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The Environment and Catalytic Converter- A Review

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Abstract: The proliferation of automobiles on the road has increased in tandem with the growth of the world economics. This has resulted in a rise in the release of harmful gases from combustion, like carbon dioxide, nitrogen oxide, particulate matter, organic volatile substances, and other pollutants. Transportation adds around 35% of CO, 30% of HC, and 25% of NOy, which are released into the environment every year. These pollutants can be harmful to both the environment and human health. Typically, the air-fuel ratio is used to describe vehicle emissions. Some approaches used to regulate exhaust gas emissions are catalytic converters, PCV (positive crankcase ventilation), EGR (exhaust gas recirculation), engine adjustments, fuel pretreatment, fuel additives, and PCV. One kind of equipment that does this is a catalytic converter that alters harmful exhaust gas pollutants by reducing their volume. Different metal oxides, such as Al_2O_3, TiO_2, and SiO_2, amongst others, as well as catalysts comprised of noble and base metals, are employed in the treatment of automobile exhaust gases. The primary subject of this review is the use of various catalytic converters and the safe removal of noble metals from catalytic converters to reduce different pollution brought on by an increase in vehicle uses.

Keywords: catalytic converter; pollutants; fuel; IC process; redox reaction.

1. Introduction

Air pollution has increased due to increasing industrial activity and the urbanization process. Besides that, the primary root causes of air quality degradation involve increased transportation and automobile gearboxes. In order to meet the conditions stated above, tree cutting has taken place. This would have drawn in automobile exhaust toxic materials from industries and other factors that change air's physical and chemical composition. Thus, pollution is the alteration of the chemical and physical components of air due to external factors. The main causes of air pollution are hydrocarbons, asbestos, or particulate matter like PM10 or PM5. Major industrial plants like cement and paper manufacturing plants discharge toxic substances into rivers and canals, like ozone, chlorine, and dust particles, which can cause diseases in humans as well as nearby living organisms [1, 2]. An additional element, such as vehicle exhausts, releases toxic substances like lead and benzene, which can cause cancer in humans as well as damage the brain [3, 4]. In human beings, asbestos can lead to lung disease. Primary and secondary pollutants are the two distinct groups that can be divided into. The primary pollutant is composed of up substances such as sulfur oxides, carbon, and particulate matter, with nitrogen oxides. Secondary pollutants: Photochemical smog, peroxyacetyl nitrate (PAN), ground ozone, and many more are examples of secondary pollutants. A method for lowering internal combustion engine pollutants is a catalytic converter engine (found in nearly every model of today's cars and trucks). The carbon fuel inside the engine cannot be fully oxidized into carbon dioxide and water since there is a lack of oxygen, which produces toxic byproducts. Catalytic converters serve a purpose in exhaust methods in order to offer a place for the reduction and oxidation of poisonous fuel byproducts, like hydrocarbons, CO (carbon monoxide), and nitrogen oxides, onto less dangerous materials, like CO_2 (carbon dioxide), water vapor, and N_2 (nitrogen gas), VOC (volatile organic compounds) [5-7].

The French mechanical engineer has dedicated his profession to creating enhanced automobile fuel. By 1950, scientists had started to understand how cars polluted the air. Houdry created the catalytic converter with the aim to purify emissions [8, 9]. The leaded gasoline used in 1950 damaged catalytic converters. Scientists developed unleaded petrol by 1975. In 1975, the widespread adoption of catalytic converters in American production cars was witnessed as a result of EPA regulations meant to lower greenhouse gas emissions [10]. All new model vehicles manufactured after 1975 were compelled by the US Clean Air Act to reduce emissions by 75%, so catalytic converters needed to be used to achieve this reduction. Vehicles that do not have catalytic converters release nitrogen oxide, carbon monoxide, and hydrocarbons. The primary cause of ground-level ozone is these gases, which harm plant life and cause environmental pollution. Catalytic converters of some kind are mounted in the exhaust method of all ICE (internal combustion engine) of vehicles, especially buses, trains, generators, and trucks. A catalytic converter fitted to the exhaust method is found in nearly all ICE vehicles. Using basic redox processes, a catalytic converter is a minimalist gadget that lowers the amount of pollution that cars release. In almost 98% of the cases, it produces less harmful gasses from harmful vehicle exhaust. It is composed of a ceramic honeycomb filled with an insulating layer and wrapped in a metal frame. Small wall channels with an aluminum oxide "wash coat" cover the inside of this honeycomb. This covering, a porous substance that expands surface area, enables additional reactions. It is composed of valuable metals like platinum, rhodium, and palladium. In converters, not less than 4 to 9 gm. of these expensive metals are used in one transaction. In catalytic converters, applying a catalyst—typically a costly metal such as platinum or palladium—accelerates the chemical reactions that transform pollutants that enter the air into less harmful byproducts such as CO_2, water-vapor, and N_2 [11]. Taking the lead worldwide, since the 1970s, ordinances requiring cars and smokestacks to have catalytic converters installed have greatly improved the overall quality of the air in urban areas. Catalytic converters remove up to 98% of contaminants from exhaust fumes by filtering them through a metal box covered in catalyst. The reduction reactions employ rhodium and platinum. They reduce exhaust's nitrogen oxides (NOy). They execute this by removing nitrogen atoms from the nitrogen oxide molecules (NO and NO_2). This indicates that oxygen gas (O_2) is produced by free oxygen atoms. Afterward, there is a reaction between the nitrogen atoms attached to the catalyst. Therefore, N_2 is produced. Breathing in both oxygen and nitrogen gases is safe.

