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A Review on Properties of Catalyst Materials for a Three Way Catalytic Converter

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Abstract : The world is being aware of the automobile exhaust emissions and the need to control them. The Three Way Catalytic Converter (TWC) is found the most effective method to control the exhaust emissions. The use TWC is made mandatory in India for passenger and heavy vehicles since 1995 for exhaust emission control. The TWC has been helping in reducing exhaust emissions but still a lot of research is required to raise the emission control level and economy. The existing TWCs are capable of reducing the exhaust emissions up to 60% for Hydrocarbon (HC) and Carbon Monoxide (CO) and 50% for oxides of Nitrogen (NOx). The important part of a TWC is the materials used for catalyst, substrate and washcoating. The selection of materials is very important step which includes detailed study of their properties and characterization. Platinum Group Metals (PGMs) were found to be appropriate materials as catalyst but due to cost considerations, its use is limited. Various methods are available to characterize a material with certain properties like ageing, Gel formation, kneading, impregnation etc. The properties which are required by a catalyst are needed to be imparted on the catalyst to achieve maximum emission performance of a TWC. The study of PGMs like Zirconium, Tungsten, Rhenium etc. will surely help to enhance the reaction rate, ultimately increasing the conversion efficiency of the TWC.

Keywords: Three way catalytic converter (TWC), catalyst, reduction catalyst, oxidation catalyst, Platinum Group Metals (PGMs), Characterization methods.

INTRODUCTION

The world is getting affected of the harmful effects like global warming, global cooling, changes in environment and human health too. The automobile exhaust emissions contribute nearly 46% of the total pollution of the world and today automobiles are inseparable part of our daily life. So these emissions need to be controlled. Various norms have been made as standards like US, EURO, Bharat Stage (B.S.), Tier etc. in respective countries. Number of technologies have been invented and presented to control automobile exhaust emissions like Diesel Particulate Filter, Lean NOx Burner, Exhaust Gas Recirculation, Selective Catalyst Reduction etc. But the most effective technology was found to be Catalytic Converter. There are two types of catalytic converter- one is Two way catalytic converter and another is Three way catalytic converter. The two way catalytic converter was used for controlling HC and CO emissions. The modification in the two way converter was made to control NOx emissions by introducing reduction catalyst in the converter which is known as three way catalytic converter. The TWC consists of substrate with catalyst support and wash coat, insulation, heat shield and outer housing. The most important parameter in accordance with emission control is the material selection and its procurements for characterization. This paper aims to review the properties required for a catalyst and substrate for maximum emission control.

LITERATURE REVIEW

The idea of a catalytic converter was first proposed in 1909 by Michel Frenkel and the first prototype was developed by Eugene Houndry in 1953. Since then, numbers of theories were proposed to enhance the performance of the catalytic converter. The focused area for research is the reduction and oxidation catalyst materials.

Said et al., 2016 [8] have conducted experiments on tantalum nitride based materials for studying the nitrogen transfer properties. The materials having different micro-structural features like channel density, surface area etc. were successfully prepared by using different synthesis techniques. The dependence of the nitrogen transfer properties upon tantalum nitride microstructure and its chemical composition was evaluated using the ammonia synthesis. It was shown that nitrogen reactivity for tantalum nitride is more dominated by lattice nitrogen stability rather than micro-structural properties. In case of non-doped tantalum nitride, only a limited improvement of reactivity with enhanced surface area was observed which demonstrates the limited impact of microstructure upon reactivity.

Chetan et al., 2016 [10] have designed a catalytic converter by using copper plate and ammonia solution for 4 stroke single cylinder 150 cc engine and conducted experiments on the same. By developed catalytic converter, reduction was found in CO by 63 % and HC by 50 % at ideal condition. While designing, they found the most important consideration is thermal conductivity of the material because it has to deal with high temperature of the exhaust gases. To obtain thermal stability and longer life of catalytic converter, rapid heat dissipation is necessary. Hence thermal conductivity is an important factor reported in the paper.

Angus et al., 2016 [13] have researched about advanced catalysts and substrates for cost effective emission control solutions for Tier III emission regulations. The catalysts were engine-aged on a dynamometer to simulate 150K miles of road aging. The substrate materials used were with standard and high porosity. They developed substrate materials Celcor and Flora having standard and high porosity respectively for experimentation. Improvements to emission performance were demonstrated when using high porosity substrates coated with an appropriate low mass catalyst technology due to faster light-off of these low thermal mass systems.

