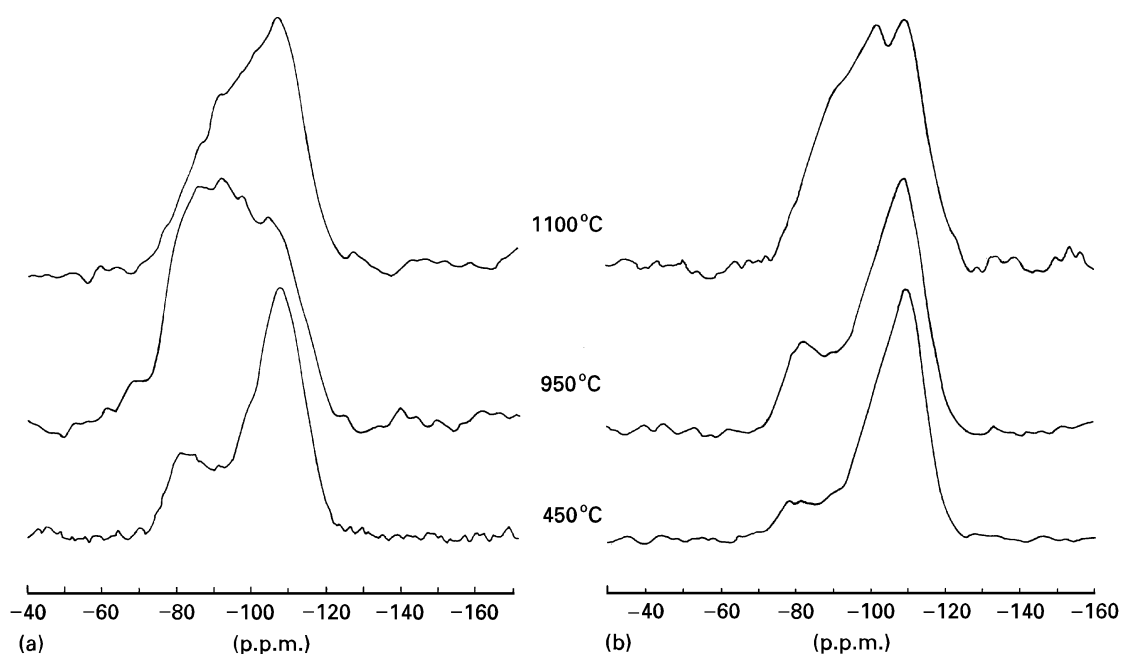


Figure 4 ^{29}Si MAS NMR spectra of M1 and M11 powders heated at 450 , 950 and 1100°C for 1 h. (a) M1, (b) M11.

