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Kaolin-based cordierite for pollution control

A. Yamuna[a], R. Johnson[b], Y.R. Mahajan[b], M. Lalithambika[c,*]

[a]Department of Physics, University of Kerala, Kariavattom, Trivandrum, India
[b]ARCI, Balapur, Hyderabad, India
[c]Regional Research Laboratory, Industrial Estate PO, Kerala, India

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Abstract

Cordierite due to its very low coefficient of thermal expansion and good thermal shock resistance is considered as promising candidate for advanced applications. Many authors have reported the preparation of cordierite by various techniques. In the present work, cordierite has been prepared from conventional method and also through sol-gel routes followed by physical, mechanical, thermal and microstructural property evaluation. The excellent properties exhibited by kaolin-based cordierite system make them suitable for the fabrication of catalyst support. Hence, honeycomb and pellet type carriers were prepared from kaolin-based cordierite composition and their efficiency in pollution monitoring has been studied in two stroke vehicles. The results clearly indicate that kaolin-based cordierite system prepared by conventional technique could remove 78% of carbon monoxide and 82% of hydrocarbons under idling conditions.

Keywords: Catalyst supports; Cordierite; Honeycombs; Pollution control; Sol-gel process

1. Introduction

The compound cordierite ($2MgO\ 2Al_2O_3\ 5SiO_2$) (2:2:5) was first reported by Rankin and Merwin in their classical work on the ternary system $MgO–Al_2O_3–SiO_2$.[1] In nature it occurs in thermally metamorphised argillaceous rocks.[2] Cordierite powders can be prepared by the solid-state reaction of stoichiometric amounts of oxides of magnesium, aluminium, silicon or by glass recrystallization.[3] Method of preparation of cordierite with stoichiometric composition of clay, talc and chlorite has been studied by Grosjean.[4] Extensive work has been carried out by many authors in the area of natural mineral resource as the raw material for the preparation of cordierite.[5–7] Kumar et al. reported that fly ash could be used as a substitute for clay in the synthesis of cordierite for refractory applications.[8] According to Sano, the addition of zircon in the magnesium aluminosilicate (MAS) system is an efficient way to widen the range of sintering temperature.[9] The use of cordierite as mirror substrate,[10] in high power superconducting devices and the effect of surface porosity on dielectric properties have been studied in details.[11–13] Das Gupta and co-workers undertook the studies on improving the mechanical properties of cordierite ceramics by the addition of ZrO_2.[14] Sumi et al. have carried out the sintering behaviour of a mixture of kaolinite and basic magnesium carbonate to form dense α-cordierite ceramics.[15] Bernier et al. have studied the preparation of cordierite from inorganic and organic precursors by the sol-gel route.[16] Many authors have described the synthesis of nanocrystalline cordierite by sol-gel methods.[17–24]

Oh et al. have examined the effects of Al/Si ratio, the crystallization behaviour and sintering of cordierite ceramics prepared by sol-gel technique.[25] Yue et al. have reported that doping of magnesium aluminosilicate gel derived glass with B_2O_3 and P_2O_5 can reduce the sintering temperature of cordierite to 900 °C.[26] The mechanical property improvement of cordierite ceramics[27] and dilatometric and dielectric properties of alkali-doped cordierite[28] have also been reported. Douy has studied the synthesis of chemically homogeneous cordierite powder by spray-drying technique.[29] Grinding effect on the synthesis and sintering of cordierite have been reported by Awano et al.[30] Preparation of

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* Corresponding author.
E-mail address: yam10emerald@yahoo.com (M. Lalithambika).

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cordierite and cordierite–mullite composite powders by the combustion route have been described by Gopichandran et al.[31,32] Cordierite ($Mg_2Al_4Si_5O_{18}$) is mainly used in glass–ceramic compositions utilized in multilayer electronic circuits, sound insulating boards, filters for separating solids from fluids and as substrate material for catalytic converters, kiln furniture and in thermal insulation materials requiring controlled porosity.[33]

