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Automotive catalytic converter: Review (Current status and some perspectives)

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Abstract
Automotive three-way catalysts (TWCs) have represented over the last 25 years one of the most successful stories in the development of catalysts. The aim of this paper is to know about the technology for abatement of exhaust emissions. In the current understanding of TWCs, the specific role of the various components, new automotive catalysts-ceramic material, which can meet future highly demanding pollution abatement at low cost, has to be considered. In this paper, exhaust and environment, legislation and some controlling techniques for gasoline engine are discussed. Attention is focused on three-way type of catalysts; the paper is focused essentially on the catalytic aspects of pollution abatement, catalysts, etc.

Keywords: exhaust emissions, honeycomb monolith, pallets, three-way catalyst

1. Introduction

Air pollution generated from mobile sources is a problem of general interest. In the last 60 years the world vehicle fleet has increased from about 40 million vehicles to over 700 million; this figure is projected to increase to 920 million by the year 2011. The environmental concern originated by mobile sources is due to the fact that the majority of engines employ combustion of fuels derived from crude oil as a source of energy. Burning of hydrocarbon (HC) ideally leads to the formation of water and carbon dioxide; however, due to non-perfect combustion control and the high temperatures reached in the combustion chamber, the exhaust contains significant amounts of pollutants which need to be transformed into harmless compounds.

2. Constituents of Exhaust gas pollution

A brief overview of major pollutants stemming from the gasoline engines are given here.

Carbon monoxide: Results from incomplete combustion of fuel. CO reduces the ability of blood to carry oxygen and can cause headaches, respiratory problems and, at high concentrations, even death.

Unburned Hydrocarbons (UBHC): HCs are emitted from vehicle exhausts as unburnt fuel and also through evaporation from the fuel tank, from the nozzle when you fill up and also at stages through the fuel supply chain. They react with NOx in sunlight to produce photochemical oxidants (including ozone), which irritate the eyes and throat.

Oxides of nitrogen: Oxides of nitrogen that are of the largest concern in the automotive applications are nitric oxide (*NO*), nitrogen dioxide (*NO*2) and nitrous oxide (*N*2*O*).The first two are usually understood under the term NOx. They are also a direct product of the combustion in the engine, while *N*2*O* is primarily a product of catalytic converter under some operating conditions. NOx is formed during combustion in the engine when oxygen reacts with nitrogen because of a high combustion temperature. It is therefore an unwanted secondary product of combustion. The amount of produced NOx is very dependent on the combustion temperature (engine load). The *NO*2/*NO* ratio is very low for gasoline engines, less than 2%. Some additional *NO*2 can also be created by the catalytic converter. While *NO* is odourless, colourless and relatively non-toxic, *NO*2 is reddish-brown, pungent and very toxic. It affects respiratory tract, damages lung tissue and increases airway resistance. It may also interfere with oxygen transport in blood via reaction with haemoglobin; provoke coughing, running noses, bronchitis, etc. The current legislation aims at NOx emission levels, while it isto be expected that also *N*2*O* will be included in the future as it is a strong greenhouse gas. NOx is also involved in secondary pollution (smog, depletion of the ozone layer). It is also, together with sulphur oxides, responsible for acid rains.

Lead oxide: For powering automobiles, the octane number has to be raised. To do this a compound of lead called Tetraethyl lead (Tel) is used. This introduces lead into the petrol raising the octane number and functions as lubricant for valve seats. The combustion of petrol is inefficient in most cases and gases and particulates are emitted as exhaust gas/particulate. One of the perturbing ones is lead particulate, which has detrimental physiological effects. Ingestion of lead has been link to several physiological disorders in man such as interference with IQ of children of school age, gastrointestinal disorder, nausea, circulatory collapse, fatigue, blindness, CNS disorder, anaemia etc.

Sulphur Oxides: The formation of Sulphur Oxides (SOx) in exhaust gases is caused by the oxidation of the sulphur in the fuel into SO_2 and SO_3 during the combustion process. In the atmosphere however, SOx combines with moisture to form H2SO4, which then falls as acid rain, and has been linked to environmental damage.

Particulate matter: Particulate matter is partly burned fuel associated mainly with diesel engines. PM10s are very small particles that can pass deep into the lungs causing respiratory complaints.

3. Legislation

In Europe, the first base directive 70/220/EEC was introduced in 1970 to set the emission limits for CO and HC.

Standards have involved since, leading to the consolidating directive 1/441/EECin 1991, which set EURO I standards. EURO I was the first mandatory European vehicle emission standard. In 1992 catalytic converters became compulsory on all new cars sold in Europe. Euro V standard is currently enforced and Euro VI standard will come to power in 2014.

