

# Effect of mechanochemical treatment on the synthesis of calcium dialuminate

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Calcium dialuminate ( $\text{CaAl}_4\text{O}_7$ ) powders were synthesised from mechanochemically treated mixtures of aluminium hydroxide + calcium hydroxide and aluminium hydroxide + calcium carbonate. On grinding, both mixtures produce X-ray amorphous precursor phases which show  $^{27}\text{Al}$  MAS NMR resonances characteristic of Al in octahedral and tetrahedral sites, and a site identified by a resonance at 37–39 ppm (possibly pentahedral Al). Although grinding does not completely destroy the carbonate XRD reflections in the carbonate mixture, both precursors show a high degree of homogeneity and behave similarly on heating, forming monophase  $\text{CaAl}_4\text{O}_7$  at  $<1050^\circ\text{C}$ . By contrast, the same unground compositions form mixtures of  $\alpha$ -alumina and various calcium aluminates (but not  $\text{CaAl}_4\text{O}_7$ ) on heating as high as  $1250^\circ\text{C}$ . Calcium dialuminate synthesised from the carbonate-containing mechanochemical precursor had a smaller particle size which may be advantageous for subsequent fabrication and sintering.

## Introduction

Failure due to thermal shock constitutes a major problem encountered with many refractory ceramics. This behaviour is due to the large thermal expansion of the commonly used basic refractory oxides with high melting points, such as MgO and CaO.<sup>1</sup> However, Jonas *et al.*<sup>1,2</sup> and Criado and De Aza<sup>3</sup> have reported that calcium dialuminate ( $\text{CaAl}_4\text{O}_7$ , mp =  $1750^\circ\text{C}$ ) shows very low thermal expansion and can be used for refractory purposes. Jonas *et al.* prepared  $\text{CaAl}_4\text{O}_7$  from  $\text{CaCO}_3$  and  $\text{Al}_2\text{O}_3$ , firing the oxide mixture in three steps, at 1200, 1300 and  $1450^\circ\text{C}$ . Sunkowski and Sawkow<sup>4</sup> prepared calcium dialuminate in a single firing at  $1500^\circ\text{C}$  from technical raw materials but their product also contained phases other than the dialuminate.

Although previous successful preparations of  $\text{CaAl}_4\text{O}_7$  required multiple high-temperature firings, it is possible to decrease the synthesis temperature of inorganic compounds by mechanochemical treatment of the reaction mixtures, especially if at least one component contains water or hydroxyl groups.<sup>5–7</sup> Such a synthesis route is described as a “soft” mechanochemical method.

The aim of the present work was to determine the influence of mechanochemical treatment on the formation of  $\text{CaAl}_4\text{O}_7$  precursors from mixtures of aluminium hydroxide with calcium hydroxide or calcium carbonate. The subsequent thermal crystallisation of these precursors was also investigated, and compared with the thermal reactions of unground mixtures of the same starting materials.

## Experimental

The starting materials were analytical grade  $\text{Al}(\text{OH})_3$  (gibbsite),  $\text{Ca}(\text{OH})_2$  (portlandite) and  $\text{CaCO}_3$  (calcite) (Reachim, Russia). X-Ray powder diffraction (XRD) showed the gibbsite and calcite to be pure, monophasic materials, but the portlandite showed evidence of a small amount of calcite resulting from atmospheric carbonation. Gibbsite–portlandite and gibbsite–calcite mixtures of molar composition equivalent to  $1\text{CaO}:2\text{Al}_2\text{O}_3$  were prepared, designated AH and AC, respectively. The mixtures were ground for 4 h using a Fritsch planetary mill (Pulverisette 5) with a rotation speed of 300 rpm. Both the pot and milling media were corundum and the weight ratio of balls to powder was 15 : 1. During the grinding the mill was stopped for 10 min every hour. After grinding, the mixtures were heated in air for 1 h at various temperatures. For comparison, a parallel set of heating experiments was carried out on the same mixtures which were not ground. The thermal behaviour of the unground and ground mixtures was examined by combined differential thermal analysis and thermogravimetry (DTA–TG) using a Rigaku Thermoplus TG 8120, and the ground precursors were characterised by XRD (Siemens D-5000 diffractometer using  $\text{Cu-K}\alpha$  radiation) and solid state  $^{27}\text{Al}$  MAS NMR at a magnetic field of 14.1 T using a Chemagnetics Infinity 600 MHz spectrometer and a 3.2 mm high-speed MAS probe in which the sample was spun at 18 kHz. The spectra were acquired at 156.374 MHz using a  $15^\circ$  pulse of 0.5  $\mu\text{s}$  and a recycle time of 1 s and were referenced by using the secondary standard of the  $\text{AlO}_6$  resonance of

