

# Formation of Mullite from Mechanochemically Activated Oxides and Hydroxides

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## Abstract

The formation of mullite from different precursors prepared by a mechanochemical method were investigated. The structural changes caused by grinding various oxide/hydroxide mixtures were characterized by the <sup>29</sup>Si and <sup>27</sup>Al MAS-NMR, FTIR, DTA and XRD. Thermal treatment of precursors prepared by mechanochemical activation from gibbsite and silica gel led to the crystallization of mullite at  $\approx 1200^\circ\text{C}$  via a spinel-phase, while precursors prepared from  $\alpha\text{-Al}_2\text{O}_3$  and silica gel or gibbsite and fused silica formed mullite at about  $1400^\circ\text{C}$  by solid state reaction between  $\alpha\text{-Al}_2\text{O}_3$  and cristobalite. MAS-NMR spectroscopy shows that the crystallization of mullite at lower temperatures is associated with good homogeneity, as judged by the amount of Si present in the aluminosilicate resonances. © 1998 Elsevier Science Limited. All rights reserved

## 1 Introduction

One conventional process for preparing mullite is by solid-state reaction between powdered raw materials (oxides, hydroxides, salts and silicates). The reaction between alumina and silica is a diffusion-controlled process in which the mullitization temperature depends on the particle size of the starting powders.<sup>1</sup> Thus, the thermal reaction between 0.3 and 0.5  $\mu\text{m}$   $\alpha\text{-Al}_2\text{O}_3$  and  $< 2 \mu\text{m}$  quartz particles requires high temperatures ( $1470^\circ\text{C}$ ) for mullite formation.<sup>2</sup> We have previously shown<sup>3</sup> that when hydroxides or hydrous starting materials are subjected to mechanical treatment, the mixture becomes more homo-

geneous due to the formation of Si–O–Al bonds, and its behavior on subsequent thermal treatment resembles that of precursor gels obtained via solution chemistry. The temperature of mullite formation in such compounds is typically about  $1200^\circ\text{C}$ , and the increased reactivity of the ground powders was found to be due to formation of Si–O–Al bonds rather than decreased particle size resulting from grinding. We have suggested that the formation of Si–O–Al bonds results from polycondensation reactions between Si–OH and Al–OH groups.<sup>3</sup>

Boehm and Kiselev have reported<sup>4,5</sup> that the chemistry of oxide surfaces is controlled mainly by the OH concentration present. On this basis, mechanical treatment of mixtures containing high concentration of hydroxyl groups should result in more homogeneous systems than in mixtures whose components contain few hydroxyls. Consequently, the mullitization temperature of these precursors should vary considerably with different starting materials. The present study was carried out to investigate the role of hydroxyl groups in the polymerization reactions initiated by mechanical treatment between the Al–OH and Si–OH groups of oxide/hydroxide mixtures. The homogeneity of the resulting precursors was characterized by their mullitization behavior, and their structures were investigated by solid-state MAS-NMR.

## 2 Experimental Procedure

The starting materials used in the investigation were gibbsite, Al(OH)<sub>3</sub>, (Showa Denko Co.Ltd., H-43M, purity 99.6%, BET specific surface area  $8 \text{ m}^2 \text{ g}^{-1}$ ), high purity  $\alpha\text{-Al}_2\text{O}_3$  (Sumitomo Chemical Co.Ltd, AKP-30, BET specific surface area  $7.49 \text{ m}^2 \text{ g}^{-1}$ ), silica gel (Wako Pure Chemical Ind.

