Exhaust emissions of much concern are Hydrocarbon (HC), Carbon Monoxide (CO) and Nitrogen Oxide (NOx) from the automotive vehicles. Catalytic converter oxidizes harmful CO and HC emission to CO and H₂O in the exhaust system and thus the emission is controlled. There are several types of problems associated with noble metal based catalytic converter. These factors encourage for the possible application of non noble metal based material such as copper as a catalyst, which may by proper improvements be able to show the desired activity and can also offer better durability characteristics due to its poison resistant nature. This paper review most common technology available and its alternatives.

KEYWORDS: Catalytic converter; non-noble material.

I. INTRODUCTION
In internal combustion engines, the time available for combustion is limited by the engine’s cycle to just a few milliseconds. There is incomplete combustion of the fuel and this leads to emissions of the partial oxidation product, carbon monoxide (CO), oxides of nitrogen (NOx) and a wide range of volatile organic compounds (VOC), including hydrocarbons (HC), aromatics and oxygenated species. These emissions are particularly high during both idling and deceleration, when insufficient air is taken in for complete combustion to occur. Carbon monoxide is a product of a partial combustion of hydrocarbons in fuel. It is always present when there is a lack of oxygen during combustion and thus directly dependent on the applied engine air/fuel ratio. There are several paths that cause hydrocarbons in the exhaust. The most obvious is, as in the case of CO, a lack of oxygen when the air/fuel mixture is rich. The other reasons that can cause hydrocarbon emissions even with lean mixtures are crevices (piston top, threads around the spark plug), the quench layer (due to a lower temperature of the cylinders’ walls), porous deposits, and absorption by oil. NOx is formed during combustion in the engine when oxygen reacts with nitrogen because of a high combustion temperature.

II. EXHAUST EMISSION CONTROL TECHNIQUE
A. Exhaust gas recirculation (EGR)
In internal combustion engines, exhaust gas recirculation (EGR) is a nitrogen oxide (NOx) emissions reduction technique used in petrol/gasoline and diesel engines. EGR works by re-circulating a portion of an engine's exhaust gas back to the engine cylinders. In a gasoline engine, this inert exhaust displaces the amount of combustible matter in the cylinder. In a diesel engine, the exhaust gas replaces some of the excess oxygen in the pre-combustion mixture. Because NOx forms primarily when a mixture of nitrogen and oxygen is subjected to high temperature, the lower combustion chamber temperatures caused by EGR reduces the amount of NOx the combustion generates. The exhaust gas, added to the fuel, oxygen, and combustion products, increases the specific heat capacity of the cylinder contents, which lowers the adiabatic flame temperature. In a typical automotive spark-ignited (SI) engine, 5 to 15 percent of the exhaust gas is routed back to the intake as EGR. The maximum quantity is limited by the requirement of the mixture to sustain a contiguous flame front during the combustion event; excessive EGR in poorly set up applications can cause misfires and partial burns.

B. Positive Crankcase Ventilation (PCV)
During normal compression stroke, a small amount of gases in the combustion chamber escapes past the piston. Approximately 70% of these “blow by” gases are unburned fuel (HC) that can dilute and contaminate the engine oil, cause corrosion to critical parts, and contribute to sludge build up. At higher engine speeds, blow by gases increase crankcase pressure that can cause oil leakage from sealed engine surfaces.

The purpose of the Positive Crankcase Ventilation (PCV) system is to remove these harmful gases from the crankcase before damage occurs and combine them with the engine's normal incoming air/fuel charge.

C. Catalytic converters
In chemistry, a catalyst is a substance that causes or accelerates a chemical reaction without itself being affected. Catalysts participate in the reactions, but are neither reactants nor products of the reaction they catalyze. A catalytic converter reduces temperature at which CO & HC convert into CO and H₂O. Generally catalytic converters uses platinum group of noble metals.

III. HOW CATALYTIC CONVERTER WORKS?
In the catalytic converter, there are two different types of catalyst at work, a reduction catalyst and an oxidation catalyst. Both types consist of a ceramic structure coated with a metal catalyst, usually platinum, rhodium and/or palladium. The idea is to create a structure that exposes the maximum surface area of catalyst to the exhaust stream.

