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Carbothermal reduction of kaolinite under nitrogen atmosphere

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Abstract

Preliminary studies on the carbothermal reduction of kaolinite ($Al_2O_3.2SiO_2.2H_2O$) in a static nitrogen gas pressure of 0.15 MPa are reported. The effect of various reaction parameters, e.g. temperature of the reaction (1550–1700°C), mole ratios of carbon to silica (4.5–9.0) in the reactant mixture and nature and source of carbon, e.g. activated charcoal (sp. surface area, 1000 m^2/gm) and carbon black (sp. surface area, 300 m^2/gm) on the carbothermal reduction have been investigated. It is observed that mullite, silicon oxy-nitride and X-sialon phases are present at low temperatures, while β'-sialons, β-SiC, Al_2O_3 and AlN are present at high temperatures. Activated charcoal is more reactive than carbon black and the reaction rate is more for higher mole ratios of carbon.

Keywords: Carbothermal reduction; Kaolinite; Nitrogen atmosphere

1. Introduction

Carbothermal reactions involving the use of fine carbons as a reactant in inert atmospheres at high temperatures has been extensively used since long for reduction of metallic oxides as well as for beneficiation of several minerals. In particular, carbothermal reduction of natural silicate minerals to obtain silicon carbide or silicon nitride or their solid solutions with oxides like alumina (e.g. β'-sialons), Al_2O_3–SiC and AlN-SiC mixed products in powder form has extensively been studied. Carbothermic reaction of alumino silicates like kaolin and sillimanite as well as of zircon under argon atmosphere has been studied by us and reported earlier elsewhere [1–3]. The same reactions have been now carried out under nitrogen atmosphere and the results are being reported in this paper.

The reduction of kaolinite ($Al_2O_3.2SiO_2.2H_2O$) by carbon under nitrogen atmosphere has been studied earlier by several authors [4–11] at temperatures ranging from 1200 to 1600°C using stoichiometric, sub-stoichiometric and over-stoichiometric quantities of carbon under flowing nitrogen atmosphere.

Although kaolinite could be mainly anticipated to produce pure β'-sialon (a solid solution of α-Al_2O_3 in β-Si_3N_4) due to the Si:Al ratio being 1:1 (general formula of β'-sialon is $Si_{6-z}Al_z N_{8-z} O_z$, where z ranges from 0 to 4.2; for kaolinite case $z=3$) this phase does not form directly. The early conversion of kaolinite into alumina rich mullite and silica which react subsequently with carbon and nitrogen at higher temperatures to give β'-sialons besides other products such as SiC, X-sialons silicon oxy nitride, AlN, Al_2O_3 in minor quantities depending upon the stoichiometry of C: kaolinite, nitrogen flow rate, temperature of the reaction, etc. Mukherjee and Bandyopadhyay [4] prepared β'-sialons with values of $z = 2$ and mixed with other phases such as Al_2O_3, mullite, AlN, AlON (spinel type aluminium oxy nitride) in minor quantities by reacting pellets of stoichiometric mixtures of kaolin and carbon black under nitrogen atmosphere.

Van Dijen et al. [5] found that the values for $\Delta G°$ for β'-sialon and β-Si_3N_4 were almost similar. They further studied the rate limiting steps of the carbothermal reduction in a packed bed reactor of carbon + kaolin and showed the sensitive dependence of products formed on reaction variables, e.g. surface area of the powders pellet sizes, nitrogen flow rate, temperature, etc. Baldo et al. [8] used different alumino silicate precursors including kaolin under control of various reaction variables to obtain β'-sialons of different z values. Lee and Cutler [9] studied the preparation of β'-sialon from carbon-clay mixtures under nitrogen and reported progressive formation of the various products given below as a function of temperature (in the range of 1400–1650°C) and carbon content:

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$$
\begin{aligned}
3Al_2O_3.2SiO_2 &\rightarrow \text{X-sialons}\\
&\rightarrow Si_2O_2N + X\\
&\rightarrow X + \beta' \text{ sialon}\\
&\rightarrow \beta' \text{ sialon}\\
&\rightarrow \beta' \text{ sialon} + 15R\,\text{phases}\\
&\rightarrow \beta\ Si_3N_4 + AlN
\end{aligned}
$$

The above phases are in confirmity with the phase diagram of Jack [10]. Higgins and Hendry [11] have proposed that around 1400°C, kaolin is converted to a mixture of mullite and silica, the latter reacts with carbon to form silicon carbide and this silicon carbide and carbon in presence of nitrogen convert mullite to β′-sialons. They also found that the presence of iron impurities have a catalytic effect on the reaction in agreement with the observation of Lee and Cutler [9]. Cho and Charles [12] have summarised the earlier studies and further studied the carbo-reduction of kaolin using different carbon precursors under nitrogen. Their findings show that the nature of the carbon precursors used as well as the nitrogen flow rates had a bearing on the products formed in the reaction.

