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Intermediate Si–Al spinel phase formation in phase transformation of diphasic mullite gel

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Al_2O_3–SiO_2 diphasic mullite gel (Si/Al = 1/3) has been synthesized by using $Al(NO_3)_3 \cdot 9H_2O$ and Ludox in basic conditions. Its phase transformation behaviour has been studied by qualitative and quantitative X-ray diffraction techniques. The results indicate that a noncrystalline alumino-silicate phase forms together with the slow crystallization of Si–Al spinel phase of a mullite-like composition up to 1250 °C. Thereafter, it transforms suddenly to orthorhombic mullite around 1325 °C. Earlier studies, e.g. alkali leaching, and measurement of co-ordination number of aluminium in 1000 °C heated diphasic gel, confirm Si–Al spinel formation as an intermediary phase.

1. Introduction

Roy and co-workers [1–5] first described the concept of a diphasic xerogel and prepared Al_2O_3–SiO_2 xerogels in three different ways. On heating, these xerogels exhibited radically different behaviour to that of single-phase or monophasic xerogels. For example, single-phase xerogels and a kaolinitic clay, exhibited a 980 °C exotherm whereas diphasic gel did not do so. Secondly, monophasic gel formed both orthorhombic mullite and Si–Al spinel at the exotherm as identified by Chakravorty and Ghosh [6] on the heated gels prepared after Hoffman *et al.* [1]. Whereas diphasic gel showed the presence of γ-Al_2O_3 and amorphous silica [7], Roy and co-workers claimed that two discrete phases present originally in the diphasic gel itself, e.g. boehmite and amorphous silica, crystallized independently up to 1000 °C. Afterwards, solid-state reaction took place between γ-Al_2O_3 and amorphous silica, and mullite developed. Thus according to them, mullite formed in diphasic gel at a higher temperature in comparison to monophasic gel which formed at 980 °C. On the contrary, Chakravorty and Ghosh [6] showed that the mullitization behaviour, particularly its growth pattern in the case of diphasic gel, was not analogous to that of the oxide mixtures of the two components because it is derived out of two discrete hydroxide particles present in the diphasic gel. However it was very similar to monophasic xerogel, which developed exclusively Si–Al spinel phase at 980 °C [8]. Obviously, it was argued that the spinel phase forming in diphasic system should be silicon-substituted spinel and not a simple γ-Al_2O_3 spinel. Accordingly, the possibility of the solid-state interaction of γ-Al_2O_3 with SiO_2 responsible for the formation of mullite even in diphasic gel, was ruled out. However by synthesizing diphasic gel using tetraethylorthosilicate (TEOS) and colloidal pseudoboehmite sol, Wei and Halloran [9] showed a lamellar feature in the electron micrographs from heated gel. Furthermore, by XRD technique they designated it γ-Al_2O_3, as proposed earlier. They further claimed that diphasic gel was an ultrahomogeneous mixture of phases of about 7–10 nm in size which crystallized independently upto 1200 °C and then reacted directly to nucleate mullite, i.e. they had gone beyond what Hoffman *et al.* [1] has proposed that the two discrete phases reacted only upto 1000 °C. Various researchers [10–16] synthesized and studied the mullitization aspect of Al_2O_3–SiO_2 gel. None has commented upon the identity of this intermediate spinel phase. As discussed earlier [17] the unit cell measurement of spinel phase [18, 19] have their limitations for obtaining a clear answer to the question of what the spinel phase is in reality.

In this paper, XRD technique has been used to compare phase transformation behaviour of diphasic gels of varying SiO_2 and Al_2O_3 contents with those of component gels. The results obtained decisively indicate that the so-called Al_2O_3 phase is, in reality a silicon-bearing spinel phase and this is associated with an amorphous alumino-silicate phase.