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Co.Ltd, Wako gel Q-63, average particle size  $\approx 18 \mu\text{m}$ ) and fused silica (Denki Kagaku Kogyo Co.Ltd., FB-301, average particle size  $\approx 7.3 \mu\text{m}$ , BET specific surface area  $4.3 \text{ m}^2 \text{ g}^{-1}$ ). The fused silica contained a small amount of crystalline quartz and cristobalite impurity. All reagents were used without pretreatment. Experiments were carried out on three combinations:  $\alpha\text{-Al}_2\text{O}_3$  + silica gel,  $\text{Al}(\text{OH})_3$  + silica gel and  $\text{Al}(\text{OH})_3$  + fused silica, denoted M1, M2 and M3, respectively. The composition of all the mixtures was  $75 \pm 1 \text{ wt}\%$  alumina/ $25 \pm 1 \text{ wt}\%$  silica, chosen to give products in the mullite + alumina system, and near the boundary of the mullite solid solution range in the  $\text{Al}_2\text{O}_3\text{-SiO}_2$  phase diagram.<sup>6</sup> The powders were ground in a planetary pot mill (Itoh Co. Ltd., La-PO.1) for 20 h at a rotation speed of 400 rpm using a silicon nitride pot and milling media. The weight ratio of milling media to powder was 20:1.

Differential thermal analysis (DTA) (Rigaku, Thermoplus 8120) was carried out at a heating rate  $10^\circ\text{C min}^{-1}$  to  $1300^\circ\text{C}$ . The amount of mullite was estimated semi-quantitatively by X-ray diffraction (Rigaku, Geigerflex) with monochromated  $\text{CuK}\alpha$  radiation using  $\text{CaF}_2$  as internal standard. The calibration material was high-purity mullite powder (Chichibu-Onoda Co. Ltd., HP-20) which was annealed at  $1500^\circ\text{C}$  for 24 h before being used as the standard. The ratio of the  $121$  mullite reflection to the  $111$   $\text{CaF}_2$  reflection was measured for each sample, and compared with the value for standard mullite (defined as 100%). Infrared spectra of samples were recorded using a (Shimadzu, FTIR 8200PC) spectrometer with the samples suspended in KBr discs.  $^{29}\text{Si}$  and  $^{27}\text{Al}$  MAS-NMR spectra were obtained at 11.7 T using a Varian Unity 500 spectrometer and Doty probe spun at 10–12 kHz. The  $^{29}\text{Si}$  spectra were acquired using a  $90^\circ$  pulse of  $6 \mu\text{s}$  and recycle time of 100 s, and were referenced to tetramethylsilane (TMS). The  $^{27}\text{Al}$  spectra were acquired using a  $15^\circ$  pulse of  $1 \mu\text{s}$  and a recycle time of 1 s, and were referenced to  $\text{Al}(\text{H}_2\text{O})_3^{3+}$ .

### 3 Results and Discussion

Figure 1 shows the XRD patterns of the mixtures ground for 20 h. Mixtures M1 and M2 show crystalline  $\alpha\text{-Al}_2\text{O}_3$  and gibbsite peaks; in M1, the  $\alpha\text{-Al}_2\text{O}_3$  peaks are broadened and of decreased intensity due to reduction of crystallite size and accumulation of microstrain. The M2 sample contains a small amount of crystalline gibbsite with unbroadened XRD peaks, but M3 is fully amorphous, suggesting that gibbsite is more readily amorphized in the presence of fused silica than with silica gel. Prolonged grinding has been shown

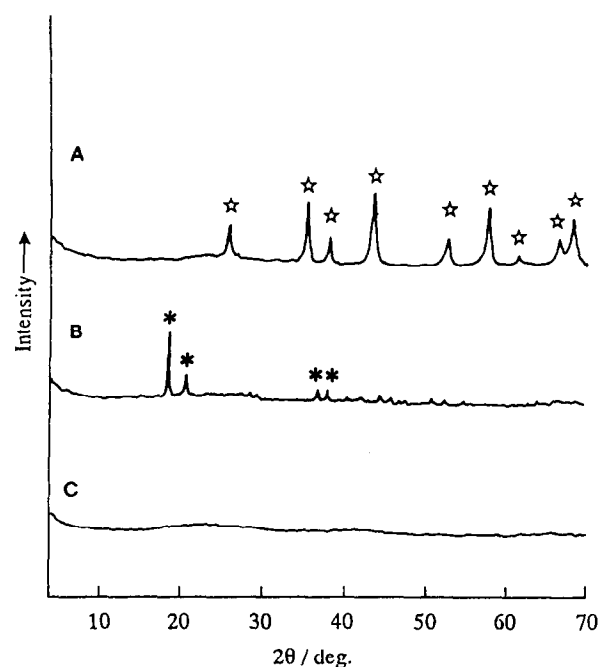


Fig. 1. XRD pattern of ground samples: A-M1; B-M2; C-M3. Key:  $\star \alpha\text{-Al}_2\text{O}_3$ ;  $\ast$  gibbsite.

