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DTA Characterisation of Three Types of Al_2O_3–SiO_2 Gels made from TEOS-Al $(OBu)_3$ Mixture with Variation of Water

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Abstract: Mixtures of TEOS and Al $(OBu)_3$ had been hydrolysed by varying the water contents at a fixed acid concentration. This led to the formation of three different kinds of gels. Diphasic gel formed when excess of water was used, which transformed to mullite at 1320°C in exothermic reaction. When the amount of water content was reduced, the resultant monophasic gel completed its mullitization at lower temperatures from an amorphous aluminosilicate phase and cubic mullite by two paths at 1150°C and 1250°C exothermic reactions, respectively. When less water is used, the monophasic gel converted directly to tetragonal mullite at 980°C in exothermic reaction. Thus, the variation of water contents during the gelation caused great variations in the course of mullitization processes. © 1996 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Mullite development via sol–gel process was undertaken with a view to attaining maximum homogeneity by involving reactive silica and alumina source materials.[1-4] The outcome of this procedure is unique in the sense that the mullitization temperature had been lowered to a great extent in comparison to its synthesis from conventional methods of firing oxide mixtures.[5] Using this sol–gel methodology four different mullitization routes have evolved which really start a new era in this field.

1. At low temperatures decomposition of aluminosilicate compounds. Mullite formation takes place as low as 450–600°C on heat treatment of the following compounds. For example, hydroxy aluminosilicate prepared from aluminium tris-isopropoxide and silicon tetrakis-isopropoxide;[6] aluminosilicate oligomers synthesized from trimethyl acetoxy silane with monodiketonate aluminium alkoxide;[7] poly organo-aluminium condensate obtained by hydrolysis of stoichiometric quantities of aluminium and silicon alkoxides;[8] aluminium siloxanes[9,10] and aluminosilicate gels,[11] etc.
2. At moderate temperatures calcination of Al_2O_3–SiO_2 precursor powder. Mullitization takes place on heating at 980°C from spray pyrollized powder[12] prepared by spraying $Al(NO_3)_3\ 9H_2O$, TEOS and alcohol mixture on a hot reaction tube and from aluminosilicate gel[4] made out of TEOS, Al $(OBu)_3$ in absolute alcohol as per the following reaction (see eqn (1)).
3. At high temperatures structural transformation of Si–Al spinel. Mullitization occurs by the polymorphic transformation of Si–Al spinel (cubic mullite or c-mullite) formed earlier on heating monophasic aluminosilicate gel[4] at 980°C as follows (see eqn (2)).

$$\begin{array}{c}Al_2O_3\text{–}SiO_2\ powder\\ or\ dried\ gel\\ (Amorphous)\end{array} \xrightarrow[Exotherm]{980^\circ C} \begin{array}{c}Tetragonal\\ mullite^{13,14}\\ (t-mullite)\end{array} \quad (1)$$

$$\underset{\text{Monophasic}}{Al_2O_3\text{–}SiO_2} \xrightarrow[\text{Exotherm}]{980^\circ C} \underset{c-\text{mullite}^{15}}{3Al_2O_32SiO_2} \xrightarrow[\text{Exotherm}]{1250^\circ C} \begin{matrix}3Al_2O_3\,2SiO_2\\ \text{Orthorhombic mullite}\\ (o-\text{mullite})\end{matrix} \tag{2}$$

$$\underset{\text{Diphasic gel}}{Al_2O_3\text{–}SiO_2} \xrightarrow{400^\circ C} \begin{matrix}\text{Oxide}\\ \text{mixture}\end{matrix} \xrightarrow[\text{Heating}]{\text{Continued}} \begin{matrix}\gamma-Al_2O_3\\ +\\ SiO_2\,(\text{Amorph})\end{matrix} \xrightarrow[\text{Independent transformations}]{1058^\circ C} \begin{matrix}\delta-Al_2O_3\\ +\\ SiO_2\,(A)\end{matrix} \xrightarrow{1200^\circ C} \begin{matrix}\delta-Al_2O_3\\ +\\ \theta-Al_2O_3\\ +\\ \beta-\text{Cristobalite}\end{matrix} \xrightarrow[\text{Exo}]{1250\text{–}1350^\circ C} \underset{\text{Mullite}}{3Al_2O_3\,2SiO_2} \tag{3}$$

4. At very high temperatures solid state reaction of component oxides. Mullitization occurs during heating diphasic gel at 1300°C[16–19] and above. In this case, two components first crystallize and then react to form mullite (see eqn (3)).