2. Experimental procedure

2.1. Gel preparation

A series of diphasic Al_2O_3–SiO_2 gels were prepared using $Al(NO_3)_3$. $9H_2O$ (E. Meck, India) and Ludox (E. du Pont de Nemours), an aqueous silica sol, as source materials. Measured quantities of the components were taken in a Pyrex beaker and diluted with distilled water; the solution was stirred vigorously with the addition of 1:5 dilute solution of NH_4OH until complete precipitation of boehmite gel and silica gel occurred. The mixture was centrifuged and washed with distilled water, dried at 60 °C and stored in stoppered bottles.

2.2. Heat treatment

All the diphasic gels were heated in an electric furnace to different temperatures with 2 h soaking time. Pure boehmite and diphasic gel of nearly mullite stoichiometry marked G-173 were heated dynamically at 10 °C min^{-1}. Samples were collected at predetermined temperatures without allowing any soaking time.

2.3. X-ray study

Dried and heat-treated gels were qualitatively analysed for crystalline phases by X-ray diffraction (Philips PW 1730 X-ray generator). The spinel phase formed on heating G-173 was quantitatively estimated by the usual X-ray internal standard method using CaF_2 and γ-Al_2O_3 as standard. A calibration curve was first drawn as per the usual method [20] and then the percentage of spinel was estimated.

3. Results

Dried and heat-treated gels were subjected to qualitative analysis by XRD. Fig. 1 shows that $Al(OH)_3$ gel G-175 forms boehmite during gelation. In addition to the formation of boehmite, G-173 shows amorphous SiO_2 as an additional phase present, as evinced by the amorphous band with its maxima at 22 ° 2θ CuK_α and so it is designated as diphasic in nature as described by Hoffman *et al.* [1]. On heating G-175, the boehmite phase decomposes at 400 °C forming an amorphous phase, as revealed by XRD. As the temperature increases (Fig. 2a) XRD peaks, e.g. 0.278, 0.238, 0.228, 0.197, 0.155 and 0.139 nm due to γ-Al_2O_3 develop.

Fig. 3 shows that the XRD peak due to γ-Al_2O_3 around the region 0.197 nm (46° 2θ CuK_α) increased with increasing heat treatment. At about 1000 °C, a portion of Al_2O_3 transforms into its higher modification θ-Al_2O_3 as observed by the appearance of the characteristic 0.274 nm peak, and finally it converts fully to its stablest form, α-Al_2O_3. Silica gel G-157 prepared out of Ludox gives a very strong 0.404 nm peak due to formation of β-cristobalite. Table I shows the appearance and disappearance of phases on heating various types of diphasic gels to different temperatures compared to pure silica gel. XRD analysis of heated gel G-168, which contains 2.5% Al_2O_3, shows a drastic diminution in the intensity of cristobalite. As the alumina content is increased further, as in G-169, cristobalite disappears and no crystalline phase corresponding to either Al_2O_3 or SiO_2 component forms. With further increase of Al_2O_3 as in G-170, G-171, etc., the gel transforms into spinel phase at 750 °C and thereafter it is converted at ~1250 °C into mullite and cristobalite. The complete XRD recording of this intermediate spinel phase termed, by Chakravorty and Ghosh [6], Si–Al spinel of mullite composition, is shown in Fig. 2b. The mode of development of Si–Al spinel phase formed on heating G-173 is shown in Fig. 4. It is qualitatively observed that the area of 0.197 nm Bragg diffraction peak (46° 2θ CuK_α increases with

