

Synthesis and characterization of cordierite precursor derived by semi-colloidal sol-gel route

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Microfine cordierite precursor powder of stoichiometric chemical composition, $2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$, can be synthesized by semi-colloidal route using dehydroxylated china clay, precipitated silica, magnesium hydroxide. The derived cordierite precursor is characterized by chemical analysis, BET surface area, particle size distribution, differential thermal analysis (DTA), FTIR spectroscopy, TG-DTA analysis, X-ray diffraction (XRD) and scanning electron microscopy (SEM) studies. The study reveals that crystallization of μ -cordierite from amorphous precursor starts at 900°C as confirmed by differential thermal analyses, X-ray. The SEM studies of the precursor calcined at 900°C focuses the uniform distribution of platelike particles in the size ranges of $0.5\text{--}4\ \mu\text{m}$.

Keywords: Cordierite precursor, $\text{MgO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ system, XRD, SEM.

Introduction

Cordierite having the stoichiometric chemical formula, $2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$ is the main phase of the $\text{MgO}\text{-Al}_2\text{O}_3\text{-SiO}_2$ system. Cordierite materials have very interesting properties like adequate refractoriness, extremely low coefficient of thermal expansion, low thermal conductivity, high mechanical strength, outstanding thermal shock resistance and excellent electrical resistivity. It finds multifunctional application such as spreads over kiln furniture, moulded honeycomb-like catalyst supports in auto emission devices, thick films, porous ceramics, high frequency insulators, high performance resistors, special furnace shapes, heating element supports, exhaust catalyst supports, burner tubes, refractory setters and substrates, welding tapes, heaters and thermocouples etc. Cordierite ceramics possess also low dielectric constant and low dielectric loss values which permit its practical applications in electronic industry as substrates, packaging and multichip module. Cordierite phase exists in three polymorphic forms: (i) the high-temperature disorder form known as indialite (α - or hexagonal-cordierite) which is stable below 1450°C , (ii) β -cordierite, called orthorhombic cordierite stable

in between 1450°C and its melting point (1460°C), and (iii) μ -cordierite, called metastable cordierite phase, the low-temperature ordered orthorhombic form¹³, which is prepared only under special conditions.

The traditional method for synthesis of cordierite ceramics involves the solid-state sintering of MgO , Al_2O_3 and SiO_2 in ratios of stoichiometric cordierite composition^{1,2}. Several methods have now been developed to synthesize cordierite over decades such as (1) solid-state reaction of MgO , Al_2O_3 and SiO_2 or their precursors^{3,4} and (2) wet chemical methods e.g. sol-gel processes, hydrothermal, spray pyrolysis and solution combustion synthesis⁵⁻⁹. The disadvantages of wet chemical processes include expensive starting materials, low yields, complex processing techniques, difficulty in large-scale preparation. From the point of cost effectiveness talc, sepiolite, kaolin, silica, gibbsite, and kaolinitic clay were used as starting materials of cordierite and allied products¹⁰⁻¹². In this study, a novel attempt has been made to synthesize stoichiometric cordierite precursor by semi-colloidal route using indigenous starting materials and characterize the precursor by various analytical and instrumental techniques.

Experimental

Preparation of cordierite precursor:

In the investigation, cordierite precursor powder was synthesized through aqueous phase interaction of ingredients in semi-colloidal route as described below. Finely milled dehydroxylated china clay and precipitated silica was thoroughly dispersed in an aqueous salt solution of $\text{Mg}(\text{NO}_3)_2$ followed by hydrolysis and gel formation by addition of 1:1 NH_4OH and engulfing the dispersion medium. This led to proper distribution of the solid particles in the $\text{Mg}(\text{OH})_2$ gel network. Rajmahal china clay, one of the best varieties of kaolinitic clay available in India was selected which was first purified from the associated impurities and then dehydroxylated at 600°C with 2 h soaking period. The mole ratio of $\text{MgO}:\text{Al}_2\text{O}_3:\text{SiO}_2$ was adjusted to stoichiometric composition of cordierite. Formation of coating of $\text{Mg}(\text{OH})_2$ was achieved by hydrolysis of the salt solution with 1:1 ammonia. The set gel was filtered and washed with hot water to remove the adhering impurities and dried at 80°C in vacuum air oven. The dried precursor was milled to fine state of subdivision. It was then thoroughly dried in an air oven at 110°C for 24 h and stored in an incubator maintained at $35\pm 1^\circ\text{C}$ for the further study.