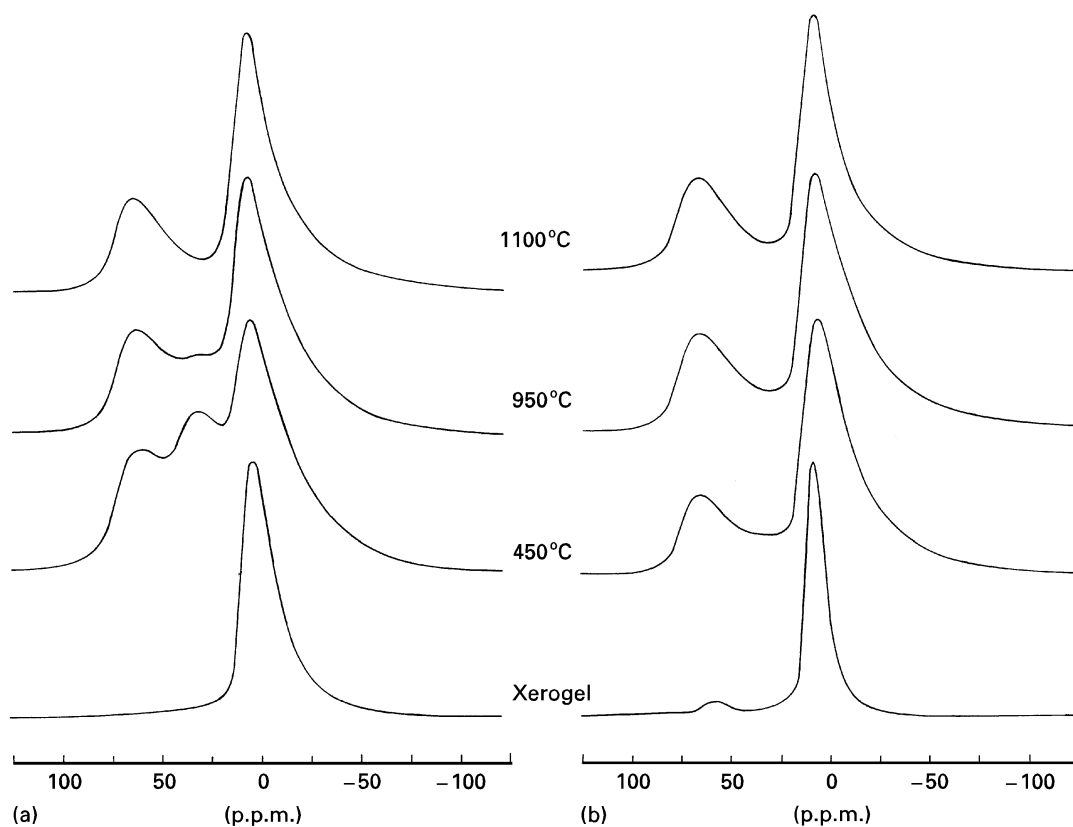


Figure 5 ^{27}Al MAS NMR spectra of M1 and M11 precursors and the powders heated at 450, 950 and 1100 °C for 1 h. (a) M1, (b) M11.

xerogel displays a single signal at 4.4 p.p.m. characteristic of six-coordinated aluminium. The M11 xerogel gives a faint peak at 58 p.p.m. and a strong signal at 7.5 p.p.m. which are, respectively, assigned to four- and six-coordinated aluminium. Note that the latter signal is much sharper than the signal given by the M1 xerogel, suggesting that crystalline phases are present in M11. This is confirmed by powder XRD (Figs 3 and 4). The spectra given by the calcined M11 precursors display two signals at 64 and 6 p.p.m. and very similar to the spectrum of γ -alumina [10]. This is in accord with powder XRD which shows that the precursors are rich in γ -alumina. The spectra of the M1 precursor heated at 450 and 950 °C display peaks at 5–6, 32 and 59–63 p.p.m. The signal at 32 p.p.m. is often observed in the spectra of non-crystalline mullite precursors and it has been assigned to five-coordinated aluminium [10, 11]. At 1100 °C no five-fold aluminium is observed and the spectrum is characteristic of γ -alumina.

In a study on the constitution of the γ -alumina phase in chemically produced (crystalline) mullite precursors, Schneider *et al.* [8] have previously suggested that the ^{29}Si NMR resonance at about -80 p.p.m. might be due (i) to the presence of silicon in an Al_2O_3 -rich non-crystalline phase, or (ii) to the incorporation of silicon in γ -alumina. However, an additional Al_2O_3 -rich non-crystalline phase should yield a ^{27}Al NMR peak at about 30 p.p.m. characteristic of five-fold aluminium [11], and this was not observed. The same result is found with our M11 (crystalline) precursor but not with (amorphous) M1. Schneider *et al.* [8] have also shown that the ^{27}Al NMR spectra of both

non-leached and NaOH-leached samples following heat treatment at 1100 °C are nearly identical and very similar to that of pure γ -alumina. Furthermore, the precursors heat treated at 900–1100 °C displayed signals at -80 and -110 p.p.m. ^{29}Si NMR spectra, while after subsequent NaOH-treatment they exhibited only the -80 p.p.m. signal. These findings led to the conclusion that the spinel phase was the only Al_2O_3 -rich compound in the precursors and that silicon was incorporated in the spinel phase. We believe that this conclusion also holds for our M11 precursors but not for M1. We note, in passing, that amorphous mullite precursors were found to give a sharp DTA exothermic peak at 980 °C while crystalline precursors do not display such a peak [8, 11]. In a similar way, the M1 precursor gives an exothermic peak at 980 °C while M11 does not. These facts suggest that the different behaviour of M1 and M11 precursors upon thermal treatment is related with their amorphous or crystalline nature.

