Development of Non-noble Metal Based Cost Effective Catalytic Converter for Engine Exhaust

By

Muhammad Habib Ur Rehman

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Session 2015-17

Supervised by:

Assoc. Prof. Dr. Naseem Iqbal

A Thesis Submitted to the U.S.-Pakistan Center for Advanced Studies in Energy in partial fulfillment of the requirements for the degree of

MASTERS of SCIENCE in

Thermal Energy Engineering

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National University of Sciences and Technology (NUST)
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THESIS ACCEPTANCE CERTIFICATE

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Dedicated to my

Parents, siblings, and friends.

Acknowledgments

First of all, I would like to pay my sincere gratitude to Allah Almighty than to my supervisor **Dr. Naseem Iqbal** (USPCASE), who made this work possible. Without his patience, friendly guidance and expert advice this dissertation would not have been completed. I could not have imagined having a better supervisor than him. His dynamism, sincerity, and motivation truly inspired me a lot. It was a great honor and privilege for me to work under his guidance.

I would also like to thank respected faculty **Dr. Majid Ali, Dr. Nadia Shahzad** and **Dr. Muhammad Hassan** for serving as my committee members and providing me their brilliant comments and suggestions whenever it was needed.

Moreover, I am thankful to many other individuals at USPCAS-E, NUST who helped me throughout this course of time, especially **Mr. Sajjad Ur Rehman** (DPA- PA to HoD-ESE). This also includes the technical staff of the Center who helped me a lot in performing my testing and analyzing data.

Last but not least, I am very thankful to all the members of my family who stood by me and helped me to complete my work. They kept me motivated and rendered me their positive energy.

“Muhammad Habib Ur Rehman”

Abstract

Exhaust gases of automobile vehicles are one of the biggest contributors towards air pollution in most cities of the world, especially in Pakistan. According to WHO report annually 3 million people die due to the ambient air pollution throughout the world. Three-way catalytic converters have been the most powerful tool to control these automobiles emissions so far. Platinum group metals e.g. platinum, rhodium, and palladium are being used as the catalyst in these catalytic converters. With the increment in the prices of these precious metals and their potential threat to the health of human beings, it is important to investigate some low cost and less threatening substitutes. In this thesis report, I am going to delineate hydrothermally produced Co_3O_4/TiO_2 catalyst and zirconia promoted Co_3O_4/TiO_2 catalyst. Cobalt nitrate hexahydrate $Co(NO_3)_2.6H_2O$ was used as a precursor material for Co_3O_4 and TiO_2 nanoparticles were used as support. Catalysts were characterized by using SEM, XRD, and TGA. In past some of the work had been progressed on Co_3O_4 as catalyst over TiO_2 support but never tested in real conditions. In this report I am presenting two catalysts one is Co_3O_4/TiO_2 which is hydrothermally produced and the other is Co_3O_4/TiO_2 promoted by ZrO_2 to investigate the effect of zirconia on conversion. The catalyst was coated on stainless steel wire mesh by using the dip-coating technique and then was tested in real-time conditions. This catalytic converter setup was mounted on the exhaust pipe of the motorcycle and the readings were taken live. RPMs of the bike were increased gradually from 1500 to 6000 with interval of 1500 and results were taken by using Crypton's exhaust gas analyzer and E instruments' E4500-2. It was seen that there was drastic decrement in the emissions. Zirconia promoted Co_3O_4/TiO_2 catalyst was observed to be more efficient towards NO_x and CO conversions. While in case of hydrocarbons Simple Co_3O_4/TiO_2 was seen more conversion efficient than the other one.

Keywords: Catalytic converter, Wire mesh, Dip Coating, Hydrothermal, Real-time testing.

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List of Abbreviations

ICE	Internal Combustion Engine
CI	Compression Ignition
SI	Spark Ignition
PM	Particulate Matter
EPA	Environment Protection Agency
PEPA	Pakistan Environment Protection Agency
PGMs	Platinum Group Metals
FTIR	Fourier Transform Infrared Spectroscopy
OSC	Oxygen Storage Capacity
CAA	Clean Air Act

Chapter 1

INTRODUCTION

1.1 Background

In 2016, 91% of the world total population was not able to have pure air, and more than 50% of the population living in cities was living in an environment where outside pollution of air had the levels of 2.5 times the standard levels set by world health organization[1]. It is reported that air pollution caused 4.2 million deaths in both city and rural areas around the globe[1]. Anything which is emitted into the environment and has a damaging effect on the living species is called air pollution[2]–[4]. The contribution of vehicle emissions towards air pollution is about 25-30% in developing countries like Pakistan while this contribution rises up to 40% in developed countries like the USA[5][6].

More importantly, internal combustion engines (ICE) are the main source of pollutants whether they are SI engines or CI engines[7]. Different methods like thermal reactors, filters or traps, selective catalytic reduction SCR and TWCC had been adopted to truncate this concern to the minimum level[8][9][10]. Three-way catalytic converters are one and most successful device so far introduced in the market to mitigate the exhaust gas toxic pollutants.

1.2 Engine emissions

Normally the composition of exhaust gases at the optimal engine operation for petrol engines values are: nitrogen 71%, carbon dioxide 14%, water vapors 13%, nitrogen oxides 0.25%, carbon monoxide 1-2%, hydrocarbons 0.25% [11][12][13]. Gases coming out from the opening of exhaust valve after the completion of a cycle, contain several toxic pollutants for human health which are needed to be removed to have a clean environment.

Diesel engines produce 100 times more particulate matter than gasoline engines. The amount of particulate matter can be reduced with efficient combustion, but this leads to more production of NO_x. The relationship between particulate matter (PM) and NO_x are called “trade-off” which is troublesome for engine producers[14]. Due to not a proper combustion inside an internal combustion engine, there are three main toxic pollutants which are most hazardous to the living lives that are unburnt hydrocarbons (HCs), carbon monoxide (CO) and nitrogen oxides (NOx)[15][16][17][18]. The main cause of CO and hydrocarbons production is the lack of oxygen in the air-fuel mixture during the combustion process that happens when the air to fuel ratio is rich. CO interferes with the blood's capability to fetch O_2 to different organs of the body causing you to suffocate[19][20].

While NO_x is produced mainly due to very high temperature in the combustion chamber when nitrogen and oxygen react together and when A/F ratio is leaner.[21][22][18]. NO absorbs oxygen like CO but is less threatening to the body because it is soluble in water[23]. Alongside these pollutants SO_x mainly SO_2 is also produced due to the presence of sulfur in fuel which affects the lungs[24]. Other than these, environmental protection agencies (EPA) is concerned with lead (Pb), ozone (O_3) and particulate matter[7].

1.3 Clean air act (CAA) 1970

After the introduction of the clean air act in the USA by President Nixon and Congress, the official formation of EPA on December 2, 1970, came into being. USA parliament gave permission to EPA to set national standards later this thing led to the implementation of catalytic converter in 1973. In the first generation technology only two-way catalytic converters were installed in cars but after the amendment in clean air act in 1977, new strict policies were introduced which forced the automakers to install three-way catalytic converters[25]. The standards which were amended and set in 1994 are the current standards implemented. The values for a lightweight car are given below in the table. All values are in gram per mile.

Table 1 USA emission standards set by federal legislation[26].

Year	Carbon monoxide	Hydrocarbons	Nitrogen Oxides
1968-69	51	6.3	-
1970-71	34	4.1	-
1972	28	3.0	-
1973-74	28	3.0	3.1
1975-76	15	1.5	3.1
1977-79	15	1.5	2.0
1980	7.0	0.41	2.2
1983	3.4	0.41	1.0
1994	3.4	0.25	0.4

1.4 PEPA, 1997

The Pakistan environmental protection act (PEPA) was approved by the lower house on 3rd Sep 1997 and by the upper house on 7th Nov 1997. This act was assented by the president of Pakistan on 3rd Dec 1997. Later Pakistan environmental protection agency (PAK-EPA) was formed in 1997[27]. This act includes many strict rules and heavy penalties for the rules breakers.

1.5 Catalytic converter

The catalytic converter was invented by Eugene Hourdy who was a French mechanical engineer who was living in the USA[28][29]. A catalytic converter is an equipment that is used to remove toxic pollutants from the exhaust of vehicles whether they are petrol or diesel based. There are three principal parts of a conventional catalytic converter that are substrate or core, clamshell, and insulation mat. Conventionally cores which are used in automotive vehicles are made of the ceramic monolith with honeycomb-like structure.

Metallic cores are also now introduced which are less costly and provide more performance[15]. Catalyst is dispersed on the wash coat material so that its active sites are available to the reactants and this mixture is coated on walls of a substrate[30]. Since the invention of the catalytic converter in 1950 it has now gone through many transformations like using different numerical and mathematical simulations, different flow models of geometry, design of two way or three-way converters and alternatives of high priced metals like Pt, Pd and Rd[22][31][32]. There are two types of converters:

1.5.1 Two-way catalytic converter

An oxidation converter has two primary tasks to perform:

Oxidation of carbon monoxide to carbon dioxide and oxidation of hydrocarbons to water vapors along with carbon dioxide[18][33].

$$2CO + O_2 \rightarrow 2CO_2 \tag{1}$$

$$HC + O_2 \rightarrow CO_2 + H_2O \tag{2}$$

These converters were mostly used in diesel engine vehicles for the oxidation of carbon monoxide and hydrocarbons. They were also used in the petrol engine till 1981 but they were taken placed by TWCC due to their limitation for not reducing nitrogen oxides[28][18].

1.5.2 Three-way catalytic converter

On the other hand, in a three-way catalytic converter along with the oxidation of carbon monoxide and hydrocarbons, reduction of oxides of nitrogen is also carried out.

$$NO + CO \rightarrow CO_2 + N_2 \tag{3}$$

NO_x is involved in smog production and also the cause of acid rain[34][35]. Discussing the conversion of NO_x from the flue gases selective catalytic reduction SCR with ammonia NH_3 has also now evolved over the decades. First SCR was used for the removal of oxides of nitrogen from emissions of big power plants but now it is used in millions of diesel vehicle technologies as well[36]. SCR is used in heavy-duty vehicles, power plants and nowadays in cars too[37]. The addition of iron oxide to vanadia-titania support resulted in the reduction of N_2O.