These four different mullite forming processes as shown, are most probably caused by variations in the choice of source materials[16] and processing conditions.[16–22] Various authors[14,20,23–28] used Si $(OC_2H_5)_4$ and Al $(OBu)_3$ as basic raw materials for synthesis of mullite by hydrolysing them either in an acidic or in an ammoniacal medium. A detailed study on the effect of acidic-to-basic hydration of the components on mullitization process was reported earlier.[16] The effect of the amount of water and alcohol used for hydrolysis of the components to the variation in gelation time and lastly to the exhibition of 980°C peak in DTA study had also been shown.[16,22,29] Interestingly, the concentration of the medium of hydrolysis used to 980°C phase development of Al_2O_3–SiO_2 gels have been the subject of great interest. Yoldas and Partlow[23] first synthesized three gels out of TEOS and $Al(OBu)_3$ by gradually reducing water by hydrolysis. It is found that the intensity of 980°C exothermic peak follows an inverse relation to the quantity of water used during gelation processes. The exhibition of 980°C exotherm had been used as an index for predicting the gel structure. They were of the opinion that the occurrence and size of 980°C peak are closely related to the intimacy or homogeneity of aluminium and silicon atoms in the gel. However, XRD tracings of those different gels heated to various temperatures were not incorporated.

In this article, Al_2O_3–SiO_2 gels derived from TEOS and $Al(OBu)_3$ with three different water contents have been studied by DTA and XRD to reveal the mechanism for their transformations leading to the formation of mullite. Results indicate that the natures of mullite gels varied and consequently these are responsible for three different modes of phase transformations.

2 EXPERIMENTAL

2.1 Gel preparation

1. The first kind of gel marked G-152 (Al:Si = 3:1) was synthesized by using a large amount of water in the following steps. A mixture of $Al(OBu)_3$, water and alcohol in the ratio of 7 ml:50 ml:10 ml followed by the addition of 2 drops of 1:10 diluted HNO_3 was hydrolysed on warming. To the resultant mixed solution, 2 ml TEOS was added and then warmed further in a boiling water bath at 65°C with occasional shaking until gelification took place. Finally, the gel was dried at 110°C and stored.
2. The second kind of gel marked G-152 (i) was synthesized in the above procedure using $Al(OBu)_3$, water, alcohol and TEOS in the ratio of 7 ml:10 ml:10 ml:2 ml followed by the addition of 2 drops of 1:10 diluted HNO_3.
3. The third kind of gel marked G-152 (ii) was synthesized using $Al(OBu)_3$, alcohol and TEOS in the above ratio but by using a negligible amount of water by the following steps. In this case, water for hydrolysis of the esters was not used directly but gelation was performed by keeping the mixed reactants in humid atmospheric conditions (room temperature 27°C, air humidity 80%–90% moisture content) for 7 days. It was assumed that under these conditions, hydrolysis of the components had taken place at a very slow rate by the moisture available from humid air only. Lastly, the semi-dried mixture was scraped away from the watch glass, dried in an air oven at 110°C and stored.

2.2 DTA study

These three dried gels and a well crystallized kaolinite were analysed for DTA in a Shimadzu Thermal Analyser System. The following measuring conditions were set. About 80 mg each of the ground gel and calcined Al_2O_3 as reference materials were taken. Both the sample and the reference were heated dynamically at a rate of 20°C/min. DTA tracings are shown in Figs 1–4, respectively.