The reaction of kaolinite with carbon being solid–solid/solid–gas in nature, the ratio of carbon to silica and the extent of their mutual physical contact would obviously influence the reaction kinetics to a considerable extent. Bandyopadhyay et al. [4] had taken C:SiO_2 ratio stoichiometrically (3 mols of carbon per mole of silica) and increased their contact by pelletisation and reactions were carried out under a continuous flow of nitrogen gas. We have carried out the reactions with varying amounts of two different types of carbon in excess of stoichiometry to generate different products under a given set of reaction conditions, e.g. temperature of the reaction (1550–1700°C), mol ratios of carbon to silica content of kaolin (4.5–9.0), and activated charcoal or carbon black on the carbothermal reduction of kaolin. The reactions were carried out in a closed reactor containing a positive pressure of nitrogen in order to minimise the loss of SiO gas generated during the carbothermal reduction. In our study, the reactant mixtures were taken in loose powder form to allow the free growth of products in whisker or other forms. The soaking period of 1 h was maintained in all the cases to study the evolution of various phases.

2. Experimental procedure

Kaolinite powder (M/s English India Clays, India) with the following impurity content: $TiO_2 = 0.5\%$, $Fe_2O_3 = 0.52\%$, $CaO = 0.06\%$, $MgO = 0.06\%$, $K_2O = 0.03\%$, $Na_2O = 0.08\%$, LOI = 14.3%, and having a particle size distribution as shown in Fig. 1 was used directly as the precursor for the reactions. Activated charcoal (M/s S.D. Fine Chemicals, India) and carbon black (M/s Degussa, Germany) possessing B.E.T. surface areas of 1000 and 300 m^2/gm, respectively, were taken as the sources of carbon. Kaolinite and carbon in the proportions of 4.5, 5.5 and 9.0 mols of carbon per mole of silica content in kaolinite were mixed in ethyl alcohol medium. After a good mechanical agitation for 30 min the alcohol was evaporated to obtain homogeneous mixture of carbon and kaolin powders. These were loaded into graphite crucibles sealed using an organic resin (Araldite, M/s Ciba Geigy, India). The lids contained small holes to enable the precursor powders to communicate and equilibrate with the outside furnace atmosphere at high temperatures. The crucibles were then placed on the hearth of a graphite furnace with internal graphite heating elements inside a carbon–carbon composite fibre board insulated hot zone. The furnace chamber containing the reactant crucibles was then evacuated to ~1 milli-bar vaccum and then back-filled with high purity nitrogen gas to a positive pressure of 0.15 MPa. The temperature inside the furnace was measured by a bare W-5% Re/W-26% Re thermocouple. The graphite furnace was heated in a programmed manner e.g. from room temperature to 1000°C at 10°C/min, from 1000 to 1250°C at 5°C/min and finally from 1250°C to the desired temperature (e.g. 1550, 1600, 1650 and 1700°C) at 3°C/min. The products were soaked for 1 h at the highest chosen temperature in all the cases before cooling to room temperature for product removal. The product powders were subsequently decarburised to get rid of excess unreacted carbon by heating in air at 700°C for 4 h.

The decarburised products were subjected to X-ray diffraction (XRD) studies using CuKα radiation with nickel filters in a Rigaku X-ray Diffractometer (M/s Rigaku Corp., Japan) for phase analysis and to Scanning Electron Microscope (SEM) in a JSM-35 Scanning Electron Microscope (M/s JEOL., Japan) and XL20 (M/s Philips, Holland) for morphological analysis of the products.