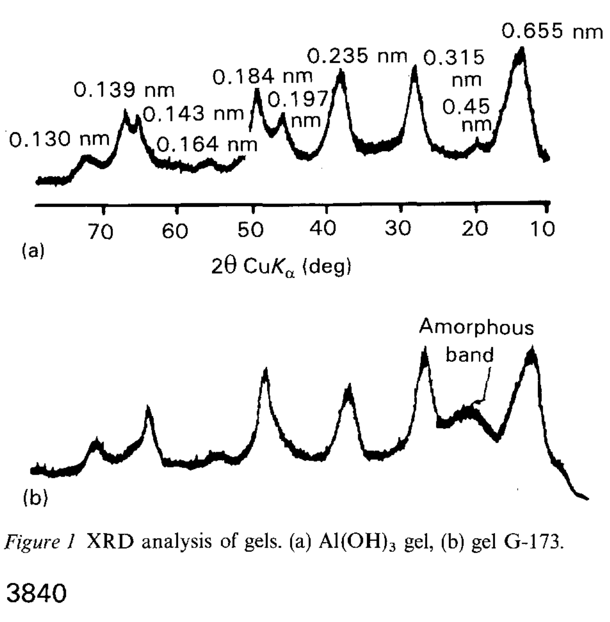

Figure 1 XRD analysis of gels. (a) $Al(OH)_3$ gel, (b) gel G-173.

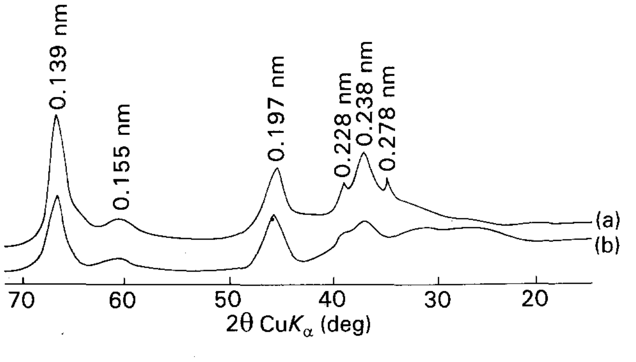

Figure 2 X-ray diffractograms of (a) γ-Al_2O_3 and (b) Si–Al spinel phase.

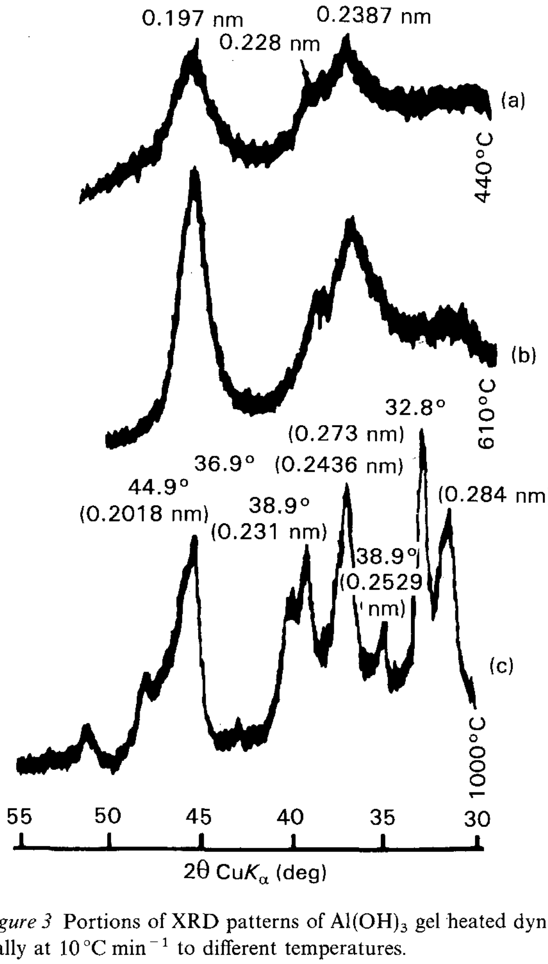

Figure 3 Portions of XRD patterns of $Al(OH)_3$ gel heated dynamically at 10 °C min^{-1} to different temperatures.