Characterization of the cordierite precursor powder:

The finely agated sample was chemically analyzed with respect to chemical constituents following standard methods of alumino-silicate analysis. Strohlein Area Meter II apparatus was employed to determine its surface area from low temperature N_2 absorption data using BET principle. Particle size distribution was measured by Malvern Master Sizer, X Ver, 1.2 b, Serial No-6449 in the size range from $0.06\text{--}6.0\ \mu\text{m}$. The FTIR absorbance spectra of the sample was recorded in a Perkin-Elmer-783 instrument in KBr phase in the frequency range of $4000\text{--}400\ \text{cm}^{-1}$. The identification of crystalline phases in precursor powder was performed by XRD analysis, using automatic X-ray diffractometer (X'PERT Pro, PW-3071). Thermogravimetric-differential thermal analysis (TG-DTA) was conducted using a NETZSCH simultaneous thermal analysis apparatus (Model STA 409 PC) in atmospheric nitrogen at the heating rate of $10^\circ\text{C}/\text{min}$. The morphology of the cordierite precursor dried at 110°C and calcined at 900°C was examined using scanning electron microscope (Quanta 200, FEI, Holland).

Results and discussion

Characterization of starting materials:

Kaolinitic clay is one of the important source alumina and silica. In the present investigation, Rajmahal china clay, one of the best variety of kaolinitic clay possessing sufficient purity and plasticity has been taken. The chemical analysis and physical properties of purified Rajmahal china clay are given in Table 1.

Table 1. Chemical analysis and physical properties of purified Rajmahal china clay

Chemical analysis and physical properties:		
Chemical analysis	Constitute	Wt%
	SiO_2	49.67
	Al_2O_3	36.64
	Fe_2O_3	0.61
	CaO	0.56
	MgO	0.02
	Na_2O	0.21
	K_2O	0.12
	Loss on ignition	12.18
Physical properties:		
Cation exchange capacity, meq/100 g of dry clay		8.21
DTA peak temperature ($^\circ\text{C}$)		600 (Endo), 980 (Exo)
Specific surface area by BET ($\text{m}^2\cdot\text{gm}^{-1}$)		20.1
Crystallographic phases by XRD		Kaolinite

Analysis of results of purified Rajmahal china clay reveal that it contained kaolinite as sole mineral phase with low percentage of Fe_2O_3 , lime and alkalis as impurities. The china clay also possessed a fairly high specific surface area with micro-fine particle size distribution.

In this investigation, synthetically prepared micro-fine precipitated silica was used as excellent source of amorphous silica to compensate SiO_2 deficit in the cordierite formulation. The physico-chemical properties of precipitated silica are listed in the Table 2.

The synthesized precipitated silica was exclusively composed of micro-fine silica particles with high specific surface area of $120.1\ \text{m}^2\cdot\text{gm}^{-1}$ and X-ray amorphous in nature. It was soft, light weight white powder.

AR grade magnesium nitrate hexahydrate and aluminum nitrate nonahydrate was taken as source of magnesia for the preparation of stoichiometric cordierite precursor via semi-colloidal sol-gel route.

Table 2. Physico-chemical properties of synthesized precipitated silica

Constituents	Wt%
SiO ₂	86.55
Na ₂ O	Trace
Loss on ignition	13.4
Physical properties:	
Loose powder density, (gm cm ⁻³)	0.16
Specific surface area by BET (m ² .gm ⁻¹)	120.1
Crystallographic phases by XRD	Amorphous

Characterization of stoichiometric cordierite precursor:

The batch compositions (wt%) and oxide equivalent of synthesized ideal cordierite precursor with corresponding empirical formulae are presented in Table 3. Gel formation in each batch was carried out in aqueous phase in such a manner that colloidal micelle of hydroxide of Mg²⁺ was formed around fine particles of dehydroxylated clay and precipitated silica at pH of 9.5. Complete gel formation was observed to occur without preferential settling. Thus more or less of uniform suspended gel of the ingredients was obtained which exhibited the important phenomenon of syneresis. After aging for 24 h, the gel mass was filtered through Buchner funnel under vacuum and thoroughly washed with distilled water to remove adhering impurities. Filter cake of each batch was vacuum dried at a low temperature of 80°C in order to minimize agglomeration of particle during drying.