4. Emission Control Techniques

The need to control the emissions from automobiles gave rise to the computerization of the automobile. Hydrocarbons, carbon monoxide and oxides of nitrogen are created during the combustion process and are emitted into the atmosphere from the tail pipe. There are also hydrocarbons emitted as a result of vaporization of gasoline and from the crankcase of the automobile. The clean air act of 1977 set limits as to the amount of each of these pollutants that could be emitted from an automobile. Some of the more popular emission control devices installed on the automobile are:

EGR valve, Catalytic Converter, Air Pump, PCV Valve, Charcoal Canister etc.

PCV System: The purpose of the positive crankcase ventilation (PCV) system is to take the vapors produced in the crankcase during the normal combustion process, and redirecting them into the air/fuel intake system to be burned during combustion. These vapors dilute the air/fuel mixture, they have to be carefully controlled and metered so as not to affect the performance of the engine. This is the job of the positive crankcase ventilation (PCV) valve. At idle, when the air/fuel mixture is very critical, just a little of the vapors are allowed in to the intake system. At high speed when the mixture is less critical and the pressures in the engine are greater, more of the vapors are allowed in to the intake system. When the valve or the system is clogged, vapors will back up into the air filter housing or at worst; the excess pressure will push past seals and create engine oil leaks. If the wrong valve is used or the system has air leaks, the engine will idle rough, or at worst engine oil will be sucked out of the engine.

EGR Valve: The purpose of the exhaust gas recirculation valve (EGR) valve is to meter a small amount of exhaust gas into the intake system; this dilutes the air/fuel mixture so as to lower the combustion chamber temperature. Excessive combustion chamber temperature creates oxides of nitrogen, which is a major pollutant. While the EGR valve is the most effective method of controlling oxides of nitrogen, in it's very design it adversely affects engine performance. The engine was not designed to run on exhaust gas. For this reason the amount of exhaust entering the intake system has to be carefully monitored and controlled. This is accomplished through a series of electrical and vacuum switches and the vehicle computer. Since EGR action reduces performance by diluting the air /fuel mixture, the system does not allow EGR action when the engine is cold or when the engine needs full power.

Evaporative Controls: Gasoline evaporates quite easily. In the past these evaporative emissions were vented into the atmosphere. 20% of all HC emissions from the automobile are from the gas tank. In 1970 legislation was passed, prohibiting venting of gas tank fumes into the atmosphere. An evaporative control system was developed to eliminate this source of pollution. The function of the fuel evaporative control system is to trap and store evaporative emissions from the gas tank and carburetor. A charcoal canister is used to trap the fuel vapors. The fuel vapors adhere to the charcoal, until the engine is started, and engine vacuum can be used to draw the vapors into the engine, so that they can be burned along with the fuel/air mixture. The tank has to have the space for the vapors to collect so that they can then be vented to the charcoal canister. A purge valve is used to control the vapor flow into the engine. The purge valve is operated by engine vacuum. One common problem with this system is that the purge valve goes bad and engine vacuum draws fuel directly into the intake system. This enriches the fuel mixture and will foul the spark plugs. Most charcoal canisters have a filter that should be replaced periodically. This system should be checked when fuel mileage drops.

Air Injection: Since no internal combustion engine is 100% efficient; there will always be some unburned fuel in the exhaust. This increases hydrocarbon emissions. To eliminate this source of emissions an air injection system was created. Combustion requires fuel, oxygen and heat. Without any one of the three combustions cannot occur. Inside the exhaust manifold there is sufficient heat to support combustion, if we introduce some oxygen than any unburned fuel will ignite. This combustion will not produce any power, but it will reduce excessive hydrocarbon emissions. Unlike in the combustion chamber, this combustion is uncontrolled, so if the fuel content of the exhaust is excessive, explosions that sound like popping will occur. There are times when under normal conditions, such as deceleration, when the fuel content is excessive. Under these conditions we would want to shut off the air injection system. This is accomplished through the use of a diverter valve, which instead of shutting the air pump off diverts the air away from the exhaust manifold. Since all of this is done after the combustion process is complete, this is one emission control that has no effect on engine performance. The only maintenance that is required is a careful inspection of the air pump drive belt.

Catalytic Converter: Automotive emissions are controlled in three ways; one is to promote more complete combustion so that there is less by products. The second is to reintroduce excessive hydrocarbons back into the engine for combustion and the third is to provide an additional area for oxidation or combustion to occur. This additional area is called a catalytic converter. The catalytic converter looks like a muffler. It is located in the exhaust system ahead of the muffler. Inside the converter are pellets or a honeycomb made of platinum or palladium. The platinum or palladiums are used as a catalyst (a catalyst is a substance used to speed up a chemical process). As hydrocarbons or carbon monoxide in the exhaust are passed over the catalyst, it is chemically oxidized or converted to carbon dioxide and water.