Ceramic substrates have been employed as automobile catalyst supports to facilitate the conversion of CO and HC emissions to CO_2 and H_2O by redox reaction. Cordierite ceramic honeycombs are currently considered as leading candidates for trapping and oxidizing the carbonaceous particulate emission from automobiles.[34] Okazaki et al. have developed a cordierite body comprising halloysite and plate shaped talc particles, which showed high crystallinity and low coefficient of thermal expansion value suitable for the fabrication of catalyst honeycomb support.[35] Many authors have studied the fabrication of cordierite bodies having low coefficient of thermal expansion (CTE) value and also the methods for producing honeycomb structures.[36–41] Platinum and palladium as catalysts are found to have a noticeable efficiency in automotive emission control systems.[42–46] In India, two stroke vehicles are the major source of pollution in urban areas. For example, the total number of all motor vehicles in India in 2003 is expected to be about 60 million, the two and three wheelers most of which use two stroke engines, numbering 38 million. The exhaust of the two stroke engines is rich in CO and HC and needs to be mainly oxidized. Exhaust emission regulations have been established for many parts of the world, which have led to the use of catalytic converters for pollution monitoring. In the present work, cordierite has been prepared by conventional and sol-gel techniques. In the former, kaolinite and talc are used as the major precursor materials. In the case of sol-gel route, aluminium nitrate, magnesium nitrate and tetra ethyl orthosilicate (TEOS) were the starting materials. The physical, mechanical, thermal and microstructural characterization of the products have been carried out. The composition that showed better performance was identified and its application as a substrate material for preparing catalytic converters to effectively control the HC and CO emission has been evaluated.

2. Experimental procedure

Kaolin, metakaolin (dehydroxylated at 650 °C/5 h), magnesium oxide [MgO] (99%), magnesium silicate (talc) [$3MgO{\cdot}4SiO_2{\cdot}H_2O$] (99.5%), aluminium nitrate [$AlN_3O_9{\cdot}9H_2O$] (99.5%), magnesium nitrate [$Mg(NO_3)_2$ $6H_2O$] (99.5%) (all E. Merck, LR), powdered quartz ($<60\mu m$), tetra ethyl orthosilicate (TEOS) [$Si(OC_2H_5)_4$] (Aldrich 99%) and fumed silica [SiO_2] (Aldrich 99%) were used as the precursor materials.

2.1. Conventional sintering methods

Kaolinite-based cordierite ceramics are prepared by the solid-state mixing of different stoichiometric compositions of kaolin/metakaolin, MgO, talc and powdered quartz/fumed silica. Typical batch compositions chosen for the study are shown in Table 1. These compositions are thoroughly mixed in a ball mill for 24 h and pelletized at 350 MPa, compaction time being 60 s. The samples are oven-dried at 110 °C for 12 h and prefired at 300 °C for 3 h. They were further sintered from 950 to 1350 °C with a rate of heating of 4 °C/min, residence time being 3 h.

2.2. Sol-gel processing

Three series of gels, viz. monophasic, diphasic and triphasic were prepared by sol-gel route.

Monophasic gel: stoichiometric amounts of aluminium nitrate and magnesium nitrate were separately dissolved in ethanol and then mixed together. To this, TEOS was added dropwise while stirring. The mixture was heated on a water bath in order to get a transparent gel, which on further heating gave a creamwhite powder. This monophasic gel composition of cordierite is represented as MPG.

Diphasic gel: Aluminium nitrate is dissolved in water and precipitated with aqueous ammonia (15%) and pH adjusted in order to obtain alumina sol. Silica sol was prepared by addition of deionized water in silica fume followed by peptization. The mixture of sols is continuously stirred for 30 min. A solution of magnesium nitrate dissolved in deionized water was then added to the mixture of sols, while stirring to maintain

Table 1
Compositions chosen for conventional sintering

Sample code	Batch composition
C1	Kaolin (<45 μm) + MgO (<45 μm) + powdered quartz (<60 μm)
C2	Metakaolin + MgO (<45 μm) + powdered quartz (<60 μm)
C3	(50% kaolin + 50% Metakaolin) + MgO (<45 μm) + powdered quartz (<60 μm)
C4	Kaolin (<25 μm) + MgO (<45 μm) + Magnesium silicate (<45 μm)
C5	Metakaolin (<25 μm) + MgO (gel) + fumed SiO_2

the homogeneity. The final milky sol is dried on a water bath to obtain the gel DPG.

Triphasic gel: The triphasic gel was comprised of three distinct sols of alumina, magnesia and silica. Alumina and magnesia sols were prepared by the co-precipitation of aluminium nitrate and magnesium nitrate salts. Fumed silica was the source for silica sol. The three sols were mixed thoroughly in a homogenizer for 15 min and dried on a water bath at 100 °C to procure triphasic gel represented as TPG.

The triphasic gel composition is sonicated using ultra sound sonicator (sonipep model 33) for 45–60 min followed by 48 h of ageing. It is then evaporated to dryness to obtain cordierite sonogel denoted as SG.