Hyeon et al., 2016 [17] have conducted experiments on Palladium (Pd) and Austin (Au) nano-particles as catalyst supported by oxides of Titanium (TiO_2) in porous medium to study Nitrogen Oxide (NO) decomposition. The 2 to 16 nm Pd–Au nano-particles were randomly dispersed in the Ti nano-fibers of diameter 117 to 185 nm. By using X-ray diffraction (XRD) patterns and X-ray photoelectron spectroscopy (XPS) Pd–Au particles formation was verified. The Pd–Au/TiO_2 fibers morphology study was confirmed by SEM, TEM and HRTEM. The crystal structures and chemical states of the Pd–Au/TiO_2 fibers were evaluated by XRD and XPS. Their final statement after the experimental study was- 'the reactivity of the Pd–Au combined fiber media were greater than Pd alone and Au alone fiber media'. The enhanced reaction activities of Pd–Au/TiO2 fiber media corresponded with decreased activation energies in the Arrhenius expression.

Mariam et al., 2016 [18] have experimented Nickel (Ni) and Molybdenum (Mo) metals as catalysts supported on Aluminium Oxide (Al_2O_3). They used sonochemical characterization technique for the synthesis of the Ni and Mo as catalysts. They studied physicochemical properties to observe the influence of ultrasound irradiation on the synthesis of bimetallic solid acid catalyst. The XRD analysis for this experiment revealed that with application of ultrasound irradiation, Ni-Mo particles were distributed homogeneously. The FESEM and TEM analysis confirmed that the nano-catalyst synthesized via sonochemical method presented with average size of 15 nm i.e. smaller than the catalyst prepared via impregnation method. FESEM images, mapping and EDX analysis showed that nano-catalysts contained particles in the range of mesoporous structure. The morphology of catalysts had changed slightly with the use of ultrasound irradiation where Nickel particles were having more pores on the support than Molybdenum and showed more interaction between Nickel and its support.

C. Ayed et al., 2015 [1] have performed the testing of a catalytic converter coated with aluminium oxide nano particles as catalyst to be used in the conventional catalytic converter. The catalytic converter was developed based on catalyst materials consisting of metal oxides such as aluminium oxide (Al_2O_3) nano-particles. The catalyst material (Al_2O_3) is inexpensive in the comparison with noble metal catalysts such as platinum or palladium. In addition, now the noble metals such as platinum group metals are recognized as human health risk due to their exhaust emissions in the environment from conventional catalytic converter. It was experimentally found that the conversion efficiencies of Al_2O_3 based catalytic converter are 99.5%, 92% for CO and HC emissions respectively.

Hussanai et al., 2015 [9] have investigated the effects of the promoter materials on physical and chemical properties of Cobalt based catalyst for hydrogenation of CO. The effects of modification with promoters on the properties of catalyst were investigated by TPSR (Transmission Surface Plasmon Resonance) Microscopy technique. The catalysts were prepared by sol-gel method and were characterized by Brunauer–Emmett–Teller theory (BET) and H_2-TPD (Hydrogen- Temperature Programmed Desorption). By analysis, it was concluded that the addition of Ruthenium (Ru), Manganese (Mn) and Zirconium (Zr) promoters can improve catalytic activity for CO hydrogenation. The findings from experimentation suggest that Mn induces both structural and electronic promotion effects and results in higher metal dispersions and lower temperature for hydrogenation of CO activity of the catalyst as well as enhancement of the catalyst selectivity.

Jonathan et al., 2015 [12] have experimented for catalyst performance by changing the platinum to palladium ratio by mass on light duty vehicle. Pt:Pd ratio by mass was varied from 0:1 to 1:0 and the performance of the catalyst was analysed. The results showed that as there is increase in Platinum content, HC oxidation was also improved. The 100% Pd sample (0:1) is significantly less active for oxidation than the other (Pt containing) samples. Pt was reported to be more active than Pd for NO oxidation. It was also found that monometallic Pt to be much more active than a 4:1 Pt-Pd catalyst for NO oxidation. NO oxidation activity to increase with Pt content for a series of Pt samples was observed.

