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# Catalytic Converters for treatment of Exhaust Gas Emission in Automobiles: A Review

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**Abstract**— Air Pollution produced from the Vehicular sources has become a big problem and going to become larger as vehicle population is projected to grow close to 1300 million by the year 2030. There are a large number of products such as $NO_X$, CO, HC etc. due to incomplete / improper combustion in engine. These pollutants influence the air quality, atmosphere, and human and animal health. Numbers of alternate technologies like improvement in design of engine, use of alternative fuels, fuel treatment, using fuel additives, exhaust gas treatment etc. are being considered to lessen the emission levels of the engine. Use of Catalytic Converter however is found to be the most suitable method to control the automotive exhaust emission amongst all other technologies. The review paper discusses automotive exhaust emissions and its effect, automotive exhaust emission control by platinum (noble) group metal based catalyst in catalytic converter, history of catalytic converter, types of catalytic converter, limitation of catalytic converter and also achievements of catalytic converter..

**Index Terms**— automotive; catalytic; pollution; efficiency; emission; environment; platinum.

## 1 INTRODUCTION

AIR pollution produced from various sources such as automobiles contributes major air quality problems in rural as well as urban and industrial areas in both developed and developing countries. About 50 million automobiles are manufactured each year and over 700 million automobiles are used globally. Vehicle populace is projected to grow close to 1300 million by the year 2030 [2].

Most vehicles operate on combustion of Petroleum, diesel and jet fuels with large amount of emission of carbon monoxide (CO), unburned hydrocarbons (HC), nitrogen oxides (NOx) and unburned particulate matter. HC and CO occur because the combustion efficiency is not 100%. The NOx is formed due to high temperatures (>1500 0C) of the combustion process causing thermal fixation of nitrogen in the air which makes NOx

Typical exhaust gas composition at the normal engine operating conditions are: carbon monoxide (CO, 0.5 vol. %), unburned hydrocarbons (HC, 350 ppm), nitrogen oxides (NOx, 900 ppm) hydrogen (H2, 0.17 vol. %), water (H2O, 10 vol. %), carbon dioxide (CO2, 10 vol. %), oxygen (O2, 0.5 vol. %) [1-3].

Carbon monoxide is a noted poison that has an affinity for hemoglobin in the blood 210 times greater than the oxygen affinity prolonged exposure to levels above 9 ppm can lead to reduce mental acuity for some individuals. HC and NOx lead to photochemical smog in presences of sun light give secondary pollutants like ozone, nitrogen dioxide & peroxyacyl nitrate which cause also global ecological problems [4].

Reduction of toxic substances emission from combustion engines can be achieved by primary (inside engine) measure and secondary (outside engine) measures. As primary measures many diverse possibilities and technical methods of reducing exhaust gas emission are used e.g. combustion of lean air fuel mixture, multistage injection fuel, exhaust gas recirculation, fuel gas after burning, loading of additional water into cylinder volume [5, 6]. Currently secondary measures, in automotive exhaust after treatment processes a variety of advanced expertise is applied based on oxidation and three-way catalyst adsorption storage and the filtration process [7]

## 2 CATALTYIC CONVERTER

The contaminants have undesirable impact on air quality, atmosphere and human health that leads in stringent norms of pollutant emission. A Catalytic Converter is an emissions regulating means that converts Toxic gases and Pollutants in exhaust gases to less Toxic pollutants. Out of various technologies available for automobile exhaust emission control a catalytic converter is found to finest choice to control Carbon monoxide, unburnt hydrocarbon and $NO_x$ emissions from petrol/LPG driven vehicles while diesel particulate filter and oxidation catalysts converter have so far been the most prospective option to regulate particulates emissions from diesel driven vehicle. A catalytic converter which is placed inside the tailpipe due to which deadly exhaust gases containing unburnt Hydrocarbon, CO gas etc. are emitted [8]. The function of the catalytic converter is to convert these gases into $CO_2$, water, $N_2$ and $O_2$ gas and currently, it is enforced for all autos plying on roads in US and Japan to have catalytic converters as they use unleaded petrol. In India, the government has made catalytic converters compulsory for registration of new cars. [9, 10]

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## 3 CONSTRUCTION

### 3.1 The Catalyst Core

For automotive catalytic converters, the core is usually a ceramic monolith with a honeycomb like structure. Metallic foil monoliths made of FeCrAl are used in some uses. This is partly a cost issue. Ceramic cores are economical when produced in large numbers. Metallic cores are less costly to construct in minor production runs, and are used in Sports cars where little back pressure and reliability under continuous high load is required.