The samples prepared under different conditions are designated using the following simple notations (precursor, nature of carbon, mol ratio of carbon: silica, nitrogen atmosphere, temperature) e.g. KCB45N1700 denotes sample derived from kaolinite precursors containing 4.5 mols (45) of carbon black (CB) (or AC for activated charcoal) per mole of silica (in the precursor) reacted in nitrogen (N) at 1700°C for 1 h. Typical XRD spectra of the products obtained in nitrogen atmosphere using activated charcoal and carbon black of different mole ratios are presented in Figs. 2 and 3, respectively. XRD patterns of all samples have been obtained taking a constant weight (100 mg) of the decarburised product,

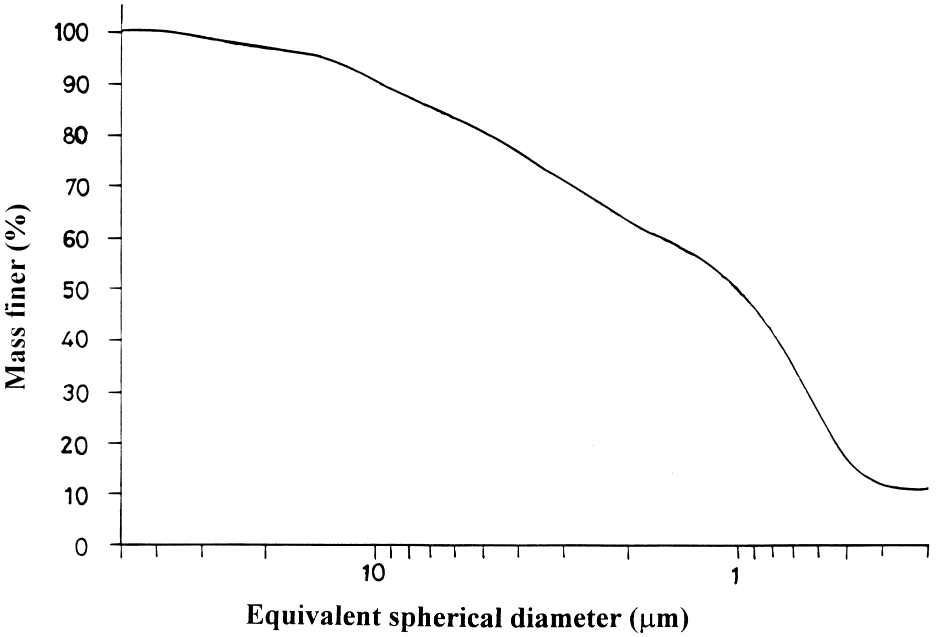


Fig. 1. Particle size distribution of kaolin.

in view of which the peak height/peak intensity of most intense non-overlapping peak of various phases present in the product could be assumed to be representative of quantity of that species present in the product. Therefore, increase or decrease of intensity of various phases could be taken to represent the progress of carbothermic reaction under a given set of experimental conditions. Thus peaks at 16.44° of 2θ ($d=0.539$ nm) of mullite, peaks at 11.23° of 2θ ($d=0.784$ nm) of X-phase sialons, peaks at 13.304° of 2θ ($d=0.665$ nm) of β′-sialons and peaks at 59.98° of 2θ ($d=0.1549$ nm) of SiC were taken as the representative XRD peaks for monitoring the progress of the reactions. The intensity of XRD peaks of various products normalised to 100% are plotted in the form of bar diagrams and are presented in Figs. 4 and 5 for activated charcoal and carbon black containing samples, respectively.

Typical SEM pictures of activated charcoal and carbon black and of some of the products of the reactions carried out in nitrogen atmosphere are presented in Figs. 6 and 7. The qualitative XRD analysis of various product phases obtained under different reaction conditions in nitrogen atmosphere are presented in Table 1.

3. Results and discussions

XRD analysis of various products at two lower temperatures (1550 and 1600°C) shows the presence of mullite, amorphous silica, X-Sialon and silicon oxynitride while β′-sialon, β-SiC and AlN are found to be major phases present at higher temperatures (1650 and 1700°C). Due to the same Al/Si ratio (Al/Si = 1) of both kaolinite and β′-sialon, carbo-nitridation of kaolinite should be anticipated to produce single phase β′-sialons. However, formation of mullite at low temperatures whose Al/Si ratio is > 1 does not allow formation of β′-sialons at low temperatures and a number of intermediate phases are formed and converted to β′-sialons. Further reactions at higher temperatures also lead to decomposition of β′-sialons and ultimate formation of AlN–SiC and some Al_2O_3.