3.2. Gel formation

The different conditions prevailing during gelation of the M1 and M11 samples could originate different gel structure which, in turn, could determine different evolutions in subsequent heat treatments, just as shown above. Out of all the processing parameters, pH value during hydrolysis and coprecipitation is considered to play a vital role in the development of gels of different characteristics [12]. Taking into consideration the results discussed above, a tentative and somewhat speculative description of the gelation

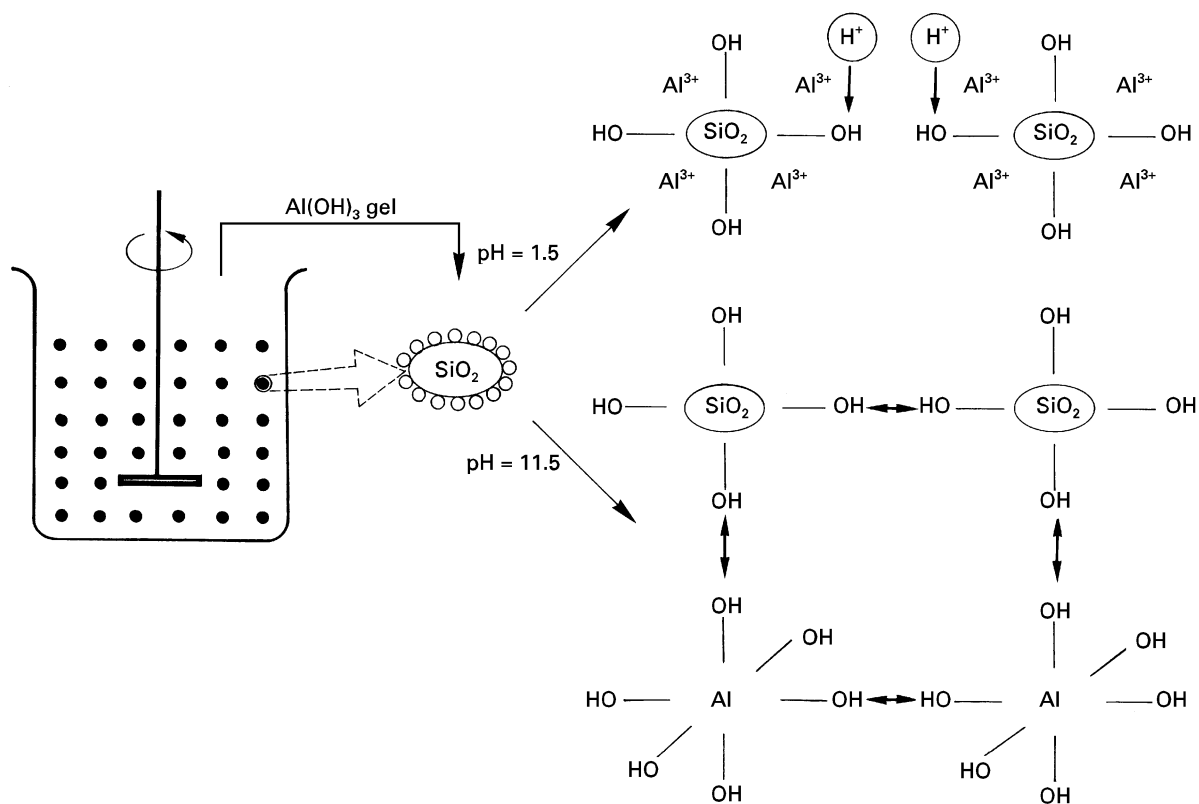


Figure 6 The schematic model for the different gelation processes.

process occurring at different pH values can be attempted.