Reduction reactions:

$$2NO \rightarrow N_2 + O_2 \tag{1}$$

$$2NO_2 \rightarrow N_2 + 2O_2 \tag{2}$$

Oxidation reactions:

First reaction:

$$O_2 + 2CO \rightarrow 2CO_2 \tag{3}$$

Second reaction:

$$CO_2 + H_2O \rightarrow HC + O_2 \tag{4}$$

In modern times, oxygen sensors are also included inside catalytic converters. It measures the quantity of air and fuel in the exhaust. After combustion, an engine having too much fuel still contains unburned hydrocarbons. Nitrogen oxide formation is increased due to excessive oxygen. The oxygen sensor modifies the amount of fuel that enters the engine if the ratio is off. Palladium and rhodium are two of the most expensive metals in the world. This is because we depend on them, and they are scarce. Catalytic converters are even stolen by robbers in order to obtain the valuable noble metals within them. Most internal combustion engines include catalytic converters installed within their exhaust pipes to lessen the number of harmful emissions and pollutants released into the atmosphere. The catalyst in the converter enables the exhaust fumes to undergo chemical reactions. However, the technology that's currently available today has its limitations. Many of these systems involve expensive platinum group metals, and the catalyst and converters only reach their optimum performance when the engine attains temperatures above 150 degrees. As a result, these systems perform less efficiently when engines are cold, vehicles are moving slowly, or stationary, which is often the case in urban areas. Whether or not the catalyst and reactant belong to the same phase determines whether a homogeneous or heterogeneous catalyst should be used. The catalyst is usually considered to be homogeneous when both are in the identical phase and heterogeneous when they are in different phases. Diesel engines also have catalytic converters, but their operation is substantially different. Rather than using three-way catalysts, diesel engines use two-way (CO and HC) catalysts engineered to cope with their exhaust, which is cooler than gasoline exhaust [17-19].

Various methods are employed in all investigations to regulate the detrimental pollutants from automobiles. According to all of the earlier studies and evaluations, most of them concentrated on use of nanoparticles as catalysts, the most recently developed and improved designs of nano-structured catalytic converters, research on the ROL profile in catalytic converters, and the modification and optimization of catalytic converters are all examples of actions taken to reduce the poisoning effect of lead fuel on catalytic converters by increasing the retention period of exhaust gas in the converter, which increases the amount of time it has to oxidize [20].

The suggested technique is especially effective for reducing the pollution that two-wheelers bring to the environment. "Air pollution occurs when the presence of a foreign substance or a large variation of its components are liable to cause a harmful effect, according to the scientific knowledge of the time, or to create discomfort," the Council of Europe stated on 14th September 1967. Based on this concept, some compounds categorized as pollutants may be trace amounts of the atmosphere's constituents. Consequently, global and local concentration effects need to be thoroughly investigated. For example, the protective shield against UV radiation diminishes when the ozone layer in the troposphere decreases, yet the concentration of ozone in urban areas increases because car pollution causes photochemical reactions that are harmful to human health and accelerate a variety of oxidation and degradation methods, comprising the decomposition of plastics [21]. Another crucial point is that, as scientific knowledge advances, the idea of pollution changes over time. The weight proportion of air to any fuel used in a combustion process is known as the A/F (air-fuel) ratio. When combustion happens, there are two possible outcomes: either controlled combustion, as in the case of an internal combustion engine or manufacturing furnace, or an explosion (such as an explosion from a thermobaric weapon, dust explosion, gas or gaseous explosion, etc.) [22].

The exhaust stream's oxygen level rises, and its CO concentration falls as the A/F ratio falls short of stoichiometry. The oxidation catalysts for palladium and platinum benefit from this highly effective operating environment. In order to enhance oxidation throughout the rich cycle, the catalyst employs cerium to store additional oxygen during the lean cycle.

Whenever the ratio of A/F is greater than stoichiometry, the exhaust has less oxygen and greater amounts of carbon monoxide. As a result, the reducing catalyst's (rhodium) operating environment was incredibly successful. While stored oxygen is let out, the oxidizing catalyst maintains its efficacious activity. An oxygen sensor in the emissions system is part of a closed-loop fuel management system that provides precise air-fuel ratio control. A computerized system monitors the air content and regulates fuel inoculation using an oxygen (λ) sensor near the catalytic converter's input, efficiently managing the A/F ratio. The information from this λ sensor offers feedback to the loop that controls fuel and air injection. A second λ sensor is installed at the catalytic converter's discharge. The engine onboard diagnostics (OBD) system is based on this arrangement [23, 24]. A/F variations can be determined by analyzing the oxygen concentrations before and after the catalyst. Significant changes in A/F at the signal system collapse result. A functional three-way catalysts (TWC) system is demonstrated by the conversion efficacy of TWC and the influence of the A/F ratio on the narrow A/F window at the stoichiometric level. In order to improve efficiency, we concentrated our review on several types of catalytic converters and more recent catalysts that are used in converters.

2. Types of Catalytic Converters:

2.1. Oxidation catalytic converter.

Carbon monoxide gets converted to carbon dioxide using an oxidation catalytic converter, which converts hydrocarbons to carbon dioxide and water. Diesel engines frequently use this converter to cut down on carbon monoxide and hydrocarbon emissions. Palladium and platinum speed up the oxidation process, burning HC and CO to produce CO_2 and water droplets.

$$HC + O_2 \rightarrow CO_2 + H_2O \quad (5)$$

$$2CO + O_2 \rightarrow CO_2 \quad (6)$$

The reduction catalytic converter is required since NOy is already an oxidized molecule that must be inserted upstream of the oxidation system to be converted back into its original components, N_2 and O_2. The first phase in the catalytic conversion process is the reduction mechanism. Rhodium (Rh) and platinum (Pt) are used to decrease the emission of nitrogen oxides. The catalyst emits oxygen in the form of O_2 as soon as the NO_y particles interact with the catalyst bed. The catalyst accomplishes this by splitting the nitrogen atom of the molecule and holding onto it. In order to produce N_2, the nitrogen atoms bound to the catalyst are bonded with each other [25-27].

2.2. Two-way catalytic converter.

Catalytic converters that operate in two directions only carry out the oxidation reaction. Diesel engines use this type of converter because the high NO_x emissions from them need to be removed using particular methods. EGR (Exhaust gas recirculation) [28] and SCR (selective catalytic reduction) systems [29] are two of these methods. In order to produce ammonia, the reagent in the reduction reaction, urea, must be injected into SCR systems and heated to a certain temperature. Because they effectively oxidize CO, HC, and particulate matter (PM), diesel oxidation catalysts (DOCs) are among the more widely used converters for diesel engines. This catalytic converter allows carbon monoxide (CO) to be turned into the less dangerous CO_2 and permits the conversion of unburned hydrocarbons, or HC, into CO_2 and H_2O. Exhaust gases are intended in this design to flow through the substrate that holds the valuable metals palladium and platinum, accelerating the chemical reaction. As the conversion process continues, the temperature of the exhaust gases increases. Because of the tremendous heat generated during this process, the exhaust gases exiting the converter are warmer than the gases going into it. This also shows the need for heat shields on a wide range of equipment. While using a low-fuel mixture, two-way converters function fairly well, and NOy (nitrogen oxides) could not be effectively controlled in three-way converters.