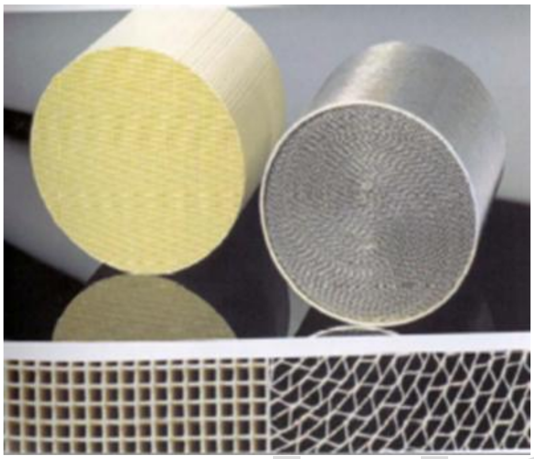

Fig 1. Substrate

Either material is designed to deliver a high surface area to support the catalyst washcoat, and therefore is often called a 'catalyst support'. The cordierite ceramic substrate used in most catalytic converters was designed by Irwin Lachman, Rodney Bagley, and Ronald Lewis at Corning Glass, due to which they were inducted into the National Inventors Hall of Fame in the year 2002. [12]

### 3.2 The Washcoat

The washcoat is a transferor for the catalytic materials and is used to scatter the materials over a high surface area. Aluminum oxide, silicon dioxide, titanium dioxide, or a mixture of silica and alumina can be used. The catalytic ingredients are suspended in the washcoat prior to applying to the core. Washcoat materials are selected to form a coarse, uneven surface, which greatly increases the surface area compared to the even surface of the bare substrate. This in turn gets the most out of the catalytically active surface available to react with the engine exhaust. The coat must hold its surface area and prevent sintering of the catalytic metal particles even at high temperatures (1000 °C). [12]

### 3.2 The Catalyst

The catalyst is most often a precious metal. Catalytic converters contain the catalytic substance in their configuration, which are a combination of Platinum Group Metals (PGMs): platinum, palladium and rhodium. Platinum retrieval process can be done by pyrometallurgical [13] or hydrometallurgical processes Platinum is the most active catalyst and is broadly used, but is not appropriate for all applications because of undesirable additional reactions and high expense. Palladium and rhodium are two additional precious metals used. Rhodium is used as a reduction catalyst, palladium is used as an oxidation catalyst, and platinum is used both for reduction and oxidation. Cerium, iron, manganese and nickel are also used, although each has its own restrictions. Nickel is not lawful for use in the European Union (since its reaction with carbon monoxide into nickel tetracarbonyl). Copper can be used universally excluding North America, where its use is banned because of the formation of dioxin. [12]

## 4 TYPES OF CATALYTIC CONVERTER

### 4.1 Reduction Catalytic Converter

A reduction catalyst to regulate NOx can be used as a distinctive system in addition to the oxidation catalytic converter.


Fig 2. Reduction catalytic converter



The reduction catalyst is fixed upstream of the oxidation system. The reduction catalyst is the 1st stage of the catalytic converter. It uses platinum and rhodium to decrease the nitrogen oxide emissions. When such molecules interacts with the catalyst, the catalyst splits the nitrogen atom out of the molecule and holds on to it, releasing the oxygen in the form of $O_2$. The nitrogen atoms link with other nitrogen atoms that are also trapped to the catalyst forming $N_2$ [14].

$$2NO \rightarrow N_2 + O_2$$

### 4.2 Oxidation Catalytic Converter

A 2-way catalytic converter has two immediate tasks:
Oxidation of carbon monoxide to carbon dioxide:

$$2CO + O_2 \rightarrow 2CO_2$$

Oxidation of hydrocarbons (unburned and partially burned fuel) to carbon dioxide and water: [12]

$$C_xH_{2x}+2 + [(3x+1)/2]\ O_2 \rightarrow xCO_2 + (x+1)\ H_2O$$

This type of catalytic converter is extensively used on diesel engines to decrease hydrocarbon and carbon monoxide emissions. They were also used on gasoline engines in American- and Canadian-market automobiles until 1981. Since their inability to control oxides of nitrogen, they were outdated by three-way converters.

