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Experimental Investigation on Cerium Oxide Nanoparticles with Alumina Catalytic Converter to Increase Emission Conversion Efficiency in Automobiles

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ABSTRACT

The increasing use of diesel passenger cars has led to considerable work in the methods resulting in the reduction of particulate emissions. Interest is centered on reduction of emission in diesel engines from the new methods and technologies, diesel particulate filter, fuel additives for particulate matter. The objective of this research is to calculate various emission factors in diesel engine using cerium oxide nanoparticles. The experimental result reveals that the influence of the addition of cerium oxide nanoparticles in the catalytic converter for oxides of nitrogen, hydrocarbon and carbon monoxide levels in a diesel engine. Cerium oxide nanoparticles act as an oxygen donating catalyst and provide oxygen for the oxidation of carbon monoxide and hydrocarbon in the catalytic converter. It was also observed that the cerium nanoparticles reduce the oxides of nitrogen effectively.

Keywords: Nanoparticles, Cerium Oxide, Alumina, Catalytic Converter, Automobile.

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INTRODUCTION

Burning of fuel or burning of anything releases harmful and toxic gases, particulate matter, smoke, etc. into the atmosphere. The major portion of the pollutants degrading the atmosphere is from transport sector and power plants. In transport sector, the engine, especially the diesel engine emissions cause serious environmental and human discomforts on global scale(Reşitoɬlu, Altinişik and Keskin, 2014). Inhaling of this diesel polluted atmospheric air, which is rich in Particulate Matter (PM) and oxides of nitrogen (NO_x) may result in serious respiratory cardiovascular bronchitis, hemorrhages, cancer etc. on human beings(Saito *et al.*, 2003). Thermally stable, high surface area (ex > 100 m^2/g) alumina in the form of small beads or as micron sized wash coat particles has long been used as a carrier for finely disperse particles of noble metals in the treatment of automobile exhaust(Bonet *et al.*, 2002). Ceric oxide (CeO_2) also called as ceria has been incorporated into the alumina particles or mixed with them as the carrier for the dispersed particles of platinum and/or palladium and rhodium. Initially, ceria was used in small amounts, about 2 to 3 percent by weight of the alumina. Now it is being used in larger proportion say about 20 to 40 percent by weight of the carrier (Liotta *et al.*, 2009). In diesel engine the combustion reactants come into contact with a surface of catalytic converter and get converted to harmless products(Pl. S., Kumar and Subramanian, 2011)(Sendilvelan, Jeyachandran and Bhaskar, 2001). To increase the probability of the reactant molecules colliding with the surface we need to increase the amount of exposed metal surface. We can increase the metal surface area by spreading the metal over a support structure. In practice, we make a very fine dispersion of metal nanoparticles which are placed on an oxide support. For a given volume of metal, making a fine dispersion of nanoparticles dramatically increases the available metal surface area on which catalytic reactions can take place (Ng *et al.*, 2013). These metal nanoparticles are highly reactive, which can make a big impact on the conversion efficiency of catalytic converters(Nithyanandan *et al.*, 2010).

The relationship between particle size and surface area has been illustrated below. Taking the same volume of metal and making many nanoparticles the surface area dramatically increases. Given below are the equations for surface area and volume.

$$\text{Surface Area of Each Parcle: SA (r)} = A = 4\pi r^2 \quad (1)$$

$$\text{Volume of Each Parcle: v(r)} = \frac{4}{3}\pi r^3 \quad (2)$$

One may solve for total surface area as a function of particle radius (r), assuming a constant total volume V and number of particles

$$\frac{\text{Total Surface Area TSA (r)}}{\text{Total Volume V}} = \frac{\text{N.SA (r)}}{\text{N.v(r)}} = \frac{\text{N.}\pi r^2}{\text{N.}\frac{4}{3}\pi r^3} \quad (3)$$

$$\text{Total Surface Area TSA(r)} = \frac{3V}{r} \quad (4)$$

The total surface area will decrease as particles size increases with a constant total volume. In the present work, it was decided to increase the surface area and increase the emission reduction with cerium oxide nanoparticle added with alumina in a new designed catalytic converter.

