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Current Developments in Catalyst of Automobile Exhaust Treatment and Scope of Photolytic Catalyst Technology: A comprehensive review

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ABSTRACT

Air pollution is at hazards level in the environment worldwide. Air pollution created by both industry and automobiles are increases very rapidly in world. Industrial pollution away from the city but more effect on the fertilize land. Automobile emitted pollutants inside the city are more dangerous for human life. HC, CO and NOx gives adverse effect on human health. Hence, pollution control boards makes stringent pollution control norms time to time. HC and CO are the polluting emittens can easily control by oxidising catalysts and advanced combustion technologies. But NOx reduction needs expensive reducing catalyst. Main source of NOx is diesel engines or petrol engine with lean combustion, where three way catalyst is required to control the all pollutant emissions including NOx. Hence, NOx reduction is challanging task Technologies to control various emittance from automobile are reviewed with scope of photolytic catalyst technology to control NOx in photolytic catalytic convertor.

INTRODUCTION

For the sake of easy and convenient living, it is predicted that automotive pollution would reach almost 1300 million by 2030. [1]. Globally, the use of two- and four-wheel vehicles is rising quickly, particularly in Asia's metropolitan regions. There are presently well over 100 million two-wheelers on the road. Additionally, this figure is increasing at a quicker rate, roughly 7 million vehicles annually.[2]. Because of improper combustion and compromised fuel quality, automobiles and industries emit mostly carbon monoxide, nitrogen oxide, hydrocarbons (unburned fuel), sulpher dioxide, and particulate matter. Known as a deadly gas, Carbon monoxide has an affinity for haemoglobin in the blood 210 times greater than the oxygen. lengthy exposure of carbon monoxide above 9 ppm level can lead to reduce mental acuity for individuals [3]. In addition, other pollutants like ozone, peroxycyl nitrate, and nitrogen dioxide that also contribute to global environmental problems, hydrocarbons and nitrogen oxide are the ones that generate photochemical smog when sunlight is present, causes serious lungs issues and reduced visibility causes accidents. The Indian government also implements standards such as BS-IV and BS-VI to polluting emittance from atuomobiles.

Table 1: Indian emission norms, BS-IV and BS-VI

Engine Type	Pollutant	BS-IV limit (mg/km)	BS-VI limit (mg/km)	Percentage decrease
Petrol	CO	1000	1000	Nil
	HC	100	100	Nil
	NOx	80	60	25%
	PM	-	4.5	-
Diesel	CO	500	500	Nil
	HC + NOx	300	170	43%
	NOx	250	80	68%
	PM	25	4.5	82%

Many technologies founded for decrease the emission level from automobiles like advanced combustion technologies, use of alternative fuel(biodiesel), fuel pre-tretment, improvement in engine design, fuel additives, exhaust gas treatment, exhausht gas recirculation etc. Among all the types of technologies developed so far, use of catalytic converters is the best way to control automotive exhaust emissions[1]. As the pollution norms strengent day by day, more advance pollution control technologies need to.

Catalytic converter

Currently Catalytic converter found on utmost automobile vehicle and other modern engines of intermidiate or bulky size. Commonly two type of catalytic converter in use Two-way catalytic converter and Three-way catalytic converter. In two-way catalytic converter reduce the concentration of two type of pollutant like CO and HC. In three-way catalytic converter reduce the concentration of three type of pollutant like CO, HC and NO_x as shown in figure 1. Catalytic convereter mounted in exahust pipe near the engine outlet and generally made from stainless stell like a container. In the catalytic converter use different type of catalyst for increasing the oxidation and reduction process[2].

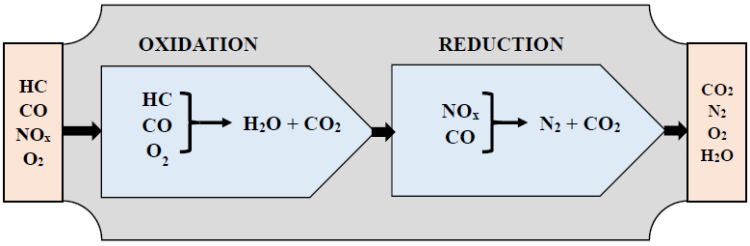

Figure 1: Working of Catalytic Converter [2]

LITERATURE REVIEW

Non photolytic catalyst

Nobel metal

Nobel metal is used for catalyst in the currently develop catalytic conveter.In this type of catalytic converter paltinum, rhodium and palladium nobel metal coated on ceramic structure. CO and HC oxides by the Paladium and platinum prmote the oxidation of CO and HC, with platinum especially active in the hydrocarbon reaction[4].

