Modification of Catalytic Converters Thereby Bettering their Performance and Reducing The Cost

Mr. Soham P. Kulkarni[1], Ms. Sapana B. kharat[2], Mr. Ajinkya K. Kulkarni[3], Mr. Vishal M. Joshi[4], Hemant Deore[5], Amar Pandhare[6]

Department of Mechanical Engineering

Smt. Kashibai Navale College of Engineering, Pune

Abstract- *With the invention of IC engines and their increased use in automobile industries, pollution has become a cause for major concern since the last two decades. We are not new to the destructive effects, global warming has had on the environment. Automobile exhausts contain hazardous gases like Nitrogen oxide gases, Carbon Monoxide and unburnt hydrocarbons. These poisonous gases pose a great threat to life on the planet and the environment that we thrive in. For the reduction of these exhaust emissions, catalytic converters have been introduced in automobiles which provide a medium to carry out simultaneous oxidation and reduction of these exhaust gases using selective catalysts. Catalysts are those substances which never participate in the reactions but speed up the reaction processes. Normally, noble metals such as Platinum (Pt), Palladium (Pd) and Rhodium (Rh) are used in manufacturing of catalytic converters. In this review an attempt is made, to study various materials like activated carbon, zeolites, sponge iron, SCR and* TiO_2*, which can replace platinum, Palladium and Rhodium from catalytic converters, to improve operating ease and economy.*

Keywords- IC engines, Exhaust emissions, Catalytic Converters, Ceramic honeycomb, Catalysts, Cost reduction.

I. INTRODUCTION

In both, the first and the third world countries, air pollution is a major cause for worry caused amongst environmentalists. It has come into observation that one of the vital causes of air pollution in both these worlds is the exhaust emitted from automobiles. Annually, over 50 million cars are produced worldwide and over 700 million cars are used all over the world. Automobile production is expected to grow close to 1300 million units by the year 2030 [1]. Combustion of fuels such as gasoline, diesel and other jet fuels (most automobiles depend upon the combustion of such fuels) lead to the emission of hazardous gases like Carbon Monoxide (CO), Nitrogen oxides (NO_x), unburnt hydrocarbons (HC) and other sulphurous oxides (SO_x) in large quantities [1-2]. Due to the combustion efficiency being less than 100%, HC and CO gases are emitted. The NOx is formed during the very high temperatures (>1500°C) of the combustion process resulting in thermal fixation of the nitrogen in the air which forms NOx. Typical exhaust consists of the following gases in the aforementioned quantities: carbon monoxide (CO, 0.5 vol. %), unburned hydrocarbons (HC, 350 vppm), nitrogen oxides (NO_X, 900 vppm) hydrogen (H_2, 0.17 vol. %), water (H_2O, 10 vol. %), carbon dioxide (CO_2, 10 vol. %), oxygen (O_2, 0.5 vol. %) [3-7]. To reduce the stress on the environment and reduce emissions, more advanced control strategies like modifications in engine design and fuel system, control of engine parameters and use of sophisticated exhaust after treatment devices have been introduced. Primary (inside engine) measure and secondary (outside engine) measures are used for the reduction of toxic gases. Methods like combustion of lean air fuel mixture, multistage injection fuel, exhaust gas recirculation, fuel gas after burning, loading of additional water into cylinder volume are used as primary methods to reduce emissions. Nowadays secondary measures for the treatment of exhaust gases includes oxidation and three-way catalyst adsorption storage and filtration process. Thus the reduction of the carbon monoxide (CO), hydrocarbons (HC), nitrogen oxide (NO_X) and particulate emissions is enabled so as to meet the demands of current and future exhaust emission regulations. This review paper discusses automotive exhaust emissions and its impact on environment, automotive exhaust emission control by catalytic converter, catalysts employed in catalytic converters and also achievements of catalytic convertor [8-10].

II. POSITION OF CATALYTIC CONVERTER

The deadly exhaust gases (NO_x, CO and HC) pass through the tail-pipe in which the catalytic converter is placed. The main purpose of the catalytic convertor is to accelerate the conversion of harmful exhaust gases into CO_2, water, N_2 and O_2. As they use unleaded petrol, it is mandatory for all the automobiles running on roads in US and Japan to have catalytic converters. In India the government has made catalytic converters mandatory for registration of new cars. It has now been made mandatory for all the vehicles, especially those which follow the BS4 norms.