MATERIALS AND METHODS

Shape and Dimensions of canister: The size of the exhaust canister is based on the engine exhaust flow rates. It was reported in the literatures that for maximizing catalyst applied surface area, the volume of catalyst must be 1.5 to 2 times the engine displacement (More *et al.*, 2015). The displacement volume of the diesel engine selected for this present investigation is 1106.28 cm^3. The total volume of catalyst used in the (revised) model is 1711 cm^3 i.e. the sum of volumes of coated wire meshes and solid catalytic beads. The modified canister volume is 5924 cm^3, the catalyst occupies 1711 cm^3 only and the remaining volume inside the canister is used for the exhaust gas to flow out freely which helps for limiting the back pressure, ensuring effective diesel oxidation catalyst (DOC) and selective catalytic reduction (SCR) systems (Colombo, Nova and Tronconi, 2010)(Watling, Ravenscroft and Avery, 2012).

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Construction of Canister: The exhaust canister designed for this study comprises two compartments. The first one is meant for filtration and DOC catalyst. The second compartment is meant for filtration and SCR system. The upstream of the first compartment is filled with steel wire meshes for about one-fourth of canister length. This wire meshes are placed vertically with their surface being parallel to the flow of gas. Sufficient gaps are provided amongst these bundles of wire meshes making the gas to flow crosswise also for better filtration as shown in Figure 1.

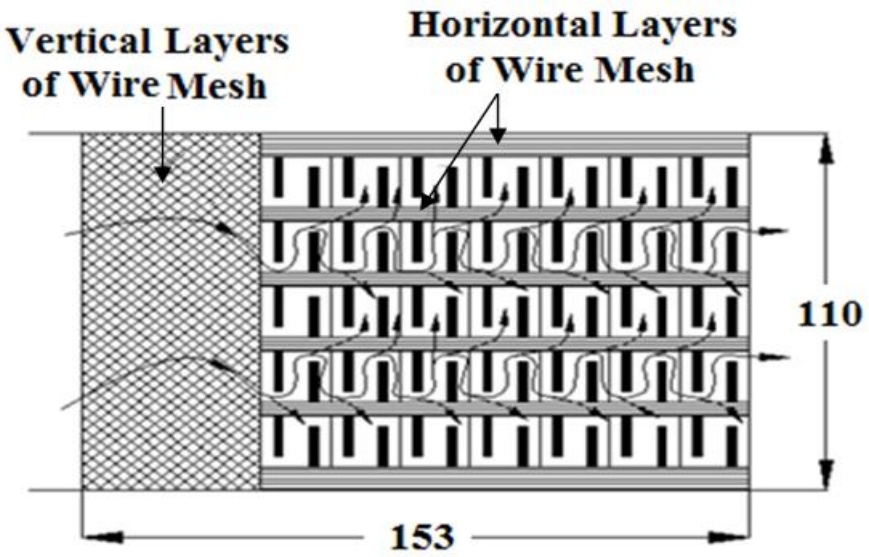

Figure 1. Compartments Filled with Catalyst and Filter Materials.

. The wire meshes provide zigzag path for the gas flow to obtain efficient contact with wire meshes which enhances better filtration as well as better catalytic action in reducing both particulate matter and oxides of Nitrogen. A set of compartments I and II which are loaded with catalytic beads and different grid size steel wire meshes are shown in Figure 2. The fully assembled catalytic converter before fitting it in the experimental set-up is shown in Figure 3. The net weight of the canister filled with two compartments is around 5.2 kg.

Figure 2. Newly Developed Exhaust Canisters

ISSN: 0975-8585

Figure 3. Assembled View.

Selection of Catalyst: The important criteria for the selection of catalyst material are higher NO_x and PM conversion efficiency, withstanding higher temperatures, avoidance of harmful by-products, cost and its availability (Shakya, Harold and Balakotaiah, 2014). Aluminium oxide is the base material used for most catalytic converters (Kašpar, Fornasiero and Hickey, 2003).

Alumina can withstand high temperatures, it remains chemically neutral, it has a very low thermal expansion, and it does not thermally degrade with age. A high surface area cerium oxide is an important component of catalyst composition, and three methods of preparing cerium oxide compound was used so that it is relatively thermally stable and retains usable surface area despite prolonged exposure to oxygen and other exhaust constituents at elevated temperatures. For purposes of comparison, alumina-ceria wash coats based on other ceria precursor materials were prepared for evaluation.