$$2CO + O_2 \rightarrow 2CO_2$$
$$4HC + 5O_2 \rightarrow 4CO_2 + 2H_2O$$

Rhodium promotes the reaction of NO_x in one or more of the following Reactions:

$$NO + CO \rightarrow \frac{1}{2}N_2 + CO_2$$
$$2NO + 5CO + 3H_2O \rightarrow 2NH_3 + 5CO_2$$
$$2NO + CO \rightarrow N_2O + CO_2$$
$$NO + H_2 \rightarrow \frac{1}{2}N_2 + H_2O$$
$$2NO + 5H_2 \rightarrow NH_3 + 2H_2O$$
$$2NO + H_2 \rightarrow N_2O + H_2O$$

There are several types of problems related with noble metal based catalytic converter[5]. The failure of catalytic converter may be due to following factors:

1. **Catalytic meltdown:** Light off temperature of catalytic converter is 250°C. So conveter continuos working at that temperature small so The converter becomes very hot and melts inside so that the small particles come separately on the inside. The broken pieces of metal can transfer from one place to another and get in position to clog the flow of exhaust gases through converter. This meltdown is instigated by converter having too much work to do.
2. **Carbon deposit:** Carbon, oil, coolant, Particulate matter or other mess are collected on the catalytic conveter surface than some time choked the converter.The converetr doesn't know how to stop; It keeps up its reaction. The inside chaber of catalytic convereter. So increase the back pressure on the engine. Also effect on Engine performance like loss of power at higher engine speeds, hard to start, poor acceleration,fuel economy. A critical analysis of all these issues infers the following significant facts: It is still problematic to attain long term robustness of converter under the circumstances of ordinary vehicle use[6][7].

Non nobel material

1. **Copper Oxide:** Copper oxide use as a catalyst. This is one of the options of remove Nobel metal from the catalytic converter. Copper oxide coated on the surface with different method and thickness. This catalytic converter light off temperature 230˚C to 250˚C.Conversion efficiency of this catalytic converter higher than ordinary catalytic converter. Comparisons of ordinary Catalytic converter and copper oxides based catalytic converter are shown in figure 2 at 3 kg load condition on engine.

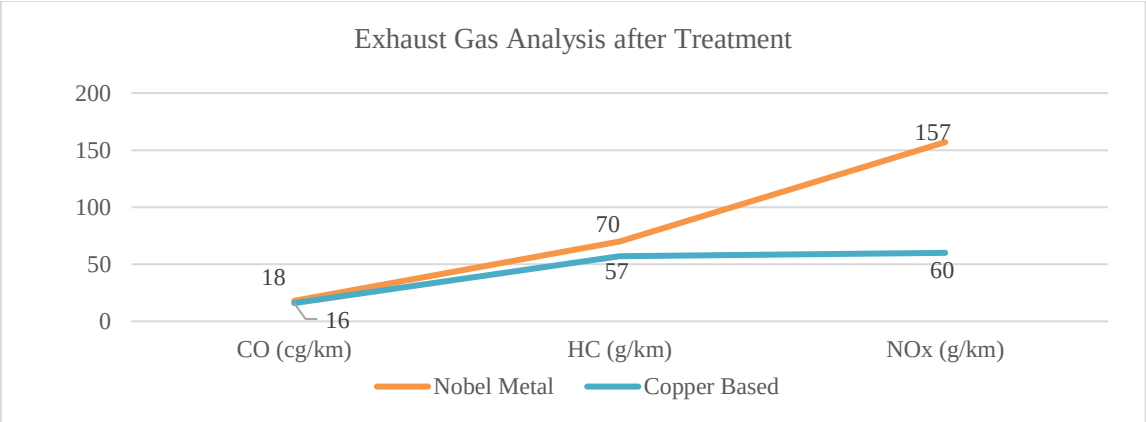

Figure 2: Comparision of Nobel metal and copper based catalyst

When exhaust gases come in contact with copper plated wire mesh, catalysis process occurs and in the presence of copper, HC and CO will be converted into H_2O and CO_2.

$$2CO + O_2 \xrightarrow{Cu} 2CO_2$$
$$HC + O_2 \xrightarrow{Cu} CO_2 + H_2O$$
$$2NO + 2CO \xrightarrow{Cu} N_2 + 2CO_2$$

Perovskite Based Catalyst Compositions

Pervosite material used as a catalyst in the catalytic convertor. Pervoskite is one of the constructin of the material like ABO_3 where, A and B is metal ions. The basic composition is $LaMnO_3$ and $LaCoO_3$. Pervoskite material activity is same as a nobel metal catalyst. Its oxidation of CO and HC and Reduction of the NO_x and SO_2. Main problem of this catalyst difficulty to find the more surface area compare to nobel metal catalyst means rection rate per area is low compare to nobel metal catalyst [6].