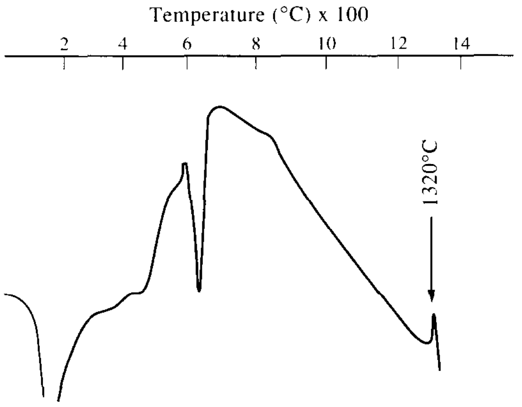

Fig. 1. DTA curve of G-152.

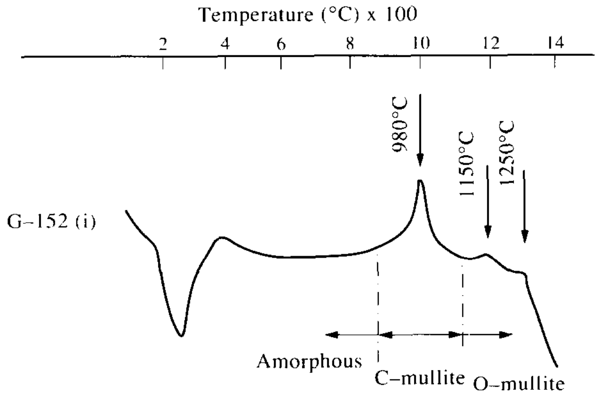

Fig. 2. DTA curve of G-152 (i).

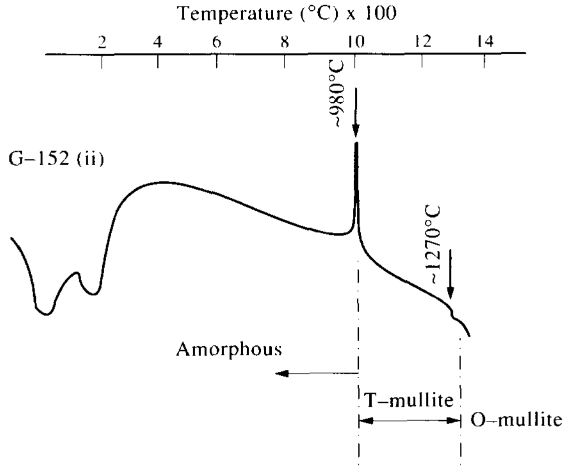

Fig. 3. DTA curve of G-152 (ii).

2.3 X-ray characterization of heat treated gels

Gel samples heated up to exothermic peak temperatures were cooled in DTA cell, ground and were analysed in a Philips XRD system for identification of the crystalline phases formed. Figures 5–8 show the X-ray diffractrograms of raw and heat treated gels. Results of DTA and X-ray analysis are summarized and shown in Table 1.

3 RESULTS AND DISCUSSION

Thermogram of gel G-152 (Fig. 1) shows two endotherms, one large at ~200°C, the other small

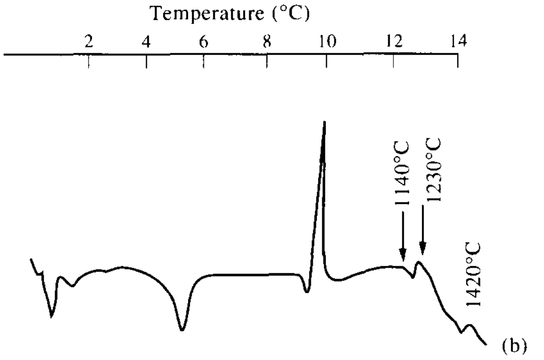

Fig. 4. DTA curve of Bhandak kaolinite.