The gel-derived cordierite compositions MPG, DPG, TPG and SG were dried in an oven at 110 °C for 12 h and pre-fired at 450 °C for 3 h to remove all volatiles. The samples were thoroughly agated and pelletized at a pressure of 200 MPa. The sintering temperature of gel-derived compositions was optimized with the help of differential thermal analysis data. The pellets were fired at temperatures 950–1225 °C with different soaking hours to obtain cordierite composition.

For conventional sintering, all the mixtures (Table 1) were thoroughly agated and dried at 110 °C for 1 h. They were sintered at temperatures 900–1450 °C in a programmable furnace (Nabertherm) with a rate of heating of 8 °C/min and with a soaking period of 1–3 h. X-ray diffraction (Philips PW 1710), Laser photoflash technique (model-TC-3000, ULVAC, Japan) and scanning electron microscopy (Jeol JSM 5600 LV) were used for the phase identification, thermal property evaluation and microstructure studies.

3. Results and discussion

3.1. X-ray diffraction studies

The compositions C1, C2 and C3 (derived from the conventional route), gave sharp cristobalite peaks in addition to cordierite and mullite. At 1250 °C/3 h, mullite and cristobalite peaks appeared, but the cordierite peaks appeared only at 1350 °C/3 h (Fig.1). The presence of pulverized quartz enhances the growth of cristobalite formation in C1–C3 compositions. But in C4 and C5 kaolin/metakaolin of particle size <25 μm were used as the precursor material and the silica percentage is compensated by magnesium silicate/silica fume. The X-ray diffraction pattern of C4 and C5 at 1350 °C/3 h clearly indicates that a reduction in particle size has much influence on the crystallinity of the sintered product (Fig.2). It is evident from the XRD analysis that the compositions C1, C2 and C3 gave a combination of three phases, viz. mullite, cristobalite and cordierite while the compositions C4 and C5 gave exclusively α-cordierite phase formation. The diffraction patterns of the composites formed from sol-gel routes are presented in Fig. 3. It is very interesting to observe that α-cordierite is the only phase formed in sol-gel systems such as MPG, DPG, TPG and SG. The volatile components

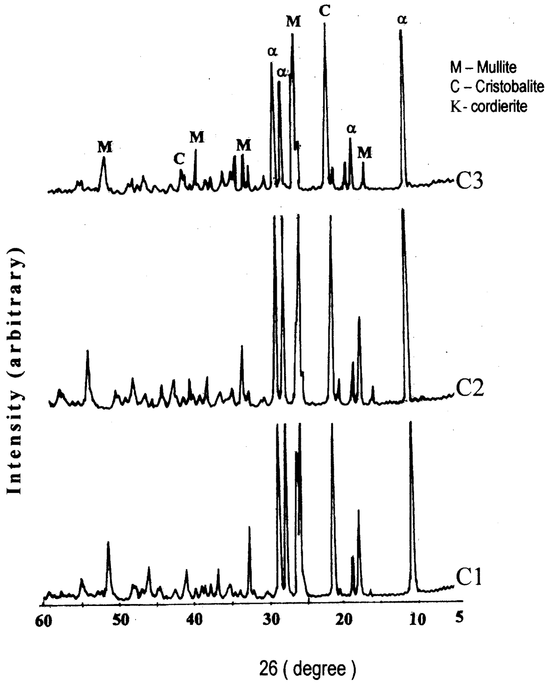


Fig. 1. XRD patterns of kaolin-based C1, C2 and C3 compositions, sintered at 1350 °C/3 h.

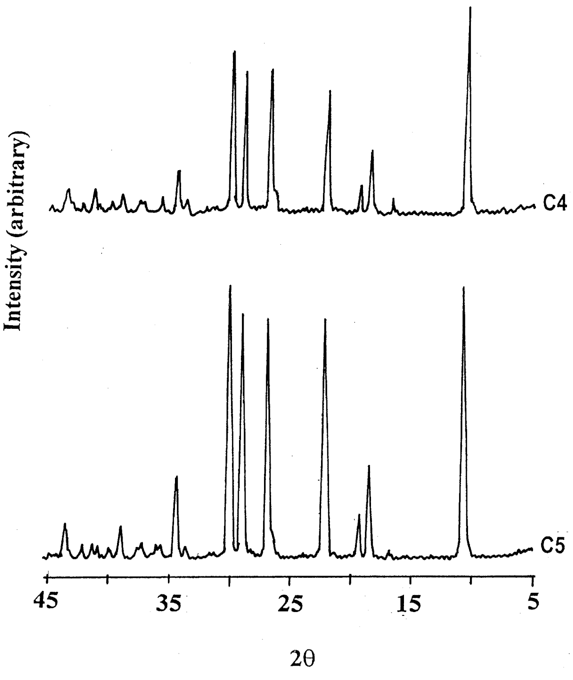


Fig. 2. XRD patterns of kaolin-based compositions C4 and C5, sintered at 1350 °C/3 h.