2.2.1. Reaction of two-way catalytic converter.

It responded in two different ways (catalytic conversion): A two-way or "oxidation" catalytic converter performs both functions at once, as explained below:

- Oxidation of CO to CO_2:

$$2CO + O_2 \rightarrow 2CO_2 \tag{7}$$

Carbon dioxide (CO_2) and water (H_2O) are produced by the partial combustion of hydrocarbons and through the oxidation of leftover fuel.

$$C_xH_{2x+2} + \left[{(3x+1)}/{2}\right] O_2 \rightarrow xCO_2 + (x+1)H_2O \tag{8}$$

Diesel engines often use this kind of catalytic converter to cut down on emissions of carbon monoxide and hydrocarbons [30]. Up until 1981, they were also utilized on automobiles powered by gasoline sold in the US and Canada. Their inability to control nitrogen oxides led to their replacement by TWC.

2.3. Three-way catalytic (TWC) converter.

Catalytic converters, in three different ways, permit the transformation of nitrogen oxides (NOy) into oxygen and nitrogen. This type of catalytic converter permits CO to be transformed into CO_2, which is less harmful and helps release CO_2 and H_2O from unburned hydrocarbons (HC) [31, 32]. Three-way additional air converters were a common component of automotive emissions systems in North America at the end of the decade of the 1970s and the beginning of the 1980s. With the help of a sophisticated catalyst and an O_2 control and monitoring system, the three-way converter releases O_2. Using one or more O_2 sensors, the blend of fuels is varied by the system among lean and rich constraints. The most efficient reduction of the three emissions is made possible by this oscillation in conjunction with the O_2 retention and release on the catalyst surface. Modern cars include OBDII diagnostic devices in addition to three-way converters. This mechanism will notify the driver when the converter fails to function at its best efficiency. Some countries (the United States and Canada) have "three-way" catalytic converters in their automobile emission control devices since 1981. Other countries have also passed strict emission laws for vehicles that, in basic terms, mandate the use of TWC in gasoline-based automobiles. Typically, the catalysts for oxidation and reduction are housed together, but sometimes they could be placed apart from others.

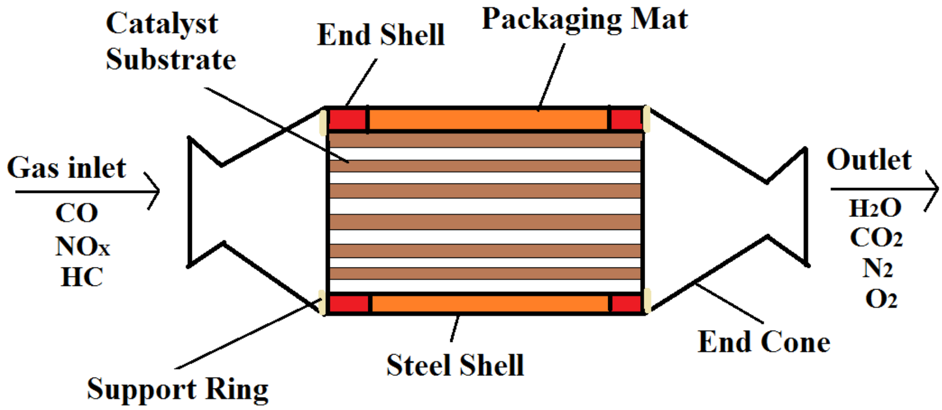

Figure 1. Three functions are carried out concurrently by a three-way catalytic converter.

Three functions are carried out concurrently by a three-way catalytic converter (Figure 1):

→Nitrogen Oxides (NO_y) undergo reduction to N_2 and O_2:

$$2NO_y \rightarrow yO_2 + N_2 \tag{9}$$

→ CO is oxidized to produce CO_2

$$2CO + O_2 \rightarrow 2CO_2 \quad 2CO + O_2 \rightarrow 2CO_2 \tag{10}$$

→Unburned hydrocarbons (HC) oxidize to yield CO_2 and H_2O as follows:

$$H_{2y+2} + \left[{}^{(3y+1)}/_{2}\right] O_2 \rightarrow (y+1)H_2O + yCO_2 \tag{11}$$

These three reactions happen most efficiently when the emission of an engine functioning slightly more than the point of stoichiometric balance is introduced into the catalytic converter. By weight, this value for petrol is between 14.6 and 14.8 parts fuel to 1 part air. The fuel ratios for ethanol, natural gas, and autogas (also known as liquefied petroleum gas, or LPG) are slightly different, and fuel system adjustments are needed when certain fuels are used. Engines with TWC converters typically use several oxygen sensors as part of a computerized feedback loop for the fuel injection system. Carburetor using feedback mixture control was also available, although at an early stage in the three-way converter's adoption. When the air-fuel ratio decreases, three-way catalytic converters have the capacity to store oxygen from the combustion air stream. The stored oxygen is released and consumed when there is inadequate oxygen available from the exhaust stream. When oxygen from NOy reduction is not available or when specific actions, such as powerful acceleration, enrich the mixture to the extent that the converter can deliver oxygen, there is a lack of oxygen available.

2.3.1. Working principle of TWC converter.

HC, NO, and CO make up the waste gases. As outlined earlier, the catalytic converter primarily decreases the release of initial hazardous gases to the minimal standard permitted by using catalyzed chemical processes. Thus, it's essential to carefully consider the layout of ICE before letting the gas out into its surroundings. Another equipment part is the metal shell that covers the catalytic converter's core. This metallic enclosure controls the emissions gas flow across the catalyst bed. The structure of the catalytic converter could not require stainless steel since lower-temperature catalysts are used, even if they are typically used for metal casing [33].