Comparison the Function of various method and advantages of catalytic convertor over the other systems.

PCV Valve /system reduce HC which entrapped in crank case. Evaporative emission control reduces evaporated HC. EGR Valve reduces NOx Excessive combustion chamber temperature creates oxides of nitrogen, which is a major pollutant. While the EGR valve is the most effective method of controlling oxides of nitrogen, in it's very design it adversely affects engine performance Air Injection system it will reduce excessive hydrocarbon emissions. Modern

catalytic converters (TWCC) Reduces HC, CO and NOx. It does not reduce vehicle performance significantly under most driving conditions because they are designed with low backpressure
as an integral part of the exhaust system. With the advances incorporated in today's engines, they perform significantly well. The modern catalytic converter is robust, one of the most reliable elements in the engine management system and corresponds to the lifetime of the car. Under Euro 4 emissions legislation, it is required that the emissions remain below the legal limits for at least 100000 km. This increased to 160 000 km with the new Euro 5 legislation as of 2009.

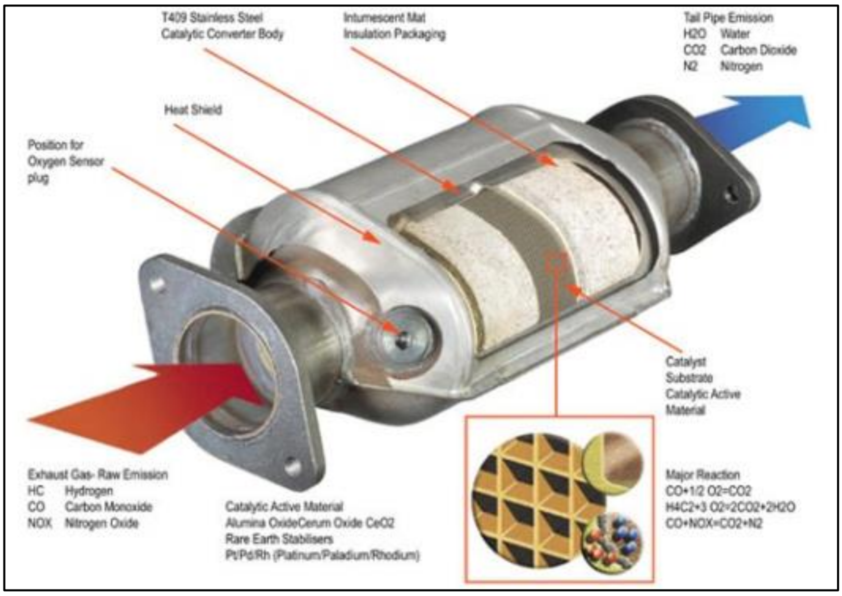

Fig 1: Catalytic converter

5. How Catalytic Converters Reduce Pollution

Most modern cars are equipped with three way catalytic converters. "Three-way" refers to the three regulated emissions it helps to reduce - carbon monoxide, unburnt hydrocarbons and nitrogen oxide molecules. The converter uses two different types of catalysts, a reduction catalyst and an oxidization 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 the catalyst to the exhaust stream, while also minimizing the amount of catalyst required (they are very expensive). There are three main types of structures used in catalytic converters - ceramic honeycomb, metal plate and ceramic beads (now almost obsolete) - most cars today use a ceramic honeycomb structure.

The Reduction Catalyst: The reduction catalyst is the first stage of the catalytic converter. It uses platinum and rhodium to help reduce the nitrogen oxide emissions. When such molecules come in contact with the catalyst, the catalyst rips the nitrogen atom out of the molecule and holds on to it, 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.

$$2NO \Rightarrow N_2 + O_2 \text{ or } 2NO_2 \Rightarrow N_2 + 2O_2$$

The Oxidization Catalyst: 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.