present in sol-gel derived composition escapes during pre-firing and the densification of α-cordierite occurs during sintering. Because of the fine particle size and atom–atom coherence, the nucleation of stable α-cordierite phase takes place at a temperature of 1225 °C/3 h. The phases formed during sintering are summarized in Table 2.

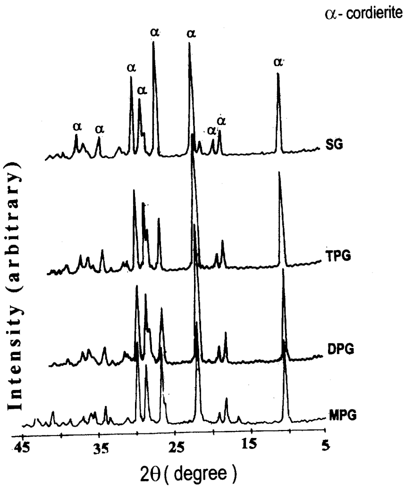


Fig. 3. XRD patterns of sol-gel derived compositions sintered at 1225 °C/3 h.

Table 2
Phases formed during sintering

Processing route	Sample code	Phases formed[a]	Sintering parameters	
			Temperature (°C)	Time (h)
Solid-state mixing	C1	M, C, α	1350	3
	C2	M, C, α	1350	3
	C3	M, C, α	1350	3
	C4	α	1350	3
	C5	α	1350	3
	MPG	α	1225	3
Sol-gel process	DPG	α	1225	3
	TPG	α	1225	3
	SG	α	1225	3

[a] M,Mullite; C,Cristobalite; α-Cordierite.

3.2. Physical property evaluation

Cordierite samples derived from conventional routes C1–C5 and sol-gel derived samples MPG, DPG and TPG were subjected to physical property evaluation as per ASTM standards.[47] The results are presented in Table 3. Compositions C1–C3 gave high volume shrinkage (15–28%) and apparent porosity values. During sintering, atom–atom coherence may be less in these compositions due to the coarse nature of pulverized quartz. The product bulk density is also found to be very low. The compositions C4 and C5 because of better homogeneity attained during sintering gave acceptable values of shrinkage, apparent porosity and bulk density. Sol-gel derived compositions gave high volume shrinkage values. The apparent porosity values are also comparatively high which could be due to the encapsulated alkoxide residues and this gel during sintering gives a product with medium porosities. The bulk density of the crystallized product however is comparable with C4 and C5.

3.3. Thermal conductivity measurements

The thermal parameter, viz. specific heat, thermal diffusivity and thermal conductivity are measured using laser photoflash method. Samples of dimension 10-mm diameter and 1–3 mm thickness were used for measurements. Among the cordierite compositions prepared, samples chosen for the specific heat, thermal diffusivity and thermal conductivity measurements include C4 (1350 °C/3 h) and gel-derived compositions MPG and TPG (1225 °C/3 h). The results are presented in Table 4. Eventhough the density values of cordierite formed from both conventional and sol-gel routes are comparable, the composition C4 has higher thermal conductivity value compared to sol-gel derived compositions. Because of the isomorphous substitution of Fe and Al and the presence of trace level impurities in kaolin can cause an increase in thermal conductivity value. The high apparent porosity values of gel-derived composite is responsible for their lower thermal conductivity values since the thermal parameters are

Table 3
Physical properties of cordierite compositions

Sample code	Volume shrinkage (%)	Apparent porosity (%)	Water absorption (%)	Bulk density (g/cc)
C1	27.5	43.68	31.61	1.38
C2	19.87	42.6	29.8	1.43
C3	15.68	42.62	30.2	1.41
C4	16.63	4.27	1.91	2.33
C5	14.32	2.56	0.89	2.53
MPG	42.62	15.83	7.02	2.25
DPG	33.50	25.79	11.56	2.23
TPG	36.03	13.46	5.25	2.56

Table 4
Thermal property data

Sample code	Sintering temperature (°C)	Sample thickness (mm)	Density (g/cc)	Specific heat (J/g/K)	Thermal diffusivity ($10^{-4}m^{-2}/s$)	Thermal conductivity (w/mk)
C4	1350/3 h	1.31	2.26	0.76	0.0260	4.4
MPG	1225/3 h	2.07	2.11	0.78	0.0068	1.1
TPG	1225/3 h	1.46	2.54	0.81	0.0076	1.6

controlled by the transport properties of the carriers responsible for heat transfer.