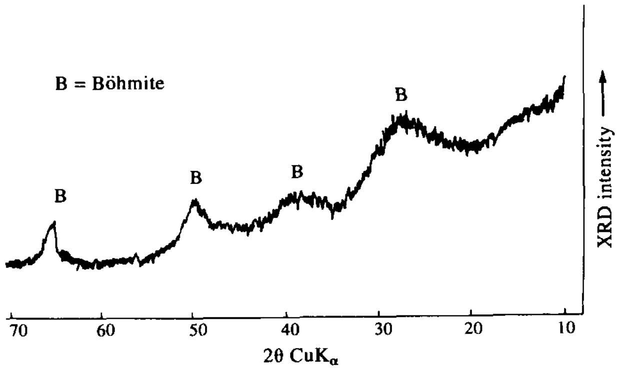

Fig. 5. XRD pattern of dried G-152, showing boehmite phase.

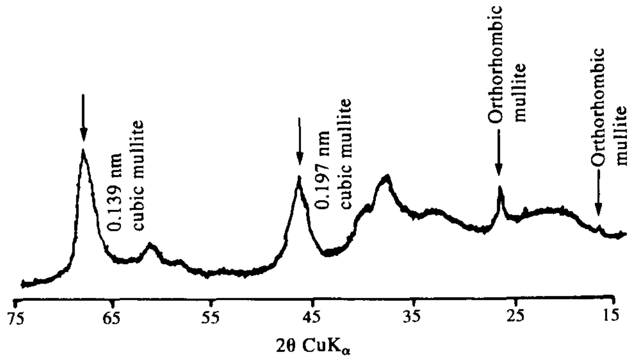

Fig. 6. XRD analysis of G-152 (i) heated in a DTA cell at 980°C exotherm, showing major cubic mullite and minor orthorhombic mullite.

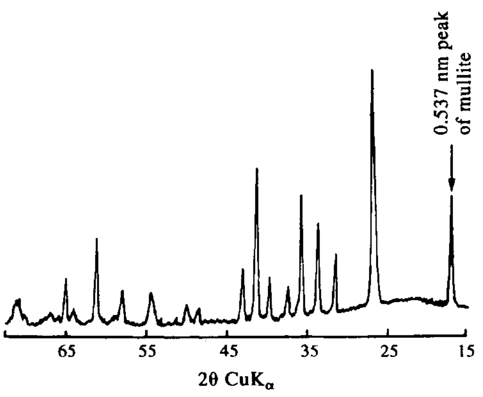

Fig. 7. XRD analysis of G-152 (i) heated in a DTA cell at 1250°C exotherm, showing orthorhombic mullite only.

at 630°C, respectively, but no exotherm at 980°C. However, a broad exothermic peak of small magnitude is observed at ~1320°C. Thermogram of gel G-152 (i) (Fig. 2) shows a large endotherm at 200–300°C and then shows 980°C exotherm and thereafter shows two more exotherms, one broad exotherm whose temperature maximum is at ~1150°C and another at ~1250°C. In the case of gel G-152 (ii), the thermogram (Fig. 3) initially shows two endotherms and then exhibits the usual 980°C exotherm. Thereafter, it shows only a small exotherm at ~1270°C. The causes of the occurrences of these exotherms are revealed by the subsequent X-ray studies.

1. In the presence of a large excess of water, as in the case of gel G-152, the resultant gel on

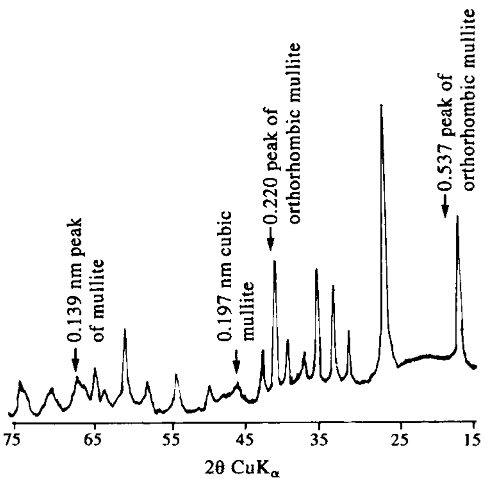

Fig. 8. XRD analysis of G-152 (ii) heated at a 1st exothermic peak temperature (980°C) showing tetragonal mullite as a major phase with a trace of cubic mullite, respectively.