Hydrolysis and condensation reactions of TEOS are ordinarily considered to proceed spontaneously [13] with relative rate depending on experimental conditions [14]. Under our conditions, large amounts of water, high hydrolysis temperature (70°C) and long hydrolysis time (8 h) are used, so the hydrolysis reaction of TEOS will be faster and the condensation reaction would control the whole process. Therefore, in the hydrolysed mixture solution, the SiO_4 tetrahedra could be considered to have been polymerized to form a three-dimensional SiO_2 framework structure. When a dropwise dilute ammonia is added to the clear mixture solution, a white milky $\text{Al}(\text{OH})_3$ precipitate occurs and coats on the surface of the SiO_2 particles.

When the as-obtained gel is adjusted into the strong acidic region with the addition of 3 N HNO_3 aqueous solution, the hydration of the OH^- groups on the surface of the silica particles can reduce the possibility of clustering during the subsequent drying process. On the other hand, the post-precipitate $\text{Al}(\text{OH})_3$ reacts with HNO_3 again and the product Al^{3+} can remain and act as a counterion absorbing on the surface of the silica particles in the gel. This will increase the proximity of Al^{3+} and SiO_2 particles and makes it possible to obtain a more homogeneous precursor. The observation of the amorphous precursor suggests, as pointed out above, no great segregation for the aluminium and silicon components. However, the mixing scale in this case is much lower than that of the "SH" xerogel with molecular-level mixing prepared by other workers [5, 15] because of the previous formation of the three-

dimensional SiO_2 framework structure. Thus, this precursor, at most, could be called a nanoscale homogeneity and a higher temperature (1200°C) is needed for this sample to finish mullitization.

When the gel is adjusted to the strong basic region, however, the gelation mechanism is quite different. The role of OH^- during gelification is detrimental to improving the mixing state of the Al–Si components. With the addition of ammonia, several reactions will take place simultaneously: the hydration of both components and the condensation reactions between $\text{Al}(\text{OH})_3$ particles, $\text{Al}(\text{OH})_3$ and SiO_2 particles, and SiO_2 particles. This will result in clusters and serious segregations of alumina and silica. The occurrence of crystalline modifications: bayerite, gibbsite and boehmite for the Al_2O_3 component is one result of the above reactions. Thus the mixing scale in the M11 precursor is even worse than that of the M1 precursor. As a result, this precursor could be called a nanoheterogeneity of Al–Si components (heterogeneity on a nanometre scale). The discrete alumina and silica phases in such a precursor behave like distinct entities during the subsequent heat treatment: $\gamma\text{-Al}_2\text{O}_3$ crystallizes before 450°C and then transforms into $\theta\text{-Al}_2\text{O}_3$ at 1200°C. 1350°C is required to complete the reaction between $\theta\text{-Al}_2\text{O}_3$ and SiO_2 for mullitization. The schematic model for the whole process could be illustrated as in Fig. 6.

The presence of the strong exothermic peak at $\sim 980^\circ\text{C}$ could only be observed in samples obtained under acidic conditions, in other words, the acidic conditions during gelation should be the main cause for the appearance of this exothermic peak. As discussed above, the mixing scale of the Al–Si

components has been greatly improved under these conditions. This $\sim 980^\circ\text{C}$ exothermic peak is generally considered to be due to the formation of either mullite or Al-Si spinel or both, depending on the various initial materials and processing adopted [12]. To determine which of the above forms is dominant in our case, further work will be needed. For the precursors obtained under basic conditions, no evident $\sim 980^\circ\text{C}$ exothermic peak is detected, probably due to the segregation of the Al-Si components in the precursor system. If this is so, the appearance of the $\sim 980^\circ\text{C}$ exothermic peak could be taken as evidence of a better homogeneity in the degree of mixing of the aluminium and silicon components in the precursors.

4. Conclusion

The effect of the pH values during gelation on the Al-Si homogeneity in the mullite precursors has been investigated. Acidic conditions are beneficial for obtaining homogeneous precursors, which is important to reduce the mullitization temperature. The observation of a pH-dependent $\sim 980^\circ\text{C}$ exothermic peak seems to be related to the degree of the Al-Si homogeneity in the obtained precursors.

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