CeO_2 and $CeZrO_2$ catalysts over titania support showed good SCR and soot oxidation activity[38]. New innovations are being introduced in three-way catalytic converters, like the introduction of oxygen storage capacity materials, Phase change materials PCMs for cold start problems, different types of beds for getting more surface area and greater strength at higher temperatures and new catalysts replacing the conventional precious metals.

1.6 Wire mesh structure

Conventionally catalytic converters contain ceramic monolithic structures with honeycomb-like straight walls. The catalysts are coated on the walls of these structures to get the maximum surface area and active sites as well[39]. Monolithic substrate has 400 to 1000 cells per square inch whereas the wire mesh structure has 1000 to 1200 cells per square inch. Wire mesh structure provides greater surface area turbulent flow compared to the honeycomb structure which provides laminar flow thus the gases have fewer chances to interact with the active sites[40][41].

With wire mesh structure we will have to live with one con that is an increment in the backpressure of the engine[40][16]. Different wire mesh structures and techniques are being tested to reduce backpressure in the engine[42][43]. Comparing the different wire mesh structures like round, square, hexagonal and elliptic shape, it has been observed that square structure gives better results. Due to the four right angles opposite to each other, more catalyst material is stuck over there and it helps more interaction and thus the reactivity of the catalysts.

1.7 Objectives

- Hydrothermal synthesis of a catalyst for a catalytic converter.
- Development of low-cost catalytic converter with wire meshes as a substrate
- To evaluate the effect of zirconia on the catalyst for NO_X reduction.
- Evaluation of the real-time performance of the catalytic converter.

1.8 Scope of study

- Identification of a low-cost alternative of PGEs as an efficient catalyst for 4 stroke engines.
- Development of a new and locally manufactured catalytic converter.
- Testing of the catalytic converter in real driving conditions ranging from low to medium RPMs.

1.9 Summary

In this chapter, there is an introduction to air pollution, sources of air pollution and different techniques that have been used to decrease the effects of this issue. Catalytic converters are one the different techniques to truncate this problem. A slight introduction of commercially available catalytic converters is discussed. New advancements in this field have also been touched.

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Chapter 2

LITERATURE REVIEW

2.1 Introduction

According to the world health organization report in 2018, about 4.2 million people died in both urban and rural areas due to air pollution in 2016[1]. There are different sources of air pollution that include power plants, burning of fossil fuels, heating or cooling systems of homes and workplaces and road vehicles[2]–[4]. It has been noted that road vehicles are the biggest contributors towards air pollution and among the road vehicles two-wheelers play a big contribution in emitting unwanted gases in the environment[5]. Asia is the largest consumer of motorcycles in the world over the last few decades especially the developing countries of Southeast Asia. Through the last few years EU had over 32 million motorcycles which were about 8% of the total passengers moving across the countries[6]. In Pakistan the growth rate of motorcycles from 1991 to 2012 increased by 450% and that of cars by 650%[7].

The problem of air pollution contributed by road traffic was recognized in the early stages of the 1940s in Los Angeles and serious efforts were being made to cope with this issue in later half of the same century[8]. Many control methods were adopted to remove the pollutants included engine improvisations like lean operating engines, fuel alterations, exhaust gas recycling (EGR) and finally catalytic converters to remove the pollutants from the environment[6][9][10].

Catalytic converters are the well-established exhaust gas treatment system that can convert most of the toxic pollutants. As it is clear by the name catalytic converters utilize the catalysts to obstruct the poisonous outflow of exhaust gases. Usually, a catalytic converter has a working life of about 160,000 km or 10,000 hours of use[11]. Catalytic converters are conventionally based on platinum group metals and they are the biggest consumer of PGMs over the last few decades. Research has been made to find the alternatives and in literature, all the metals have been discussed as alternate to PGMs. Here we will only discuss non-noble based catalysts based on the oxides of base metals.

2.2 Non-noble metal-based catalysts

Since the introduction of PGMs in catalytic converters in the 20th century, researchers have been doing research to find alternatives to these sources. PGMs are rare metals, very costly and thus the chances of theft from the vehicles also increase. Researchers are trying to increase the efficiency by introducing materials having greater oxygen storage capacity, experimenting different PCMs to solve the cold start problem, the heat losses issues from the walls of the converter and the different substrate structures to find out maximum surface area plus the required strength[12][13][14].

As the automotive industry has been the biggest user of PGMs, its reserves are getting low and low while the cost is getting high and high. So, researchers are trying to find the alternative at a low cost. All the base metals oxides have been tested so far and the results are quite promising for few of them[15]. Mostly in literature non-noble metal-based catalysts have been discussed to remove one pollutant but somewhere multi pollutants have been coped using a non-noble metal-based catalyst.

2.3 Oxidation over non-noble materials

CO and HCs are oxidized in the presence of excess oxygen in the converter shell. Carbon monoxide and hydrocarbons are both products of incomplete combustion in the combustion chamber of an engine. Carbon monoxide is a poisonous gas and it is very dangerous for all the living organism which inhale as it combines with the hemoglobin in the blood and reduces its ability to carry the oxygen[16]. Exposure to CO even to small amount can cause damage to the nervous system of body. Keeping in mind all hazards to human life by CO, researches is made to oxidize CO to CO_2 which is less alarming to human health. Low-temperature oxidation of CO by using Cobalt oxides as catalyst has been discussed in literature[17]. Oxidation of CO at low temperature is perhaps the most extensively searched reaction as far as heterogeneous catalysis is concerned as it is very important to provide fresh air to the atmosphere by lowering exhaust gas emissions.

Jonas Jansson[17] studied the oxidation of CO by using Co_3O_4 at low temperature in a flow reactor experiment. He studied that the catalyst showed higher activity towards CO conversion, but he also found that catalyst deactivated during the course of the reaction. He regenerated the catalyst by using 10% O_2/Ar mixture. He found the presence of carbonyl, carbonates and oxygen species on surface of the catalyst by using the FTIR analysis. He also came to know that there was an alternation in chemical structure and oxidation state with help of XRD. However, he concluded that the possible reason behind the deactivation of catalyst might the change in surface reconstruction of the catalyst.

Wang[18] experimented by preparing a cobalt oxide catalyst with three different supports like TiO_2, Al_2O_3, and SiO_2 by using incipient wetness impregnation method. He expressed that the type of cobalt oxide and the type of support used had a great effect on the activity and the surface area. He concluded that CoO_x/TiO_2 showed very significant results in CO conversion. Hu[19] performed the oxidation of CO on cobalt oxides nanobelts and nanotubes. He revealed that the shape Co_3O_4 had a great effect on the catalytic activity towards CO as nanobelts depicted more conversion efficiency than nanocubes.

Jia[20] prepared Co_3O_4-SiO_2 nanocomposite as a catalyst with a high surface area for the oxidation of CO. He observed that the catalyst showed activity at a very low temperature of even -76°C. He concluded that there was some adsorption of water molecules on the exterior of catalyst which caused abnormal behavior in the activity of catalyst. Xie[21] reported that Co_3O_4 showed high activity for carbon monoxide conversion surprisingly at a temperature of -77°C and remained stable under moist conditions. He observed that under the stoichiometric conditions, conversion efficiency of Co_3O_4 catalyst was 96% at temperature of 200°C but the conversion efficiency decreased at temperature of 150°C to 40% due the presence of moisture content.

In conventional catalytic converter where PGMs are used as the catalysts and light-off temperature of these catalysts is about 300°C which takes a lot of time for a vehicle converter to reach its light-off temperature. Mostly the unburned hydrocarbons skip through the exhaust system and reach the outer environment during this period of time[22]. So, it is important to find the alternatives which have a low light-off temperature. Hydrocarbons are very toxic and carcinogenic like benzene (C_6H_6) which can block the regular production of red blood cells[23]. Hydrocarbons produce ozone (O_3) by reacting in the presence of NO_X and direct light which is biggest contributor towards smog. It causes eye irritation, lung damage and respiratory problems[24], [25]. Oxidation of hydrocarbons over Co_3O_4 has been studied extensively since it is very important reaction related to clean environment. Liotta[26] studied Co_3O_4, CeO_2 and Co_3O_4-CeO2 mixed oxides prepared by precipitation method for the conversion of propene. She concluded that mixed oxides attained the maximum conversion efficiency of propene at temperature of 250°C. Tian[27] also studied the oxidation of different hydrocarbons in lean conditions in a monolith reactor. He studied most of the reactants had the light off temperature ranging from 250°C to 290°C.

Alalwan[28] studied the conversion of methane over tri cobalt tetraoxide and noticed that in the temperature range of 500-700°C, methane oxidation to CO_2 was at maximum. Chun Ma[29] reported that at very low temperature 0°C ethylene was oxidized by mesoporous Co_3O_4. He promoted the catalyst by using Au and achieved the conversion of ethylene to 76% at 0°C. Wang[30] demonstrated the oxidation of hydrocarbons especially methane by using highly stable Co_3O_4. He carried out the reaction in an oxygen-rich environment with temperature ranging from 25-700°C. He noticed that light-off temperature was about 200°C and the conversion of CH_4 to CO_2 remained over 60% for 20 hours and 100% selectivity of the catalyst towards CO_2. He reported that with the passage of time selectivity of the catalyst did not alter and remained 100%.

Li[31] studied the conversion of methane over Co_3O_4 with Pd loading in a reaction gas mixture. He studied that Co_3O_4 achieved the 100% conversion of methane at 480°C under the specific conditions used and the reactivity of the catalyst remained stable for the full reaction time period of about 90 min. Prior[32] studied the combustion of some chlorinated compounds over Co_3O_4 with SBA-15 silica as support. He reported that oxidation reaction could be accelerated by the incorporation of Co_3O_4 in pores of silica moreover with the concurrent corporation of both the acid sites and redox sites.