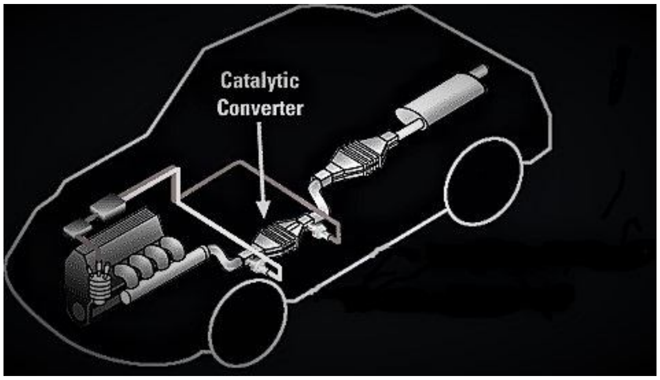

Fig 1.1: Location of Catalytic Converter in a Vehicle.

III. DIFFERENT VARIATIONS OF CATALYTIC CONVERTERS

The three main variations of catalytic converters are listed below with a brief introduction:

- **Oxidation catalytic converter-** The oxidation catalytic converter performs the oxidation of carbon monoxide to carbon dioxide and that of hydrocarbons to carbon dioxide and water. This converter is widely used on diesel engines to reduce hydrocarbon and carbon monoxide emissions. Platinum and Palladium accelerate the oxidation process thereby burning HC and CO and convert them into CO_2 and water droplets.

$$HC + O_2 \longrightarrow CO_2 + H_2O$$

$$2CO + O_2 \longrightarrow CO_2$$

- **The reduction catalytic converter-** As NOx is already an oxidized compound, therefore, to transform it into its original elements (N_2 and O_2) a reduction catalyst is required which is fitted upstream of the oxidation system. Reduction mechanism forms the first stage of the catalytic conversion. Platinum (Pt) and Rhodium (Rh) are used to reduce Nitrogen Oxides emission. As soon as the NO_X molecules establish contact with the catalyst bed, the catalyst rips the nitrogen atom out of the molecule and holds on to it thereby freeing the oxygen in the form of O_2. The nitrogen atoms bond with other nitrogen atoms that are also stuck to the catalyst forming N_2 [8-10].

$$2NO \longrightarrow N_2 + O_2$$

- **Three-way oxidation-reduction catalytic converters (TWCs)-** First world countries like USA and Canada employ the maximum use of TWCs. Due to stringent emission norms, it has now been made mandatory to use catalytic converters in almost all the countries. These converters have come to be recognized as one of the most important inventions in the history of the automobiles. These converters perform three simultaneous tasks, namely, reduction of nitrogen oxides to nitrogen and oxygen, oxidation of carbon monoxide to carbon dioxide, and oxidation of unburnt hydrocarbons to carbon dioxide and water.

TWCs carry an added advantage of oxidising carbon monoxide (CO), hydrocarbons (HC) and reducing nitrogen oxides (NO_x), both simultaneously. Noble metals are usually used as the active phase in TWCs. Palladium (Pd) catalysts are especially attractive since Palladium is by far the cheapest noble metal in the market and has better selectivity and activity for hydrocarbons. Rhodium the other essential constituent of three-way catalysts is widely recognized as the most efficient catalyst for promoting the reduction of NO to N_2. High temperatures (> 600 °C) vastly affect the performance of TWCs in emission controls. The major 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 also found [11, 12]

Reactions in a Three Way Catalytic Converter [11, 12]

Oxidation	$2CO + O_2 \longrightarrow 2CO_2$ $HC + O_2 \longrightarrow CO_2 + O_2$
Reduction	$2CO + 2NO \longrightarrow 2CO_2 + N_2$ $HC + NO \longrightarrow CO_2 + H_2O + N_2$ $2H_2 + 2NO \longrightarrow 2H_2O + N_2$

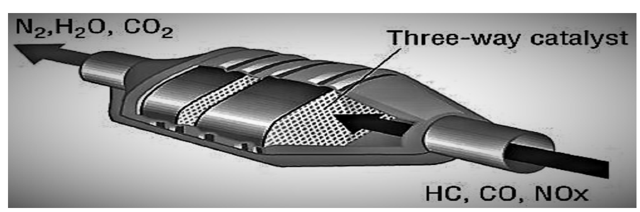

Fig 1.2: 3-way Catalytic converter

IV. BASIC COMPONENTS OF CATALYTIC CONVERTER

• **Substrate**: It is ceramic honeycomb like structure with thousands of parallel channels that provide a large surface area for the engine exhaust.