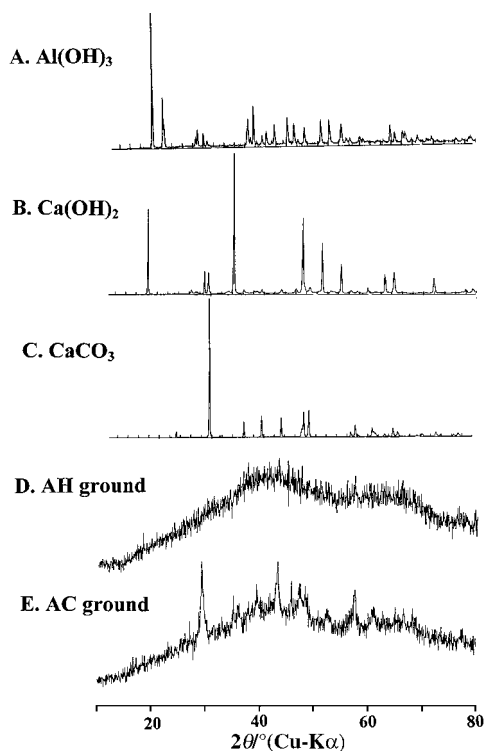


Fig. 1 XRD traces of the unground starting materials and their mixtures ground for 4 h.

$\text{Y}_3\text{Al}_5\text{O}_{12}$  at 0.7 ppm. The heated powders were examined by XRD, and their particle size distribution was determined by a Malvern MasterSizerE using samples ultrasonically dispersed in 0.2% aqueous sodium hexametaphosphate.

## Results and discussion

### Effect of grinding on the structure of the $\text{CaAl}_4\text{O}_7$ precursors

Fig. 1 shows the XRD patterns of the unground starting materials and the ground mixtures. Grinding causes mixture AH to become fully amorphous (Fig. 1D) but mixture AC shows some residual crystalline calcium carbonate reflections (Fig. 1E). When ground by itself, gibbsite has been shown<sup>8</sup> to become fully amorphous, with the formation of internal structural vacancies;<sup>7,9</sup> amorphization of the  $\text{Ca}(\text{OH})_2$  component could similarly occur without combination of the amorphized components by a “soft” mechanochemical mechanism<sup>5</sup> to form a reactive precursor. However, the thermal reaction sequence (see below) suggests that the precursor is a compound rather than a physical mixture of amorphous constituents.

The  $^{27}\text{Al}$  MAS NMR spectra of the unground and ground samples are shown in Fig. 2. The  $^{27}\text{Al}$  spectrum of the unground material shows the characteristic octahedral resonance of gibbsite,  $\text{Al}(\text{OH})_3$ , at 9.5 ppm (Fig. 2C). On grinding for 4 h. with either calcium hydroxide (Fig. 2A) or calcium carbonate (Fig. 2B), the octahedral resonance is broadened and two new NMR resonances appear. The peak at 70–74 ppm corresponds to new tetrahedral sites created during grinding. The peak at 37–39 ppm has been observed in a number of other amorphous aluminates, including  $\text{CaAl}_4\text{O}_7$  gel precursors prior to their thermal crystallisation.<sup>10–12</sup>  $^{27}\text{Al}$  NMR resonances in this vicinity are often attributed to Al in five-fold coordination with oxygen,<sup>13</sup> but alternatively may be associated with distorted tetrahedral sites in the vicinity of tricluster oxygen vacancies, such as found in the mullite structure.<sup>14</sup> Studies of other aluminate and aluminosilicate gels<sup>10</sup> indicate a strong