2.4 Reduction over non-noble materials

Due to very high temperature and pressure in the combustion chamber, oxygen and nitrogen react together to form NO_x which is a prominent source of acid rain and smog. Nitrogen oxides are very toxic to the plant species as they blemish leaves and mitigate growth[33]. Oxidation of CO and HCs over Co_3O_4 is now proven in literature, it can give conversion efficiency even greater than PGMs and has high selectivity towards CO_2. On the other hand conventionally in catalytic converters NO_x undergo the reduction reaction where Pt/Rh or Pd/Rh supported by AL_2O_3 are used as the reduction catalysts[34]. Recently many advances have been made to reduce NO_x with other than precious metals whether it is catalytic converters or SCR technology. There are generally two practical methods that are now implemented for NO_x removal one is catalytic converters and other is selective catalytic reduction by using NH_3 as a reducing agent[35], [36]. Wang[37] developed Cu-chabazite catalyst for the removal of NO_x by selective catalytic reduction with NH_3. The catalyst showed higher stability at all temperatures even at 750°C than the other zeolites-based catalysts used in SCR.

Yao[38] studied the reduction of NO_x on CeO_2 supported by different forms of TiO_2 like anatase, brookite, and rutile. He differentiated the effect of the crystal structure of TiO_2 on the reduction property of the catalyst. He reported that the CeO_2 based catalyst supported by rutile form of TiO_2 showed greatest activity in NH_3-SCR reaction for NO_x removal. He added these catalysts not only had greater reduction ability but had large acid sites and great amount of oxygen storage capacity (OSC) for rich operating condition. Boningari[39] synthesized different metal oxides catalyst supported over TiO_2 while NH_3 as reducing agent for NO_X reduction. He reported that vanadium oxide supported by titania exhibited maximum efficiency in monometallic while mixture of ceria and manganese oxide were excellent in bimetallic category.

Lu[40] studied the catalytic reduction of NO_X over Mn/Ce oxides using NH_3 as a reducing agent while supported on TiO_2-graphene. He reported that the catalyst with lower loading of Ce-Mn showed higher efficiency towards NOx reduction and higher selectivity towards N_2. The introduction of graphene with titania helped to curtail H_2O and SO_2.

2.5 Summary

In this chapter literature or the work which has been published related to my thesis has been discussed. Different alternative metals and metal oxides which have been alternative to the precious metals as less costly materials have been described. Conversions of NO_X, CO and HCs which are toxic pollutants over different materials have been briefly discussed. These conversions over materials that I am using are also discussed.

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Chapter 3

MATERIALS AND METHODS

All the chemicals used in this research work were of analytic grade. Titanium oxide (Panreac) was used to synthesize titania nanoparticles. H_2O_2 was used as an oxidizing agent in the hydrothermal method. Potassium hydroxide KOH was used to achieve the required pH of the solution for catalyst synthesis. Sodium silicate solution and sodium metabisulfite were used in a mixture of binding agents. Cobalt nitrate hexahydrate $Co(NO_3)_2.6H_2O$ was used as precursor material for getting cobalt oxide Co_3O_4. Zirconium oxide was used as promoter of the catalyst.

3.1 TiO_2 nanoparticles synthesis

60 g of titania powder was added 400 ml of distilled water. The mixture was stirred for 24 hours at 800 rpm and then it was allowed to settle down for 12 hours. Then settled material was dried in the oven for 12 hours at 100°C. The dried material was continuously crushed by using pestle and mortar and then it was allowed to calcine at 500°C for 6 hours in a furnace.

3.2 Catalyst preparation

3.2.1 Simple Catalyst

The catalyst was prepared by using the hydrothermal synthesis method. 2.75 g of cobalt nitrate hexahydrate $Co(NO_3)_2.6H_2O$ was added in 30 ml of distilled while stirring at room temperature as shown in figure 1.

Figure 2: Co(NO3)2.6H2O stirring with *water*

Figure 1: Addition of KOH

Figure 3: Addition of H_2O_2

Figure 4: Mixture of TiO2 nanoparticles and prepared suspension of $Co(NO_3)_2$.6H2O in autoclave

A mixture of potassium hydroxide KOH and water was added dropwise as a precipitating agent for the formation of $Co(OH)_2$ as shown in figure 2. The color of the mixture changed from pink to purple after addition. The pH value of the solution was continuously monitored while adding KOH so that it should reach 8-9. After that 30% mass fraction of H_2O_2 was added dropwise in the solution as an oxidant for the formation of spinel Co_3O_4 as shown in figure 3[1]. The color of the mixture started turning into brownish from purple after addition of hydrogen peroxide. 4g of titania nanoparticles were stirred in 40ml of water for one hour and then poured into a stainless-steel autoclave along with the suspension already prepared as shown in figure 4. The autoclave was sealed and was put in a furnace at 180°C for 10 h. Distilled water and ethanol were respectively used to wash the obtained powder and then it was dried in an oven at 100°C for 8 h.

3.2.2 Zirconia promoted catalyst

8% wt. zirconia was dissolved in the required amount of distilled water and was dropped on the already prepared Co_3O_4/TiO_2 catalyst so that it completely soaked the powder. Then it was kept in oven at 100°C for 5 hours and then calcined at 400°C for 6 hours.

3.3 Preparation and Pretreatment of wire meshes

An SS-304 wire mesh sheet of 4×4 feet size was cut into circular pieces of 6 cm diameter each shown in figure 6 by using a manual table cutter shown in figure 5. Before coating the catalyst on the wire meshes, they were pretreated with 10% HCL. For this purpose, wire meshes were kept dipping in HCL for half an hour as shown in figure 7. After that distilled water was used to wash them and kept in an oven for drying for an hour at 100°C. In this way impurities were removed from the stainless-steel structure.

Figure 5: Table cutter

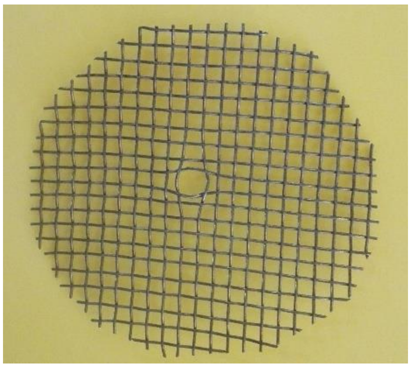

Figure 6: Wire mesh piece

Figure 7: Wire meshes immersed in HCl

3.4 Catalyst slurry formation

Catalyst slurry was prepared for coating it onto the wire mesh substrate. For this purpose, 3 g sodium metabisulfite and 270 g of sodium silicate were added together for each catalyst separately while stirring. 30 g of each catalyst was added in this mixture and stirred for 12 hours as shown in figure 8 and then it was coated on wire meshes[2].

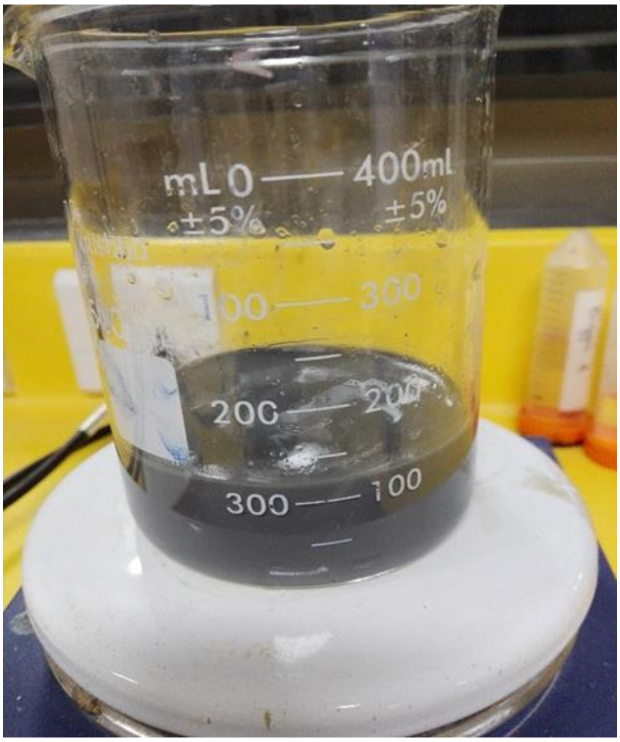

Figure 8: Catalyst slurry preparation

3.5 Catalyst coating on wire meshes

Catalysts were deposited on the pretreated wire meshes by using the dip-coating method. After coating a blower was used to remove the extra material from the wires of structure. This coating and blowing were repeated three times to achieve uniformity. The coated wire meshes were calcined in a furnace for 5 hours at 500°C to remove the impurities and then cooled at the room temperature.

3.6 Wire meshes specification

Wire meshes used in this study are woven with SS 304. Grade 304 is a standard “18/8” stainless steel which is a low cost, widely used and most versatile form of steel. It is very corrosion and heat resistant can survive up to 925°C of temperature[3]. Composition of the wire mesh steel is prescribed in table 2 below.

Table 2 Composition of SS-304[4]

Element	Weight %
Cr	18-20
Ni	8-10.5
C	0.08
Mn	2.0
P	0.045
S	0.030
Si	0.75
Ni	0.10
Fe	Balance

3.7 Substrate arrangement

24 wire meshes (for each catalyst) of the circular diameter of 6 cm were cut by a manual table cutter with a punch hole in the center. Then circular meshes were arranged on a threaded bar having a diameter of 4 mm with a washer between each of them to maintain a gap and closed by hexagonal nuts on both sides as shown in figure 9.