In a nutshell, the three-way system in a TWC converter controls emissions by means of the reduction of NO_y and the oxidation of CO and HC. In contrast, NO_y cannot escape into the atmosphere because two-way catalytic converters only go through two oxidation steps. As a result, the following applications for the TWC converter would be achievable [34]:

Oxidation of HC: In this step, the bonds between the HC and oxygen are split by the oxygen gas present in the exhaust gas. The outcome is CO_2 and water vapors. The following reaction occurs due to benzene getting oxidized.

$$2C_6H_6 + 15O_2 \rightarrow 12CO_2 + 6H_2O \quad (12)$$

Some may use platinum or palladium in this particular method. Palladium would be preferred over platinum despite its similar chemical qualities because of the converter's diminishing efficacy. Because platinum deactivates more quickly than palladium, the converter's efficiency would start to fall off swiftly.

Oxidation of CO to CO_2 with palladium nitrate or platinum catalysts. The equation given below indicates that oxygen gas from exhaust fumes is adsorbed to the honeycomb ceramic surface, loosening the oxygen link and permitting the oxygen atom to combine with CO to yield CO_2.

$$O_2 + CO \rightarrow CO_2 \quad (13)$$

Due to their remarkable resemblances in their physical and chemical characteristics, either palladium or platinum can be used as a catalyst for this type of reaction.

N_2O reduces to yield stable nitrogen and oxygen gas. Instead, rhodium is used since this reaction is a reduction. Because rhodium is a rare category of noble metal, it is generally alloyed with palladium or platinum.

$$yO_2 + N_2 \rightarrow 2NO_y \quad (14)$$

The percentage of oxygen gas in the exhaust gas is a crucial parameter for these redox processes. The system is regarded as lean if extra oxygen gas is in the exhaust gas than necessary. As there is less fuel in the car, oxidation of HC and CO is more likely to occur.

2.3.2. Structure of TWC converters.

Different parts are present in the TWC converter. Some are discussed below.

Substrate, or catalyst core: Catalytic converters frequently consist of an open-channel ceramic monolith or a metallic core substrate comprised of a honeycomb that gives the catalyst zone [35]. The honeycomb ceramic development, which is the most often utilized, is made for the greatest surface area. A higher response rate would be generated by a bigger surface area [36]. The most prevalent monolith type is cordierite (2MgO-2Al2O3 -5SiO2), with a large surface area, an extensive open frontal area, lower heat capacity, and strong mechanical ability. The positioning of the catalyst on the monolith channel is shown in Figure 2.

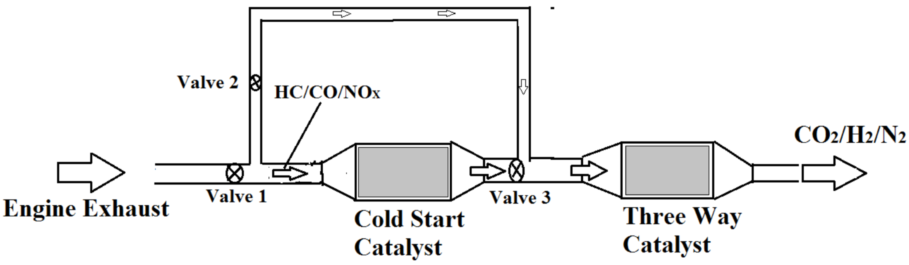

Figure 2. Positioning of the catalyst on the monolith channel.

b. Wash Coat: The honeycomb ceramic configuration's surface is coated with a layer of supported catalysts. The highly porous material is immediately covered with a skinny layer of wet-dependent slurry, which contains zeolites, other metal oxides, and alumina [37]. As γ-Al_2O_3 has excellent adaptability to higher temperatures, it is usually employed to cover the honeycomb ceramic structure [38]. It comprises 20% cerium oxide, 0.1–0.15% catalyst materials, and stabilizers such as barium oxide is utilized [38]. Alkaline and rare earth ions may improve reliability. Cerium oxide is incorporated with the catalyst materials to boost the thermal stability of alumina. Cerium oxide has the ability to store and release oxygen in lean and rich situations, respectively [39].

The wet slurry's thin layer is thereafter dried and heated through calcination, which is a method of heating particles to a high temperature to eliminate volatile compounds. Research has been carried out by applying metal catalysts directly to the honeycomb ceramic surface, avoiding the requirement for drying and calcination. This process uses the electrolysis, or electroplating, technique, where the FeCrAl substrate is electroplated on a nickel oxide (NiO) catalyst with a wash coat of γ-Al_2O_3. The honeycomb ceramic is then submerged in a solution, which shifts alumina ions directly to the honeycomb surface. Consequently, it was discovered that the CO emissions were less than 7 parts per million while the demonstration's catalytic converter was used.

c. Catalyst solutions: Since noble metals may be strengthened to withstand colder temperatures, they are the most frequently utilized heterogeneous catalysts. Another outstanding feature is their capacity to provide comparable catalytic activation in smaller quantities than base metals. Thus, a honeycomb ceramic surface is coated with a couple of noble metals in the form of solutions (like palladium, platinum, and rhodium nitrates). Platinum group metals (PGM), considered the best catalyst solution for a catalytic converter due to their exceptional resistance to chemical assaults, corrosion, and high temperatures, make up this sort of heterogeneous catalyst solution, commonly referred to as a PGM Solution. The PGM Solution is applied to the honeycomb ceramic structure and is reinforced by a layer of supported catalysts made up of heat-resistant metals. It contains platinum, palladium, and rhodium. The type of vehicle, manufacturer, country, year, and other variables all affect how much platinum, palladium, and rhodium are used in auto catalysts [40]. Pt/Rh is five to one in TWC Converters, and Pd/Rh is seven to one. The need for PGM is rising, along with the need for TWC converters. Used catalytic converter recycling provides between 15 and 20 percent of the world's platinum consumption; nevertheless, the quantity of platinum needed to supply this expanding demand is inadequate, which is why platinum reserves are depleted and prices are rising. Consequently, PGM recovery from utilized catalytic converters has been encouraged by the substantial value of PGM and is now widely utilized. The figure shows one common PGM recovery approach. PGM recycling is crucial as it offers another source of income for mining these metals, safeguarding the environment through reduced waste disposal, conserving the exploitation of natural resources, spending less energy, and releasing fewer pollutants.