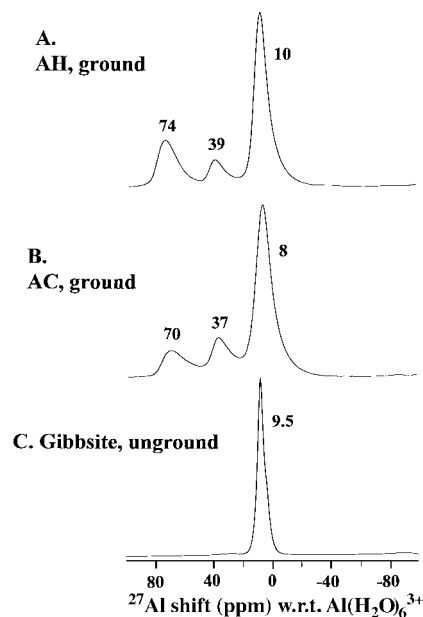


Fig. 2 14.1 T  $^{27}\text{Al}$  MAS NMR spectra of unground gibbsite and the mixtures ground for 4 h.

correlation between the presence and intensity of this resonance and the homogeneity of the amorphous material, which in turn influences its crystallisation temperature. Accurate simulation of such spectra requires a detailed determination of the mean interactions and their distributions.<sup>15</sup> However, semi-quantitative estimates of the relative intensities of the present resonances were made by direct spectral integration. These suggest that the carbonate-based mixture AC contains 16.7% of the 37 ppm resonance and 13.9% of the tetrahedral resonance, by comparison with the AH mixture derived from the two hydroxides, which contains 9.5% of the 37 ppm resonance and 23.5% of the tetrahedral resonance. On the basis of the intensity of the 37 ppm resonance, sample AC would appear to be more highly amorphized and homogeneous than AH. However, this conclusion is not reflected in the thermal behaviour of the two ground mixtures (see below). Since the final product,  $\text{CaAl}_4\text{O}_7$ , contains only tetrahedral Al,<sup>16</sup> a more accurate measure of the reactivity of the precursor appears in this case to be reflected by the intensity of the tetrahedral site formed by grinding, which is greatest in AH. The appearance of tetrahedral and 35 ppm NMR peaks has been reported in gibbsite ground by itself,<sup>8</sup> in which significantly more tetrahedral intensity was observed (20% tetrahedral, 7% 35 ppm resonance). The present behaviour of gibbsite ground with  $\text{Ca}(\text{OH})_2$  is therefore more typical of the gibbsite itself, which forms X-ray amorphous  $\rho$ -alumina on grinding.<sup>8</sup> Although the X-ray reflections of the gibbsite are similarly removed by grinding in the presence of  $\text{CaCO}_3$ , the resulting atomic environments of the Al are slightly different, suggesting a different interaction with the Ca component in this case.

### Thermal behaviour of the ground and unground samples

The TG and DTA traces of the unground and ground mixtures are shown in Fig. 3. The thermal behaviour of the unground mixture AH (Fig. 3A,B) is as expected for these component hydroxides. The  $\text{Al}(\text{OH})_3$  dehydroxylates endothermically at 297 °C with a total observed weight loss of 29.5% up to 600 °C, in reasonable agreement with the theoretical loss of 28.0% for the gibbsite component of this mixture. A small endotherm at 531 °C, which contributes a small weight loss of 2.8% to this total value, is probably due to the presence of a small amount of boehmite resulting from the decomposition of the gibbsite.<sup>17</sup> The dehydroxylation of the  $\text{Ca}(\text{OH})_2$  occurs at 706 °C with a

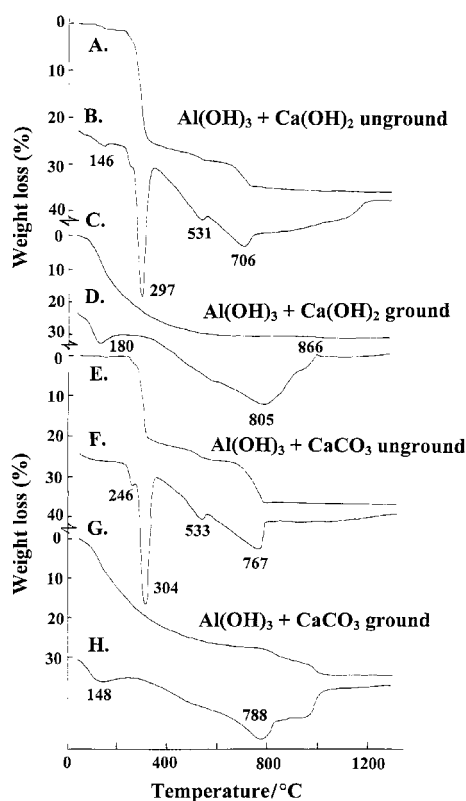


Fig. 3 Thermal analysis traces of the unground and ground mixtures in static air, heating rate  $10\text{ }^{\circ}\text{C min}^{-1}$ .