From the XRD analysis of various products, it is observed that kaolin first decomposes to mullite and amorphous silica. Mullite then reacts with carbon in the presence of nitrogen and forms X-phase sialon as per the equations given below in agreement with observations of Lee and Cutler [9].

$$\underset{\text{Kaolin}}{3(Al_2O_3.2SiO_2.2H_2O)} \rightarrow \underset{\text{Mullite}}{3Al_2O_3.2SiO_2} + \underset{\text{Amorphous Silica}}{4SiO_2} + 6H_2O \quad (1)$$

$$3(Al_2O_3.2SiO_2.2H_2O) + 3C + N_2 \rightarrow \underset{\text{X-phase}}{2(Si_2Al_3O_7N)} + 2SiO_2 + 3CO + 6H_2O \quad (2)$$

$$2SiO_2 + 3C + N_2 \rightarrow \underset{\text{Silicon oxy-nitride}}{Si_2N_2O} + 3CO \quad (3)$$

Bandopadhyay et al. [4] noticed the conversion of amorphous silica to SiC in the initial stages and there is no mention about X-phase while we observed the formation

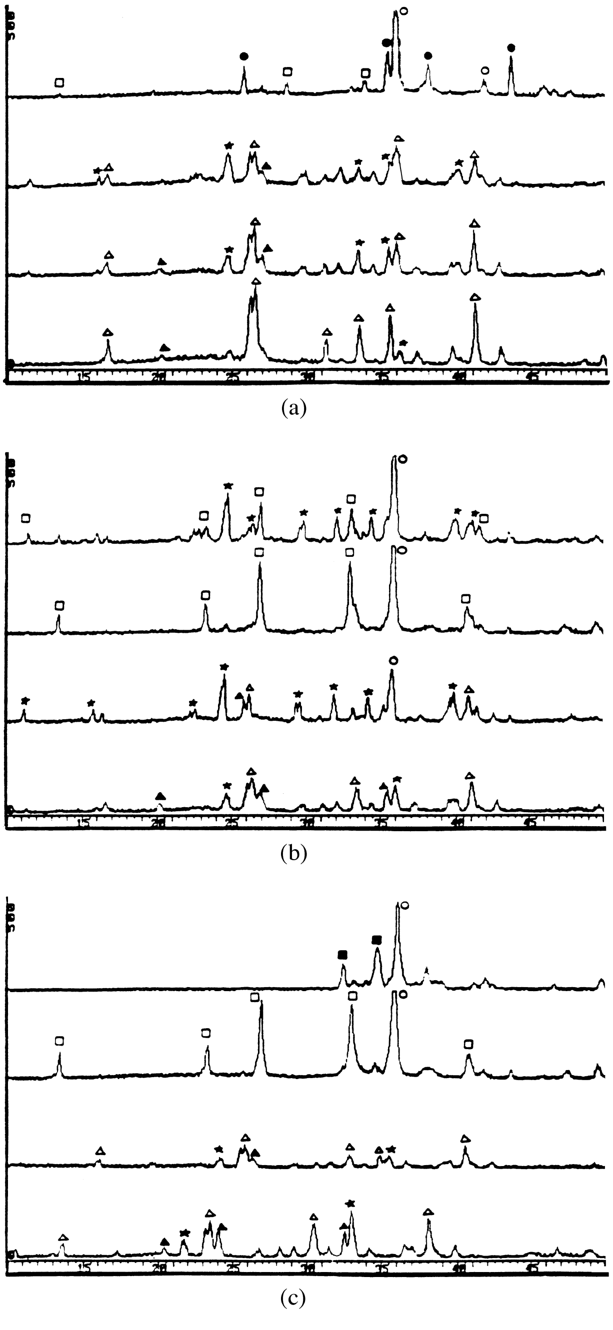


Fig. 2. XRD patterns taken at 50°C intervals of the products obtained when (a) 4.5 (b) 5.5 (c) 9.0 mol ratios of activated charcoal are reacted between 1550°C (bottom trace) and 1700°C (top trace): (△) mullite; (○) β-SiC; (●) α-Al_2O_3; (*) X-phase sialon; (□) β′-sialon (■) AlN; (▲) Si_2N_2O.