X-ray analysis shows pseudoboehmite as a crystalline phase (Fig. 5) besides the usual $Si(OH)_4$ gel. As such, this gel is characterized as diphasic and obviously its thermal transformation behaviour should be analogous to diphasic mullite gel synthesized earlier by the present author.[30] In fact, 980°C peak is not observed in the thermogram of G-152 since Si–Al spinel (c-mullite) crystallized much earlier to 980°C and it continued beyond 980°C.[30] This may be the reason why Yoldas and Partlow[23] did not observe a 980°C exothermic peak in DTA analysis of their mol-

Table 1. DTA and X-ray characteristics of three different Al_2O_3–SiO_2 gels compared to kaolinite

Samples	Water used during gelation	Nature of the gel formed	DTA results	X-ray characterisation of crystalline phases formed in DTA analysed sample
G-152	Excess amount than that required for hydrolysis of mixed esters	Diphasic	At 980°C no exotherm At 1320°C small exotherm	Formation c-mullite continued[30] Forms o-mullite
G-152(i)	Moderate amount	Monophasic	At 980°C sharp exotherm	Forms major c-mullite
			At 1150°C broad exotherm	Forms o-mullite
			At 1250°C less sharp exotherm	Forms additional c-mullite
G-152(ii)	May be very small (not quantified)	Monophasic	At 980°C very sharp exotherm	Forms major t-mullite and minor o-mullite
			At 1150°C no exotherm	
			At 1270°C very small exotherm	Forms o-mullite
Kaolinitic clay[32]	—	—	At 980°C very sharp exotherm	Forms c-mullite
			At 1100–1400°C broad exotherm	Forms o-mullite
			At 1250°C sharp exotherm within the above broad exotherm	Forms o-mullite

$$\begin{array}{l}\text{Mixed Boehmite} + Si(OH)_4\ \text{Gel } G-152 \xrightarrow[200\text{–}600°C]{\text{Endo}} Al_2O_3\,(A) + SiO_2\,(A) \xrightarrow[1300°C]{600-} \text{Si–Al Spinel } (c-\text{mullite}) \\ \xrightarrow{1320°C} 3Al_2O_3\,2SiO_2\ o-\text{mullite}\end{array} \quad (4)$$

$$\text{Metakaolinite} \xrightarrow[\text{Reaction}]{980°C} \begin{array}{l} (i)\ Si-Al\ \text{spinel (cubic mullite)} \xrightarrow[\text{Exotherm path}-I]{1250°C} \text{Mullite (Orthorhombic)} \\ (ii)\ \text{Aluminosilicate phase (amophous)} \xrightarrow[\text{path}-II]{1300°C} \text{Mullite (Orthorhombic)} \\ (iii)\ \text{Mullite (Orthohombic, weakly crystalline)} \\ (iv)\ SiO_2\ \text{(amorphous)} \\ \quad (980°C\ \text{reaction products of kaolinite}) \end{array} \quad (5)$$

ecular gel marked 'A'. The amorphous SiO_2 component of the gel does not crystallize to β-cristobalite as reported by Hyatt and Bansal.[18] DTA result shows that the temperature of mullitization increases above 1250°C since no exotherms at 980°C and 1250°C are noted as reported earlier in the case of monophasic gels.[15] Only at ~1320°C exotherm, mullitization ensues rapidly, and it may be explained as in a previous case[30] as caused by polymorphic transformation of accumulated c-mullite to o-mullite (Table 1) (see eqn (4)).

2. When water involvement is reduced from 50 ml to 10 ml as in the case of gel G-152(i), colloidal hydrolysed species of silicon and aluminium interact mutually and form monophasic aluminosilicate hydrate gel (amorphous to X-ray). DTA of such gel shows 980°C exotherm of reduced intensity which is similar to that noted by Yoldas and Partlow.[23] XRD of this gel heated to 980°C shows major c-mullite and minor o-mullite as crystalline phases (Fig. 6). Besides 980°C exotherm, another two exotherms at 1150°C and 1250°C tally with those occurring in the DTA trace of a kaolinitic clay (Fig. 4), but differ only in their temperature of occurrences. Comparing these DTA phenomenon, it can be concluded that the thermal transformation sequence of G-152 (i) bears a similarity to the high temperature reaction sequence of kaolinite as substantiated[31,32] and shown in eqn (5).