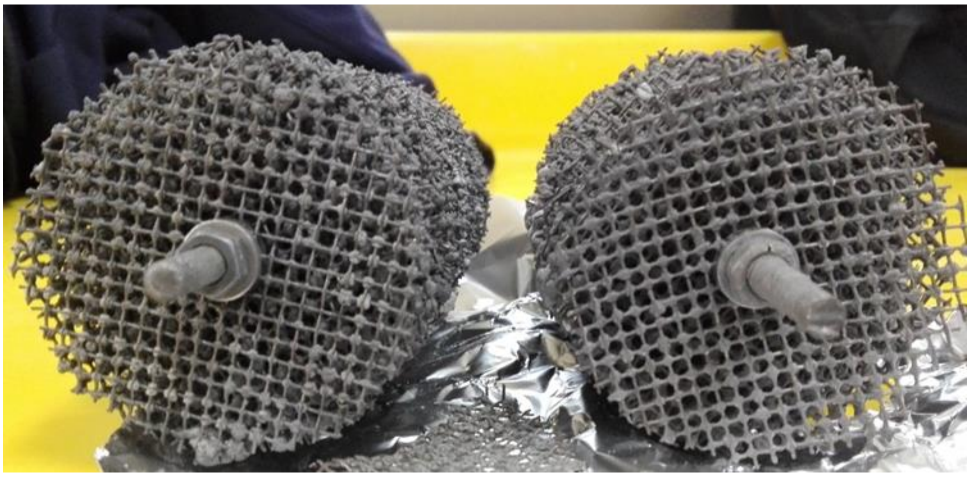

Figure 9: Wire meshes arranged on a threaded bolt

3.8 Characterization

3.8.1 X-ray diffraction

XRD analysis of TiO_2 and the catalysts was carried out by using an X-ray diffractometer. The analysis was done by Cu Kα radiation at voltage of 20 kV and current of 30 mA. The analysis was done from 10° to 80° at rate of 2° per minute. Catalysts' crystal size was determined by using Scherer equation.

$$L = \frac{K\lambda}{\beta cos\theta} \tag{4}$$

Where,

K = is a dimensionless shape factor

λ = 0.154 nm Cu kα wavelength

β = full width at half of the maximum intensity (FWHM)

θ = Bragg angle of the crystal phase

3.8.2 Scanning electron microscopy (SEM)

A scanning electron microscope provides images of high resolution with high focus. The focused beam of electrons provides us information about form, size and elemental composition of under analysis material. Tescan vega 3 scanning electron microscope was used to analyze the prepared catalysts. The compositional analysis of the catalyst was done by using EDS.

3.8.3 Thermogravimetric analysis (TGA)

The thermogravimetric analysis gives data about change in weight according to change in temperature. Weight loss or the weight gain curves give statistics about alterations in composition of sample, how stable sample is and other parameters. Schimadzu DTG-60H was used to analyze the thermal stability and the oxygen storage capacity (OSC) of the catalyst. TGA measurements were observed under cyclic heat treatment of samples in flowing air. In the first cycle, sample was treated under 800°C then cooled to 169°C. In second cycle sample was again heated to 800°C. All the heating and cooling rates were 10°C per minute. TGA data of weight loss of sample in second heating cycle was used to measure the oxygen storage capacity (OSC)[5].

3.8.4 Real time testing

The fabricated catalytic converters were mounted at the exhaust of a 70-cc petrol engine as shown in figure 10. The motorcycle engine having 72 cm^3 displacement, 47 mm of bore and 41.4 mm of stroke length was used. Test readings were taken by using Crypton’s gas analyzer for CO and HC but for NO_x readings, E instruments’ E4500-2 was used as shown in figure 11 and figure 12. Readings were taken at 1500, 3000, 4500 and 6000 RPM respectively.

Figure 10: Catalytic converter mounted on motorcycle's exhaust for final testing

Figure 11: Engine Exhaust gas analyzer

Figure 12: E4500-2 NOx analyzer

3.9 Summary

In this chapter Co_3O_4/TiO_2 and zirconia promoted catalyst synthesis technique and their real-time testing have been described. Catalysts are synthesized by using hydrothermal synthesis technique. Then they were coated on wire meshes and mounted at the exhaust of a motorcycle engine by putting it in clamshell. Tests were carried out at 1500, 3000, 4500 and 6000 rpms.

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Chapter 4

RESULTS AND DISCUSSION

4.1 X-ray Diffraction (XRD)

All phases of the prepared catalyst were identified by using the JCPDS powder diffraction file. In XRD analysis of titania (TiO_2), phase identified as rutile and no peaks of other forms of titania were noticed. XRD graph of TiO_2 shows peaks at 2 theta values 27.45°, 36.07°, 41.25°, 44.18°, 54.43°, 56.73°, 62.89°, 64.15°, and 69.13°. The particle size of titania nanoparticles was calculated by Sherrer equation which was 20.67 nm. In XRD analysis of the catalyst the spinel structure of cobalt oxide Co_3O_4 was identified. The pattern in figure 13 shows strong peaks at the 2 theta values of 31.4°, 36.90° and 44.85° indicating it a spinel structure of cobalt oxide Co_3O_4. The particle size of cobalt oxide was determined by using Sherrer equation at strongest peak of 2 theta value 36.90° which came out to be 30.6 nm. No other peaks of $Co(OH)_2$ or CoO were observed. No peaks of cubic structure of Co_3O_4 were observed at all. Zirconia (ZrO_2) peaks were observed at 28.26°.

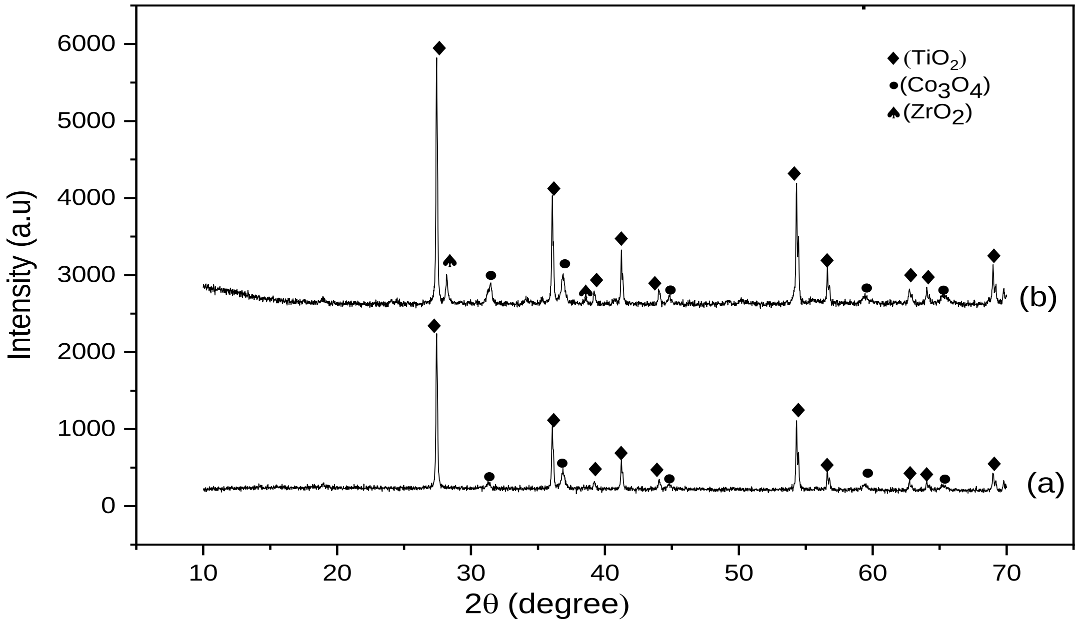
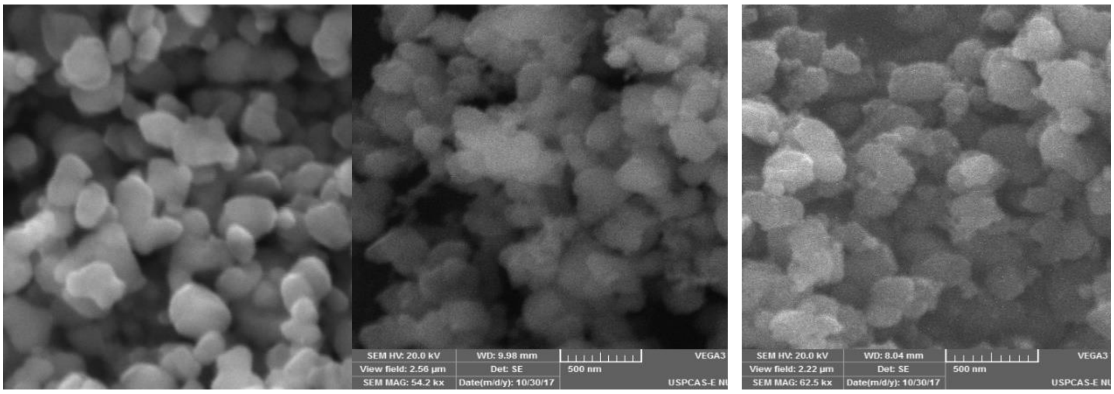


Figure 13: XRD patterns of Catalysts (a) Co_3O_4/TiO_2 (b) 8% wt. ZrO_2-Co_3O_4/TiO_2

4.2 Scanning Electron Microscopy (SEM)

SEM images of the samples are shown in figures with different scaling. It was observed that the particles were spherical in shape and the size was less than 50nm. Size and the shape of the particles are uniform without many variations as shown in figure 14 (a), (b) and (c).



(a) **(b)** **(c)**

Figure 14: SEM images of catalysts (a) TiO_2 nanoparticles, (b) Co_3O_4/TiO_2, (c) 8%wt.ZrO_2-Co_3O_4/TiO_2

4.3 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was carried out to analyze the stability of the zirconia promoted at higher temperatures as well as to find out the oxygen storage capacity of the catalyst for the redox reactions. The catalyst powder of 6.78 mg was put in furnace of TG analyzer. For this purpose, catalyst was heated from room temperature to 800°C in the presence of air stream to provide atmospheric condition with flow rate of 10 ml/min and the weight loss was calculated as 7.22%. This loss of weight corresponds to both loss of water and also oxygen molecules. Then it was cooled to 169°C in the presence of air stream with same flow rate during which it gained weight of about 1.76% which corresponds to oxygen gaining of catalyst[1]. There was 2.2% weight loss observed in second heating cycle as shown in figure 15 which corresponds to the oxygen releasing capacity of the catalyst in atmospheric conditions.