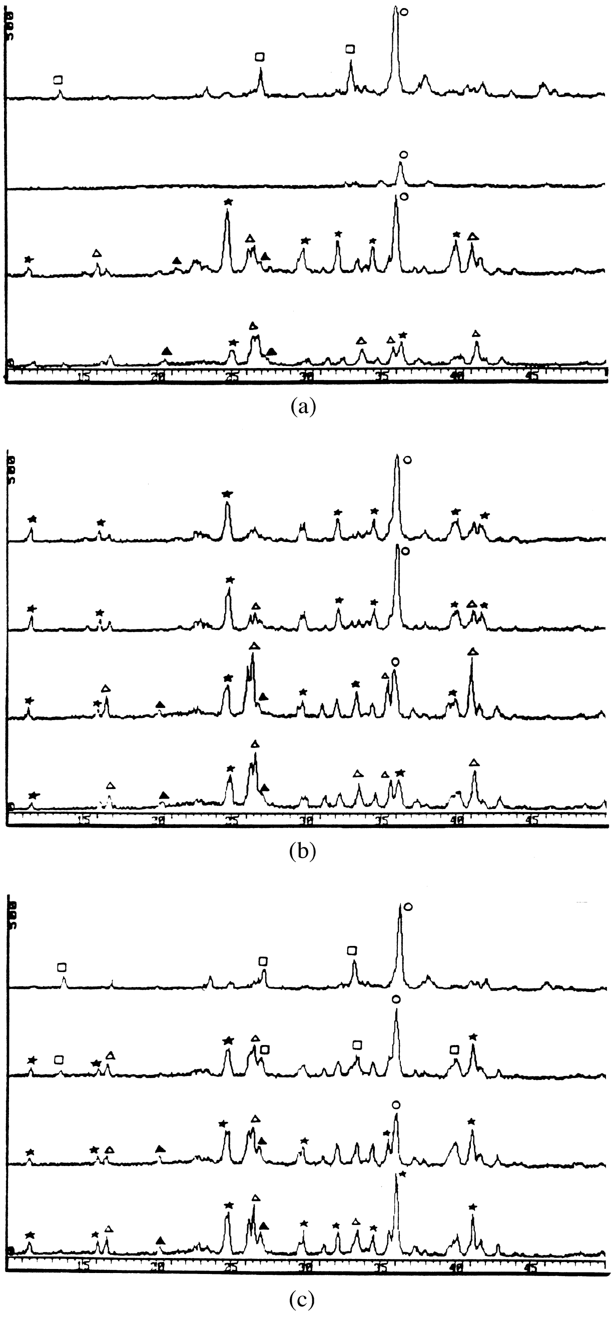


Fig. 3. XRD patterns taken at 50°C intervals of the products obtained when (a) 4.5 (b) 5.5 (c) 9.0 mol ratios of carbon black are reacted between 1550°C (bottom trace) and 1700°C (top trace): (△) mullite; (○) β-SiC; (●) α-Al_2O_3; (*) X-phase sialon; (□) β′-sialon; (■) AlN; (▲) Si_2N_2O.

of amorphous silica, X-phase sialon and silicon oxy nitride (Si_2N_2O) at lower temperatures of 1550 and 1600°C. The reason might be due to higher reactivity in the former case due to pelletisation causing direct formation of β′-sialon. In case of activated charcoal, due to high reactivity, β′-sialon further decomposes to Al_2O_3, SiC and even AlN at 1700°C. The presence of β′-Sialon, β-SiC, Al_2O_3 and AlN obtained in this study and by other authors[4,9,12] can be explained as per the following reactions.

$$3Al_2O_3.2SiO_2 + 2Si_2Al_3O_7N + 3Si_2N_2O + 6N_2 + 18C \rightarrow \underset{(\beta'-\text{sialon})}{Si_3Al_3O_3N_5} + 18CO \qquad (4)$$