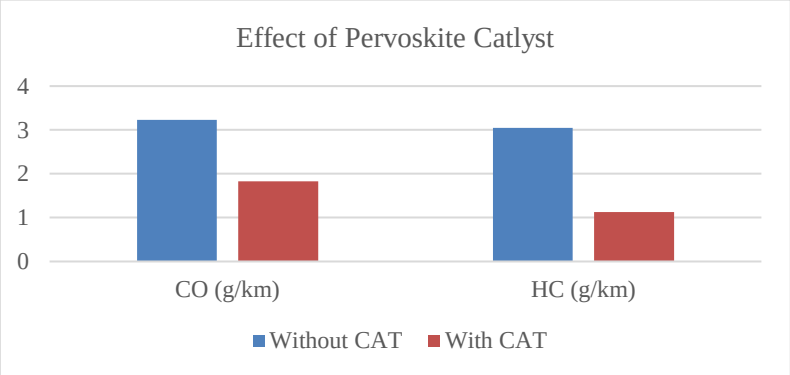

Figure 2: Pervoskite catalyst Conversion [6]

Nickel Catalyst

In this converter nikel as a catalyst. It is work as a oxidizing agent. Its non poisonous nature, low cost and availibility makes it preferred carries in oxidation from the stationary pollution sources. Stainless steel material use a substrate, it is generally use in all catalyst. By using this catalyst HC reduce by 40% and CO reduce by 35%. This result is same as nobel metal catalytic converter [2].

Iron exchange zeolite Catalyst

Iron-exchanged X- zeolite catalyst used in catalytic converter. The Fe-exchanged X-zeolite has been developed by ion exchanging of 13X zeolites in pelleted form with anhydrous Ferric chloride ($FeCl_3$). 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. From the experimental results, it is observed that the NO and CO reaction plays an important role in NO conversion. The working temperature of this catalyst is in the range 275˚C to 375˚C [12].

$$2NO + 2CO \rightarrow N_2 + 2CO_2$$

TiO_2 &CoO Catalyst

In this catalytic convereter use mix solution of TiO_2 and CoO. TiO_2 matalic powder mix with sodium silicate solution and CoO mix with sodium metabesulphate. This mixture coated on the substrate surface. It is experimentally found that the conversion efficiencies of TiO_2/CoO based catalytic converter are 93%, 89% and 82% for NOx, CO and HC emissions respectively at above the 500˚C temperature.

Light off temperature of this catalyst is 270°C to 360°C. Operating temperature of this catalyst is very high so this is difficulty to use in automobile vehicle [13].

Photolytic catalyst

1. Photolytic Degretion of NO_x using TiO_2

In this experiment, TiO_2 poweder mix with paint and painted on the car parking all surface and roof of the parking is made by acralic transperent sheet with TiO_2 paint.

UVA lamp(36W/2500lm) fitted inside parking and exhaust gas of car is relese inside the parking by pipe connection.Consentration of UV light on surface is 1 W/cm^2.

Result of this experiment, NO and NO_2 remove by photolytic effect 19% and 20% respectively [14,15].

2. TiO2 Coating on Concret

In this reserch paper, we have seen that TiO_2 powder coated on the exterior surface of the concreat which exposed to UV light.

Processor of the experiment in this reserch paper,10 ppm NO/N_2 mix with compressed air and make 1 ppm mixture of NO/N_2 than pass on the TiO_2 coated block in side the chamber. After 5 minitue time NO/N_2 concentration in the air is reduce to 0.05 ppm.so conversion efficiency of this experiment is 95% [16].

Comparition of conversion efficiency between various catalysts are shown in figure 4.