Three Way Catalytic Converter

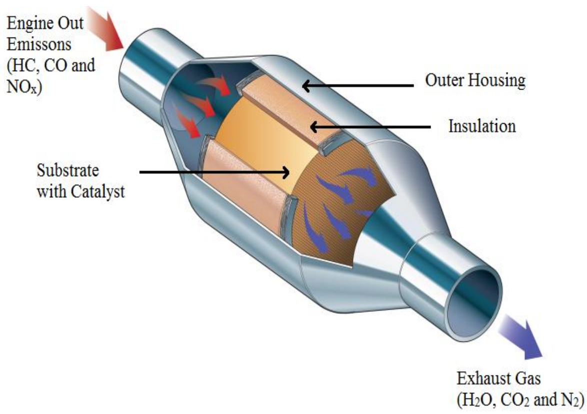

Fig. 1 Three way catalytic converter

Whenever it comes to the emission control of automobiles especially passenger and heavy vehicles, the Three Way Catalytic Converter comes into the picture. In many countries including India the use of TWC is made essential. So the study of TWC is important in the field of automotive emissions. Figure 1 shows the different parts of a three way catalytic converter.

The different parts of a TWC are as follows:

1. Catalyst:
a. Oxidation catalyst
b. Reduction Catalyst
2. Substrate / Catalyst Support
3. Insulation with cover
4. Coating
5. Outer Housing with Heat Shield

The catalysts and substrate are key elements of the TWC which are responsible for emission control. The materials react with the exhaust pollutants and convert them into environmental gases like Nitrogen, Carbon Dioxide etc. As the catalytic converter works at higher temperatures due to high temperature of exhaust gas, it needs the insulation and housing with heat shield.

Catalyst

There are two different types of catalysts used in the TWC namely Oxidation catalyst and Reduction catalyst. The oxidation catalyst reacts with CO and HC molecules from exhaust emissions and they are oxidized to CO2 and H2O respectively and the reduction catalyst reacts with NOx to form Nitrogen gas. Various materials have been incorporated as a catalyst like precious metals of Platinum (Pt) group or Non- noble metals. Higher costs of the precious and noble metals and scope to raise emission control encourage the manufacturers to search means to use low cost metals while simultaneously maintaining the catalytic performance and durability.

The methods which have been proposed and presented for improving catalyst performance and durability include the selection of supports with required morphological characteristics (like optimized porosity and specific surface area, geometry of the support, the addition of the base metals to improve durability of the converter and to enhance the activity of noble metals) and attention to the location of the noble metal within the support.

The basic design criteria for the catalyst is as following-

1. To remain unchanged in mass and chemical composition at high temperature.
2. Maximum optimum temperature.
3. High conversion efficiency.

The catalysts must possess flexibility in their chemical compositions to resist the poisoning of TWC. The exhaust gases escape with high temperatures so to avoid melting of the catalyst, materials with high melting point and high thermal conductivity. Conversion efficiency is the most important Criteria. More the conversion efficiency of TWC, lesser emissions are observed. When the conversion efficiency is lesser than the standards, the converter needs to be replaced.

Materials and their properties

Selection of material for catalyst is considered to be the most important as it has got lead role in TWC. It deals with the exhaust gas molecules to form non hazardous emissions like Nitrogen, Carbon Dioxide, Hydrogen Dioxide and can also be aimed at reduction in back pressure by design optimization. Numbers of materials have been used as catalyst from precious metals like Platinum (Pt), Rhodium (Rd) (which cost up to 40,000 Rupees per gram) to Non Noble Metal Catalyst like Copper, Cobalt, Zirconium etc. The emission performance of a converter is primarily function of properties of the catalyst. Platinum Group Metals (PGM) are considered to be the standard for catalyst properties. The Non-Noble metals possess similar properties to some extent but they can be made to have required properties by characterization. The following Table 1 shows the properties required for catalyst and its effect on the performance of TWC or other system of the vehicle like engine.

TABLE I
Properties Of Catalyst And Their Effect On TWC

Sr. No.	Properties required	Effect on Catalytic Converter
1.	High Thermal Stability	a. Avoids converter meltdown b. Retains Properties of Catalyst at higher temperatures c. Constant working condition can be achieved.
2.	Non-Poisonous Nature	Lesser toxic emissions
3.	Surface and Morphological Characteristics	a. Increase in reaction rate, ultimately the conversion efficiency. b. Reduction in back pressure or pressure drop c. Characterization of catalyst for required properties.
4.	Cell Density and Structure	a. Reduction in back pressure b. Optimized flow distribution c. Optimized resistance for flow distribution
5.	Active Oxidation or Reduction State	a. Increase in emission control b. Better conversion efficiency c. Lesser failure due to poisoning d. Better durability
6.	More Thermal Conductivity	a. More heat dissipation so temperature can be maintained b. Better durability
7.	Less Flow Resistance	Minimum back pressure

The properties like surface and morphological characteristics, cell density and structure etc. are very important due to their effect on the pollutants. Specific surface area and cell density are important factors to be considered. More the specific surface area and the cell density, more control on the pollution can be obtained. But the problem arises is increase in the backpressure in the TWC. The backpressure reduces the engine performance. So the specific surface area and the cell density are needed to be optimized.