TABLE I Sequential phase developments in some diphasic gels compared with pure gels

Gel	Composition (wt %)		Phases present at room temp	Phases formed on heating to various temperatures with soaking						
	SiO_2	Al_2O_3		400 °C	600 °C	750 °C	900 °C	1000 °C	1100 °C	1250 °C
G-157	100	0	Amorphous (band)	A	A	A	Cristobalite (A)	Cristobalite (vs)	Cristobalite (vs)	Cristobalite (vs)
G-168	97.5	2.5	A	A	A	A	Cristobalite (w)	Cristobalite (w)	Cristobalite (vw)	
G-169	92.5	7.5	Boehmite + amorphous band	A	A	A	A	A	A	A
G-170	85	15	Boehmite + amorphous band	A	A	Si–Al spinel (vw)	Si–Al spinel (vw)	Si–Al spinel (vw)	Si–Al spinel (vvw) + mullite (vw)	Mullite + cristobalite (w)
G-171	75	25	Boehmite + amorphous band	A	A	Si–Al spinel (vw)	Si–Al spinel (w)	Si–Al spinel (w)	Si–Al spinel (w) + mullite (vw)	Mullite (w) + cristobalite (s)
G-172	55	45	Boehmite + amorphous band	A	A	Si–Al spinel (vw)	Si–Al spinel	Si–Al spinel	Si–Al spinel + mullite (w)	Mullite (s) + cristobalite (ms)
G-67	40	64	Boehmite + amorphous band	A	A	Si spinel	Si–Al spinel	Si–Al spinel	Si–Al spinel + mullite	Mullite (vs) + cristobalite (vvw)
G-173	31	69	Boehmite + amorphous band	A	A	Si spinel	Si–Al spinel	Si–Al spinel	Si–Al spinel + mullite	Mullite (vs)
G-64	20	80	Boehmite + amorphous band	A	A	Si spinel	Si–Al spinel	Si–Al spinel	Si–Al spinel + γ-Al_2O_3	Mullite (s) + corundum (w)
G-174	10	90	Boehmite + amorphous band	A	γ-Al_2O_3	Si–Al spinel phase + γ-Al_2O_3	Si–Al spinel γ-Al_2O_3	Si–Al spinel + γ-Al_2O_3	Si–Al spinel + corundum	Mullite (ms) + corundum (s)
G-175	0	100	Boehmite	A	γ-Al_2O_3	γ-Al_2O_3 (vs)	Al_2O_3	$\gamma + \theta$ Al_2O_3	Corundum	Corundum (vs)

vs, very strong; ms, medium strong; s, strong; w, weak; vw, very weak; vvw, very very weak; A, amorphous

increasing temperature up to 1258 °C. Thereafter, orthorhombic mullite formation ensues as is shown by the appearance of 0.255, 0.22 nm, etc., Bragg diffraction peaks. At 1325 °C, drastic reduction in the XRD intensity of 46° 2θ CuK_α peak of spinel phase takes place with consequent development of large amounts of orthorhombic mullite. The intensity of cristobalite decreases from G-171 to G-172 to G-67 and no cristobalite is observed in G-173 when heating such gels to 1250 °C. The intensity of corundum decreases from pure $Al(OH)_3$ gel G-175 to G-174 to G-64 and no corundum is observed in heated gel marked G-173. Variations in the XRD intensities of cristobalite and corundum of different gels are shown in Fig. 5.

4. Discussion

4.1. Evidence of the formation of non-crystalline aluminosilicate

Silica gel shows the formation of β-cristobalite at 900 °C. However, a completely different picture is observed when diphasic gels are heated (Table I). For example, when a small quantity of aluminium nitrate is used during gelation, the resultant gel G-168 does not develop boehmite. Boehmite is found in the gel G-169 when the Al_2O_3 content in the gel has been increased to 7.5%. On heat treatment it is found that as the weight per cent of alumina in the gel increases, cristobalite development decreases, as is apparent from G-157 to G-168. In G-169, cristobalite vanishes.

The X-ray patterns of this diphasic gel heated to various temperatures are completely amorphous, i.e. the boehmite portion of the gel does not show any crystallization. This result thus indicates that a non-crystalline aluminosilicate phase has formed during heating G-169. Obviously, this is true in the case of other diphasic gels also, and there may be a reaction between the two amorphous oxide phases with the formation of a noncrystalline alumino silicate. This is due to high free-energy possessed by dehydrated boehmite containing enormous concentration of pores [22] as well as the high reactivity of the very low particle size (~20 nm) of silica phase. This view confirms the theoretical expectation of the formation of a glassy phase as in the *G–T* diagram shown by Hoffman *et al.* [1].