From the chemical analysis (Table 3) of dried precursor, the empirical formula was calculated. The chemical analysis result was found as per with reacting batch composition. Thus the chemical analysis of precursor confirmed total interaction of the ingredients and complete precipitation of Mg²⁺ and Al³⁺ ions at pH value of 9.5

The physical properties of stoichiometric precursor indi-

Table 3. Chemical analysis and empirical formula of the cordierite precursor powder

Constituents	Wt%
MgO	10.50
Al ₂ O ₃	27.95
SiO ₂	41.50
H ₂ O	20.05
Empirical formula	2MgO.2Al ₂ O ₃ .5SiO ₂ .8H ₂ O

cated its low loose bulk density that made the powder soft, floppy and porous (Table 4).

Table 4. Physical properties of the cordierite precursor

Loose powder density (gm cm ⁻³)	0.346
Specific surface area by BET (m ² .gm ⁻¹)	25.28
DTA peak temperature (°C)	130, 450 (Endo), 960 (Exo)

The synthesized precursor is off white in appearance. The texture of cordierite powder and its optical appearance clearly indicated the existence of mixed phase materials. From the Table 4, it is quite evident that all the precursor powder was characterized by micro-fine particles having high specific surface area. However, some agglomeration and cluster formation during gelation and drying process may be responsible for exhibiting somewhat lesser surface area.

Particle size distribution of the synthesized cordierite precursor highlighted that 75% of the particles remained within

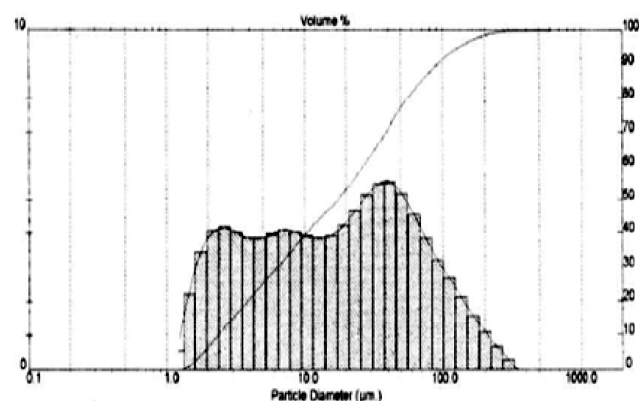


Fig. 1. Particle size analysis of cordierite precursor powder.

the range of 50 µm in batch mixes and about 40% of the particles lying below 10 µm (Fig. 1).

Infrared spectroscopy analysis of the cordierite precursor was carried out to understand on the nature of different IR active bonds present in the sample. In the sample, mostly OH stretching, OH bending, Si-O, Mg-O stretching vibrations give rise to different IR absorption bands. The sharp OH stretching peak was visible at 3694 cm⁻¹ attributing to the presence of loosely bound water. It indicates that significant surface charge was developed in the precursor. The broad absorption band at around 3447 cm⁻¹ assigned to stretching

vibration of bound OH groups. The bending vibration of OH groups was observed at 1640 cm^{-1} . The IR absorption band at 1078 cm^{-1} is assigned to Si-O stretching vibration. The weak IR absorption spectra at 803.6 cm^{-1} corresponds to Al-O stretching vibration of AlO_4 tetrahedral unit. The strong absorption peaks appeared at 464.0 cm^{-1} being assigned to the Mg-O stretching vibration.