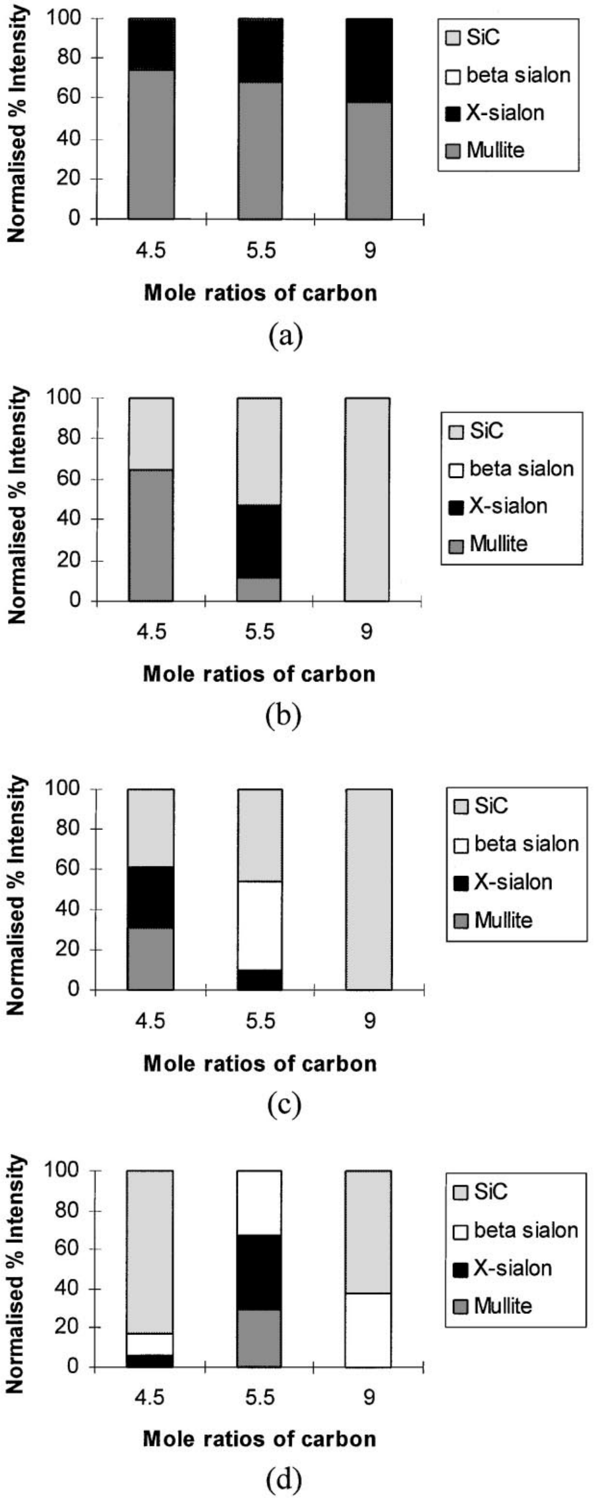


Fig. 4. (a)–(d) Bar graphs of intensity of product phases at temperatures 1550°C (top)–1700°C (bottom) for different mole ratios (4.5–9.0) of activated charcoal.