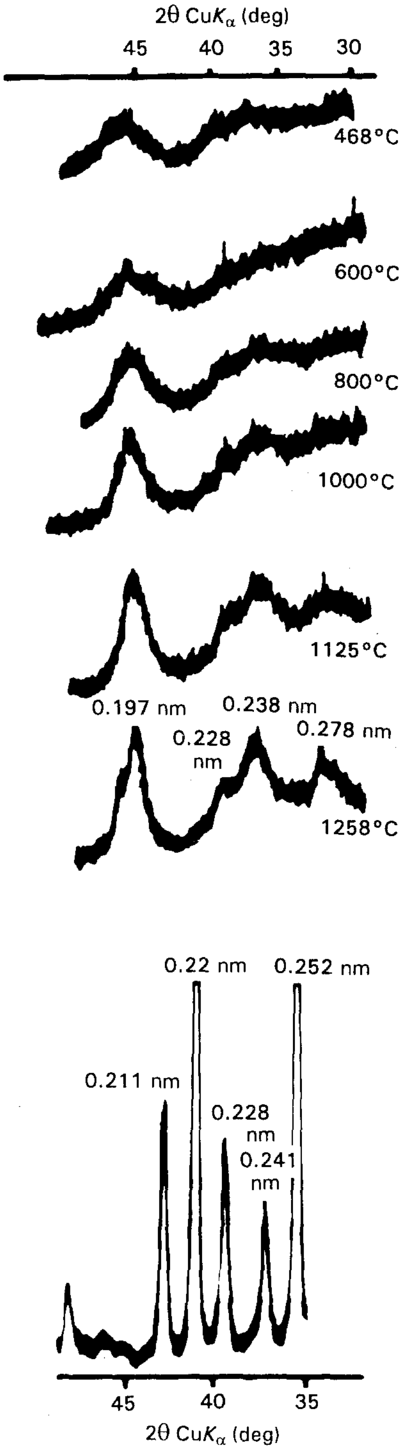

Figure 4 Portions of XRD patterns of gel G-173 heated to different temperatures at 10 °C min^{-1} and 0 h soaking in all cases.