$$2CO + O_2 \Rightarrow 2CO_2$$

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

6. TWCS: principles and operation

A typical design of a modern three-way catalytic converter is reported in Fig. Basically, it is a stainless Fig. Diagram of a typical catalytic converter (1) and a metallic honeycomb (a monolith from Emitec GmbH) (2).steel container which incorporates a honey comb monolith made of cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) or metal. Although this aspect is sometimes neglected in the scientific literature, in must be underlined that the choice and geometrical characteristics of the honeycomb monolith play a key role in determining the efficiency of the converter. In fact, high conversion must be achieved in the converter and therefore the catalyst works under conditions where severe mass and heat transfer limitations apply. Typically, both metal and ceramic monoliths are employed nowadays. The major advantage of the metallic substrate is that the wall thickness is limited by the steel rolling mill's capabilities, not strength. In a typical automotive 400 cell/in.2 application, the frontal flow area in a ceramic monolith is 69% open (31% closed), while the metallic version has 91% open area. This is due to the higher wall thickness of ceramic monoliths(0.007 in. (0.178 mm)) compared to metallic ones(0.002 in. (0.050 mm)) [17,18]. However, even in this field there has been a strong improvement of the technology, cell densities as high as 900 cell/in^2 or even higher are now commonly available on the market for both types of monoliths. Traditionally, cordierite monoliths have been employed quite extensively,

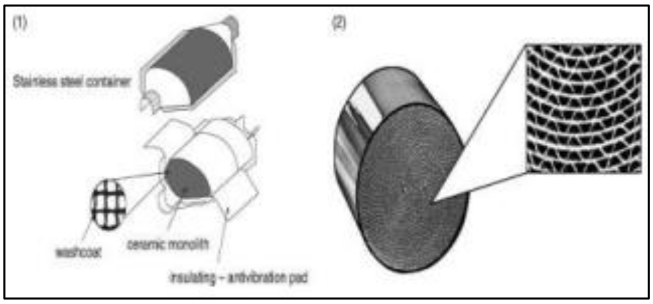

Fig 2: Typical catalytic converter (1) and a metallic honeycomb (a monolith from EmitecGmbH) 2).

Primarily due to their lower production cost. However, a major advantage of the metal monoliths resides in their high thermal conductivity and low heat capacity, which allow very fast heating of the CCCs during the phase-in of the engine, minimising the light-off time. The monolith is mounted in the container with a resilient matting material to ensure vibration resistance. The active catalysts is supported (wash coated) onto the monolith by dipping it into a slurry containing the catalyst precursors. The excess of the deposited material (washcoat) is then blown out with hot air and the honeycomb is calcined to obtain the finished catalyst. This is clearly a very simplified and schematic description of the wash coating process as multiple layer technology, or multiple catalyst-bed converters are also employed. The exact method of deposition and catalyst composition is therefore highly proprietary and specific for every wash coating company. For example, the metallic honeycombs are non-porous, which makes adhesion of the wash coat difficult. Accordingly a FeCrAl based alloy is employed, which contains up to 5 wt. % of aluminium; after an appropriate pre-treatment this element then acts as an anchoring centre for adhesion of the wash coat. However, there are some common components, which represent the state-of-art of the wash coating composition:

- Alumina, which is employed as a high surface area support.
- CeO_2–ZrO_2 mixed oxides, principally added as oxygen storage promoters.
- Noble metals (NM = Rh, Pt. and Pd) as active phases.
- Barium and/or lanthana oxides as stabilisers of the alumina surface area.

7. Proposed catalytic convertor system

It is proposed in this research work that the Indian metal oxides readily available in the market can be utilized as catalyst to convert the polluting gases to nonpolluting gases. These catalysts are

1. Calcium oxide
2. Magnesium oxide
3. Zink oxide
4. Nickel oxide
5. Tin oxide

The oxide with glycere as binder can be prepared in form of pallets and these pallets can place in the pipe attached to the exhaust pipe of the vehicle. The pallets can be supported or unsupported. If the pallets are unsupported then they can be prepared by mixing the oxide powder with the binder and preparing the balls of the think jelly of the powder. These balls can be drying in sunlight and then dry balls of the oxides are placed in the pipe which acts as catalytic convertor. The supported pallets can use the simple glass balls on which the oxide powder mixed with binder can be coated and dried after coating. These are supported pallets which can be placed in the pipe which is attached to the exhaust pipe. Khandare *et al.* found that these catalysts show some encouraging results during the experimentations. The high conversion efficiency can be expected from these catalysts being used in the catalytic convertor system. The cost of the catalytic convertor is also low and economical.

8. Conclusion

The development of automotive converters has proceeded by a continuous improvement of the catalytic performances and durability of the automotive catalysts over the past 25 years. It is now clear that a TWC is a complex system and that its lifetime must be equivalent to that of the car. The achievement of such targets requires strong research efforts. Summarising, the technologies or automotive pollution control, TWC, are playing key role in reducing air pollution. Indian metal oxides can be utilized as catalyst to convert the polluting gases to non-polluting gases. The high conversion efficiency can be expected from these catalysts being used in the catalytic convertor system. The cost of the catalytic convertor is also low and economical.

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