to convert all hydrated aluminas into an amorphous state.<sup>7</sup> The particles of fused silica are considered to be composed mainly of polygrains and hardly vitreous state. The breakdown of the particles during milling occurred readily in the fused silica, starting from the grain boundary within each particle, without aggregation with gibbsite. The silica gel contains a large concentration of (OH) groups and adsorbed water; during grinding the aggregation of silica gel with gibbsite decreases the effect of grinding, retarding the full amorphization of the gibbsite. An alternative explanation for the behavior of M3 is the formation of aluminosilicate resulting from the mechanical treatment. Liao and Senna have reported<sup>8–10</sup> that mechanochemical dehydration and amorphization of hydroxides is substantially enhanced by grinding with  $\text{SiO}_2$  and have explained this phenomenon by suggesting that hydroxide decomposition and incipient formation of metal silicates are mutually enhanced reactions.

Figure 2 shows the FTIR spectra of the starting materials and ground powders, which confirm the conclusions drawn from the XRD data (Fig. 1). The M1 spectrum shows the absorption bands due to alumina and silica. The spectrum of M2 shows the (OH) vibration of crystalline gibbsite and the tetrahedral Si–O vibration at about  $1000\text{--}1100 \text{ cm}^{-1}$ , overlapping the (OH) bending vibration of gibbsite at about  $1020 \text{ cm}^{-1}$ . In the M3 spectrum, the (OH) stretching vibration of gibbsite at about  $3500 \text{ cm}^{-1}$  has merged into one broad absorption band, and the (OH) bending vibrations of gibbsite at about  $1020 \text{ cm}^{-1}$  have disappeared.

All the spectra of the ground mixtures show the virtual disappearance of the band at  $800\text{ cm}^{-1}$  arising from three-dimensionally bonded  $\text{SiO}_4$ .<sup>8</sup>

Figure 3 shows the DTA traces of the ground samples. Mixture M1 shows a small exothermic peak at about  $970^\circ\text{C}$ . M2 contains endothermic peaks attributed to the dehydration of adsorbed water at  $130^\circ\text{C}$  and dehydroxylation of residual gibbsite at  $260^\circ\text{C}$ , a broad exothermic peak at  $963^\circ\text{C}$  and small exothermic peak at  $1260^\circ\text{C}$ . M3 contains an endothermic peak due to dehydration of adsorbed water at about  $130^\circ\text{C}$  and broad exothermic peaks at  $810\text{--}860^\circ\text{C}$  and  $1020\text{--}1040^\circ\text{C}$ . The thermal behavior of sample M2 is similar to those previously reported by us<sup>3</sup> and M3 is similar to

mechanochemically treated gibbsite studied by Tsuchida and Ichikawa,<sup>7</sup> who found that mechanochemically amorphized gibbsite transforms into  $\eta\text{-Al}_2\text{O}_3$  at about  $850^\circ\text{C}$ , then to  $\alpha\text{-Al}_2\text{O}_3$  at about  $1000^\circ\text{C}$  accompanied by a small exothermic effect. The small  $970^\circ\text{C}$  exothermic peak in M1 is probably due to the formation of a small amount of transition alumina or  $\alpha\text{-Al}_2\text{O}_3$  arising from  $\text{AlO}(\text{OH})$ , which has been reported<sup>11</sup> to form on the surface of  $\alpha\text{-Al}_2\text{O}_3$  during grinding. To characterize the origin of the exotherm, X-ray powder diffraction patterns taken at  $1000^\circ\text{C}$  for 2 h are shown in Fig. 4.