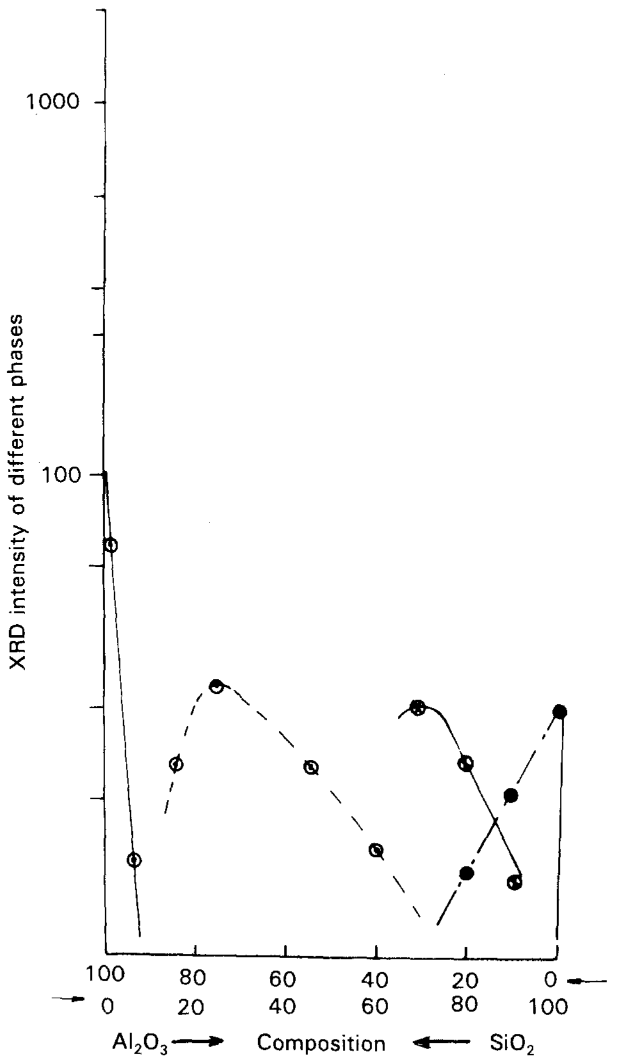

Figure 5 Variation of XRD intensity of corundum and β-cristobalite (arbitrary scale) versus composition of various diphasic gels. (○) 0.404 nm peak of crystobalite, (⊗) 0.537 nm peak of mullite, (●) 0.208 peak of corundum.

4.2. Identification of the spinel phase

γ-Al_2O_3 crystallizes from boehmite gel G-175 very rapidly, as shown by a pronounced increase in XRD intensity of the 0.197 nm peak (Fig. 3) in the temperature range 400–600 °C. However, in presence of silica boehmite component of G-173 produces spinel phase very slowly, as shown by the gradual increase of 0.197 nm Bragg peak as noted in the XRD recording of successive heat-treated gels (Fig. 4). Firstly, retardation of crystallization of the spinel phase during heating of the diphasic gel suggests that amorphous silica, after dehydration of the gel, reacts with amorphous alumina formed after decomposition of the boehmite component of the gel and thus stops its normal crystallization sequence. The resultant aluminosilicate reacted product starts to crystallize as a silicon-incorporated spinel phase, followed by a separate growth pattern which is clearly distinguishable from the growth of γ-Al_2O_3 from boehmite gel.

Secondly, boehmite gel transforms on heating to its other modifications of alumina whereas the alumina component in diphasic gel does not follow its independent crystallization behaviour, e.g. G-173 on heating does not form, θ, κ and α forms but forms only the spinel phase. The complete inhibition in nucleation of the above three alumina modifications definitely suggests the incorporation of silicon in the spinel phase.

Thirdly, as shown in the XRD patterns (Fig. 4) some Bragg diffraction peaks of spinel phase become more and more sharp. This observation confirms the earlier XRD study of Al_2O_3–SiO_2 gels by Iller [23]. One can explain this behaviour as due to the fact that the added SiO_2 physically surrounds the amorphous Al_2O_3 particles formed after dehydration of boehmite. If that be the case then each individual particle or grain will independently crystallize at the same transformation temperature. Physical restraint is not a factor in this case. In fact, it is only the spinel phase which develops gradually on heating and it does not transform to corundum but forms mullite. However, in the thermal sequence of boehmite, the oxygen network of the first phase, i.e. boehmite, and the last phase, i.e. corundum, are both hexagonal close packed. The intermediate forms have a cubic close packed oxygen layer. Therefore, the determining factor for the sequence of thermal changes of $Al(OH)_3$ gel is the persistence of the original oxygen network. In the presence of SiO_2, as in the above discussion, the transformation of boehmite does not follow the same topotactic sequence that occurs in the pure state, as noted by previous authors [24–26].

Fourthly, spinel phase derived from diphasic gel is found to exist up to 1250–1300 °C, which is higher than the crystallization temperature of corundum from boehmite gel. The high-temperature stability of this spinel phase definitely indicates that it must contain Si^{4+} in its structure and, consequently, as the temperature increases during heating, no nucleation of aluminous phase takes place. The possibility of introduction of silicon in certain sites of the alumina structure has been reported by Yoldas [27]. He explained that the introduction of some Si^{4+} caused no disturbance in the lattice and remained essentially undetectable, i.e. some Si^{4+} substitutes for Al^{3+} in the tetrahedral interstices and the replaced Al^{3+} sit in the octahedral sites of the alumina phase. The question now is: what will be the maximum limit of Si^{4+} substitution? Two pieces of evidence are presented below regarding the concentration of Si^{4+} in Si–Al spinel phase.