Each of the wash coats was prepared to contain gamma alumina and ceria in the proportion of 72 weight percent alumina and 28 weight percent ceria. The wash coats were calcined and impregnated with the platinum and rhodium applied onto a designed metal monolith. In a first comparison wash coat, the precursor of the ceria was cerium carbonate. All the ceria content of the wash coat came from cerium carbonate $Ce(CO_3)_3$ which was added into the mill and calcined as a part of the wash coat, followed by impregnation with platinum and rhodium. A second wash coat comparison sample was prepared in which the sole source of the ceria was cerium nitrate, $Ce(NO_3)_3$. An aqueous cerium nitrate solution was added with the alumina in the ball mill and upon coating of the cerium nitrate impregnated alumina on the metal monolith and calcining the cerium nitrate was converted to ceric oxide, followed by impregnation with platinum and rhodium. A third comparison wash coat material was prepared utilizing our high surface area ceric oxide as the source of ceria in conjunction with the gamma alumina. The high surface area ceria and gamma alumina were ball milled together and the resulting slurry applied to a metal monolith. After calcining, a wash coat of finely divided particulate ceria and gamma alumina was obtained. The wash coat was impregnated with platinum and rhodium.

DEVELOPMENT OF FILTER MEDIUM

Selection of Filter Medium: The purpose of providing filter medium inside the canister is to filter the solid particle of particulate matter that is present in the diesel engine exhaust emission. The accumulation of PM on the surface of filter medium causes the pressure drop inside the canister. This results in increased back pressure having an adverse effect on maximum power of the engine and fuel economy. Wire mesh of a coarse category with 1.96 mm gap (100 CPSI) was selected along with medium category, wire mesh with 1.61 mm gap (144 CPSI). Wire mesh with 1.01 mm gap (324 CPSI) categorized as fine and wire mesh with 0.65 mm (576 CPSI) gap which is very fine category were also selected. Since the number of steel wire mesh pieces were stacked one over the other as a bunch, the gas flow cannot be laminar, rather it would be turbulent flow. Thus, the laminar flow of exhaust gas is interrupted, thereby creating turbulence for improved mass transfer. This type of flow provides increased travel length and contact time so that more amount of DOC and SCR catalytic actions can take place and hence more PM and NO_x reductions are achievable(Sendilvelan, Jeyachandran and Bhaskar, 2001)(Sendilvelan, Jeyachandran and Bhaskar, 2001).

ISSN: 0975-8585

Next to the vertical wire mesh bundles there is a window plate having 14 mm wide openings of 14 mm size at 21mm pitches, i.e. 7 mm width metal portion of window plate is placed just opposite to the 6 mm gap available in between wire mesh bundles. This 7 mm width metal portion prevents the gas flowing straight and diverts it to pass through the wire meshes, which helps better DPF and DOC actions. The diverted gas will leave out through 14 mm opening of the window plate.

Analysis of Exhaust Gas:

Velocity:

Diameter of piston	D= 80 mm
Stroke length,	L = 110 mm
Speed,	N= 1500 rpm
Diameter of valve port,	d= 20 mm
Valve lift,	l= 9 mm

No. of inlet & outlet valve per cylinder, m = 1 each
Valve is opened by 14° earlier & closed 48° later. i.e. $\lambda = 180 + 14+48 = 242°$

Volume of gas flowing through the valves $= \frac{\pi}{4} D^2 L$ (5)

Time for the valve opening $= \frac{60}{N} \times \frac{\lambda}{360}$ seconds (6)

The average volume rate of flow/sec

$$= \frac{\pi}{4} D^2 L \times \frac{360N}{60\lambda} = \frac{3\pi D^2 LN}{2\lambda} = \frac{1.5\pi D^2 LN}{\lambda} \quad (7)$$

Area of flow in the valves = 0.6 x πdl x m (Where the average discharge co-efficient is assumed as 0.6)

Velocity of flow $= \frac{\text{Volume/sec}}{\text{area}} = \frac{1.5(\pi D^2 LN)}{\lambda(0.6\,\pi dlm)} = \frac{1.5}{0.6} \times \frac{D^2 LN}{dlm\lambda}$ (8)

$$= \frac{2.5 \times (0.08)^2 \times 0.11 \times 1500}{0.02 \times 0.009 \times 1 \times 242} = 60.60606 \text{ m/sec.}$$

Velocity of exhaust gas flow = 60.61 m/sec

Regeneration Period:

1kWh = 1.341 hp: $\therefore$ 1 hp = $\frac{1}{1.341}$ kWh

On an average 5.2 hp of power and 45 km/h of speed are assumed.

kWh equivalent of the assumed hp of 5.2 = $\frac{1}{1.341}$ x 5.2 = 3.877 kWh

This means 3.877 kWh energy is consumed to cover 45 km distance in one hour time. $\therefore$ The distance covered while spending

1 kWh energy = $\frac{45}{3.877}$ = 11.607 km

i.e. for every 11.607 km distance covered, 1kWh energy is consumed.