• **Wash Coat**: A coating that increases the effective surface area of the substrates & facilitates the application of precious metal catalyst onto the surface of the ceramic surface of the ceramic substrate.

• **Catalyst**: Precious metal catalyst-the heart of catalytic converter, applied to wash coated ceramic substrate.

• **Mat**: It provides thermal insulation & protects against mechanical shock & chassis vibration.

• **Case**: A metal package that encases all the above components.

• **Heat Shields**: They are used to protect various parts surrounding the catalytic converter, from thermal shocks.

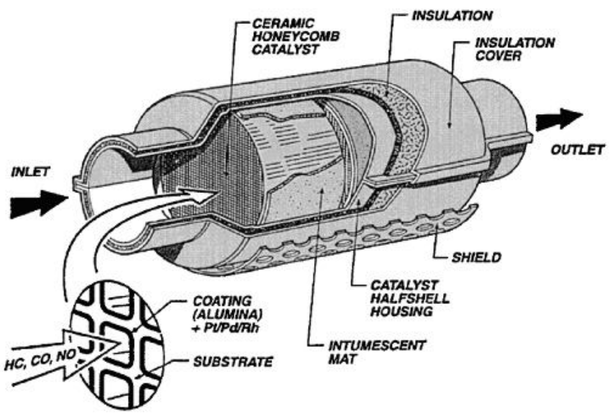

Fig 1.3: Schematic Diagram of Catalytic Converter [13]

Catalysts: These include oxides of base metals e.g. copper, chromium, nickel, cobalt etc. and the noble metals Platinum (Pt), Palladium (Pd) and Rhodium (Rh). Base metal oxides although found to be effective at higher temperature but they sinter and deactivate when subjected to high-end exhaust gas temperature of conventional SI (Spark-Ignition) engine operation. Also, their conversion efficiency is severely inhibited by sulfur dioxide resulting from sulfur in fuel. The base metal catalysts are required in a relatively large volume and consequently due to high thermal inertia they took longer to heat up to operating temperature. Therefore in practice only the noble metals are used as they have high specific activity high resistance to thermal degradation, Superior cold start performance and low deactivation caused by fuel sulfur. The noble metals are more expensive but the amount required for an automotive catalytic converter is small about 1 to 2 gm only. The loading of noble metals typically varies from about 1.0 to 1.8 g/l (30 to 50 g/ft3) of catalytic converter volume. A mixture of platinum and palladium in 2:1 mass ratio is usually employed as oxidation catalyst. Palladium has higher specific activity than Pt for oxidation of CO, olefins and methane. For the oxidation of aromatics, Pd and Pt have similar activity while for the oxidation of paraffin hydrocarbon (higher than propane) Pt is more active than Pd. Palladium has a lower sintering tendency than platinum at high temperatures of about 980 0C in the oxidizing atmosphere. Rhodium is primarily a NO reduction catalyst. The NO reduction activity of noble metals is in the order Rh>Pd>Pt. when simultaneous conversion of CO, HC and NOx is desired in the 3-way catalytic converters, mixture of Pt + Pd is used with Rh in a ratio of 5:1 to 10:1. The active metals in catalytic converter (Pt, Pd and/or Rh) is very small (0.1 to 0.15% by weight of monolith) which are highly dispersed on the surface of the catalyst support. The particle size of the noble metal particles when fresh is around 50 nm or smaller. At high temperature the noble metals sinter and particles may grow to a size of around 100 nm.

Zeolites and Sponge Iron can also be used as a substitute for expensive noble metals: Platinum, Palladium and Rhodium [12, 13].

Shell: Manufactures make converter housing of shell of two stamped metal pieces welded to gather to form a round or oval assembly.