1. By identifying the mode of crystallization of cristobalite and corundum during the heating of diphasic gels having varying ratios of SiO_2 and Al_2O_3 contents. Table I shows that on heating to 1250 °C, cristobalite does not develop from diphasic gels having 0%–28% SiO_2 content; it is found to form only when SiO_2 is in excess of that of the composition of 3:2 mullite (Fig. 5). After that, its crystallization increases with increasing SiO_2 content of the diphasic gel. Pure boehmite gel G-175 forms only γ-Al_2O_3 on heating. Its intensity decreases more with further addition of SiO_2. At 3:2 mullite composition, no α-Al_2O_3 is found to form at 1250 °C, but it develops only a maximum amount of mullite (Fig. 5). Therefore, the spinel phase from which mullite develops during the course of heating may be of the composition of 3:2 mullite.

2. Estimation of amorphous SiO_2 liberated on heating diphasic gel containing of varying ratios of SiO_2 and Al_2O_3. It was found earlier [28] that with 5% NaOH solution or even with 10% NaOH [16] under boiling-water bath conditions, negligible amounts of SiO_2 and Al_2O_3 could be extracted from 1000 °C heated diphasic gel of mullite stoichiometry. This result definitely indicates that component oxides are not present in free states at 1000 °C, as assumed for the γ-Al_2O_3 hypothesis. It was also shown that diphasic gels of SiO_2 content more than 28%, discarded the excess silica during heating at 1000 °C, which showed that the saturation limit of SiO_2 in the spinel phase is 28%. As a result, the excess SiO_2 is found to be leachable by NaOH solution and the residue left after leaching is nearly of the composition of 3:2 mullite. Such gels will form cristobalite during heating at higher temperatures along with the usual mullite phase. Thus by correlating the alkali leaching study with XRD analysis of heated diphasic gels, it is concluded that the intermediate phase is silicon-bearing and it is of the composition of mullite. However Okada and Otsuka [29] and Hsi *et al.* [30] believed the intermediate spinel phase is $SiO_2 \cdot 6Al_2O_3$. Okada and Otsuka [29] showed that the amount of spinel phase was maximum when the silica content was 8% and decreased with decreasing SiO_2. The fall in intensity of spinel in the range between 8% and 0% is not theoretically possible, and therefore is not realistic.

4.3. Quantitative amount of spinel phase detected by the XRD technique

The amount of spinel phase in G-173 heated to 1000 °C/2 h is estimated to be 79%–80% compared to the initial 69% Al_2O_3 content of the gel, as determined by chemical analysis. These data exemplify two aspects regarding the characterization of spinel phase. Firstly, the observed value of 79% is greater than the theoretically expected value of 69%, which is the total alumina content of the diphasic gel. This indicates that spinel phase formed during transformation of boehmite in the presence of SiO_2 is not γ-Al_2O_3. In other words, the entrance of Si^{4+} in the spinel structure is responsible for the higher value. Thus, out of the total 31% SiO_2 present in the gel G-173, some of the silica is responsible for the formation of 80% Si–Al spinel of mullite-like composition, and the rest remains associated with Al_2O_3 and develops ~20% non-crystalline aluminosilicate phase. Therefore, the phase transformation in the case of diphasic mullite gel follows Equation 1.

$$\begin{matrix}\text{Ludox}\\ +\\ Al(NO_3)_3 9H_2O\end{matrix} \xrightarrow[NH_4OH]{H_2O} \begin{matrix}\text{Diphasic}\\ \text{gel}\end{matrix} \xrightarrow{400\,^{\circ}C} \begin{matrix}Al_2O_3\\ (\text{Amorphous})\\ +\\ SiO_2\\ (\text{Amorphous})\end{matrix} \xrightarrow[\text{heating}]{\text{Gradual}}$$

$$\begin{matrix}\text{Aluminosilicate}\\ \text{phase (amorphous)}\\ +\\ Al_2O_3, SiO_2 \text{ (residual}\\ \text{amorphous phases)}\end{matrix} \xrightarrow{600\text{–}1200\,^{\circ}C} \begin{matrix}3\ Al_2O_3 2\ SiO_2\\ \text{Si–Al spinel } (\sim 80\%)\\ +\\ \text{Alumino silicate phase } (\sim 20\%)\\ \text{(residue)}\end{matrix} \qquad (1)$$