M1 shows the presence of  $\alpha\text{-Al}_2\text{O}_3$ , M2 contains  $\gamma\text{-Al}_2\text{O}_3$  or spinel-phase and a very small amount

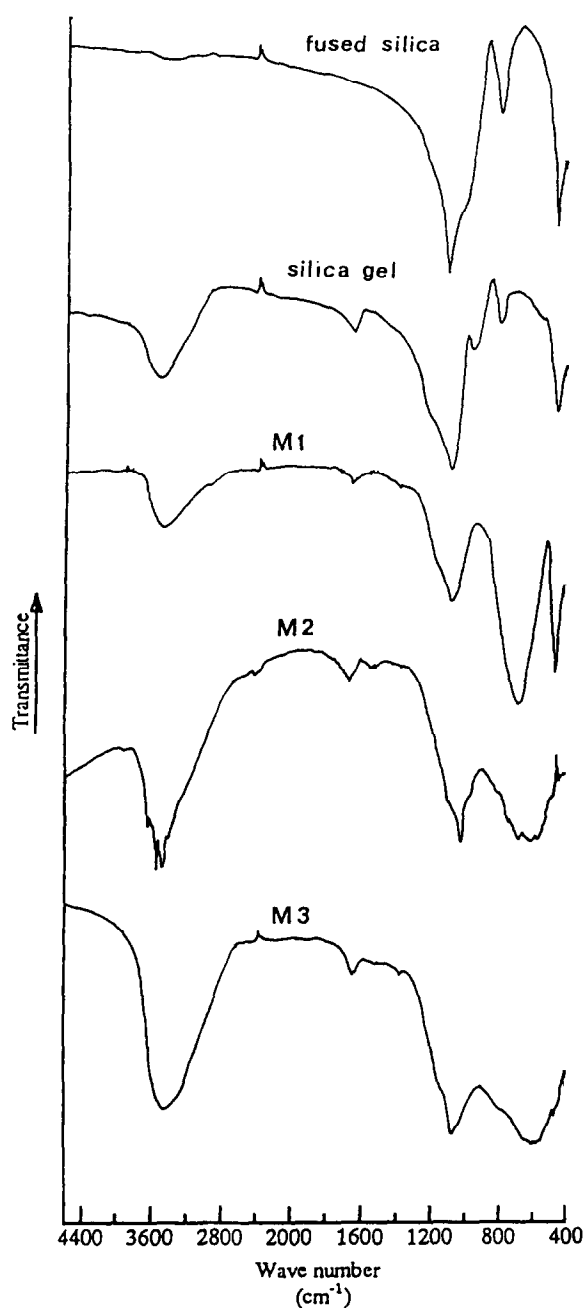


Fig. 2. FTIR spectra of silica starting materials and ground mixtures.