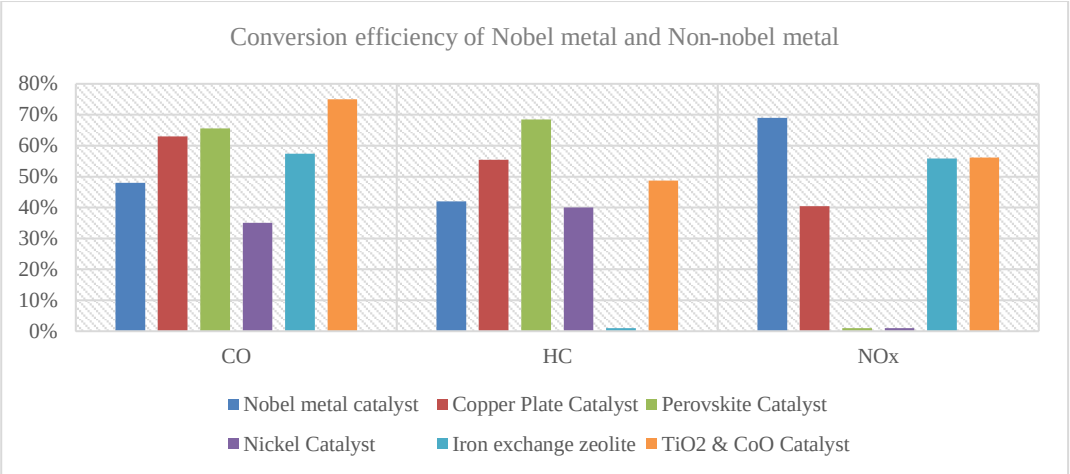

Figure 3: Conversion efficiency of various catalyst

Table 2: Summary on application photolytic catalyst for pollution reduction

Sr. No.	Author	Title	Fact Finding
1.	M. Machida, S. Ikeda, D. Kurogi, T. Kijima [11]	Low temperature catalytic NO*x*–H_2 reactions over Pt/TiO_2-ZrO_2 in an excess oxygen	TiO_2 Oxide layer on Pt-catalytic converter effectively working near 100°C
2.	J.S. Dalton, P.A. Janes, N.G. Jones, J.A. Nicholson, K.R. Hallam, G.C. Allen [12]	Photocatalytic oxidation of NOx gases using TiO_2: a surface spectroscopic approach	Reaction of NOx with TiO_2 using UV light on surface
3.	Yoichi Ishibai, Junya Sato, Shoichi Akita, Takashi Nishikawa [13]	Photocatalytic oxidation of NO*x* by Pt-modified TiO_2 under visible light irradiation	Greatly increased photocatalytic degradation of NO*x* under visible light irradiation.
4.	Th. Maggosa, J.G. Bartzis, M. Liakou, C. Gobin [14]	Photocatalytic degradation of NO*x* gases using TiO_2-containing paint: A real scale study	Photocatalytic rate and NOx conversion for same concept.
5.	Mingfeng Xu, Yi Bao, Kai Wua, Tian Xia, Herek L. Clack, Huisheng Shi [15]	Influence of TiO_2 incorporation methods on NOx abatement in Engineered Cementitious Composites.	TiO_2 in cement block and reduce NOx by sunlight effect.
6.	Masaaki Kitano, Masaya Matsuoka, Michio Ueshima, Masakazu Anpo [16]	Recent developments in titanium oxide-based photocatalysts	Method of TiO_2 Coating
7.	Guido Buscaa, Luca Liettib, Gianguido Ramisa, Francesco Bertic [17]	Chemical and mechanistic aspects of the selective catalytic reduction of NOx by ammonia over oxide catalysts	Reduction of NOx by ammonia and disadvantages.
8.	Lijun Liao, Steven Heylen, Sreeprasanth Pulinthanathu Sree, Brecht Vallaey, Maarten Keulemansa [18]	Photocatalysis assisted simultaneous carbon oxidation and NOx Reduction	TiO2 Photocatalyst use for carbon black oxidation
9.	Rajesh B. Biniwale, N. K. Labhsetwar, R. Kumar and M. Z. Hasan[19]	A Non-noble Metal based Catalytic Converter for Two-stroke, Two-wheeler Applications	Non-Nobel metal catalytic converter; Material: Perovskite catalyst ($LaCoO_3$ and $LaMnO_3$).
10.	Chirag Amin, Pravin P. Rathod [20]	Catalytic converter based on non-noble material	Nobel metal catalytic converter disadvantages; Iron-exchange zeolite

			and TiO_2 & CoO catalyst conversion efficiency
11.	P.R. Kamble and S.S. Ingle [21]	Copper Plate Catalytic Converter: An Emission Control Technique	Non-Nobel metal catalyst conversion efficiency

CONCLUSION

Based on above summery table 2 it can be conclude based on temperature of operation, Conversion efficiency and economic aspect.

Temperature

From the above discussion we can say that Catalytic converter efficiency is highly depended on the temperature in Non-photolytic process, Increase the temperature than increase the conversion efficiency. But in the photolytic process required low temperature or room temperature for reduction of pollutant.

From the above discussion we have conclude that optimum efficacy of non photolytic catalytic convereter required 250˚C to 450˚C.

If the temperature of catalyst is above 450˚C than all the catalyst give the maximum conversion efficiency in range of 90% for all three pollutants.

Coversion Efficiency

From the Figure 4 in Non-photlytic process, Non- nobel metal conversion efficiency same as Nobel metal Catalyst. But in this process NO_x reduction is low compare to other main pollutants. In Photolytic process mainly reduce the concentration of the NO_x.

Econoimic

In both process, Non-Nobel metal Catalyst and Photolytic process is economical compare to Nobel metal Catalyst.

Literatures we can conclude that Non photolytic process catalyst has not working sufficiently in cold starting condition. Also this conversion efficiency of catalytic converter is not able to fullfill the demand of BS-VI norms at low temperature. Photolytic catalyst requires comparatively lower temperature to control NOx emission enables to solve the existing problem.

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