weight loss of 4.7% (theoretical value 4.7%). The temperature of this decomposition is higher than reported ( $590\text{ }^{\circ}\text{C}$ <sup>16</sup>), possibly due to the presence in the reaction atmosphere of  $\text{CO}_2$  from decarbonation of the carbonate impurity known to be present, since the reaction temperature is increased in a  $\text{CO}_2$  atmosphere.<sup>17</sup> The thermal analysis results for this portlandite heated alone show a similar endothermic event at this temperature with an associated weight loss (22%) in reasonable agreement with the theoretical value of 24.3% for  $\text{Ca(OH)}_2$  dehydroxylation. The lack of further well defined thermal events suggests that any higher-temperatures reactions are occurring sluggishly.

By contrast, the ground mixture AH (Fig. 3C,D) is considerably broadened, showing an endotherm at about  $180\text{ }^{\circ}\text{C}$  due to the removal of adsorbed water, a very broad endothermic feature which reaches a maximum at  $805\text{ }^{\circ}\text{C}$  and a weak exotherm at  $866\text{ }^{\circ}\text{C}$ . The sample loses weight continuously up to  $600\text{ }^{\circ}\text{C}$  in the typical manner of a gel-like material,<sup>18</sup> the total observed weight loss (31.4%) is in reasonable agreement with the theoretical weight loss of 32.7% for reaction (1)



Although the endothermic peaks at  $300\text{--}700\text{ }^{\circ}\text{C}$  and the associated discrete weight losses found in the unground mixture AH were not observed in the ground samples, the overall expected weight loss still occurs, indicating that the mechanochemical precursor formation reaction does not involve dehydration.

The unground carbonate-based mixture AC shows the expected gibbsite decomposition endotherms at  $304$  and  $533\text{ }^{\circ}\text{C}$  and an endotherm at  $860\text{ }^{\circ}\text{C}$  resulting from decomposition of the  $\text{CaCO}_3$ . This temperature is at the low end of the range reported for the decarboxylation of  $\text{CaCO}_3$ ,<sup>17</sup> possibly as a result of the small particle size of the sample, which is known to lower the reaction temperature.<sup>17</sup> The associated weight losses of these endotherms are in good agreement with the

theoretical values for the reactions in a mixture of this composition: 26.1% for the gibbsite dehydroxylation up to  $600\text{ }^{\circ}\text{C}$  (theoretical value 26.2%) and 11% for decarboxylation (theoretical value 10.7%).

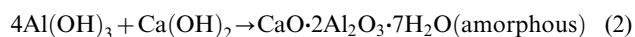
The ground mixture AC shows endothermic effects at about  $148\text{ }^{\circ}\text{C}$  and  $788\text{ }^{\circ}\text{C}$ . The weight loss occurs in two stages, a slow gel-like loss of 27.2% up to about  $650\text{ }^{\circ}\text{C}$  and a further 7.4% loss in at least two stages up to  $1020\text{ }^{\circ}\text{C}$  corresponding to the decomposition of the unreacted  $\text{CaCO}_3$ . The total observed weight loss is in reasonable agreement with the theoretical value of 36.9% for this mixture.

The DTA-TG results are in agreement with the XRD data (Fig. 1) in suggesting that mixture AH is more homogeneous than AC.

The XRD patterns of the ground and unground mixtures of AH heated for 1 h at two temperatures are shown in Fig. 4. After heating at  $850\text{ }^{\circ}\text{C}$ , the ground mixture sample (Fig. 4B) shows the major lines of  $\text{CaAl}_4\text{O}_7$  (JCPDS card 23-1037) superimposed on the background intensity of the amorphous precursor. Heating to  $1050\text{ }^{\circ}\text{C}$  completely transforms this sample into well-crystallised  $\text{CaAl}_4\text{O}_7$  (Fig. 4C). Since the thermal analysis experiments were conducted under dynamic heating conditions, it is not unexpected for the thermal analysis temperatures to lag behind those of the XRD samples which were isothermally heated for 1 h at each temperature.<sup>11</sup> Therefore, it is likely that the small exotherm at  $866\text{ }^{\circ}\text{C}$  in ground AH (Fig. 3D) corresponds to the formation of  $\text{CaAl}_4\text{O}_7$  from the amorphous precursor phase.