3.4. Thermal shock resistance (spalling resistance)

Thermal shock—a highly complex property of ceramic materials is the fracture of the body resulting from thermal stresses induced by rapid temperature changes. In order to assess the spalling resistance of cordierite composition, cylindrical pellets of dimension (1 inch×1 inch; diameter×height) were used for measurements. Spalling resistance of C1–C5 compositions has been determined. The results (Table 5) clearly indicate that C4, which contains kaolin and magnesium silicate (talc) as the major precursor materials, is found to be the best composition. Both raw materials have good plasticity and fine particle size, which in presence of MgO powder resulted in the formation of well-crystallized cordierite during sintering. The poor performance of C2 is due to the lack of plasticity of matrix material resulted during dehydroxylation.

3.5. Mechanical property evaluation

The compressive strength measurements of conventionally prepared cordierite samples have been carried out as per ASTM standards.[48] Compositions C1 and C2 show poor strength values because of the inhomogeneity in the microstructure of sintered products. The coarse SiO_2 particles enhance the cristobalite phase and formation of glassy matrix during sintering. C3, C4 and C5 show very good compressive strength values (Fig. 4). These compositions constitute materials having fine particle size distribution.

Table 5
Thermal shock properties of kaolin-based compositions

Sample code	Temperature (°C)	No. of cycles	Remark
C1	950±50	9	Micro cracks developed
C2	950±50	3	Shattered
C3	950±50	14	Major cracks developed
C4	950±50	19	3–4 Micro cracks
C5	950±50	11	Starts to warp

Thermal shock resistance and compressive strength measurements of sol-gel derived cordierite compositions were not studied since they show high shrinkage values (Table 3).

3.6. Microstructure evaluation

The fresh fracture surface of C4 composition sintered at 1350 °C/3 h was subjected to microstructure evaluation. Fig. 5 (A–D) represents the microstructure of sintered samples. General morphology of the psuedohexagonal cordierite crystals (Fig. 5A) clearly indicates the homogeneity of the crystallized product. A typical hexagonal cordierite crystal formed in C4 System is shown in Fig. 5B. Microstructure developed in triphasic gel derived system is presented in Fig. 5C. It is very interesting to note that the composition SG shows bigger crystals of mullite and cordierite (Fig. 5D). The enhanced crystal growth can be attributed to the cross-linking of small crystallites during the ageing period followed by sonication.

3.7. Application studies

The selection of cordierite as substrate material for catalytic converter is due to its low CTE value and moderately high melting point ∼1465 °C. In the present study, cordierite composition C4 was chosen as the substrate material for catalytic converter in the honeycomb form and C1, C2, C3 and C4 as pellet type carriers. The properties viz. melting point, strength, coefficient of thermal expansion, thermal conductivity,

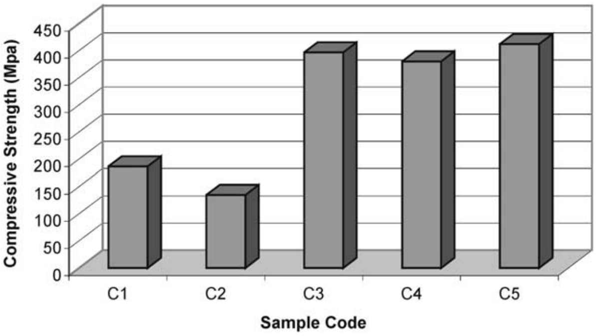


Fig. 4. Compressive strength plot of kaolin-based cordierite compositions.

density and specific heat of kaolin based C4 composition are summarized in Table 6.