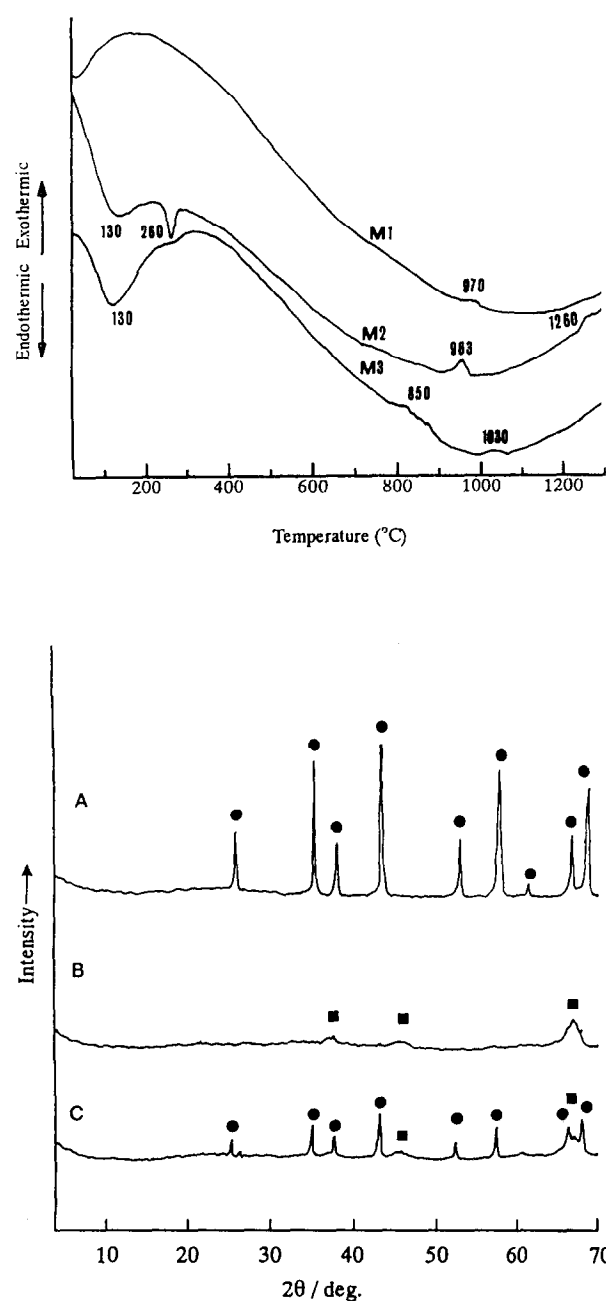


Fig. 4. XRD pattern of ground mixtures calcined at  $1000^\circ\text{C}$  for 2 h; A-M1; B-M2; C-M3. Key:  $\bullet$   $\alpha\text{-Al}_2\text{O}_3$ ,  $\blacksquare$  spinel-phase or  $\gamma\text{-Al}_2\text{O}_3$ .

of  $\alpha$ - $\text{Al}_2\text{O}_3$ , and M3 contains  $\alpha$ - $\text{Al}_2\text{O}_3$  and  $\gamma$ - $\text{Al}_2\text{O}_3$  or spinel-phase. The XRD patterns indicate that in the M2 samples the exothermic effect at about  $980^\circ\text{C}$  is due to the formation of  $\gamma$ - $\text{Al}_2\text{O}_3$  or spinel-phase. The DTA curve of M3 samples did not show the exothermic effect at about  $980^\circ\text{C}$ . The formation of a large amount of  $\alpha$ - $\text{Al}_2\text{O}_3$  at  $1000^\circ\text{C}$  in the M3 samples but not in M2 cannot be explained by M3 being fully amorphous, because we have previously shown<sup>3</sup> that fully amorphized ground mixtures of gibbsite and silica gel form spinel-phase at about  $1000^\circ\text{C}$  but no  $\alpha$ - $\text{Al}_2\text{O}_3$ . Although the M3 sample contains  $\gamma$ - $\text{Al}_2\text{O}_3$  or spinel-phase, these phases were not responsible for the exothermic effect at about  $980^\circ\text{C}$ . Therefore, the exothermic effect at about  $980^\circ\text{C}$  is related to the formation of spinel-phase into which is incorporated a small amount of silica from the aluminosilicate precursors; the phase formed in M2 is assigned as spinel-phase whereas it is  $\gamma$ - $\text{Al}_2\text{O}_3$  in M3. In the XRD patterns of samples calcined at  $1200^\circ\text{C}$  for 2 h (not shown here), M1 sample contains  $\alpha$ - $\text{Al}_2\text{O}_3$ , M2 contains mullite,  $\alpha$ - $\text{Al}_2\text{O}_3$  and a small amount of transition alumina, M3 contains  $\alpha$ - $\text{Al}_2\text{O}_3$  and a trace of transition alumina. At  $1300^\circ\text{C}$ , M1 contains  $\alpha$ - $\text{Al}_2\text{O}_3$  and cristobalite, M2 contains mullite and little  $\alpha$ - $\text{Al}_2\text{O}_3$  and M3 contains  $\alpha$ - $\text{Al}_2\text{O}_3$  and cristobalite. The second exothermic effect in the DTA curve of the M2 probably represents the formation of mullite from transition alumina and amorphous silica.