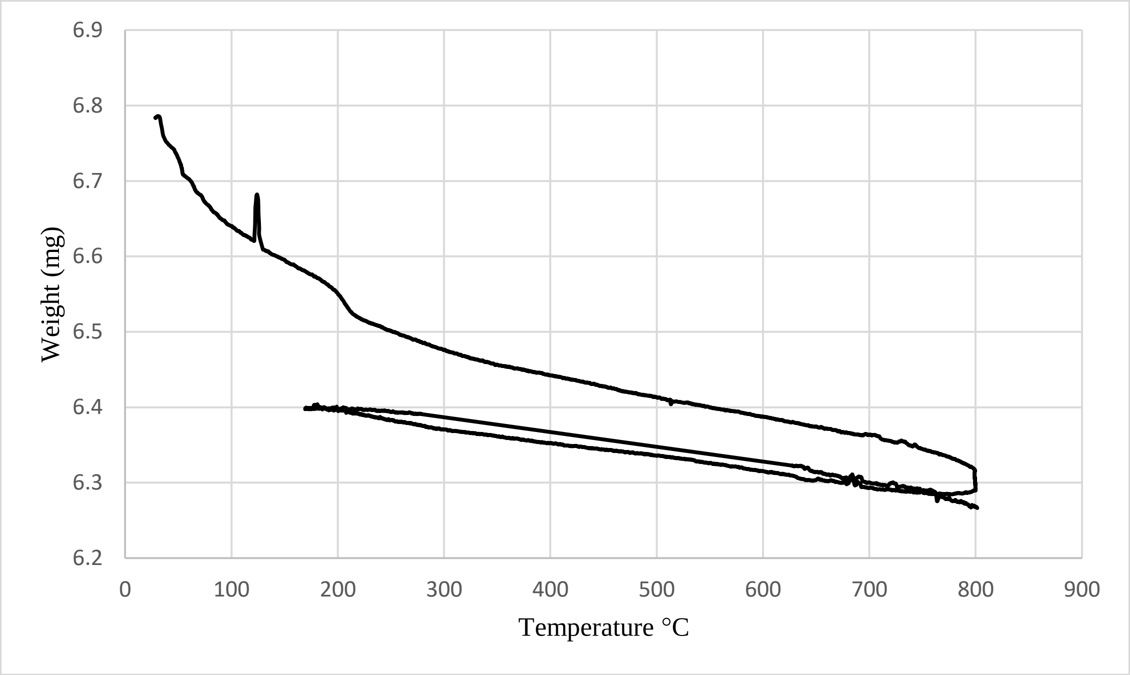


Figure 15: Graph between weight and temperature

4.4 Catalytic Activity Test

The activity of the catalysts was measured in real-time testing conditions and the conversion efficiencies of CO, HCs and NO_X were also noticed. The newly fabricated catalytic converters were mounted at the exhaust of the 70-cc motorcycle. The RPMs of the engine shaft were increased manually from 1500 to 6000 with the interval of 1500. The temperature of the exhaust gases also increased giving values 121°C, 257°C, 284°C and 391°C with respect to RPMs of 1500, 3000, 4500 and 6000. With the increment in temperature, it was noticed that the amounts of HCs and CO coming out of combustion chamber decreased but for NO_X it was the reverse case.

4.4.1 NO_x Conversion

In the case of NO_X, the maximum conversion efficiency was noticed at 1500 RPMs as shown in figure 16 which was 71.4% for simple catalyst but Zirconia promoted catalyst showed higher efficiency of 75% for NO_X reduction shown in figure 17. At this point the exhaust gas temperature was minimum and NO_X amount in the gas stream was minimum in its range proving that NO_X is produced at higher temperatures as mentioned in literature[2]–[4]. While lambda value at this point was 1.323 which showed that the compression ratio inside the combustion chamber of motorcycle was 19.5:1 and the air-fuel mixture was lean.

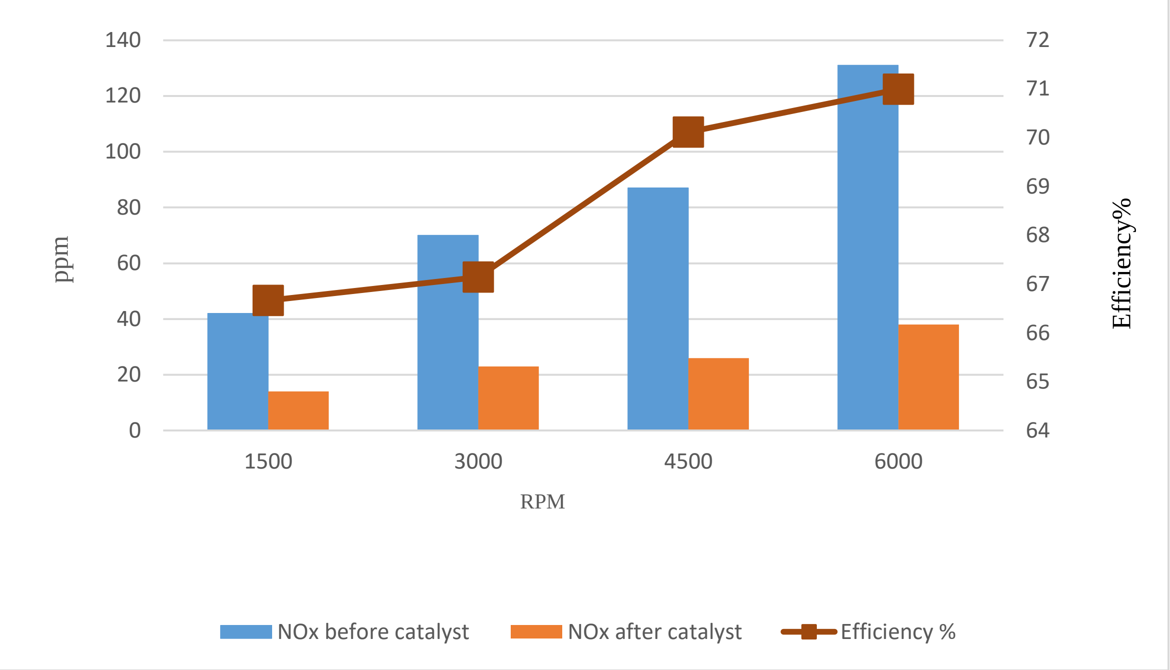


Figure 16: Conversion of NOx with Co_3O_4/TiO_2

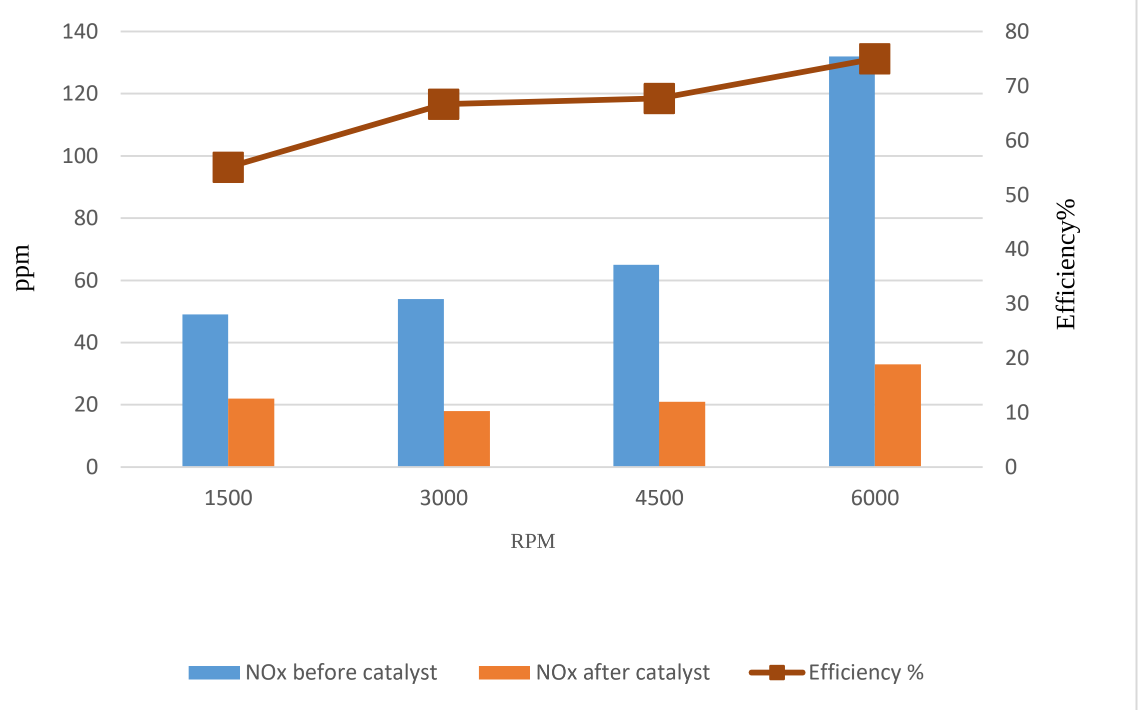


Figure 17: Conversion of NO_X with 8 wt. % ZrO_2-Co_3O_4/TiO_2

4.4.2 CO Conversion

In the case of CO, maximum conversion efficiency was noticed at 1500 RPMs which was 78.15% for simple catalyst and slightly higher 78.65% for zirconia promoted catalyst as shown in figure 18 and 19. At this point CO amount in exhaust gas was maximum in its range which decreases drastically with temperature increment from 1500 to 6000 RPMs. The inlet lambda value was noticed to be same 1.323 thus the compression ratio of 19.5:1. A higher compression ratio indicating that the air-fuel mixture is lean thus oxidation reactions are more favorable[5]. The outlet lambda value was recorded as 6.02 which means that catalyst is working properly.