A catalytic converter is the only techno-economically feasible device to effectively control the exhaust emission from automobiles. It is placed ahead of the noise suppression silencer, as near to the exhaust manifold as possible. It normally takes the form of a stainless-steel cylindrical or oval shaped casing with conical or semi-conical front and rear ends which merge with short flanged tubes to provide the inlet and exit for the polluted and treated exhaust gases, respectively as shown in Fig. 6. The catalytic bed may take different forms such as ceramic pellets and ceramic honeycomb. In the present study, a working model of the catalytic converter assembly for pellet type and honeycomb carriers was developed and their efficiency in pollution monitoring has been evaluated. Catalytic converter systems with pellet and honeycomb type catalyst beds are as shown in Figs. 7 and 8.[49]

Table 6
Material properties of cordierite (C4) composition

Material properties	As observed
Melting point	1467 °C
Coefficient of thermal expansion	1.64×10^{-6}/°C
Thermal conductivity	1.6 W/mK
Compression strength	562.32 MPa
Density	2.6 g/cc
Specific heat	0.76 J/g/K

Pellet or bead type carriers can function as support for the catalyst. They are easy to produce and are unbreakable. This type of catalyst support assembly consists of layers of spheres resting on top of each other. The passageways and large surface area exposed to the exhaust gases are created by the interstices, or spaces, surrounding the spherical contact points of the pellets. These ceramic pellets of about 4–5 mm diameter have good crush and abrasion resistance when sintered at a temperature of 1350 °C.

The honeycomb substrates are produced by the extrusion process using an indigenously designed extrusion die. Initially a homogenous mixture of raw materials was kneaded into extrudable dough with the addition of methylcellulose as binder and polyethylene glycol as plasticizer along with water in a sigma kneader. The plastic dough thus obtained was extruded into honeycomb structures of dimension 6×4 cm (diameter×height) with a cell density of 16 cells/cm^2 The honeycombs were subjected to controlled drying and were further sintered at 1350 °C/3 h, with a rate of heating of 50 °C/h. Fig. 9A and B represent the pellet type and

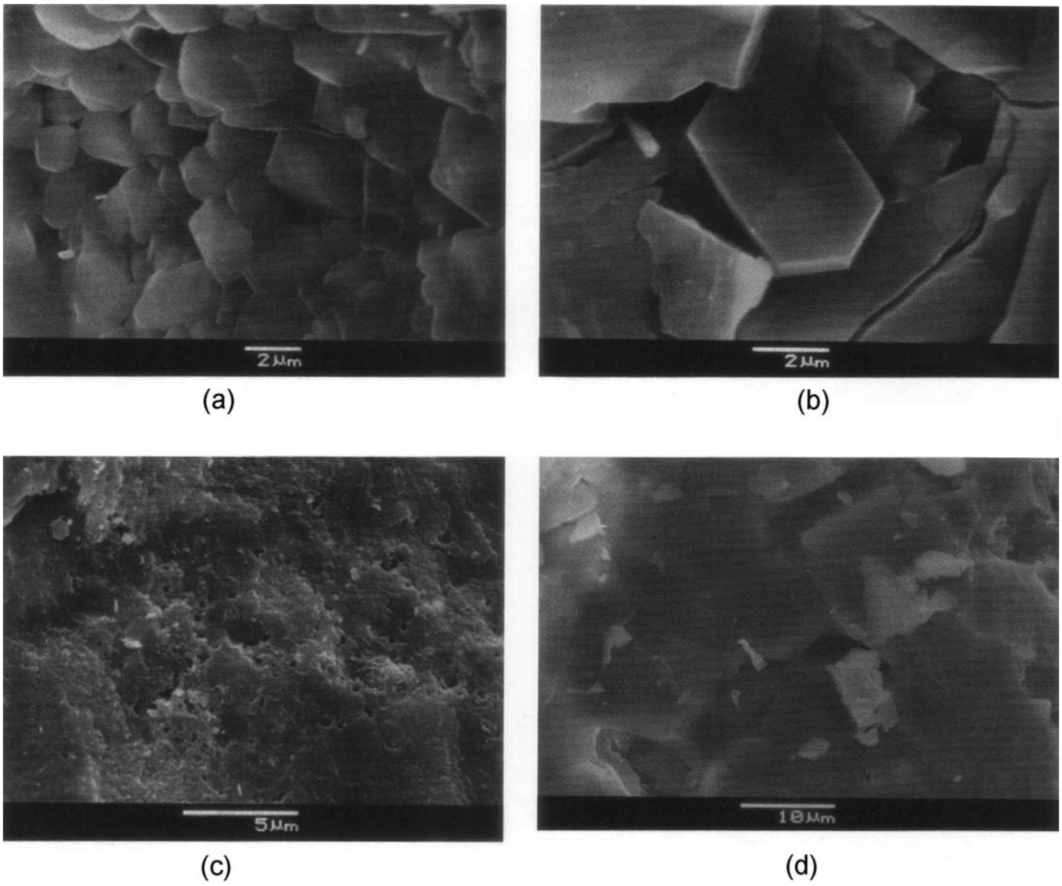


Fig. 5. (A–D) SEM images of C4, TPG and SG systems sintered at 1350 °C/3 h.