For an average aged engine, when 1kWh energy is consumed, a maximum of 0.02 gram of particulate matter is permitted to accumulate as per Euro IV and Euro V norms.

i.e. = $\frac{0.02}{11.607}$ g of particulate matter is deposited for every one km of the distance covered. i.e. 1.7231×10^{-3} g of particulate matter accumulation is permitted per km of distance covered

Compartment I:

Void volume in the first compartment = 597.368 cm^3
PM of 10% deposit (assumed) = 597.368 x 0.1
= 59.7368 cm^3 (9)

Compartment II:

Void volume in the first compartment = 557.357 cm^3
PM of 10% deposit (assumed) = 557.354 x 0.1
= 55.735cm^3 (10)

Volume of beads = Surface area x Thickness of PM deposit
50 microns of PM deposit is assumed on beads body surface
= (14.953 x 644) x 0.005 cm
= 48.1486cm^3 (11)

Total volume of PM deposit = (9) + (10) + (11)
= 59.7368 + 55.735 + 48.1486
= 168.6208 cm^3
Bulk density of PM = 0.075 g/cm^3
∴ Mass of PM deposit = 168.6208 x 0.075
= 12.2715 g

i.e. when 10% volume of void space is filled with PM deposit on wire meshes and 50 microns of PM deposit on catalytic beads, the total mass of PM deposit = **12.2715 g.** This means during this 12.2715g of PM is getting accumulated, the distance covered

$$= \frac{12.2715}{1.7231 \times 10^{-3}} = \textbf{7121.875 km}$$

From the observed results, it was concluded that for every 7000 km of engine run, regeneration (i.e. cleaning of canister) is a must.

RESULTS AND DISCUSSION

Catalytic performances: Figures 4, 5 and 6 present the conversion of carbon monoxide, hydrocarbon and NO_x under stoichiometric conditions (λ =1) over fresh cerium oxide using three wash coat methods, the precursor of the ceria was cerium carbonate, the precursor of the ceria was cerium nitrate, and cerium oxide gamma alumina catalysts.

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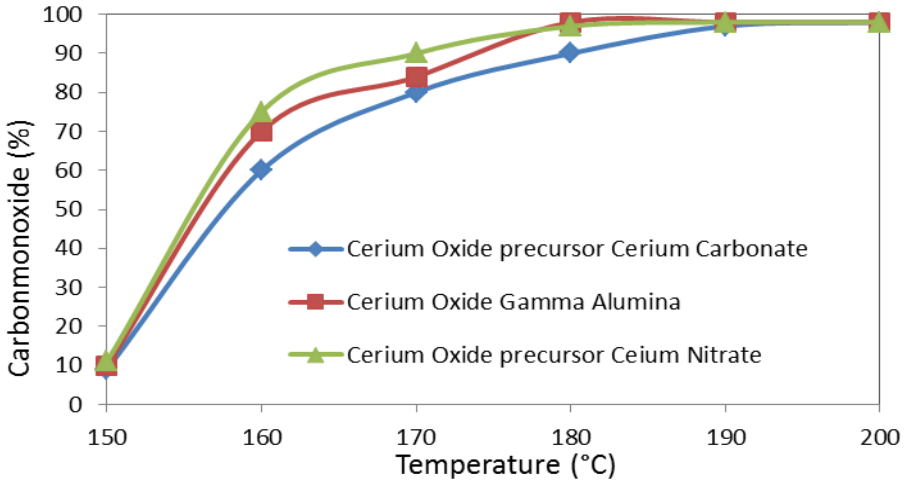

Figure 4. Variation of Carbon monoxide Conversion Efficiency with Temperature.