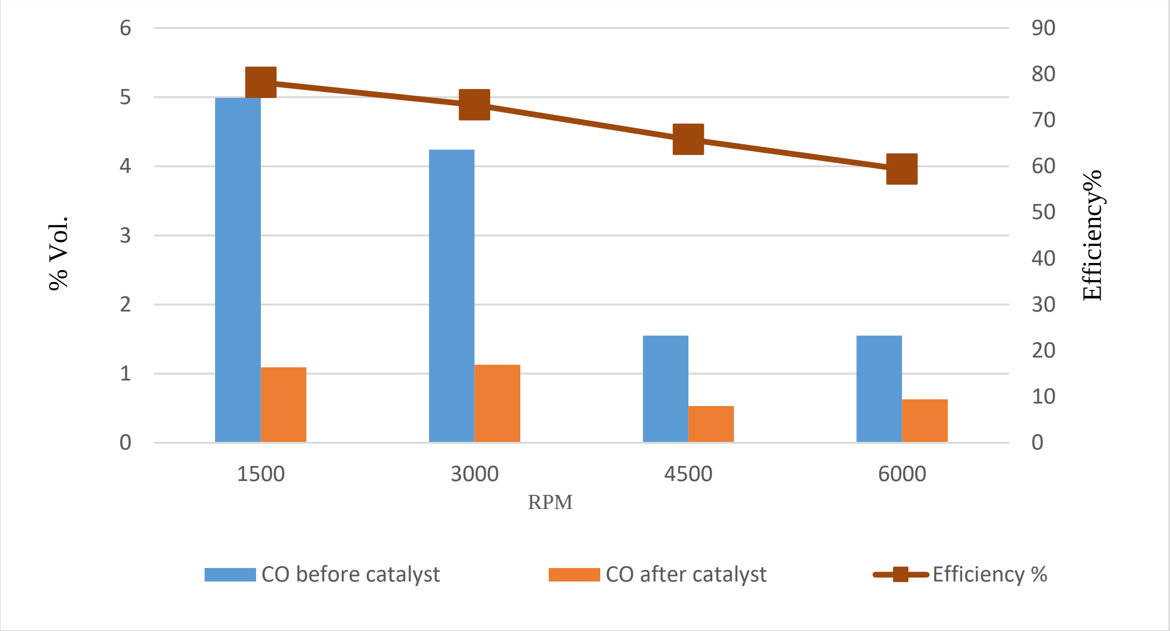


Figure 18: Conversion of CO with Co_3O_4/TiO_2

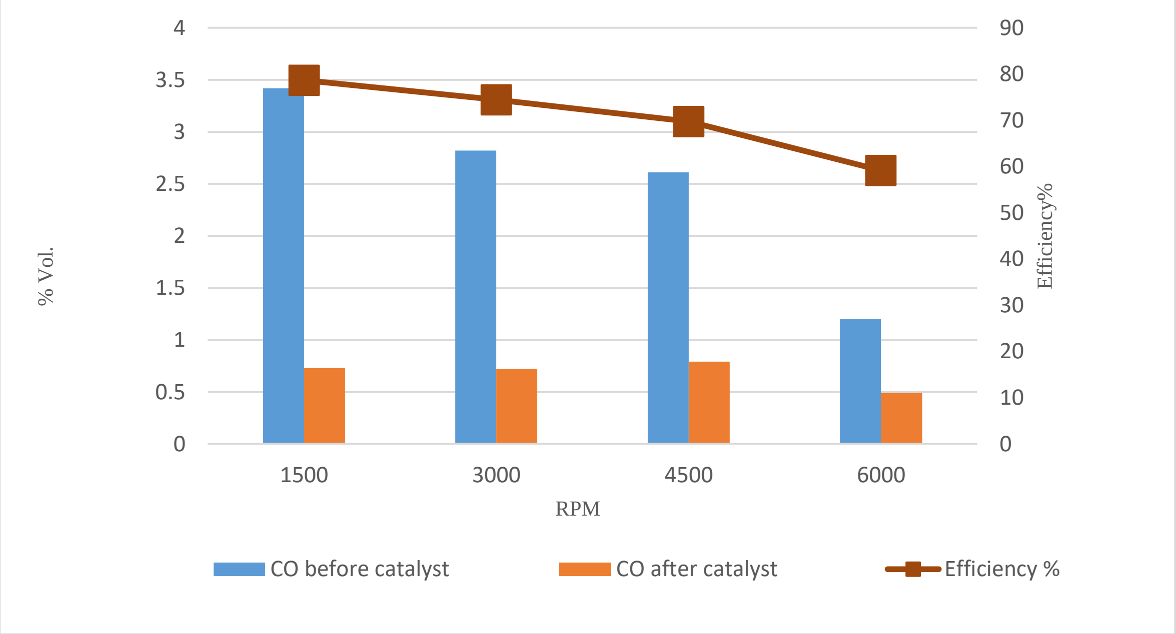


Figure 19: Conversion of CO with 8 wt. % ZrO_2-Co_3O_4/TiO_2

4.4.3 HC Conversion

Hydrocarbons conversion efficiency was noticed as 82.56% for simple catalyst at 4500 RPMs as shown in figure 20 but in the case of promoted catalyst HC conversion decreased and gave highest value of 81.3%. Graph representation is shown in figure 21. With increasing RPMs temperature also increased but the ppm of hydrocarbons decreased. Thus confirming that amount of CO, NO_x, and HCs producing inside the combustion chamber depending on the temperature inside[6].

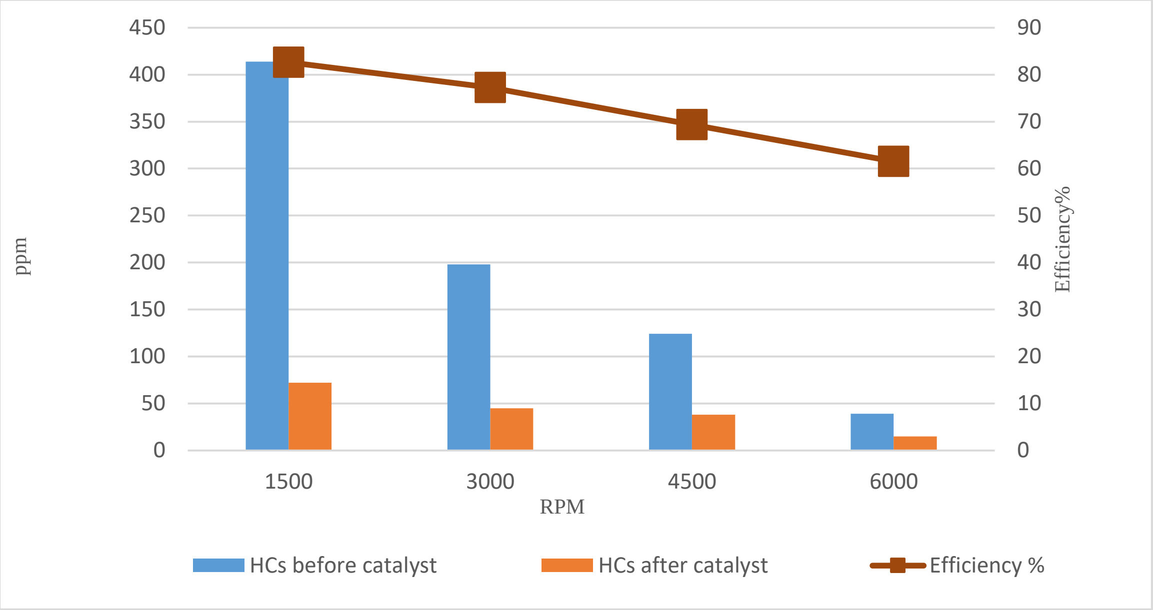


Figure 20: HC Conversions with Co_3O_4/TiO_2

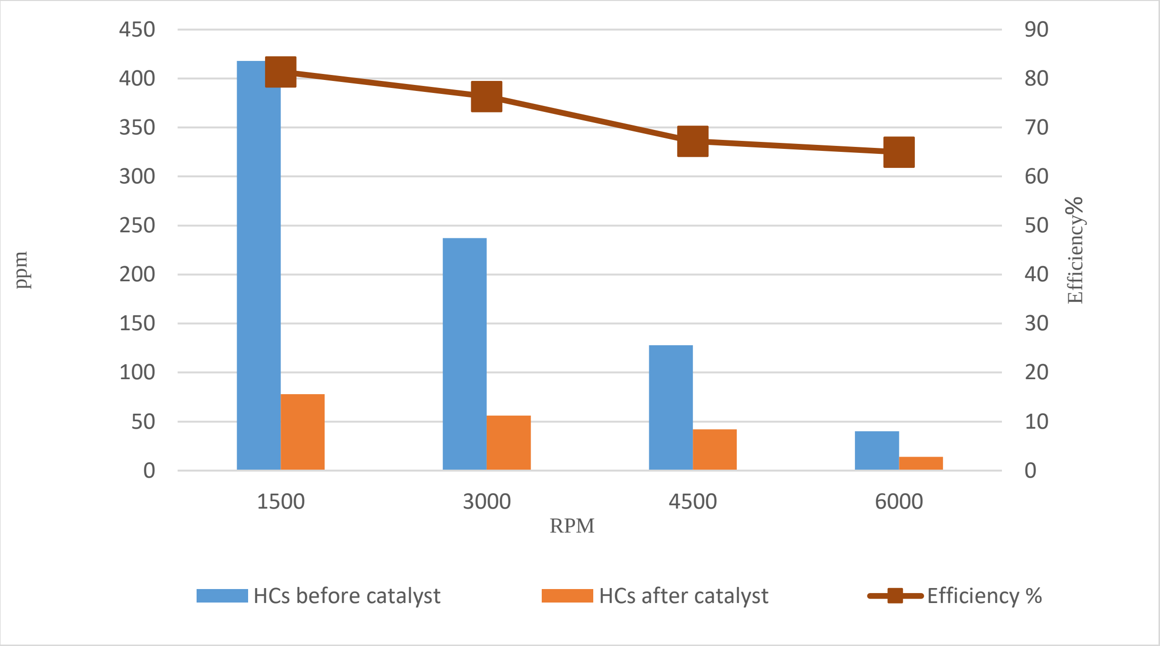


Figure 21: HC conversions with 8 wt. % ZrO_2- Co_3O_4/TiO_2

4.5 Summary

In this chapter results of the characterizations and testing are discussed. Real-time activity tests of both catalysts show very significant results. Zirconia promoted catalyst show better conversion results compare to the simple catalyst. Promoted catalyst has more efficiency of NOX conversion than the simple catalyst.