Monolith: A monolith is a ceramic block consisting of a large number of small straight and parallel channels. The monoliths are made by extrusion. A special mixture of clay binders and additives is pushed through a sophisticated dye to create the monolith structure. The material is dried cut to the required length and fired at high temperatures. The monolithic structure has a diameter of about 15 cm and can have different shapes. The diameter of the channels ranges from 0.5 to 10 mm and the length of the monolith can be up to 1 meter long. On the walls of the channels a catalytic active layer can be applied in which chemical reactions can take place. Because of the large number of channels the contact area between the catalytic layer and the fluid that travels inside the channels is very large. Further the channels are straight and parallel so that the flow is not obstructed. The ceramic and metallic monolithic allows high conversion efficiencies at high gaseous throughput, provides a high geometric surface area with lower pressure drop, excellent high temperature and thermal shock resistance and can be conveniently oriented in the exhaust train in any number of directions. The monolithic catalyst is mounted in a stainless-steel container with a matting material wrapped around it to ensure resistance to vibration [14].

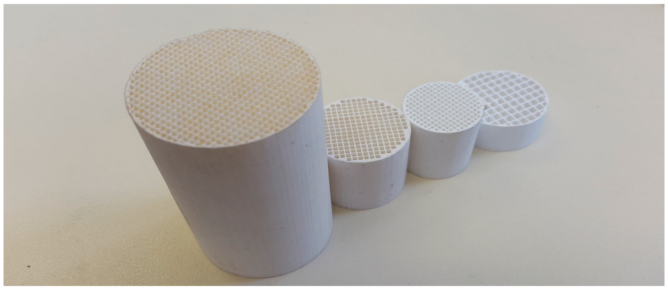

Fig 1.4: Ceramic Honeycomb Structures of different shapes [15]

Wash coat: Ceramic and metallic monoliths have a geometrical surface area of 2.0-4.0 m^2/l of substrate volume. A thin layer of inorganic oxides known as wash coat is applied to the cells in monolith structure to increase effective surface area for dispersion of active catalyst that increase its contact with the reacting gases. The wash coat has pores of varying sizes ranging from 20 to 100 Å. The ceramic monoliths generally have some wall porosity or surface roughness that results in good adhesion of wash coat. The wash coat constitutes about 5 to 15 % of the weight of ceramic monolith. Its thickness typically varies in the range 10-30 μm on the walls and 60-150 μm on the corners of the square cells which reduces the open flow area of the catalyst. Wash coat increase surface area of the catalyst substrate to 10000-40000 m^2/l of monolith volume. The wash coat components support the catalyst function and to improve resistance of catalyst to thermal de-activation processes [16].

V. COATING PROCESS

Catalytic converters used in automobile and industries for regulating pollution are usually made of cordierite ceramic. Cordierite ceramics are extruded to form a structure of honeycomb-like cells that extend as channels along the length of catalytic converter. The channel walls are coated with an emulsion-like liquid which contains the noble metal catalyst. A final layer of protection against heat damage is applied by ribbing of the shield while reinforcing the structural stability of the entire converter. A ceramic is encased by a ribbed body to reduce expansion and distortion when the converter reaches its high operating temperature. The channels formed by the ribs hold the ceramic in proper alignment and protect the cushioning mat from direct exposure to exhaust gases. The variations in size and shape are different for every automobile company but typically, they are about 10-12 cm in diameter and 7-10 cm in long with multiple honeycomb catalysts.

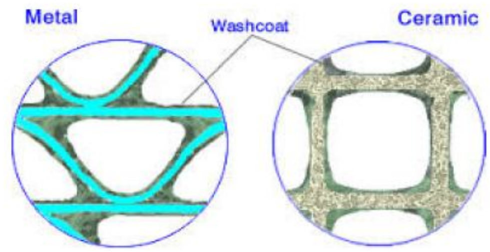

Fig 1.5: Internal Structure of Ceramic and Metallic Monolith [17, 13]

VI. ACHIEVEMENTS OF CATALYTIC CONVERTER

Latest automobile standards require emission reductions of up to 99 percent for HC, CO and NO_x compared to the uncontrolled levels of automobiles sold in the 1960s. Automobiles installed with catalytic converters are able to achieve these reduction standards. Now, catalytic converters have also found working on trucks, buses and motorcycles as well as on construction equipment lawn and garden equipment marine engines and other non-road engines; basically every mobile machine which runs on an IC engine. Catalytic converters have also been able to reduce emissions coming from alternative fuels such as natural gas, methanol, ethanol and propane. Across the globe, more than 500 million vehicles equipped with catalytic converters have been sold so far. In 2005, all the new cars that were sold in the U.S came installed with a catalytic converter by default and more than half of new cars sold worldwide, were equipped with a catalyst. Catalytic converter has been called as automobile industries greatest achievement in the past century by Car and Driver magazine [18, 19].