The optimum design should be such that maximum performance of the emission control to be obtained with minimum backpressure. So study of these characteristics becomes necessary to raise the emission performance. These characteristics can be analyzed by following methods-

a. Scanning Electron Microscopy (SEM)
b. Transmission Electron Microscopy (TEM)
c. Volumetric Desorption
d. Gravimetric Desorption
e. Dynamic Desorption

Materials and their performance in TWC

The control of emissions by TWC is basically done by the reaction between catalyst materials and exhaust gases. This reaction depends on the physical and chemical properties of the catalyst material incorporated in TWC. Many of modifications and developments have been done in materials using different metals except PGM like Ferrous, Chromium, Aluminium, Copper, Cobalt, Zirconium etc. which possess required properties as PGM to some extent claiming cost effectiveness. The metals in PGM group having similar properties as the Platinum, Rhodium and are required to be evaluated as catalyst materials. The characterization can be done if some particular properties if material demands for it as a catalyst. Individual metals catalyst was not observed as effective as combination of the metals.

The following Table II shows the materials used in TWC and their effects on performance parameters like conversion efficiency (η_c) and/or emission reduction (E.R.).

TABLE II
Materials And Their Performance In TWC

Catalyst Materials	**Performance Parameter**	**Reduction/ Efficiency (in %)**		
		HC	CO	NO_x
Iron and Zeolite	η_c	-	57.4	55.8
Titanium and Cobalt Oxides	η_c E.R.	82 24	89 40	93 41
Copper, Nickel and Chromium	E.R.	28	93	-
Limestone	E.R.	56	50	-
Perovskite	η_c E.R.	85 84	55 53	- 17
Copper	E.R.	38	33	-
Copper, Silver, Cerium and Zirconium Oxides	η_c	62	64	60
Nickel	E.R.	40	35	-
Aluminium Nano Particles	η_c	92	99	49
NH3 Solution	E.R.	-	-	63
Monoethanolamine (MEA)	E.R.	-	-	28

The combination of the metals not only reduces the exhaust emissions but helps to reduce the backpressure phenomenon and improves the engine performance. The combination of the metals shows the morphological characteristics which are essential for the catalyst materials. So the study of morphological characteristics becomes important in order to reduce backpressure in the TWC. The table III shows the combinations of the metals and their effect on the backpressure.

TABLE III
Catalyst Materials And Their Effect on Backpressure

Materials	**Effect on Backpressure**
Combination of Oxides of Copper, Cerium and Zirconium	Backpressure reduced by 78 to 290 mbar
Combination of Oxides of Copper, Silver, Cerium and Zirconium	Backpressure reduced by 46 to 148 mbar

Cost effectiveness of materials in TWC

The cost aspect in any engineering work is always considered to have economical flexibility for the system. The conventional TWC with Platinum, Rhodium and Palladium costs more than 45,000 rupees per converter. The costs of Platinum, Rhodium and Palladium vary from 38 to 41 thousand rupees per gram and the quantity required is 1 to 2 grams. So the cost considerations become essential for catalyst materials. There are other metals in the PGM group like Iridium, Osmium, Zirconium etc. which possess same properties as that of Platinum, Rhodium and Palladium with lower costs. The other metals in the group are needed to be evaluated for their properties as a catalyst material.

The TWC made with combination of Copper, Nickel and Chromium has excellent oxidation properties for CO emissions and the costs are very less compared to PGMs nearly 50, 2000 and 7 rupees per gram respectively. So this combination can be used in the converters which need to have better oxidation characteristics.

CONCLUSIONS

The study of parameters related to the catalyst materials like physical & chemical properties and cost effectiveness needs to be done in all directions. The materials which possess the same properties as that of Platinum, Rhodium and Palladium should get attention for better emission control and cost effectiveness. The characterization methods are required to be studied to impart certain properties on the catalyst materials so that the catalyst will be able to perform better in emission performance.

For example, Aluminium nano-particles have excellent conversion efficiency for CO and Nickel has poor reduction control of 35% for the same. So we should aim at characterizing the properties of Aluminium over Nickel to have more emission control by increasing the conversion efficiency. The Perovskite metal shows excellent oxidation state for HC and CO but poor reduction state for NO_x. So it should be used in combination with the metal having good reduction characteristics or it should be characterized with better reduction properties by suitable characterization method.

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