The  $^{27}\text{Al}$  and  $^{29}\text{Si}$  MAS-NMR spectra of the ground samples and some of their component phases are shown in Fig. 5. The  $^{27}\text{Al}$  spectrum of M1 [Fig. 5(C)] is identical to that of the  $\alpha$ -alumina starting material, which shows a single octahedral resonance at 13–15 ppm (our unpublished data). By contrast, in samples M2 and M3, in which the starting material is gibbsite, the single octahedral Al site of unground gibbsite [Fig. 5(A)] is partially replaced in the ground samples by a tetrahedral site (62–68 ppm) and a site characterized by a resonance at 34 ppm. The latter has been ascribed in amorphous materials either to pentacoordinated Al, or to a tetrahedral site associated with a tricluster structure surrounding an oxygen vacancy;<sup>12</sup> this structure occurs in mullite, where it resonates characteristically at about 45 ppm but has been suggested to relax to about 35 ppm in gels and other amorphous compounds.<sup>13</sup> The formation of new frequencies in  $^{27}\text{Al}$  MAS NMR spectrum are related to alumina [Fig. 5(D) and (E)], rather than to silica, since they are observed in the mixture of gibbsite ground alone under the same conditions [Fig. 5(B)]. These conclusions are confirmed by the  $^{29}\text{Si}$  NMR spectra [Fig. 5(F)–(I)]. The  $^{29}\text{Si}$  spectrum of M1 [Fig. 5(G)] indicates no

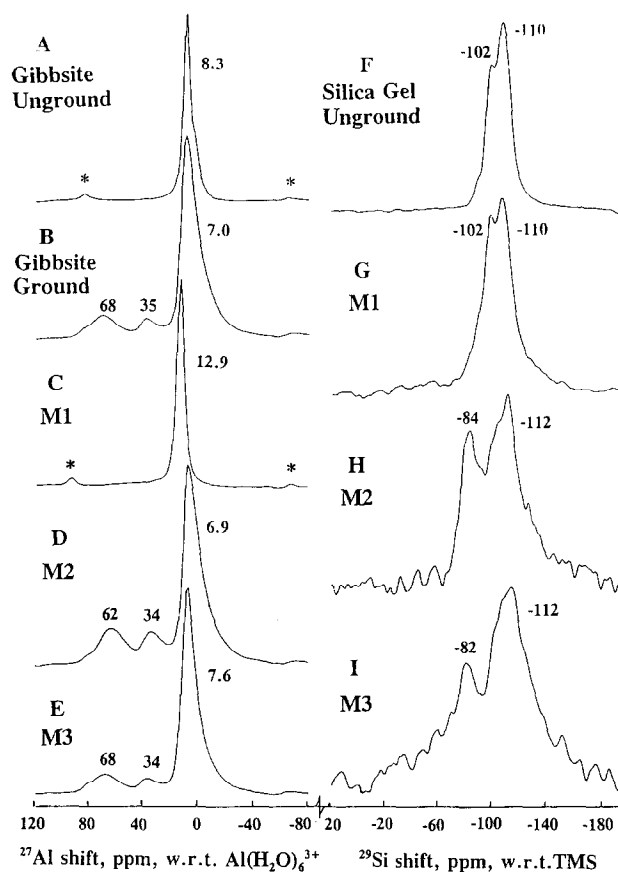


Fig. 5. 11-T  $^{29}\text{Si}$  and  $^{27}\text{Al}$  MAS-NMR spectra of starting materials and ground samples as indicated: A–E,  $^{27}\text{Al}$  spectra; F–I,  $^{29}\text{Si}$  spectra. The symbols \* in the  $^{27}\text{Al}$  spectra represent spinning side band.