The formation of calcium dialuminate from ground AH may occur as follows.

Grinding forms a homogeneous precursor in which the constituents are intimately combined [eqn. (2)]:



The formation of a compound rather than a mixture of

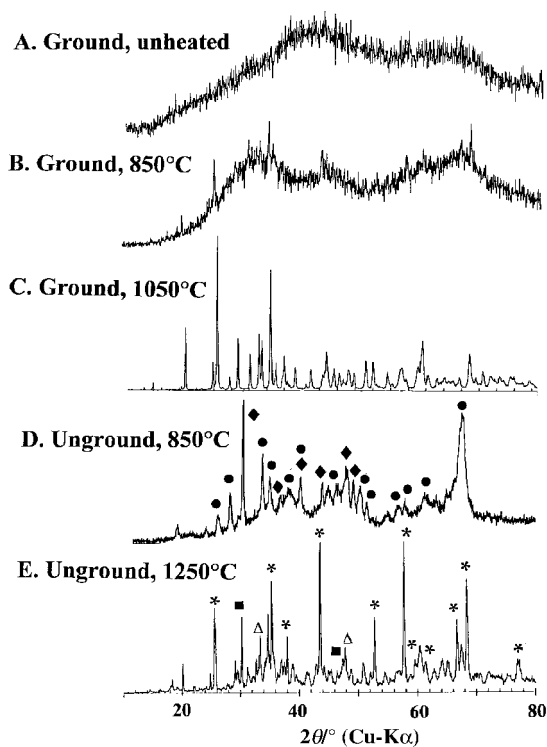
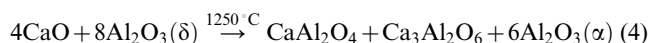


Fig. 4 XRD traces of ground and unground mixture AH, heated as indicated. Key:  $\blacklozenge$  =  $\text{CaO}$  (PDF no. 28-0775),  $\bullet$  =  $\delta\text{-Al}_2\text{O}_3$  (PDF no. 16-0394),  $*$  =  $\alpha\text{-Al}_2\text{O}_3$  (PDF no. 46-1212),  $\blacksquare$  =  $\text{CaAl}_2\text{O}_4$  (PDF no. 23-1036),  $\triangle$  =  $\text{Ca}_3\text{Al}_2\text{O}_6$  (PDF no. 38-1429), unmarked peaks correspond to  $\text{CaAl}_4\text{O}_7$  (PDF no. 23-1037).

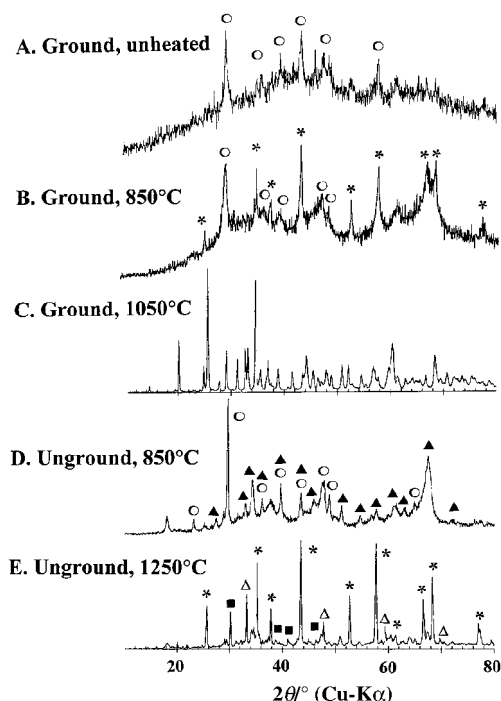
amorphous constituents is evidenced by the lack of  $\alpha$ -alumina after heating at 850 °C since this phase would be formed by amorphous ground gibbsite if present on its own.<sup>8</sup> Furthermore, the amorphous precursor is shown by thermal analysis to be fully hydrous, but the water occurs in gel-like sites and is gradually given off over a wide temperature range during heating. A similar formation of hydrous calcium aluminate in ground  $\text{Al}(\text{OH})_3$ - $\text{Ca}(\text{OH})_2$  mixtures has been reported by Kano *et al.*<sup>19</sup> The precursor, formed as in eqn. (2), transforms directly to  $\text{CaAl}_2\text{O}_7$  on heating <1050 °C without the formation of intermediate phases.