   Two high temperature reaction paths of mullite formations, namely path-I and path-II as shown above, reveal the origin of two separate exotherms in the DTA trace of kaolinite (Table 1). The XRD study shows that G-152 (i) first forms a major amount of c-mullite at 980°C exotherm (Fig. 6) as in kaolinite and then transforms to o-mullite at ~1250°C exotherm with the complete elimination of c-mullite (Fig. 7). This path of mullitization is analogous to path-I as in kaolinite which was explained as being caused by the polymorphic transformation of c-mullite formed earlier during the 980°C exotherm to o-mullite at 1230°C exotherm (Fig. 4). The exhibition of another exotherm in the same kaolinite at ~1140°C (Fig. 4) was explained as being caused by mullitization in the amorphous aluminosilicate phase by nucleation and crystallization mechanism constituting path-II. Thus, the exhibition of exotherm at ~1150°C in G-152(i) is analogous to the exhibition of exotherm at ~1140°C in case of kaolinite. This similar phenomenon in two cases suggests to us that some amount of amorphous aluminosilicate phase likely liberates out along with c-mullite and o-mullite crystallization at the 980°C exotherm of gel G-152(i).

3. When direct use of water is not made, the gel marked G-152 (ii) directly transforms to t-mullite with the exhibition of a very sharp exothermic peak at 980°C (Table 1). This observation tallies exactly with the finding of molecular gel made by Yoldas and Partlow.[23] In addition to the 980°C peak, this gel also exhibits a small exothermic peak at ~1270°C.

By X-ray analysis, this gel shows the formation of a major amount of t-mullite[29] and a minor amount of c-mullite (Fig. 8) as crystalline phases during 980°C exotherms. Obviously, the formation of these two phases is responsible for the 980°C exotherm in DTA. The later phase, i.e. c-mullite, transforms to o-mullite on further heating and it could be explained that the cause of exhibition for this small exotherm at ~1270°C may be due to the transformation of the accompanying c-mullite phase developed at the 980°C exotherm. As there is no other exotherm in the vicinity of 1200°C as in G-152 (i), it is assumed that aluminosilicate is not present in association with t-mullite and c-mullite at 980°C. By comparing the mullitization behaviours of G-152 (i) and G-152 (ii) it is inferred that water used during hydrolysis reaction is responsible for the formation of aluminosilicate phase. The present study also indicates that the formation of c-mullite could be minimized by performing the gelation in a very slow and restricted way by use of absolute alcohol only and possibly by slight absorption of moisture from a humid atmosphere as in gel G-152 (ii).

4 CONCLUSION

Using TEOS and $Al(OBu)_3$ as sources for SiO_2 and Al_2O_3 components and by maintaining same acid concentration, three different kinds of Al_2O_3–SiO_2 gels have been synthesized by only varying the amount of water used. These three gels show three different modes of phase transformation sequences. Of the three processes of gel synthesis, gel made by using an excess amount of water shows mullitization at a temperature as high as 1320°C exotherm, since this gel is diphasic in character, i.e. inhomogeneous in nature. Gel prepared by the use of a moderate amount of water shows major mullitization at 1250°C exotherm which most researchers in this field noted. It is explained as being caused by the polymorphic transformation of c-mullite crystallized earlier from amorphous aluminosilicate gel at 980°C exotherm. The minor amount of residual aluminosilicate phase associated with c-mullite at 980°C also crystallizes at 1150°C and adds to the major mullite development. So mullitization of this gel is found to be analogous to kaolinite. Gel synthesized with the help of minor moisture absorption from air shows mullitization as early as 980°C in comparison to the other two gels. This gel is supposed to be most homogeneous of the three kinds and it may be formed very slowly by the chemical interaction of hydrolysed monomeric species of the two component raw materials. This view is in confirmation with Yoldas' observation.[23]

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