VII. LIMITATIONS OF A CATALYTIC CONVERTER

The metal in the catalyst is prone to deactivation by sintering because of exhaust streams with temperatures up to 1000 degrees Celsius. This leads to a reduction in surface area and therefore catalytic activity. The orthodox way to meet tightened legislative emissions control targets is to simply increase the amount of PGM in the auto catalyst. The catalyst performance over the typical vehicle lifetime of 80,000 km must be guaranteed. However, this also means that metal must be added in excess, since the performance of the catalyst drops off over time. The rising PGM demand and costs are incentives towards achieving lower metal loadings and higher activity, additionally. The catalytic converters in the exhaust system become deteriorated by several mechanisms e.g. thermal deterioration and poisoning. Thermal deterioration occurs as a result of exposure of the catalyst to high temperature conditions. This cause sintering of the PGM, loss of support surface area and phase transformation. Poison also cause loss of activity mainly by blocking the pores leading to active sites or even by direct blockage of the active sites themselves [19-22].

VIII. SUGGESTED MODIFICATIONS IN THE CATALYTIC CONVERTER

As discussed earlier, Catalytic Converter contains precious noble earth metals such as Platinum, Palladium and Rhodium. These metals are very expensive and are present in the earth's crust in very less quantities. Hence an alternative for these metals must be found. The main criteria for the selection of catalysts are as follows:

- Catalyst disintegration temperature
- Desorption temperature
- Saturation pressure
- Back pressure
- Commercial availability and feasibility

Taking these parameters into consideration, activated carbon, BEA zeolite and ZSM-5 zeolite have been evaluated.

- **Zeolite:**

Because of its higher affinity towards absorbing/adsorbing carbon materials, ZSM-5 is an ideal substitute. Additionally, its higher disintegration, desorption temperature and availability shows practical usage. ZSM-5 no matter what the pore size, is able to absorb and adsorb hydrocarbons. Some other carbon based emissions are also absorbed to some extent. 4.6 Angstroms to 5.4 Angstroms is the ideal pore size. It does not deteriorate up to 1100 degrees Celsius temperature. Its limiting factor is calculated as 1.75 which is well in the limits of limiting factors for adsorption-desorption cycle (1.5-2.0). Desorption starts at a temperature, significantly above the light off temperature of the commercially available catalytic converters. It's hardly expensive as compared to noble metals and is available in varied sizes, powders and extrusions [23-31].

- **Sponge Iron:**

Sponge iron has been developed by a process of reducing iron-ore by non-cocking coal; a process developed by an Indian scientist, Bharati. It is used as a raw material in many steel plants. Sponge iron can be used to reduce Nitrogen Oxide (NOx) emissions from the exhaust of IC engines. Its chemical composition is as follows:

- Iron: 93.4%
- Silica: 2.1%
- Carbon: 2.5%
- Residue: 2.0%

It has come into observation that the NO_x conversion efficiency was improved as the CO% was increased. Absolute NOx conversion was relatively constant between 1 and 2.5% CO variation [32-36].

IX.CONCLUSION

The norms on emissions have recently, been made very stringent due to the adverse impact of hazardous effluents on environment, human health and nature. Among all the types of technologies developed so far, use of catalytic converters is the best way to control auto exhaust emission. Three-way catalyst with stoichiometric engine control systems remain the state of art method for simultaneously controlling hydrocarbon, CO and NOx emissions from vehicle. The economic reasons, limited resources of platinum group (noble) metal and some operating limitations of platinum group metal based catalytic converters have motivated the investigation of alternative catalyst materials like activated carbon, zeolites, sponge iron, SCR and TiO2 etc.

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