By contrast, the thermal reactions in the unground mixture AH consist of the normal thermal decomposition of the reactants, followed by solid state reaction of the anhydrous oxide products. The products of heating at 850 °C (Fig. 4D) are CaO from decomposition of the  $\text{Ca}(\text{OH})_2$  and a mixture of transition aluminas (principally  $\delta$ -alumina) from decomposition of the gibbsite. Heating at 1250 °C (Fig. 4E) results in a mixture of  $\alpha$ -alumina,  $\text{CaAl}_2\text{O}_4$  (PDF no. 23-1036) and  $\text{Ca}_3\text{Al}_2\text{O}_6$  (PDF no.38-1429). These reactions may be written as eqns. (3) and (4):



By contrast with the ground mixture, no  $\text{CaAl}_4\text{O}_7$  is formed in the unground sample even at 1250 °C, reflecting its considerably lower degree of homogeneity.

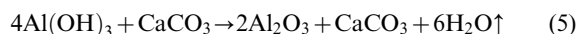
Typical XRD traces of the ground and unground mixture AC heated to different temperatures are shown in Fig. 5. The ground sample AC heated at 850 °C (Fig. 5B) shows the broad background intensity of the amorphous precursor, with a few superimposed reflections of  $\text{CaCO}_3$  (PDF no. 5-0586) and  $\alpha$ -alumina (PDF no. 46-1212). Low-temperature crystallisation of the latter from an amorphous phase produced by mechanochemical activation of gibbsite has previously been reported.<sup>16</sup> However, heating at 1050 °C produced crystalline monophase  $\text{CaAl}_4\text{O}_7$  (Fig. 5C), but with slightly less intense



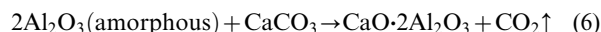
**Fig. 5** XRD traces of ground and unground mixture AC, heated as indicated. Key:  $\circ$  =  $\text{CaCO}_3$  (PDF no. 5-0586),  $*$  =  $\alpha$ - $\text{Al}_2\text{O}_3$  (PDF no. 46-1212),  $\blacktriangle$  =  $\text{CaAl}_{12}\text{O}_{19}$  (PDF no. 25-0122),  $\blacksquare$  =  $\text{CaAl}_2\text{O}_4$  (PDF no. 23-1036),  $\triangle$  =  $\text{Ca}_3\text{Al}_2\text{O}_6$  (PDF no. 38-1429), unmarked peaks correspond to  $\text{CaAl}_4\text{O}_7$  (PDF no. 23-1037).

diffraction lines than in AH. Thus, even though mechanochemical processing does not fully amorphize the carbonate reactant, it apparently induces sufficient homogeneity to permit the mixture to behave similarly to the more amorphous ground AH, and to fully crystallise to  $\text{CaAl}_4\text{O}_7$  at 1050 °C.

The behaviour of the ground mixture AC is different from ground AH; the observed first weight loss of 27.2% up to 650 °C is slightly greater than the theoretical loss of 26.2% for reaction (5)



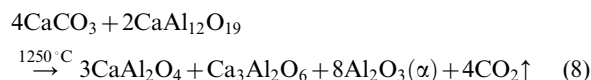
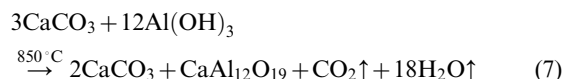
whereas the observed second weight loss of 7.4% at 650–1020 °C is smaller than the theoretical value of 10.5% for reaction (6)