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Chapter 5

CONCLUSION AND FUTURE WORK

5.1 Conclusion

- Two alternative catalysts Co_3O_4/TiO_2 and 8% wt. ZrO_2 promoted Co_3O_4/TiO_2 have been found active for CO, HC and NO_X conversions.
- Zirconia promoted catalyst showed more promising results towards NO_X and CO conversion.
- The lower efficiency of zirconia promoted catalysts towards HCs is due to the non-availability of the vacancies of oxygen for oxidation.
- Both the catalyst showed selectivity towards CO, $NO_{X,}$ and HC.
- Results revealed that the addition of zirconia played a positive role in stability and oxygen storage capacity of the catalyst.

5.2 Future Work

- By using wire mesh structure there is backpressure on the engine which needs to be evaluated.
- By changing and optimizing the loadings of zirconia and cobalt oxide even high conversion results can be achieved.
- Proper CFD analysis of cell density and wire mesh structure needs to be done to get maximum efficiency and minimum backpressure.
- As there is a lot of temperature loss that can be restrained to give a higher temperature inside for more efficient reactions.
- SEM images of the coated wires before and after testing showed some agglomeration so the coating technique needs to be further studied.

Annexure

Effect of Zirconia on hydrothermally synthesized Co_3O_4/TiO_2 catalyst for NO_x Reduction from engine emission

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Abstract

We looked into the effect of zirconia on the 6 wt. % Co_3O_4/TiO_2 catalyst for NO_x reduction. Co_3O_4/TiO_2 catalyst was prepared by using hydrothermal method and then was promoted with zirconia by impregnation to get 6 wt. % $Co_3O_4/Ti_{0.92}Zr_{0.08}O_2$ catalyst. Catalysts were characterized by using XRD, SEM and TGA. Catalysts real time activity was tested by coating them on stainless steel wire meshes, containing them in a mild steel shell and mounting them at the exhaust tailpipe of a 72 cm^3 motorcycle. Zirconia promoted catalyst showed higher conversion efficiency of NO_X than the simple Co_3O_4/TiO_2 catalyst.

1. Introduction

Gases coming out of automobile vehicles are one of the biggest contributor towards the air pollution in most cities of the world[1]–[4]. Annually 4.2 million people die due to the ambient air pollution throughout the world [5][6]. Since the introduction of clean air act in 1970 a numbers of efforts have been made to reduce the engine exhaust pollution. Engine exhaust emissions contain three major pollutants that are carbon monoxide (CO), nitrogen oxides (NOx) and hydrocarbons (HCs) which needed to be tackled[7]. Different methods like thermal reactors, diesel particulate filters (DPFs), selective catalytic reduction SCR, changes in engine design, oxygenated fuels and catalytic converters had been adopted to truncate this concern to the minimum level[8][4]. Gasoline blended with 3% oxygen by weight reduces 30% of CO emissions but NO_X concentration increases which can swell ozone problems[9]. Conventionally catalytic converters employ Pt, Pd and Rh as catalysts with innovations like introduction of CeO_2 or CeO_2-ZrO_2 composite for managing the time lag from switching between lean to rich condition or vice versa[10][11]. These metals are emitted out due to high temperatures, mechanical friction, stresses and chemical reactions to the roadside soils which cause disruption in plant growth[12]. Due to high solubility of PGEs with various compounds, presence of these metals in environment can cause many health threats like nausea, tumor, sensitization, pregnancy loss and other human health issues[13][14]. Moreover due to thermal aging Rh_2O_3 reacts with Al_2O_3 to form an inactive compound, Pt sintering occurs at 700°C and at high temperature of 900°C sintering of γ-AL_2O_3 occurs and it transforms to α-AL_2O_3 which has less surface area[15]. These metals are rarest of the elements present on the earth ranging from 5 to 15 ppm in ores mines and from 0.022 ppb for Ir to 0.52 ppb for pd[16], [17]. Automotive industry consumed 37% of platinum, 72% of palladium and 79% of rhodium in 2013[16]. Due to scarcity of these metals, increasing prices and health hazards, it has been a requirement to find a replacement which is less rare, less expensive and competitively active. Over the period of time many pure metals and metal oxides have been tested as alternatives to these PGEs for redox reactions in catalytic converters i.e. Au, Ni, Cu, MnO_2, CoO, Co_3O_4 and CuO[16], [18]–[20]. Co_3O_4 over different supports has been investigated as catalyst for oxidation of CO and HC in exhaust emission control system and has demonstrated low temperature activity[21], [22]. Wang et al. [23] experimented by preparing cobalt oxide catalyst with three different supports like TiO_2, Al_2O_3 and SiO_2 by using incipient wetness impregnation method. He expressed that the type of cobalt oxide and type of support used had a great effect on the activity and the surface area. He concluded that CoO_x/TiO_2 showed very significant results towards CO conversion. Hu et al. [24] performed the oxidation of CO on cobalt oxides nanobelts and nanocubes. He revealed that the shape Co_3O_4 had a great effect on the catalytic activity towards CO as nanobelts depicted more conversion efficiency than nanocubes. Jia et al. [25] prepared Co_3O_4-SiO_2 nanocomposite as catalyst with high surface area for oxidation of CO. He observed that the catalyst showed activity at a very low temperature of even -76°C. He concluded that there was some adsorption of water molecules on the exterior of catalyst which caused abnormal behavior in the activity of catalyst. Xie et al. [26] reported that Co_3O_4 showed high activity for carbon monoxide conversion surprisingly at temperature of -77°C and remained stable under the moist conditions. He observed that under the stoichiometric conditions, conversion efficiency of Co_3O_4 catalyst was 96% at temperature of 200°C but the conversion efficiency decreased at temperature of 150°C to 40% due the presence of moisture content.

On the other hand due to high thermal stability, high surface area and highly resistant towards poisoning TiO_2 has been used widely for catalyst support as an alternate to alumina[27], [28]. Titanium dioxide exists in three crystalline phases that are anatase, brookite and rutile however anatase and rutile play a role in applications of titanium dioxide. Anatase is less dense and less stable than rutile at ambient temperature and pressure conditions[29]. Zhu et al. [30] studied the effect of TiO_2 structure on catalytic properties of copper oxide supported by anatase or rutile for NO reduction by CO reaction. He concluded that copper oxide supported by rutile TiO_2 was more active than supported by anatase TiO_2. Nowadays commercially available three way catalysis systems have ceria or ceria-zirconia along with alumina and precious metal to increase the conversion efficiency. The incorporation of ceria-zirconia mixture into automotive catalysts was to enhance the OSC for the redox reactions by releasing/storing oxygen depending upon A/F ratio and other factors[31]. Extensive studies have been carried on ceria, zirconia and mixture of both as OSC is very important for increment of CO oxidation as well as the reduction of NO at the same time. Transition metal oxides have shown a great potential to have oxygen vacancies on the surface like TiO_2, ZrO_2 and V_2O_5[32]. Yu et al. [33] studied the adsorption and oxidation of CO by O_2 at the surface of rutile TiO_2. Li et al. [34] calculated the oxygen vacancies on anatase and rutile TiO_2 and concluded that both phases have oxygen vacancies but in case of rutile more stable oxygen vacancy was found on the surface rather on subsurface. In case of zirconia oxygen vacancies are produced by doping but undoped zirconia also contains bulk concentration of oxygen vacancies[35]. In this work we are going to present the effect of zirconia on hydrothermally produced Co_3O_4/TiO_2 catalyst for petrol engine emissions control system. Zirconia was impregnated on catalyst and new 8% wt. ZrO_2-Co_3O_4/TiO_2 was prepared. Both catalysts were coated on round wire meshes then placed in a mild steel clam shell and mounted on exhaust of motorcycle. Zirconia promoted catalyst showed more qualities of reductive catalyst as less NO_x were seen after the reaction inside the catalytic converter.

2. Experimental

2.1 Catalyst preparation

For synthesis of TiO_2 nanoparticles, 60 g of titania powder was added 400 ml of distilled water. The mixture was stirred for 24 hours at 800 rpm and then it was allowed to settle down for 12 hours. Then settled material was dried in oven for 12 hours at 100°C. The dried material was continuously crushed by using pestle and mortar and then it was allowed to calcine at 500°C for 6 hours in a furnace. Catalyst was prepared by using hydrothermal synthesis method. 2.75 g of cobalt nitrate hexahydrate $Co(NO_3)_2.6H_2O$ was added in 30 ml of distilled while stirring at room temperature to give 6 wt. % loading. A mixture of potassium hydroxide KOH and water was added dropwise as precipitating agent for the formation of $Co(OH)_2$. Color of the mixture changed from pink to purple after addition. The pH value of the solution was continuously monitored while adding KOH so that it should reach 8. After that 30% mass fraction of H_2O_2 was added dropwise in the solution as shown in figure 3. Color of the mixture started turning into brownish from purple after addition of hydrogen peroxide. 4g of titania nanoparticles were stirred in 40ml of water for one hour and then poured into a stainless steel autoclave along with the suspension already prepared. The autoclave was sealed and was put in a furnace at 180°C for 10 h. Distilled water and ethanol were respectively used to wash the obtained powder and then it was dried in an oven at 100°C for 8 h. 8% wt. zirconia was dissolved in required amount of distilled water and was dropped on the already prepared Co_3O_4/TiO_2 catalyst so that it completely soaked the powder. Then it was kept in oven at 100°C for 5 hours and calcined at 400°C for 6 hours to have 8% wt. ZrO_2-Co_3O_4/TiO_2.