The reduction catalyst is the first stage of the catalytic converter. It uses platinum and rhodium to help reduce the NOx emissions. When an NO or NO₂ molecule contacts the catalyst, the catalyst rips the nitrogen atom out of the molecule and holds on to it, freeing the oxygen in the form of O₂. The nitrogen atoms bond with other nitrogen atoms that are also stuck to the catalyst, forming N₂. For example:

\[2\text{NO} \rightarrow \text{N}_2 + \text{O}_2 \text{ or } 2\text{NO}_2 \rightarrow \text{N}_2 + 2\text{O}_2\]
The oxidation catalyst is the second stage of the 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 with the remaining oxygen in the exhaust gas. For example:

\[ 2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2 \]

There are two main types of structures used in catalytic converters -- honeycomb and ceramic beads. Most cars today use a honeycomb structure.

A. Types of converter
   a) Monolithic converters
      The monolithic catalytic converter uses ceramic material made in a honeycomb pattern to control the exhaust gases flowing through it. The catalytic elements in the ceramic are encased in stainless steel. When ceramic beads are used instead of a honeycomb structure, the unit is known as a pellet catalytic converter.
   b) Oxidation Converter / two-way catalytic converter
      This type is also known as a two-way catalytic converter, because it can only operate with hydrocarbons (unburned fuel) and carbon monoxide (caused by partially-burned fuel). Oxidation converter elements are usually covered in platinum.
   c) Reduction Converter / Three-way catalytic converter
      Similar to the oxidation converter, the reduction catalytic converter helps eliminate hydrocarbons and carbon-monoxide emissions, plus oxides of nitrogen emissions, or NOx. NOx emissions are produced in the engine combustion chamber when it reaches extremely high temperatures more than 2,500 degrees Fahrenheit, approximately.
   d) Dual-Bed Converter
      This is perhaps one of the most efficient converters. The dual-bed uses a combination of two and three way catalytic converters housed in a single unit. Both converters are connected through a chamber where incoming emissions are mixed. An air line plugs into the mixing chamber to force air into the chamber to react with the combined emissions and help reduce hydrocarbon and carbon-monoxide emissions.

B. Automobile exhaust catalysts
   Conversion efficiency of a catalytic converter is low at low temperature and efficiency increases as exhaust temperature increase. It means that catalytic converter is less effective during cold starting, when pollution constituents in the exhaust gas are maximum. The technology race to develop suitable methods to control cold start HC’s included both catalytic and some unique system approaches:
   - Close-coupled catalyst;
   - Electrically heated catalyzed metal monolith;
   - Hydrocarbon trap;
   - Chemically heated catalyst;
   - Exhaust gas ignition;
   - Pre-heat burners;

   The concept of using a catalyst near the engine manifold or in the vicinity of the vehicle firewall to reduce the heat-up time has been practiced. Electrically heated catalyst are used to overcome the cold temperatures during start up & provide heat to the exhaust gas or the catalytic surface using resistive materials and a current/voltage source. Another approach investigated was the hydrocarbon adsorption trap in which the cold HC’s are adsorbed and retained, on an adsorbent, until the catalyst reaches the light off temperature. All of these approaches contain under floor catalysts of various compositions. The chemically heated catalyst uses highly reactive specie, usually H\text{3}, which is generated in a device onboard, the vehicle. Since this reacts at room temperature over the catalyst, the heat of reaction warms up the catalyst to react during cold start. The exhaust gas igniters involve placing an ignition source (e.g. glow plug) in between two catalysts. During cold start, the engine is run rich and a small amount of air is injected to make the mixture flammable. This is then ignited and heats the catalyst.

   The pre-heat burner uses the gasoline fuel in a small burner placed in front of the catalyst. The burner is turned ‘on’ during cold start and the heat generated warms up the catalyst. So, the catalyst is hot when the cold exhaust from the manifold reaches the catalyst.