d. Metal casing: The metal casing is important because of the high-temperature strains and internal mechanical vibrations of the vehicle's frame. Moreover, the exhaust gas stream is directed by a metal casing since gas movement is a scalar value, meaning it is directionless but has a magnitude. High temperatures may vary the physical shape of the substrate quickly; therefore, the ceramic needs to be kept together by a metal shell. This could give rise to irreversible plastic deformations at elevated temperatures. The canning technique can be used to create the metal casing. It is better to have a metal container with thinner walls because it can improve heat transfer to the surroundings while preventing the catalytic converter from overheating beyond 1000°C. Yet, given that high temperatures may cause the catalytic converter to deform, lifespan and efficiency problems have been considered. Another design addresses the possibility of utilizing a support mat as thermal insulation, which can be set up between the steel shell and the honeycomb ceramic. The main purposes of a support mat are to reduce the likelihood of shell deformation, offer thermal insulation, and serve as a mechanical support for the monolith. Shells are a crucial component of the system for exhaust and come in a range of grades of stainless steel. Consequently, the engineer has to prepare for the differences in yield strengths and thermal expansion throughout various materials [41-43].

There is a gap between both catalytic converter components since the steel shell and the substrate have varying thermal coefficients of thermal expansion. During execution, the converter's temperature leads the gap to expand and shrink. By modifying the stainless-steel shell's layout, gap expansion can be reduced. Ferritic steel shells are recommended since they have a 50% lower thermal expansion than austenitic steel shells.

e. Catalysts: Catalysts are typically used to oxidize pollutants, reducing their toxicity. Most frequently, the catalyst is composed of a valuable metal. The most common and active catalyst is platinum. Its cost and unanticipated side effects make it inappropriate for all applications. Two more precious metals that are employed are rhodium and palladium. Platinum and palladium are oxidation catalysts, whereas rhodium is used as a reduction catalyst. Typically, the catalyst is an expensive metal in and of itself. The most active catalyst and most often employed is platinum. Not all applications may justify it due to costs and undesirable extra answers. Two more valuable metals that are used are palladium and rhodium. Palladium and platinum are used as an oxidation catalyst, and rhodium and platinum are used as a reduction catalyst. Cerium, iron, manganese, and nickel are also used, although each has certain limitations [44, 45]. Figure 3 shows the working principle of the catalyst.

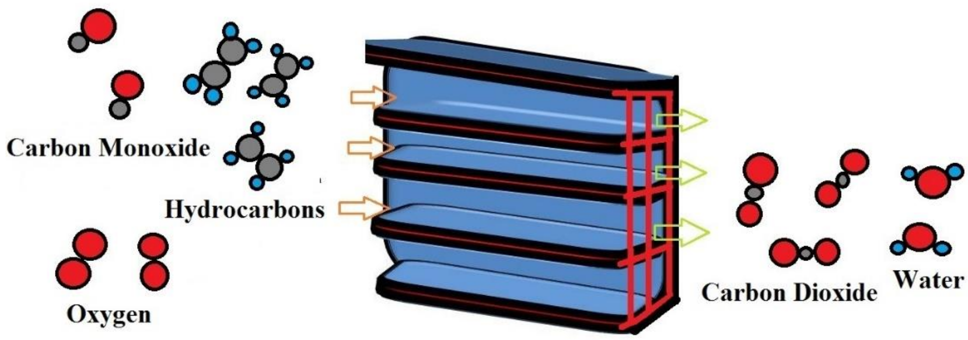

Figure 3. Working principle of catalyst.

One might use a homogeneous or heterogeneous catalyst, though usually depending on whether or not the catalyst and the reactant are in the same phase. When both are in the same phase, the catalyst is said to be homogeneous; when they are in separate phases, they are commonly referred to as heterogeneous. Catalytic converters can and are used in diesel engines, yet their operation differs significantly from that of petrol engines. Diesel engines employ two-way (CO and HC) catalysts, which are particularly made to operate with their exhaust, which is colder than petrol exhaust, in place of three-way catalysts.

2.3.3. Thermodynamics of catalytic converters.

Remember that the laws of thermodynamics are capable of predicting a reaction's or process's chances of happening spontaneously under certain circumstances, not the process's pace. Without a catalyst, the redox reactions below go slowly; even in cases where the processes are thermodynamically advantageous, they cannot take place with enough power. This energy is known as the activation energy (Ea), which is necessary to overcome the first energy barrier that stops the reaction. Although a catalyst does not make a product by itself, it can affect the amount and rate at which the products are formed, which accelerates the reaction by lowering the activation energy [46, 47].

Nitrogen oxides are converted to elemental nitrogen and oxygen:

$$NO_y \rightarrow N_y + O_y \tag{15}$$

Carbon monoxide oxidizes to produce carbon dioxide (CO_2).

$$CO + O_2 \rightarrow CO_2 \tag{16}$$

Hydrocarbons oxidize to produce carbon dioxide (CO_2) and water (H_2O).