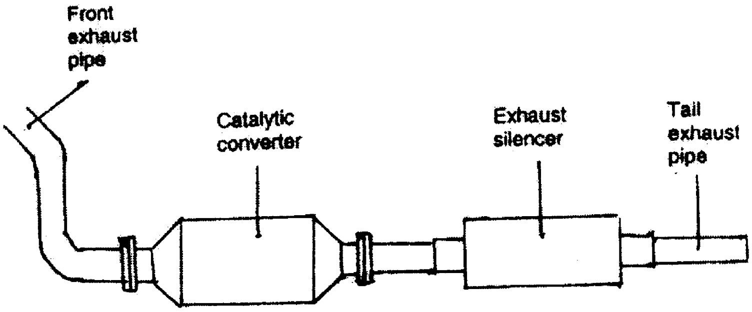


Fig. 6. Schematic representation of catalytic converter system connected to the exhaust manifold.

honeycomb structures prepared from C4 composition. Care was taken to maintain the volume of pellet type and honeycomb catalytic converter as similar.

The cordierite bodies, both pellet type and honeycomb thus obtained are immersed in ammonia solution (pH 11.8) after which the interstices/ channels were air blown to make it free from liquid. It was then directly immersed in boehmite–aluminium hydroxide slurry for 15 seconds. After keeping in air for 10 s, excess slurry was removed by gentle air blowing. It was dried again with hot air for 15 min. On calcining at 550 °C for 2 h in air atmosphere, the substrate surface gets completely covered with a homogeneous layer of γ-alumina, which becomes the support for the noble metal catalyst. Catalyst is supported by dip coating technique. Substrate material is dipped in 1.5 μmol hexa chloro platinic acid solution and was dried at 120 °C for 30 min. The samples were then heated in air at 550 °C for 40 min.

The performance evaluation of a catalytic converter with cordierite-based pellet type and honeycomb catalyst carriers connected to a two-stroke vehicle under idling condition was carried out using NETEL Environment Exhaust Gas Analyzer using a high-speed medium duty petrol engine with Indian reference fuel (ULP). Engine operating parameters along with the concentration of CO and HC were monitored and percentage reduction in each case was determined. The results are summarized in Table 7. It is clear from the table that C1 and C2 pellet type carriers could remove 68% of carbon monoxide and hydrocarbon. Composition C3 showed higher efficiency as an oxidation catalyst compared to

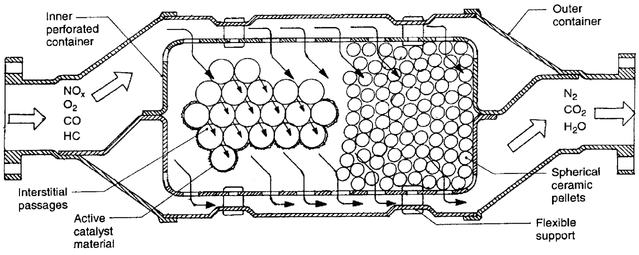


Fig. 7. Ceramic palletized type catalyst converter.[49]