reaction between the  $\alpha$ -alumina and silica gel, which shows the resonances at  $-102$  and  $-110$  ppm present in the spectrum of unground silica gel [Fig. 5(F)] and assigned to Si–OH and uncombined  $\text{SiO}_2$  respectively. By contrast, the  $^{29}\text{Si}$  spectra of M2 and M3 [Fig. 5(H) and (I)] indicate that reaction has occurred to form Al–O–Si linkages typified by the resonance at  $-82$  to  $-84$  ppm. This resonance is smaller in M3, suggesting that the fused silica is less reactive than hydroxylated silica gel. These results indicate that the presence of hydroxyls is a prerequisite for the mechanochemical formation of aluminosilicate precursors, and that the hydroxyls must be associated with the alumina starting material but not necessarily with the initial silica.

Semi-quantitative estimates of the mullite formed in the various samples are plotted as a function of calcining temperature in Fig. 6, which shows similar mullitization behavior in M1 and M3. This results from solid state reaction between  $\alpha$ - $\text{Al}_2\text{O}_3$  and cristobalite at elevated temperatures. The greater amount of mullite formed in M3 than in M1 at  $1500^\circ\text{C}$  may be due to enhanced diffusion of Al resulting from the defects present in the

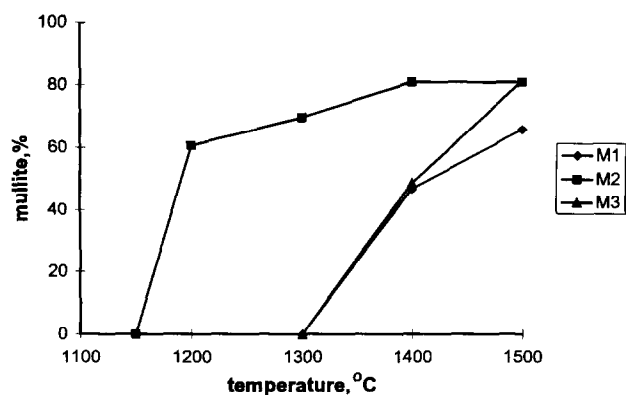


Fig. 6. Amount of mullite in the ground mixtures plotted as a function of calcining temperature.

ground gibbsite, in which some silica has also been incorporated. The improved homogeneity of the M2 sample results in the formation of mullite via spinel-phase at about 1200°C. Yoldas has suggested<sup>14</sup> that differences in the ultrastructure of mullite precursors are the main factor in determining the difference in their thermal behavior of them. Figure 6 shows large differences in the mullitization temperature of M2 and M3. These differences may be caused by differences in the homogeneity of the samples, as reflected by the amount of Si associated with aluminosilicate units (21% in M2 and 10% in M3).

The fused silica used in M3 is vitreous and monolithic, with low specific surface area leading to few Al–O–Si bonds formed between the active sites of gibbsite and fused silica surfaces, resulting in precursors of low homogeneity. By contrast the silica gel and gibbsite used in M2 has a greater reactivity which gives more homogeneous precursor with low mullitization temperature.

Even though the M1 and M3 samples form mullite only at higher temperatures ( $\approx 1400^\circ\text{C}$ ), these mixtures are more reactive than unground  $\alpha\text{-Al}_2\text{O}_3$  and quartz,<sup>2</sup> reflecting the increased long-range order introduced into these samples by grinding.

#### 4 Conclusions

The formation of mullite has been studied in aluminosilicate precursors prepared by mechanochemical treatment of these different combinations of alumina and silica. The most homogeneous precursors, judged on the basis of their  $^{27}\text{Al}$  and  $^{29}\text{Si}$  spectra, are formed from hydroxylated alumina and silica gel compounds. The presence of hydroxyls in the silica component is neither a necessary nor sufficient condition for mechanochemical precursor formation. The more

homogeneous precursors, formed from gibbsite and silica gel, produce mullite at 1200°C. Less complete mullitization occurs in precursors formed from gibbsite and fused silica, while the substitution of  $\alpha$ -alumina for gibbsite leads to the least reactive precursor, judged both by its NMR spectra and its mullitization behavior.

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