$$yCO_2 + 2yH_2O \rightarrow C_yH_{4y} + 2yO \tag{17}$$

2.4. The four-way catalytic (FWC).

Diesel engines have higher thermal efficiency, require less maintenance, and emit less CO_2 than gasoline-powered ones. The great thermal efficiency is due to a high compression ratio (7:1-20:1) and fuel-lean operation, with a high air-fuel ratio (A/F >18) [48, 49]. The A/F mixture is not uniform and contains both fuel-rich and lean zones. Diesel engines emit pollutants due to heterogeneous fuel-air mixtures in the combustion chamber [50]. Emissions comprise more particulate matter (PM) and oxides of nitrogen (NOy) than unburned hydrocarbons (HC) and carbon monoxide (CO). The FWC system combines all the distinct control mechanisms into a single compact device. The FWC technology, which employs a combination of oxidation-reduction catalysts under various techniques, has been examined for its ability to remove CO, HC, PM, and NOy emissions from diesel engines at the same time. In a three-way catalytic converter, the noble metals are used, which are precious. Hence, the FWC is introduced. Toyota pioneered the use of an FWC system in vehicles in 2003, employing a DPNR (diesel particulate-NOy reduction) catalytic converter with a sulfur level of around ten ppm [51]. Millet *et al*. [52] reported the concurrent conversion of a generated gas fusion of CO, HC, NOy, and PM through a single commercialized FWC converter filled with soot. Liu *et al*. conducted a study on non-noble metal catalysts using two layers of $La_{0.6}K_{0.4}CoO_3/Al_2O_3$ and W/H-ZSM5 in an FWC system [53]. Several studies have evaluated Cu-ZSM5 and Ag/Al_2O_3 catalysts for reducing NOy to N_2 [54, 55]. The FWC catalytic mechanism is particularly effective at controlling all diesel engine emissions contaminants in a single modular component. The results of the activity testing of FWC using a mixture of 2 layers of catalysts, oxidation ($La_{0.6}K_{0.4}CoO_3$ SG) and reduction (Cu-ZSM5), indicate superior performance to that of a single mixed layer. The perovskite catalysts are capable of oxidizing CO, HC, and PM, whereas the Cu-ZSM5 catalyst efficiently reduces NO to N_2. The varied layer assembly sequences reveal that the performance of the FWC system improves when the oxidation catalyst is situated on top and the reduction catalyst on the bottom [56].

3. Different Types of Catalysts Used in the Catalytic Converter

3.1. Noble metal catalysts.

In general, a catalytic converter in a car is what uses noble metals (Pt, Pd, Rh, Ir, Au, and Ag) to convert hazardous and poisonous engine gasses into less harmful gases like CO_2 and H_2O. Pt/SnO_2 and Pd/SnO_2 catalysts are the extremely low-temperature CO oxidation catalysts that are most frequently used. Cost is the main limitation of noble metal catalysts. Platinum is employed as a catalyst for both reduction and oxidation, with palladium as a catalyst for oxidation and rhodium as a catalyst for reduction in noble metal catalysts. Gold exhibits a high degree of activity when distributed on suitable metal oxides and combination oxides for the low-temperature oxidation of carbon dioxide. It is known that gold supported on reducible oxides can effectively catalyze CO oxidations at extremely low temperatures—even below zero degrees Celsius. The gold catalytic system might be essential for CO_2 laser air screening, CO sensors, and safety gas masks [57].

3.2. Metal base catalyst.

Co, Ni, Cr, Fe, Mn, and Cu base metal catalysts are the most active. Base metal oxides, such as CCo_3O, CuO, and MnO_2, have been shown to possess considerable catalytic activity per unit surface area for CO oxidation processes. There is a lot of promise for using affordable, highly efficient base metal catalysts in catalytic reactions. Based on their CO oxidation catalytic activity, the components that support base metal oxide catalysts are placed in the following sequence: Fe_2O_3 > $CuCr_2O_4$ > Co_3O_4 > Cu_2O > Fe_2O_3; Cr_2O_3 > V_2O_5 > NiO > MnO > Fe_2O_3. In addition to CO, the supported Cu oxide catalysts have been used to oxidize NH3 and volatile organic compounds (VOCs). Compared to other base metals, copper catalyst mounted on CeO2 or Al2O3 is a significantly more effective catalyst at oxidizing CO. Numerous surface characteristics found on base metals modify compounds' surface energy, influencing their chemical properties. It contains transition metals bound to oxygen atoms. The bimodal pore structure of base metal catalysts will offer a more favorable pore size for reactant chemisorption [58].

3.3. Hopcalite.

In 1920, Lamb, Bray, and Frazer found a mixture of several oxides, including Cu, Mn, Ag, and Co. At room temperature, this catalyst is especially efficient in oxidizing CO. This group includes equal amounts of MnO_2 and Ag_2O along with a four-component combination, known as the typical hoplite, that is composed of 50% MnO_2, 30% CuO, 15% Co_2O_3, and 5% Ag_2O. Hopcalites are quite resilient when it comes to oxidizing CO in dry conditions. The catalytic abilities of catalysts are enhanced by the addition of Au, Ag, Ce, Co, Fe, and Ni. CuMnOx prepared using the sol-gel technique, compared to commercial hoplite, possesses higher catalytic activity. It has also been noted that the crystalline Cu_2MnO_4 is also active in the CO oxidations at low temperatures. It has been examined to replace noble metal materials like platinum (Pt), palladium (Pd), and rhodium (Rh) with novel catalysts [57]. It has been found that compounds like zeolite, nickel oxide, and metal oxide may properly reduce pollutants more so than commercial converters. The process of manufacturing the catalyst has additionally evolved over time with the aim of guaranteeing that it has the desirable characteristics of a good monolith catalyst. The authors suggest that the discovery of stabilizing isolated palladium species on industrially relevant support, including alumina, might affect the field of automotive catalysis, other heterogeneous catalysts, and enhanced comprehension of sintering and dispersion. In reducing the need for pricey precious metals such as platinum or palladium, single isolated transition metal atoms grant the highest degree of atom efficiency. Palladium is used as an oxidation catalyst, rhodium as a reduction catalyst, and platinum as a multipurpose catalyst. Although each has limitations, cerium, iron, manganese, and nickel are utilized. Because nickel reacts with carbon monoxide to produce the toxic nickel tetra carbonyl, nickel is not permitted for usage in the European Union. Japan is the sole nation where copper cannot be utilized.

4. Mechanism Through the Catalytic Converter

The catalytic converter is a part of an automobile's exhaust system that reduces the quantity of pollutants in the vehicle's exhaust emissions. The parts of a catalytic converter include an insulated chamber with a porous substrate, or bed, covered with catalytic. Material that hot exhaust gas must go through in order to be liberated into the atmosphere. The catalyst is one of many metal oxides—mostly palladium or platinum—that are heated to around 500 degrees Celsius (900 degrees Fahrenheit, or 737 Kelvin) by exhaust gas. At this temperature, carbon monoxide and unburned hydrocarbons continue further oxidation, while nitrogen oxides continue chemical reduction in a separate chamber employing a different catalyst.