The precursor powder is a mixed phase material whose hydrated nature was reflected from its thermal analysis. The initial endothermic peak (130°C) was due to the removal of loosely bound gel water. The second endotherm in the range of $280\text{--}420^\circ\text{C}$ was due to dehydroxylation of the hydroxides of Mg^{2+} and Al^{3+} which was due to the dehydration of $\text{Mg}(\text{OH})_2$. The synthetic hydrogel had formed a thin coating on surfaces on porous dehydroxylated clay and silica particles. The process of dehydration determines the nature of dehydrated material which subsequently undergoes solid state reactions at elevated temperature. The sharp exothermic peak above 960°C might be related to formation of either alumina-silica spinel or metastable cordierite from the dehydroxylated clay prior to mullitization or cordierization.

Powder XRD patterns of the cordierite precursor dried at 110°C , preheated at 500°C and 900°C exhibit diffused characteristic peaks of disordered boehmite (Al-O-OH) and bayerite [$\alpha\text{-Al}(\text{OH})_3$] phases. XRD pattern of the stoichiometric precursor powder after calcination at 500°C revealed the transformation of crypto-crystalline precursor into a X-ray amorphous material by heat treatment at 500°C . However, the amorphous material started crystallization to μ -cordierite at about 900°C as evidenced by the presence of sharp characteristic peaks of μ -cordierite phase in the sample on heat treatment at 900°C .

The average crystallite size calculated by Debye-Scherrer equation for the precursor preheated at 900°C was 0.73 nm only.

The SEM micrographs of dried cordierite precursor dried at 110°C and precursor calcined at 900°C are represented in Fig. 2 and Fig. 3. SEM micrographs of cordierite precursor powder heat treated at 900°C focused that plate-like particles were present in agglomerated condition with particle size distribution ranging from 0.5 to $4\ \mu\text{m}$.

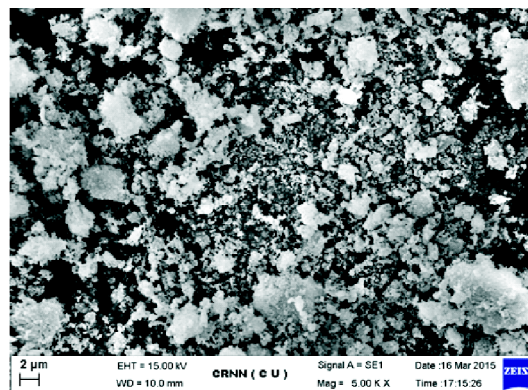


Fig. 2. SEM micrograph of cordierite precursor dried at 110°C .

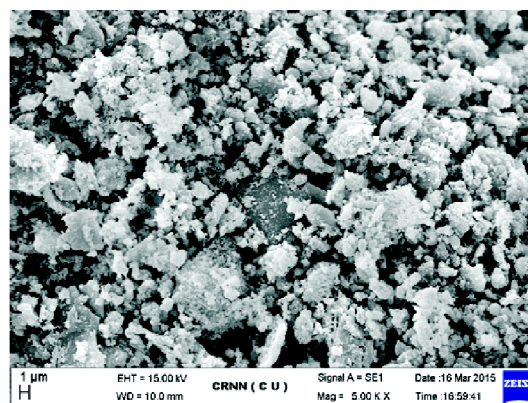


Fig. 3. SEM micrograph of cordierite precursor calcined at 900°C .

Conclusion

- (i) Stoichiometric cordierite precursor can cost effectively be synthesized through unconventional semi-colloidal sol-gel route by dispersion of the fine particles of dehydroxylated kaolinite and precipitated silica into the coprecipitated gel matrix of $\text{Al}(\text{OH})_3$ and $\text{Mg}(\text{OH})_2$.
- (ii) Thermogram of synthesized cordierite precursor upto 1000°C exhibits two endothermic peaks and one exothermic peak. Initial loss of physically adsorbed water; interlayer water occurs at around 130°C followed by the removal of hydroxyl groups from their complex structure at around 405°C . The exotherm at 960°C corresponds to the formation of transient μ -cordierite.
- (iii) Average crystallite size of the derived cordierite calcined at 900°C as calculated by Debye-Scherrer

equation is of the order of 0.73 nm while SEM micrograph calcined at 900°C exhibited particle size distribution within the range from 0.5 to 4 μm.

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