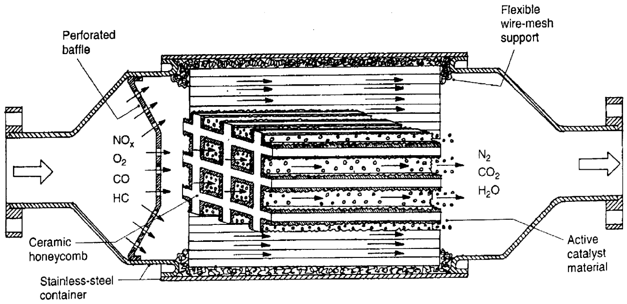
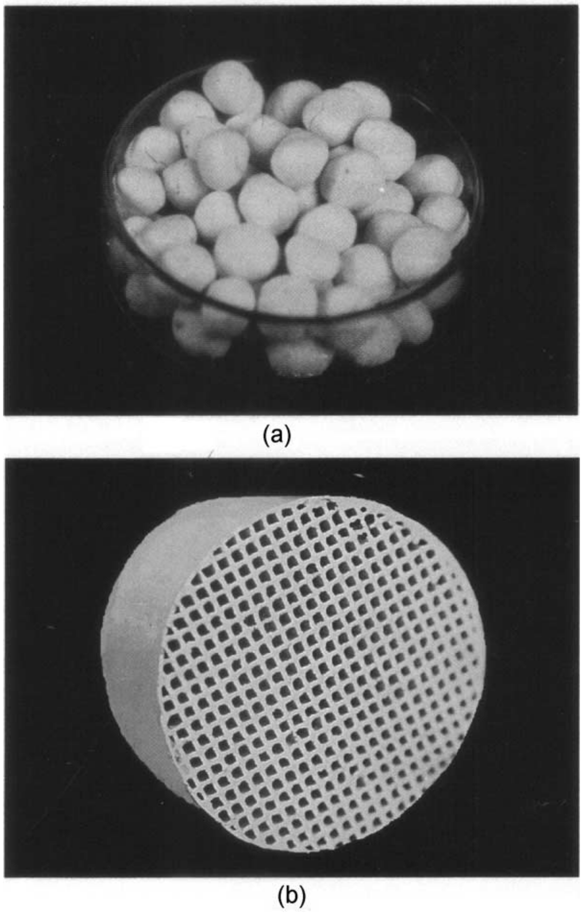


Fig. 8. Ceramic honeycomb or monolith type catalyst converter.[49]


(a)

(b)

Fig. 9. (a,b) Kaolin-based cordierite catalyst supports.

Table 7
Performance evaluation of kaolin-based catalytic converters

Type of substrate	Pollutants	Without converter	With converter	Conversion efficiency
C1 (Pellet type)	CO	4.84%	1.51%	68.8
	HC	7800 ppm	2260 ppm	71.63
C2 (Pellet type)	CO	4.84%	1.58%	67.85
	HC	7800 ppm	2570 ppm	67.05
C 3 (Pellet type)	CO	4.84%	1.12%	76.86
	HC	7800 ppm	2003 ppm	74.32
C4 (pellet type)	CO	4.84%	1.04%	78.5
	HC	7800 ppm	1610 ppm	79.36
C4 (Honeycomb)	CO	4.84%	0.94%	80.58
	HC	7800 ppm	1372 ppm	82.41

C1 and C2. When bead type C4 composition was used as the catalyst bed, carbon monoxide and hydrocarbons are reduced with the conversion efficiency of 78 and 79%, respectively, indicating better efficiency. The typical reaction that takes place in auto exhaust converters are oxidation of CO and HC as represented below.

$$(\mathrm{HC}) + (\mathrm{O_2}) \longrightarrow \mathrm{CO_2} + \mathrm{H_2O}$$

$$\mathrm{CO} + \tfrac{1}{2}\mathrm{O_2} \longrightarrow \mathrm{CO_2}$$

$$\mathrm{CO} + \mathrm{H_2O} \longrightarrow \mathrm{CO_2} + \mathrm{H_2O}$$

The advantages of bead catalysts are that they are easy to prepare, impregnate and use. However they caused backpressure diminishing engine efficiency. This backpressure increased with use due to attrition and formation of fines during use. Hence the necessity of ceramic honeycombmonoliths.

Since C4 composition show better physical, mechanical, thermal and microstructural properties and also acts as a good support for oxidation catalyst, this composition alone was chosen for the preparation of honeycomb monoliths. It is quite interesting to note that C4-based honeycomb monolith could remove 80% of CO and 82% of HC. This increased efficiency of honeycomb catalytic converter over the bead type catalytic converter is due to its increased surface area arised from the structure. Monoliths having 16-cells/cm^2 with wall thickness 2 mm are found to be thermally very stable and due to the large voids produced by the channels, which cause negligible pressure, drop.

4. Conclusions

Among the various compositions studied, the C4 composition gave pure cordierite phase during sintering at 1350 °C/3 h. The shrinkage characteristics, low coefficient of thermal expansion, good compressive strength and better extrudability of this material was found to be suitable for its use as catalyst support. Honeycomb and pellet-type structures were made with this composition. Platinum was coated on to the support by dip coating technique and performance evaluation showed that 70–80% of CO and ~82% HC could be removed by the clay-based cordierite honeycomb catalytic converter under idling conditions. The advantages of these converters are low cost, ready availability of the precursor materials and acceptable firing properties.

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