Issues with catalysts include their intolerance for leaded fuels (lead-free petrol is required; otherwise, the catalyst's beads would get coated with lead and stop working) and the requirement to avoid overheating. Nevertheless, the transformation of carbon monoxide to carbon dioxide leads to a rise in greenhouse gases, and eliminating hazardous gases reduces non-toxic gases, leading to the greenhouse effect.

$$HC + O_2 \rightarrow CO_2 + H_2O \qquad (18)$$

This reaction is the oxidization of the hydrocarbon.

$$2CO + O_2 \rightarrow 2CO_2 \qquad (19)$$

This reaction is the oxidization of Carbon monoxide.

$$2NO \rightarrow N_2 + O_2 \qquad (20)$$

This process leads to a reduction in nitrogen oxide. We may decrease the activation energy of the HC, CO, and NO so that they react more quickly and generate fewer dangerous substances by utilizing both a reduction and an oxidizing catalytic converter. The replies are caused by a catalyst that takes place within the catalytic converter. The initiator is often referred to as a heterogeneous, or contact, catalyst when it exists in a phase different from the reactants. Materials that possess the ability to adsorb liquid or gas molecules onto their surfaces are known as contact catalysts. Diesel engines operate cooler than petrol engines, resulting in catalytic converters less efficient. Higher temperatures are ideal for catalytic converter performance. Particles like soot are generated by diesel engines as well. However, ultra-fine particle emissions can be reduced by up to 99% by adding a diesel particulate filter (DPF) to the catalysts within the catalytic converter.

5. Extraction of Platinum Group Metals from Catalytic Converters

Platinum group metals (PGMs) are highly stable chemical substances under various environmental conditions, making them valuable in chemical engineering and chemistry.

The PGMs—platinum, palladium, rhodium, ruthenium, osmium, and iridium—have long been desirable and have become highly esteemed in a variety of industrial fields. A contemporary three-way auto-catalyst is composed of a cordierite ($2MgO.2Al_2O_3.5SiO_2$) skeleton with a honeycomb structure. This is covered in a thin layer of washcoat (90% γ-Al_2O_3), catalytic metals (PGMs), and additional additives (oxides of Ce, Zr, La, Ni, Fe, and alkaline earth metals).

The manufacturer, the vehicle's specifications, such as engine power, weight, fuel type (diesel or petrol), and the necessary catalytic functions, all affect the number of PGMs in catalysts [59]. A three-way automotive catalytic converter is estimated to contain 3.7–7 g Pt, 1.5–5.0 g Pd, and 0.8–1.5 g Rh [60]. The International Energy Agency (IEA) estimates that 6.6 million EVs (electric vehicles) were bought in 2021. That number is predicted to rise in the upcoming years as EV sales finally shift from internal combustion engines (ICEs) to fuel cells or batteries. From 2017 to 2022, the number of electric and hybrid vehicles sold increased from approximately one million to over ten million in just five years. Because battery-electric vehicles have a lower total cost of ownership than alternatives like hydrogen and e-fuels, this will likely be the main trend in light vehicles in the near future. Hydrogen or e-fuels, however, can be good substitutes for batteries since they are heavy and cannot be readily used to power ships, airplanes, or heavy-duty vehicles. PGMs are required by some EVs that are based on alkaline fuel cells (AFC), direct methanol fuel cells (DMFC), phosphoric acid fuel cells (PAFC), and polymer electrolyte membrane fuel cells (PEMFC). Although platinum and palladium are not essential components of batteries, they will likely be required by next-generation lithium-ion battery technology in order to improve overall battery performance [61-63].

Rather, PGMs are primarily used in the technologies for producing green hydrogen through water electrolysis, which is currently the most promising method of producing green hydrogen that may be without greenhouse gas emissions. Renewable energy sources drive this method. Alkaline water electrolysis (AWE) and proton exchange membrane water electrolysis (PEMWE) are the two low-temperature water electrolysis techniques currently in use in the commercial world [64]. On the other hand, high-temperature solid oxide electrolysis (SOE) equipment cannot be scaled up due to high degradation and thermal variations resulting in thermomechanical stress in the cell.

PGM catalysts such as rhodium (Rh), palladium (Pd), and platinum (Pt) are commonly used in automotive catalytic converters. A cordierite shell ($2MgO•2Al_2O_3•5SiO_2$) with a honeycomb structure and cell density that vary between 60 to 120 cells per square centimeter usually makes up these catalytic converters. The partitions that divide the cells are roughly 150 µm thick [65- 68].

The walls of the cordierite framework receive a smooth-textured surface coating that makes up between 20 and 30 percent of the catalyst's total weight. It is anticipated that this coating will have certain properties, such as the ability to promote noble metals in an organized manner and exhibit chemical inertness in reaction environments. These requirements are satisfied by using a variety of materials, including alkaline earth metals, oxides such as CeO_2, La_2O_3, ZrO_2, BaO, TiO_2, Y_2O_3, NiO, WO_3, and gamma alumina (γ-Al_2O_3) Figure 4 [68].

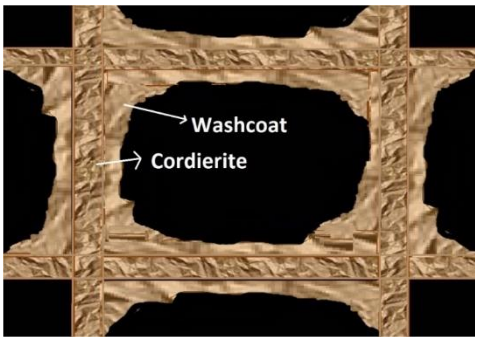

Figure 4. A catalytic converter's cordierite shell is coated with γ-Al_2O_3. Based on analysis from [66].

Utilizing solutions containing H_2PtCl_6 x $6H_2O$ (hexachloroplatinic acid), $PdCl_2$ (palladium chloride), and rhodium chloride ($RhCl_3$), platinum group metals are impregnated onto the γ-Al_2O_3 surface. Catalytic efficiency loss that occurs over a vehicle's lifetime is a well-known phenomenon. Sulfur compounds from diesel fuel can build up on an aging catalytic converter's surface, reducing the converter's catalytic efficiency [69]. Furthermore, higher operating temperatures may cause platinum nanoparticles to clump together, decreasing their effective surface area (agglomeration). A decline in conversion efficiency is directly correlated with decreased surface area of precious metals associated with the catalytic processes with exhaust emissions [70].