These results suggest that although the major part of the mechanochemical energy is expended on the modification of the  $\text{Al}(\text{OH})_3$  structure, a small proportion of the  $\text{CaCO}_3$  is also affected, and may take part in precursor formation. Part of the remaining  $\text{CaCO}_3$  is also affected by grinding, and decomposes gradually up to about 920 °C, whereupon the remainder decomposes in the more typical fashion of  $\text{CaCO}_3$ , in a rapid reaction which is completed at 1010 °C. Grinding apparently enhances the reactivity of these thermal decomposition products, since, unlike the unground mixture (below), the stoichiometric dialuminate is formed directly and without intermediates at <1050 °C. Previous studies of reactions in calcium aluminate cements without mechanochemical treatment report<sup>20</sup> the formation of  $\text{CaAl}_2\text{O}_4$  at 900 °C, with some dialuminate beginning to appear at 1200 °C. The present results show that mechanochemical treatment of gibbsite mixtures containing Ca either as the hydroxide or as the carbonate results in the formation of monophase calcium dialuminate below 1050 °C.

This behaviour is in complete contrast to that of the unground mixture AC, which at 850 °C (Fig. 5D) contains unreacted  $\text{CaCO}_3$  and some poorly crystalline  $\text{CaAl}_{12}\text{O}_{19}$  (PDF no. 25-0122), reflecting the onset of some decarboxylation, followed by solid state reaction with the excess transition alumina from the gibbsite, which by this stage is fully dehydroxylated. At 1250 °C, decarboxylation is complete; the solid state reaction products are similar to unground AH, consisting of  $\text{CaAl}_2\text{O}_4$  and  $\text{Ca}_3\text{Al}_2\text{O}_6$ , with some unreacted  $\alpha$ -alumina also present (Fig. 5E).

These reactions may be written as eqn. (7) and (8):



Measurements of the particle size distribution of samples synthesised at 1050 °C from the ground mixtures indicated median particle sizes ( $d_{50}$ ) of 7.65  $\mu\text{m}$  and 3.85  $\mu\text{m}$  from AH and AC, respectively. Thus, although the precursor formed from mixture AC is apparently less homogeneous, the crystalline product derived from it might exhibit superior sintering properties.

## Conclusions

1. Mechanochemical treatment (grinding) of a mixture of  $\text{Al}(\text{OH})_3$  (gibbsite) and  $\text{Ca}(\text{OH})_2$  in the molar proportions of  $\text{CaAl}_4\text{O}_7$  produces an X-ray amorphous precursor in which some of the octahedral Al sites of the original gibbsite are converted to tetrahedral sites and others which are possibly pentahedral. Grinding causes no loss of water, but converts the

original structural hydroxyl groups to water which on thermal treatment is gradually evolved in a gel-like manner over an extended temperature range (400 °C). The ground precursor phase behaves homogeneously on heating, transforming directly to monophase  $\text{CaAl}_4\text{O}_7$  at  $<1050^\circ\text{C}$  without the formation of intermediates. By contrast, this unground mixture forms predominantly  $\delta$ -alumina and  $\text{CaO}$  at  $850^\circ\text{C}$ , which react at  $1250^\circ\text{C}$  to form a mixture of  $\alpha$ -alumina (corundum) and calcium aluminates (but not  $\text{CaAl}_4\text{O}_7$ ).

2. Grinding an analogous mixture of gibbsite with  $\text{CaCO}_3$  produces a precursor in which the XRD reflections of the alumina are destroyed but some of the carbonate reflections survive. The Al sites in this precursor are similar to those formed in the mixture containing  $\text{Ca}(\text{OH})_2$ , but the proportion of tetrahedral Al sites is slightly lower. On heating at  $850^\circ\text{C}$  this ground precursor loses the water from its gibbsite component in a gel-like manner, forming some  $\alpha$ -alumina. Heating to  $1050^\circ\text{C}$  produces monophase  $\text{CaAl}_4\text{O}_7$ , as with the precursor derived from  $\text{Ca}(\text{OH})_2$ . Without grinding, this mixture produces a mixture of calcium aluminates but no  $\text{CaAl}_4\text{O}_7$  when heated at  $1250^\circ\text{C}$ .

3. The precursor derived from the present  $\text{CaCO}_3$  produces  $\text{CaAl}_4\text{O}_7$  powder of smaller particle size when heated at  $1050^\circ\text{C}$ , suggesting that this product may exhibit superior post-synthesis fabrication and sintering behaviour.

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