An oxidation catalyst is a device located on the tailpipe of a car. The oxidation catalyst is the 2nd stage of the

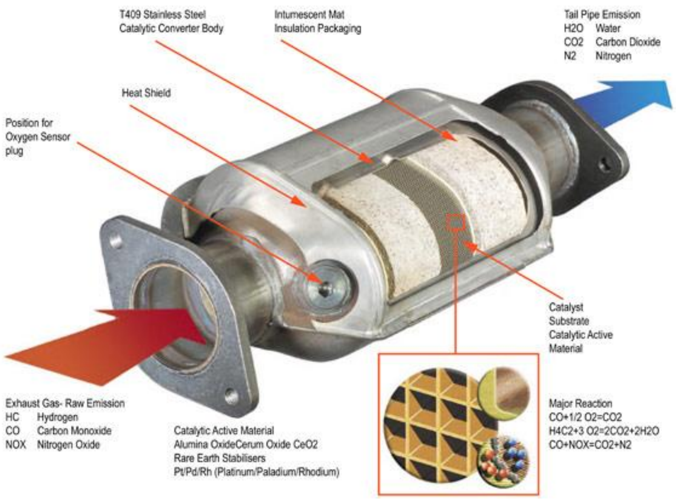


Fig 3. Oxidation catalytic converter

catalytic converter. It reduces the unburned hydrocarbons and carbon monoxide by burning (oxidizing) them over a platinum and palladium catalyst. This catalyst aids the reaction of the CO and hydrocarbons using the remaining oxygen in the exhaust gas [14-15].

$$HC + O_2 \rightarrow CO_2 + H_2O \quad \text{--- (1)}$$
$$2CO + O_2 \rightarrow CO_2 \quad \text{--- (2)}$$

### 4.3 Three-way Catalytic Converter

TWCs have the benefit of performing the oxidation of carbon monoxide (CO), hydrocarbons (HC) and the reduction of nitrogen oxides (NOx) concurrently. Noble metals are generally used as the active phase in TWCs. Pd catalysts are specifically attractive since Pd is by far the most inexpensive noble metal in the marketplace and has better selectivity and activity for hydrocarbons. Rhodium the other important constituent of three-way catalysts is usually renowned as the most efficient catalyst for encouraging the reduction of NO to $N_2$.

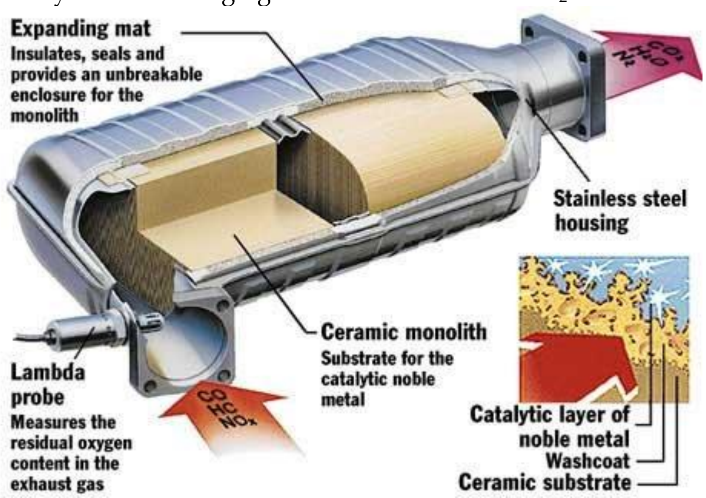


Fig 4. Three way catalytic converter

The TWCs performance in the emission control can be affected by functioning the catalyst at high temperatures (> 600°C). Reactions happening on the automotive exhaust catalysts are very complex as listed below. The main reactions are the oxidation of CO and HC and the reduction of NOx. Also, water gas shift and steam reforming reaction occur. Intermediate products such as $N_2O$ and $NO_2$ are as well produced. The NOx storage concept is centered on assimilation of a storage module into the three-way catalyst (TWCs) to store NOx through lean conditions for a time period of minutes [14].

Reactions in a catalytic converter:

Oxidation :
$$2CO + O2 \rightarrow 2CO2$$
$$HC + O2 \rightarrow CO2 + H2O$$

Reduction/three-way :
$$2CO + 2NO \rightarrow 2CO2 + N2$$
$$HC + NO \rightarrow CO2 + H2O + N2$$
$$2H2 + 2NO \rightarrow 2H2O + N2$$

Water Gas Shift:
$$CO + H2O \rightarrow CO2 + H2$$

Steam reforming :
$$HC + H2O \rightarrow CO2 + H2$$

## 5 AIR-FUEL RATIO

Conversion efficiency of NO, CO and HC as a function of the air-fuel in a three way catalytic converter. There is a fine range of air- fuel ratio near stoichiometry in which great conversion efficiencies for all three pollutants are realized.