Major quantities of organic sulfur compounds can be found in petrol and diesel fuels; these compounds burn in the engine to produce different sulfur dioxide gases [71]. These sulfur compounds can quickly impair the palladium-based catalysts' ability to catalyze reactions.

PGMs are extracted from catalytic converters using a variety of techniques, such as pyrometallurgical and hydrometallurgical techniques alongside afterward element recovery [72-79]; biological methods [80, 81]; leaching methods [82-85]; solvometallurgical methods [86-88]; molecular recognition technology [89-92] and biometallurgical methods [93-95]. When combined, these techniques guarantee efficient and environmentally responsible PGM processing. The choice of a particular technique mostly depends on elements like PGM quantities and the existence of other substances.

In addition, new catalyst processing approaches have been developed to be more economical and environmentally sound [96, 97]. One such technique, for example [98], dissolves platinum in aqueous solutions despite using hazardous chemicals. The procedure entails the interplay between magnesium vapor and platinum group metals, forming PGM-Mg alloy. The alloy is then chlorinated using metal chlorides, such as copper chloride. Dissolving compounds containing platinum in a hydrochloric acid (HCl) solution is possible without additional oxidizing agents.

A separate study [99] describes an alternative method for extracting PGMs from catalytic waste. This process directly concentrates these metals via magnetic separation from catalytic converter wastage. Using a disproportionation reaction, ferromagnetic iron is applied to PGM particles through exposure to ferric chloride vapor in this procedure.

$$Fe_{(s)} + FeCl_{2\,(g)} \rightarrow FeCl_{3\,(g)} \qquad (21)$$

As a result, the PGMs take on magnetic characteristics that enable them to be effectively separated from non-magnetic elements, such as the catalytic converter's ceramic shell [100].

5. Future Aspects

The need for catalytic converters for hybrid vehicles, which have both gasoline/diesel engines and electric cars, might seem unusual as they have a tiny internal combustion engine called a range extender that helps generate strength when the battery gets low. In order to decrease emissions, these engines require catalytic converters. In addition, fossil fuels and greenhouse gases are manufactured during the electric car's manufacturing process. Therefore, hybrid vehicles become even more environmentally benign when catalytic converters are installed.

There are several benefits to installing catalytic converters in hybrid vehicles, i.e. (i) Reduced emissions of hazardous gases: Catalytic converters have been designed to transform poisonous gases, such as nitrogen oxide, hydrocarbons, and carbon monoxide, into harmless ones, assisting in creating an environment that is cleaner and better; (ii) Conforming with regulations: Vehicle emissions are governed by stringent laws in numerous countries. Environmental norms and laws are met whenever hybrid automobiles have catalytic converters; (iii) Lengthening the battery's life: Range extenders having catalytic converters can prolong the battery's life by decreasing the need for charging, particularly on long journeys.

Studies are investigating catalysts based on non-precious metals, like iron, cobalt, and nickel, in an effort to alleviate concerns about PGM scarcity and cost. Nanotechnology is being used to produce catalysts with increased surface area and reactivity. Catalytic performance may be improved, and reliance on limited resources may be reduced with the aid of nanomaterials. Real-time assessment of catalytic converter performance can be achieved by integrating advanced sensors and monitoring systems. This enables the application of adaptive control strategies in various operating conditions, maximizing the efficiency of pollutant conversion. Advanced monitoring makes a longer converter lifespan and faster maintenance possible, which makes it simpler to spot catalyst degradation or problems early on.

At the forefront of catalyst design innovations is catalytic material structure optimization. This includes modified nanostructures and composite materials to increase catalytic activity and stability. Research is being conducted to create effective catalysts over a wider temperature range to guarantee efficient operation in both cold-start conditions and high-temperature operations. As the automotive industry transitions to electric and hybrid vehicles, research examines the role of catalytic converters in these newly developed technologies. The top priorities are reducing emissions from non-combustion resources and ensuring that emerging powertrain technologies are compatible. Future developments will concentrate on increasing the recyclable nature of catalytic converters, reducing their environmental impact, and reducing their need for new raw materials. The objective is to develop catalyst compositions that are as cost-effective as feasible without compromising performance, thereby raising the catalytic converter technology's affordability and accessibility. Precious metals like rhodium, palladium, and platinum can be detected in catalytic converters and can be recycled and used again. Catalytic converter recycling is an increasing industry due to the expensive nature and limited supply of these metals. In order to recover the precious metals, the catalyst has to be taken out of the substrate and purified. Though the substrate is typically less valuable than the catalyst, it can still be recycled.

6. Conclusion

The results indicate a correlation between exhaust systems missing a catalytic system or experiencing catalyst failure and releasing potentially dangerous gasses. As demonstrated, with proper application of the catalyst, it is possible to reduce NOy, PM, CO_2, and VOC emissions among additional toxic pollutants. This research also suggests a catalyst monitoring paradigm that makes use of the catalyst efficiency sensor. This reduces the expense of treating respiratory conditions brought on by pollution and allows better planning, upkeep, or renewal of the catalytic system, thereby lowering the emission of toxic pollutants and enhancing the quality of life. This study suggests that the monitoring system should be simple to build since NOy sensors are commonly utilized in the automotive industry due to their small size, quick reaction, low cost, extended service life, and capacity to function at low and high temperatures. The findings show an association between the emissions of harmful gases and exhaust systems without a catalytic system or with catalyst failure. Addressing the population's respiratory health is the value found. As shown, with suitable application of the catalyst, among other polluting substances, reducing the emission levels of NOy, CO_2, and VOC is feasible. Additionally, this paper proposes a model for monitoring the catalyst using the catalyst efficiency sensor. This allows for better planning, maintenance, or replacement of the catalytic system, reducing the emission of polluting gases and improving quality of life while lowering the cost of treating respiratory issues caused by pollution.

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Conflict of Interest

The authors declare that they have no conflict of interest.

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