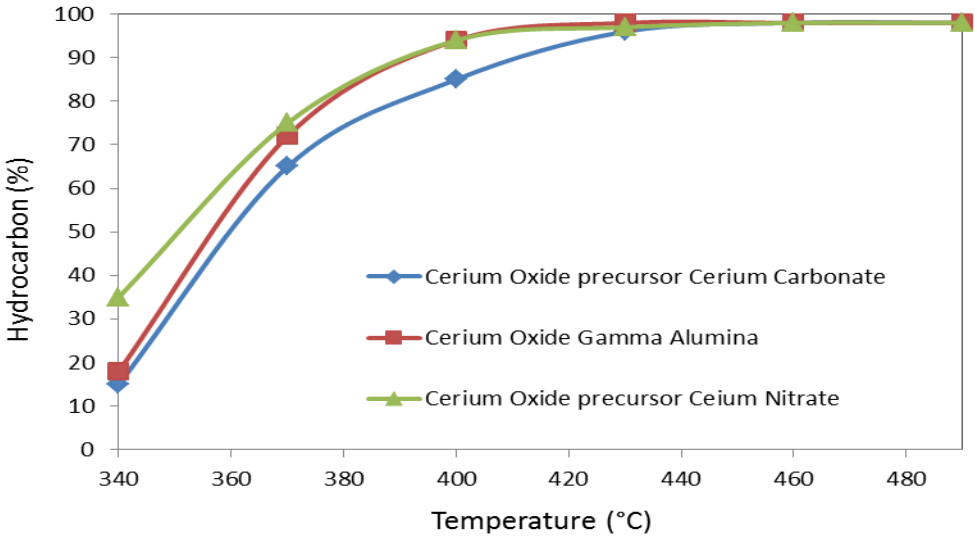

Figure 5. Variation of Hydrocarbon Conversion Efficiency with Temperature.

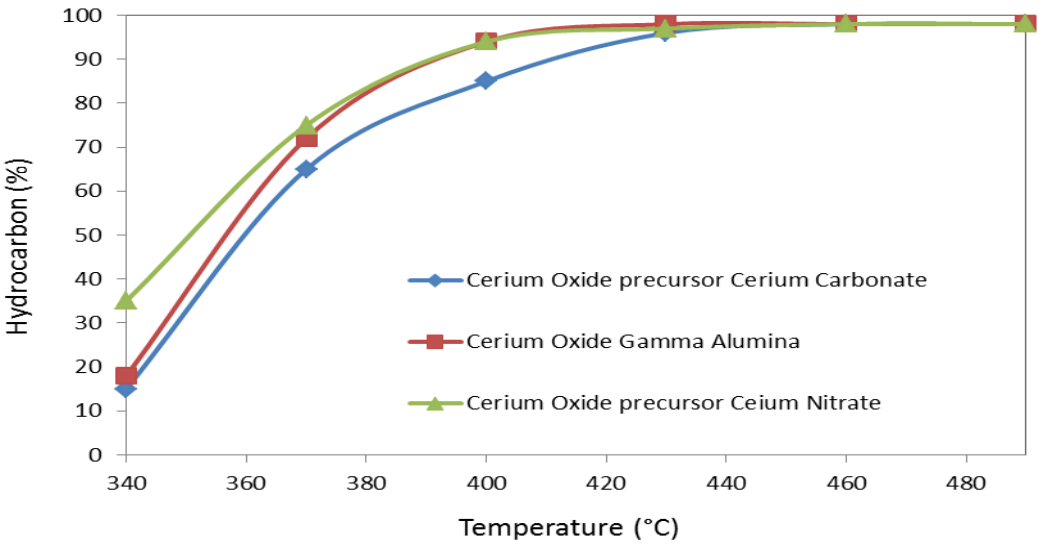

Figure 6. Variation of Oxides of Nitrogen Conversion Efficiency with Temperature.

The temperature range from 150 to 200°C, HC and NO_x did not take part in the reaction, while the reactions of CO were predominated (Theis and Gulari, 2007)[14]. The catalytic behavior in the higher temperature range enhanced the conversion of hydrocarbon and oxides of nitrogen, cerium nitrate precursor showed the highest activity. Above 250°C, the conversion of HC, NO_x increased as the temperature increased. These results show that the presence of ceria promotes the catalytic activities associated with HC and NOx removal. Thus, the cerium oxide precursor of cerium nitrate catalyst was also seen to exhibit better activity than the other catalysts. The experimental tests revealed that cerium nanoparticles can be used as an additive in the diesel catalytic converter to improve the exhaust emission reduction.

CONCLUSION

In the present work, it was proposed to increase the surface area of catalyst and to increase the emission reduction with cerium oxide nanoparticle added with the alumina in a new designed catalytic converter. Based on the experimental analysis the following observations were made.

- The experimental results reveal that there is a reduction of CO, HC and oxides of nitrogen using cerium oxide nanoparticle in well-designed metal monolith.
- From the velocity of exhaust gas flow and particulate accumulation rate calculated for the new design, it was concluded that for every 7000 km of engine run, regeneration is a routine necessity.
- The cerium oxide nanoparticles act as an oxygen donating catalyst and provide oxygen for the oxidation of CO and HC in the catalytic converter.
- It was also observed that the cerium nitrate catalytic behaviour in the higher temperature range was enhancing the conversion of HC and NO_x.

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