The width of this gap is narrow about 0.1 air-fuel ratio for catalyst with high stretch use and depends on catalyst design and engine working conditions.

***1) When the A/F ratio is leaner than stoichiometry***

The oxygen content of the exhaust stream increases and the carbon monoxide content decreases. This provides a high efficiency working environment for the oxidizing catalysts (platinum and palladium). During this lean cycle the catalyst (by using cerium) also keeps excess oxygen which will be released to encourage improved oxidation during the rich cycle.

***2) When the A/F ratio is richer than stoichiometry***

The carbon monoxide content of the exhaust increases and the oxygen content decreases. This providing a high efficiency operating setting for the reducing catalyst (rhodium). The oxi-

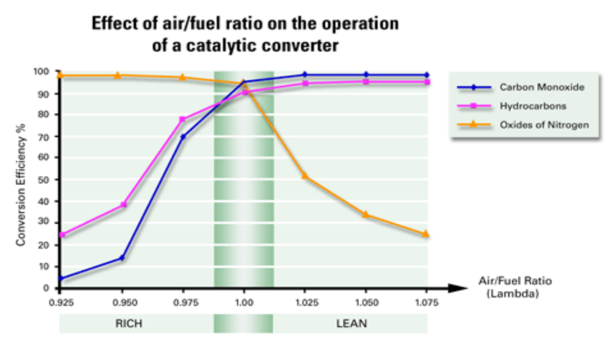


Fig 5. Effect of Air/Fuel Ratio

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dizing catalyst maintains its efficiency as kept oxygen is released [16, 17].

A closed loop feedback fuel managing system with an oxygen sensor in the exhaust is used for accurate control of air-fuel ratio. To obtain a proficient control of the A/F ratio the amount of air is measured and the fuel injection is controlled by a high-tech system which uses an oxygen (λ) sensor situated at the inlet of the catalytic converter. The indication from this λ sensor is used as a feedback for the fuel and air injection control loop. A second λ sensor is located at the outlet of the catalytic converter (Fig. 6.). This configuration constitutes the foundation of the so-called engine on-board diagnostics (OBD).

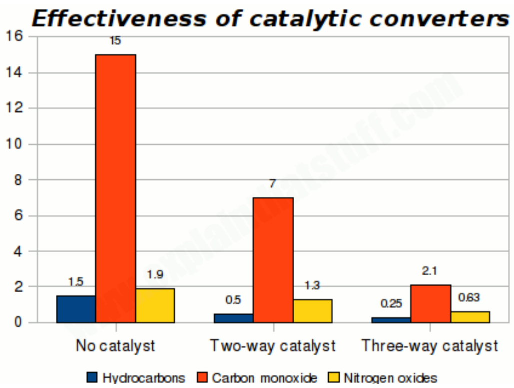


Fig 5. Effect of Air/Fuel Ratio

By comparing the oxygen concentration earlier and subsequently the catalyst, A/F fluctuations are detected. Extensive variations of A/F at the outlet signal system failure. Effect of A/F ratio on the conversion efficiency of three-way catalysts constricted A/F window at the stoichiometric point is the thumbprint of an effective TWC system [18].

## 6 Limitations

In unforgiving conditions experienced in the exhaust stream with temperatures up to 1000 °C the metal in the catalyst is prone to deactivation by sintering, leading to a reduction in surface area and hence catalytic action. The orthodox means to meet constriction statutory emissions control goals is just to increase the amount of PGM in the auto catalyst. The need to surety catalyst performance over the distinctive vehicle lifetime of 80,000 km also means that additional metal must be added, since the performance of the catalyst descents over time. In addition escalating PGM request and costs are enticements towards attaining lesser metal loadings and greater activity. [19] The combinations of the PGM are usually considered exceedingly toxic while the Pd and Rh are cancer-causing in nature. Due to the fact that the PGM are produced due to the scrape of an automotive catalyst wash coat. That is why the road traffic is liable for metallic and organic pollutant – emissions which foul the environment [20]. The catalytic converters in the exhaust system become weakened by several mechanisms e.g. thermal deterioration and poisoning.

Thermal deterioration occurs as a consequence of interaction of the catalyst to high temperature conditions. This reasons sintering of the PGM, loss of provision surface area and phase transformation. Poison also cause loss of action mainly by hindering the pores leading to active sites or even by direct deadlock of the active sites themselves. [21, 22].