IV. WHY CATALYTIC CONVERTER BASED ON NON-NOBLE MATERIAL?
Generally catalytic converter uses platinum group of metals like Pt, Pd and Rh. These noble metals are known to promote the oxidation processes. There are several types of problems associated with noble metal based catalytic converter. The failure of catalytic converter may be due to following factors:
   - Converter meltdown
   - Carbon deposit
   - Catalyst fracture
   - Poisoning

The converter becomes too hot and melts inside so that the small particles come apart on the inside. The broken pieces can move around and get in position to plug up the flow of exhaust through converter. This meltdown is caused by converter having too much work to do. There is too much HC or CO to clean up. The converter doesn’t know how to stop; It keeps up its reactions. The inside chamber of the catalytic converter gets coated with some contamination, like carbon, oil, coolant or other stuff, or they are just melted enough and reduce surface area. Poor engine performance may happen as a result of a clogged or choked converter. Symptoms of clogged converter include loss of power at higher engine speeds, hard to start, poor acceleration and fuel economy. A red hot converter indicates exposure to raw fuel causing the substrate to overheat. A critical review of all these factors infers the following important facts: It is still difficult to achieve long term durability of converter under the conditions of normal vehicle use.
V. NON-NOBLE MATERIAL BASED CATALYST
A. Iron-exchange zeolite
Zeolite is crystalline, hydrated alumina silicates, formed in nature or can be synthesized. Zeolite is formed of Al₂O₃ and SiO₂ bonded together via the oxygen atoms and assembled in such a way as to constitute cavities, cages and channels, uniformly penetrating the entire lattice volume and thus generating a high internal surface area available for adsorption and catalytic processes. The properties of zeolites or molecular sieves which make them particularly suitable for use as catalysts are their large surface area, well defined and uniform pore structure, well defined crystal structure, temperature stability, easy ion-exchange method and reproducibility in various forms. The iron-exchanged X-zeolite (Fe±X) has been developed by ion-exchanging of 13X zeolite in pelleted form (3.0 mm average diameter) with anhydrous Ferric chloride (FeCl₃). The amount of the metal salt used for ion-exchanging is 5% of the mass of X-zeolite.

Randip K. Das et al. conducted experiment with the exhaust of a stationary, 4-stroke, 3-cylinder, water-cooled, SI engine with a total displacement volume of 800 cc and coupled to a hydraulic dynamometer. Maximum conversion efficiencies of 55.8% and 57.4% were recorded for NOx and CO, respectively. The catalyst also maintains its high performance through a wide range of temperatures.

B. TiO₂ & CoO
M A Kalam et al. presented characteristics of a new catalytic converter (catco) to be used for natural gas fuelled engine. The catco were developed based on catalyst materials consisting of metal oxides such as titanium dioxide (TiO₂) and cobalt oxide (CoO) with wire mesh substrate. Both of the catalyst materials (such as TiO₂ and CoO) are inexpensive in comparison with conventional catalysts (noble metals) such as palladium or platinum. The TiO₂/CoO based catalytic converter and a new natural gas engine such as compressed natural gas (CNG) direct injection (DI) engine were developed under a research collaboration program. The original engine manufacture catalytic converter (OEM catco) was tested for comparison purposes. The OEM catco was based on noble metal catalyst with honeycomb ceramic substrate. It is experimentally found that the conversion efficiencies of TiO₂/CoO based catalytic converter are 93%, 89% and 82% for NOx, CO and HC emissions respectively. It is calculated that the TiO₂/CoO based catalytic converter reduces 24%, 41% and 40% higher NOx, CO and HC emissions in comparison to OEM catco respectively.

C. Copper as in-cylinder catalyst
In order to investigate the application of catalytic combustion, Ramesh B. Poola et al. carried out experiment with various catalysts; such as copper, chromium, and nickel, was coated on the combustion chamber wall for determining their effect on engine performance, combustion, and emission characteristics. The effect of lean fuel-air mixture and higher compression ratio was studied with the best catalyst among all the catalyst tested. These catalysts were deposited on the top of piston and cylinder head surface, using standard electroplating process. Copper was coated by using a cyanide copper bath which produces a coating of porous nature and a fine deposition of metal on surface. Among the different catalysts investigated, copper was found very effective in reducing both HC and CO emissions, and brake thermal efficiency was also improved. At a high CR of 9:1 and with a lean mixture (A/F=15.7), copper catalyst increases the absolute brake thermal efficiency from 17.7% to 22.8%, decreases HC emissions from 3200 to 2300 ppm, and lowers CO emissions from 3.6 to 0.25% by volume when compared to the normal engine (CR=7.4, A/F=13.2) at 2 kW, 3000 rpm.

VI. CONCLUSION
This paper reviewed the most common existing technologies available to reduce exhaust emission and catalytic exhaust after treatment. Methodologies to increase temperature of catalytic converter during cold starting were also discussed. Finally, current research going on to replace noble catalyst were discussed.

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