$$Si_3Al_3O_3N_5 + 6C \rightarrow 3SiC + 3AlN + 3CO + N_2 \qquad (5)$$

or

$$Si_3Al_3O_3N_5 + 3C \rightarrow 3SiC + AlN + Al_2O_3 + 2N_2 \qquad (6)$$

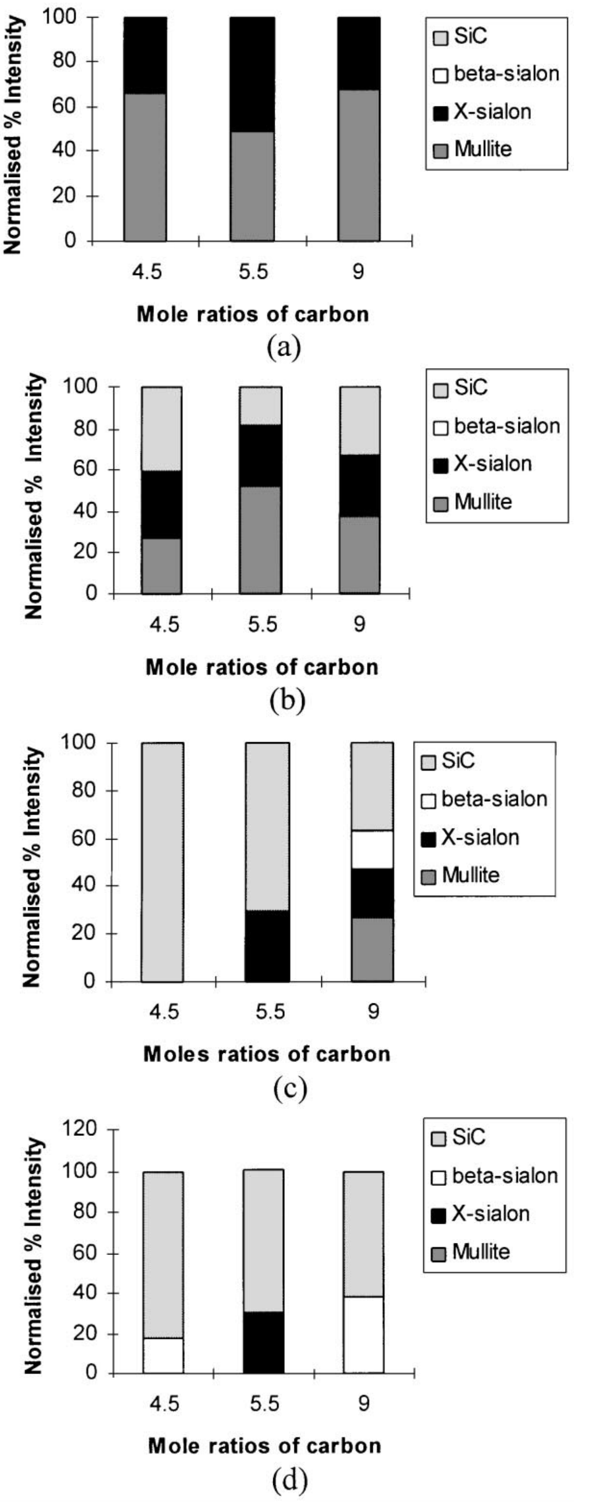
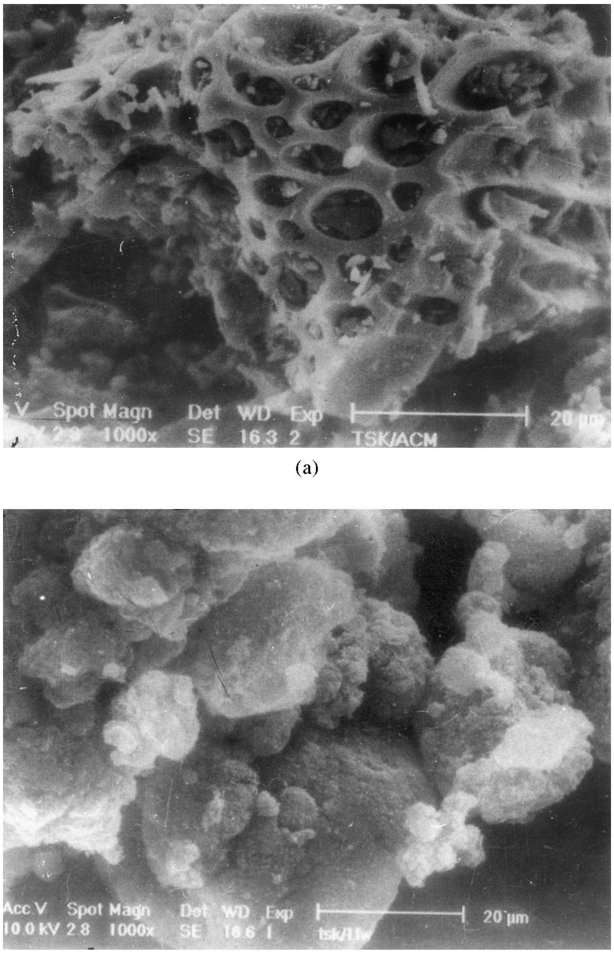


Fig. 5. (a)–(d) Bar graphs of intensity of product phases at temperatures 1550°C (top)–1700°C (bottom) for different mole ratios (4.5–9.0) of carbon black.

Due to the gaseous nature of SiO gas, sialons and silicon carbide formed were found to be mostly having a whisker morphology.



(a)

(b)

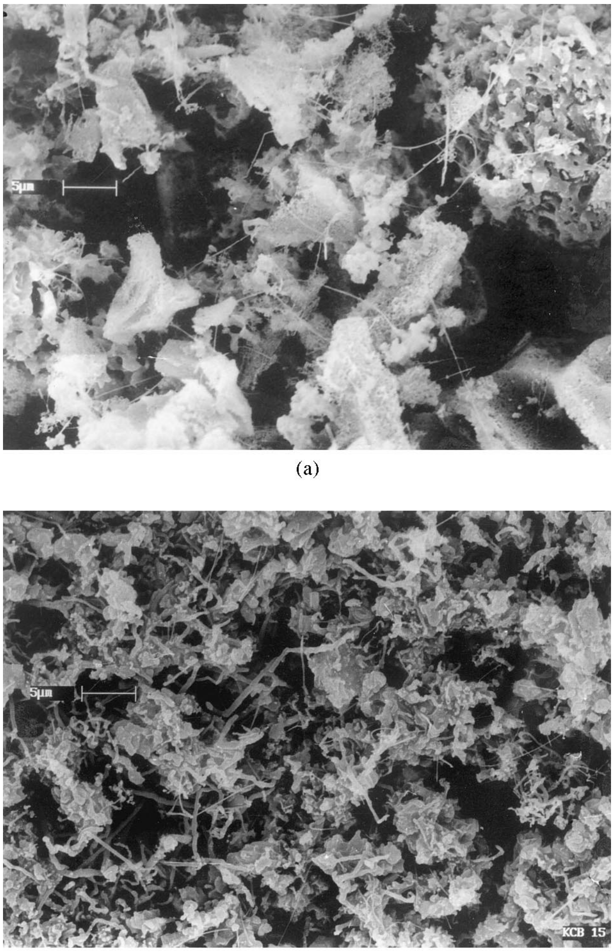
Fig. 6. SEM micrographs of (a) activated charcoal and (b) carbon black used in the experiment.