4.4. Explanation of previous works

4.4.1. Co-ordination of aluminium

Komarneni *et al.* [2] measured the ^{27}Al MAS-NMR of diphasic mullite gel heated to 1010 °C and showed the tetrahedral to octahedral ratio of aluminium was 0.45. This is very different from the corresponding value of 37.5/62.5 = 0.6 for γ-Al_3O_3. This result definitely suggests that the intermediate spinel phase formed on heating the diphasic gel is not simple γ-Al_2O_3. On the other hand, the observed lower value of the tetrahedral to octahedral ratio indicates that Si^{4+} has substituted Al^{3+} in the tetrahedral holes of the oxygen network of the spinel structure and, as a result, the octahedral occupancy by Al^{3+} has increased. In order to test the reliability of Equation 1, tetrahedral-to-octahedral ratio for aluminium in the diphasic mullite gel heated to 1000 °C was calculated theoretically. The AlO_4 content in 79% Si–Al spinel is 29 × 79/100, i.e. 16.59%. (The tetrahedral aluminium content in pure Si–Al spinel of a mullite-like composition is 21%, and the rest is octahedral [19]). The AlO_4 content in 21% aluminosilicate is 55 × 21/100, i.e. 11.55%, and the total AlO_4 content in 1000 °C heated diphasic mullite gel is 16.59 + 11.55, i.e. 28.14%. Therefore, the ratio of AlO_4 to AlO_6 is 28.14/71.86, i.e. 0.39%. This value is closer to the measured value of 0.45 than to 0.6 for the transformation to the theoretically expected γ-Al_2O_3 phase. Thus Si–Al spinel formation is the most probable phase in the thermal transformation of the diphasic gel.

5. Conclusion

By comparing the thermal change of pure $Al(OH)_3$ and $Si(OH)_4$ gels with those of diphasic gels of different Al_2O_3:SiO_2 ratios, the following conclusions have been drawn.

1. Boehmite gel hinders the crystallization sequence of the silica gel component of the diphasic gel (Al_2O_3 7.5%, remainder SiO_2) during heating. On the other hand, it will not transform to its own high-temperature modifications and thus indicates the formation of a non-crystalline aluminosilicate phase.

2. On heating diphasic gel containing 28% SiO_2, the boehmite component will not transform topotactically to θ, κ, etc., modifications, as it does when it is present in the free state, but it will form Si–Al spinel as an intermediate phase and then transforms to mullite on further heating rather than forming corundum. Side by side, the silica components in the gel will not transform to cristobalite, but when either of the percentages of SiO_2 or Al_2O_3 is higher than its percentage in 3:2 mullite, then either β-cristobalite or α-Al_2O_3 will crystallize.

3. Growth of γ-Al_2O_3 from pure boehmite gel is very rapid and occurs in the temperature range 500–750 °C. On the other hand, Si–Al spinel forms from the diphasic mullite gel and crystallizes slowly over a long temperature range, being stable to a temperature as high as 1300 °C, which is higher than the transformation temperature of γ-Al_2O_3 to corundum.

4. The amount of spinel phase formed as estimated by the QXRD technique is ~79% which is higher than the amount of Al_2O_3 (69%) used during preparation of the diphasic gel. These results, together with the previous results of our leaching study indicate that on heating, the diphasic gel forms Si–Al spinel of a mullite-like composition (cubic mullite) to the extent of 79%–80%, with 21% non-crystalline alumino-silicate phase. These quantitative data agree with the co-ordination number of aluminium in 1000 °C-heated diphasic gel measured by the ^{27}Al MAS–NMR study.

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