## 7 Future Trends

As above discussed, three-way catalysts signify a quite mature, highly effective technology for contamination abatement which, however, has some inherent limitations which need further enhancement and development. These aspects are essentially related to: (i) low activity at low temperatures (start-up of the engine) and (ii) use of stoichiometric A/F. As far as the first aspect is on our concern, it should be noted that approximately 50–80% of HC emissions during the test procedures are emitted before the Three-way catalyst reaches the light-off temperature. When, in recent years, the release limits have been pushed down, it seemed clearly that minimization of warm-up HC emissions was the chief problem in automotive pollution reduction. This issue was been consequently addressed by introduction of the CCCs onto the market. This made development of Three-way catalysts featuring thermal stabilities well above 1000◦C [23]. In truth, the matter of the start-up emissions can be addressed by different tactics.

A first possibility is that of gathering the HC emitted during the warm-up of the converter in a HC trap, naturally composed of hydrophobic zeolite. In an ideal trap, HC are trapped at low temperatures and as the temperature is augmented above 250–300 ◦C, HC are on the loose and converted on the Three-way catalysts [23]. An appropriate trap must also feature very high thermal stability under hydrothermal situations, which often is not the case for zeolite-based systems. We recollect that temperatures as high as 850–900◦C may possibly be reached in the under-floor catalysts. While such systems are still under examination, alternative approaches have been indicated [23, 24]. It must be accepted that to minimize the emissions, the catalysts must be heated-up in a lowest time. This can be accomplished, for example, by electrically or combustion/chemically heated catalysts. In the latter case hydrogen and oxygen, or CO-rich feed is run over the catalysts [24].

Oxidation of both CO and H2 are easy and exothermic reactions, which occur at low temperatures over the Three-way catalysts [25], leading to rapid heating of the catalyst. However, storing of H2 on the vehicle or usage of rich A/F which produces high CO and H2 emissions, brings struggle to the de-pollution system. Huge amounts of HC are in-fact emitted at a rich A/F, which require a supplementary HC trap. Use of composite technology clearly increases costs while the simplest technology is needed. Therefore, there has been a strong effort intended at improving the thermal stability of the washcoat [34]. With the convenience of thermally stable washcoats, application of a start-up converter, i.e. converter that is meticulously attached to the exhaust manifold, became possible. This converter allows tremendously rapid heating of the catalyst, leading to enhanced conversions during the warm-up of the engine. Metallic converter can be easily shaped into the exhaust manifold and are very suitable for such application also due to their low heat capacity. In general, the composition of the CCC is related to that of the typical Three-way catalyst in that NM metals and particularly Pd are engaged to encourage HC conversion. The OSC promoter may be omitted from these formulations since it encourages CO conversion, leading to local overheating due to this highly exothermic reaction [23].

An alternative approach is that of evolving new catalysts presenting high conversion efficiency at low, nearly ambient, temperature [25]. A large part of these investigations have been activated by the observation by Haruta et al. [28, 29] that gold catalysts are able to proficiently oxidise CO even at sub-ambient temperature provided that nano-dispersed Au particles are equipped on the support. Thus, light-off temperatures in the conversion of the exhausts as low as 100 ◦C could be achieved by putting small Au particles on reducible oxides such as $CeO_2$ and $TiO_2$ [30]. However, the durability of gold catalysts under punitive conditions is still an issue, noteworthy deactivation of cobalt oxide promoted Au catalysts was detected already after 157 h of reaction at 500 ◦C under computer-generated exhaust simulation [31]. There is in fact a prosperous activity in the field of low temperatures catalysts [29,32,33], other noble metals, in addition to Au, being effective in low temperature oxidation reactions, provided that suitable synthesis methodology is employed [32]. To our acquaintance, however, due to the Nano-dispersed nature of these catalysts, the issue of thermal stability, even at discreetly high temperatures has not been solved as yet. Sustained metal Nano-particles are, in fact, quite mobile on the surface, even at ambient temperature in the case of gold [33], which makes inhibition of sintering phenomena difficult. We believe that thermal stabilization of nano-dispersed metals may signify a new breakthrough point in the growth and enhancement of these environmental catalysts.

## 8 Conclusion

With almost all the current study on catalytic converters, it is imaginable to expect a day where automobiles are no longer identified to pollute and damage the environment. Today's automobiles are meeting emission standards that need to decrease of up to 99 percent for CO, Unburned Hydrocarbons and NOx compared to the unrestricted levels of automobiles sold in the 1960s. Three-way catalyst with stoichiometric engine control systems tolerates the state of art technique for simultaneously controlling hydrocarbon, CO and NOx emissions from automobiles. The financial reasons, limited resources of platinum group noble metal and some working limitations of platinum group metal based catalytic converters have driven the study of alternative catalyst materials.

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