4. Effect of mole ratios of carbon

From the following observations made from the plots of bar graphs of various phases present at different reaction temperatures and for different mole ratios of carbon (Figs. 4 and 5), it is concluded that the rate of reaction increases with increase in carbon content (mole ratios of carbon).

At 1550°C, mullite and X-phase sialons are the two phases formed. The relative intensity of X-sialon generally increases with increase in molar ratios of carbon.

1. At 1600°C, the intensity of mullite decreases with increase in molar ratios. The fact that X-phase is absent at 4.5 mols, appears at 5.5 mols and finally converts to β′-sialon at 9.0 mole ratio proves the increase in reaction rate with increase in mole ratios of carbon.
2. At 1650°C, mullite and X-phase are present at 4.5 mole ratio while they efficiently disappear at higher mole ratios of carbon and converts to a mixture of β-SiC and β′-sialon.



(a)

(b)

Fig. 7. SEM micrographs of products obtained with (a) activated charcoal (b) carbon black.

3. At 1700°C, X-phase is observed at 4.5 mol ratio and is completely absent at 9.0 mole ratio of carbon.
4. All samples contain appreciable amounts of silicon carbide at temperatures > 1600°C owing to the existence of a very high carbon activity in the furnace.

Similarly, the absence of amorphous silica in the samples containing 9.0 mols of carbon black proves to be high reactivity compared to 4.5 and 5.5 mols.

5. Comparison of activated charcoal and carbon black

The two types of carbon used in this study have very different morphologies (Fig. 6). While carbon black consists of agglomerated fine primary grains, active charcoal is lumpy and contains large number of fine channel pores which account for the latter's high surface area and reactivity.

The formation of β′-sialon is completed at 1650°C for higher mole ratios of activated charcoal while it is com-

Table 1
Various product phases (analysed by XRD) obtained by carbothermal reduction of kaolin in nitrogen atmosphere[a]

Reactants	C: SiO_2	Product phases (as analysed by XRD) at temperatures			
		1550°C	1660°C	1650°C	1700°C
Kaolin + A.C.	4.5	M, X, AS, Sion	M, X, sion	M, X, AS, sion	A, S, SLN
	5.5	M, X, sion	M, X, S	SLN, S	X, S, SLN
	9.0	M, X, sion	M, X, sion	SLN, S	SiC–AIN
Kaolin + C.B.	4.5	M, X, sion	M, X, sion, S	S, AS, SLN	SLN, S
	5.5	M, X, AS, sion	M, X, S, sion	X, M, S	X, S
	9.0	M, X, sion	M, X, S, sion	M, X, SLN, S	SLN, S

[a] M, mullite; S, silicon carbide; A, aluminia; AS, Amorphous silica; SLN, β'-sialons; X, X-sialon; sion, silicon oxy-nitride.

pleted only at 1700°C for higher mole ratios of carbon black. This shows that activated charcoal is more reactive than carbon black. Due to the high reactivity of activated charcoal, β′-sialon further decomposes to other products like Al_2O_3, AlN and SiC at 1700°C for higher mole ratios of carbon and to α-alumina and β-SiC for lower molar ratios of carbon. This is again attributable to the higher surface area of activated charcoal compared to carbon black.

6. Presence of minor phases in the products

In the reactions, alumina and silicon oxy-nitride phases form at lower temperatures (1550–1600°C) but they disappear at higher temperatures (Figs. 2 and 3). There is no evidence of AlN phase in the XRD patterns and even if formed they are below detectable limits in this study. However, considerable quantity of silicon carbide in whisker form formed in our studies.

7. Conclusion

From the above discussions, it can be concluded that mullite, X-phase sialons and silicon oxy-nitride form at low temperatures, while β′-sialons, SiC, AlN, Al_2O_3, and SiC are formed at high temperatures. The higher mole ratios of carbon increases the rate of reaction and activated charcoal has better reactivity than carbon black due to its higher surface area.

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