2.2 Characterization

Powder X-ray diffraction (XRD) patterns were recorded by using – operates using Cu-kα radiation operating at 40kV and 30mA with 0.02° step size. Samples were scanned ranging the 2θ values from 10° to 70°. Tescan Vega3 scanning electron microscope was used to analyze the morphology of prepared catalysts operating at 20kV. Schimadzu DTG-60H having alumina pan was used to analyze the thermal stability and the oxygen storage capacity (OSC) of the zirconia promoted catalyst with temperature ranging from 28°C to 800°C with heating and cooling rate of 10°C/min.

2.3 Fabrication and testing of catalytic converter

2.3.1 Preparation of wire meshes

A SS-304 wire mesh sheet of 4×4 feet size was cut into 48 circular pieces of 6 cm diameter each by using a manual table cutter. Before coating the catalyst on the wire meshes, they were pretreated with 10% HCL. For this purpose wire meshes were kept dipping in HCL for half an hour. After that distilled water was used to wash them and kept in an oven for drying for an hour at 100°C. In this way impurities were removed from the stainless steel structure.

2.3.2 Catalyst slurry

Catalyst slurry was prepared for coating it onto the wire mesh substrate. For this purpose 3 g sodium metabisulfite and 270 g of sodium silicate were added together for each catalyst separately while stirring. 30 g of each catalyst was added in this mixture and stirred for 12 hours then it was coated on wire meshes.

2.3.3 Catalyst coating

Catalysts were deposited on the pretreated wire meshes by using dip coating method. After immersing a blower was used to remove the extra material from the wires of structure. This immersion and blowing was repeated three times to achieve uniformity. The coated wire meshes were calcined in a furnace for 5 hours at 400°C to remove the impurities and then cooled at the room temperature.

2.3.4 Wire meshes arrangement

24 circular wire meshes (for each catalyst) after being coated were arranged on a threaded bar having 4 mm diameter with 1mm thick washers between them to keep them away from intermingling. Both sides of the bar were closed by using hexagonal nut. These catalysts coated wire mesh structures were respectively placed in mild steel clam shell for activity testing having inner diameter of 6.2 cm and sealed with Teflon lining to prevent any leakage of gases.

2.4 Activity test

The fabricated catalytic converters were mounted at the exhaust pipe of a 70 cc petrol engine having 72 cm^3 displacement, 47 mm of bore and 41.4 mm of stroke length was used. Test readings were taken by using Crypton's gas analyzer for CO and HC conversions but for NO_x readings E instruments' E4500-2 was used. Catalytic activity readings were taken at 1500, 3000, 4500 and 6000 revolutions per minute which were manually set. Engine shaft angular speed was measured by a tachometer.

3. Results and discussions

3.1 X-ray diffraction (XRD)

All phases of the prepared catalyst were identified by using JCPDS powder diffraction file. In XRD analysis of Co_3O_4/TiO_2, phase identified was rutile and no peaks of other phases of titania were noticed. XRD pattern of Co_3O_4/TiO_2 nanoparticles is shown in figure 1(a). XRD graph of TiO_2 shows peaks at 2 theta values 27.45°, 36.07°, 41.25°, 44.18°, 54.43°, 56.73°, 62.89°, 64.15° and 69.13°. Particle size of titania nanoparticles was calculated by Sherrer equation which was 2.67 nm from highest peak at 27.45°. In XRD analysis of the catalyst the spinel structure of cobalt oxide Co_3O_4 was identified. The pattern in figure1(a) shows strong peaks at the 2 theta values of 31.4°, 36.90° and 44.85° indicating it a spinel structure of cobalt oxide Co_3O_4. Particle size of cobalt oxide was determined by using Sherrer equation at strongest peak of 2 theta value 36.90° which came out to be 3.6 nm. No other peaks of $Co(OH)_2$ or CoO were observed. No peaks of cubic structure of Co_3O_4 were observed at all. XRD pattern of 8% wt. ZrO_2-Co_3O_4/TiO_2 is shown in figure 1(b). Co_3O_4, TiO_2 and ZrO_2 were detected successfully. Highest peak of zirconia (ZrO_2) was observed at 28.24˚, one more of zirconia was observed at 38.6˚. Particle size of zirconia was calculated at highest peak which came out to be 2.7 nm.

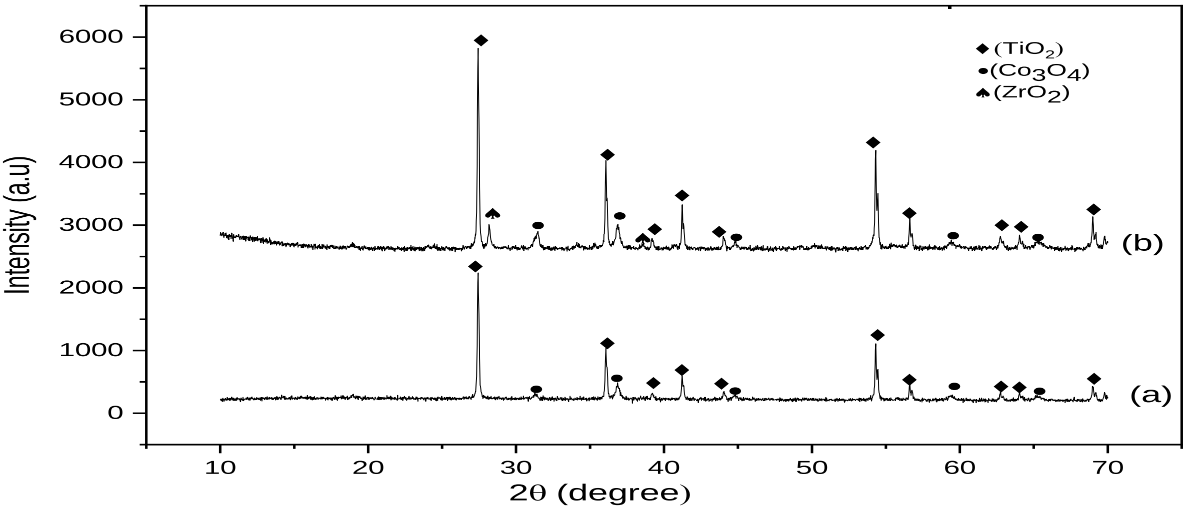
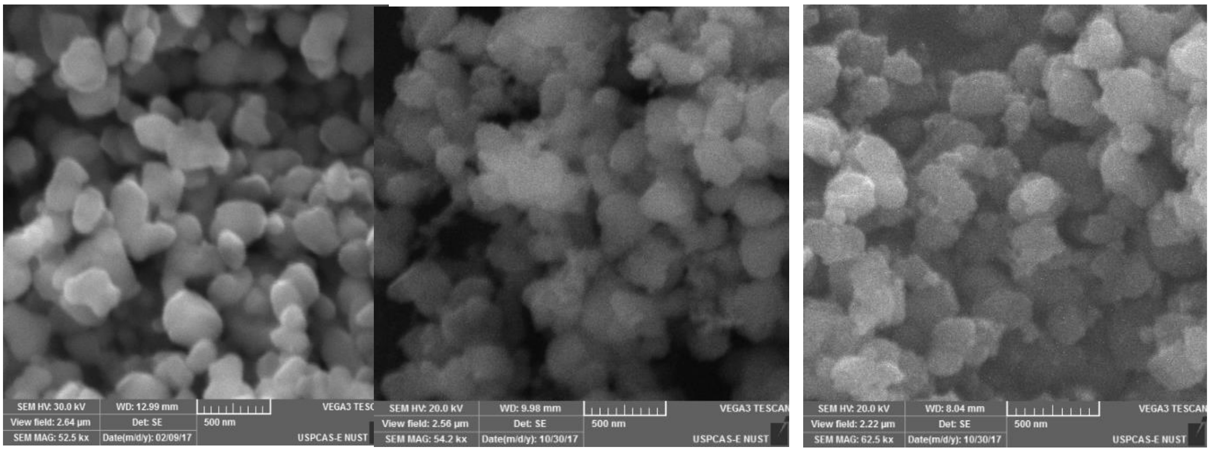


Figure 22: XRD patterns of Catalysts (a) Co_3O_4/TiO_2 (b) 8% wt. ZrO_2-Co_3O_4/TiO_2

3.2 Scanning Electron Microscopy (SEM)

SEM images of the samples are shown in figures with different scaling. It was observed that the particles were spherical in shape and size was less than 10 nm. Size and the shape of the particles are uniform without many variations. SEM images of the samples at the same scale are shown in figure (a), (b) and (c).



(a) TiO_2 nanoparticles

(b) Co_3O_4/TiO_2 catalyst

(c) 8% wt. ZrO_2-Co_3O_4/TiO_2 catalyst

3.3 Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out to analyze the stability of the zirconia promoted catalyst at higher temperature as well as to find out the oxygen storage capacity (δ) of the catalyst for the redox reactions. 6.78 mg of catalyst powder was put in furnace of TG analyzer and was heated from room temperature to 800°C in the presence of air stream to provide atmospheric condition with flow rate of 10 ml/min. The weight loss in the first heating cycle was calculated as 7.22% which corresponds to both loss of water and also oxygen molecules[36]. Then it was cooled to 169°C in the presence of air stream with same flow rate during which it gained weight of about 1.76% which corresponds to oxygen gaining of catalyst. The OSC value (δ) of zirconia promoted catalyst is observed to be 1.4 µmol/g which is quite significant value as per literature[37]. There was 2.2% weight loss observed in second heating cycle as shown in figure 2 which corresponds to the oxygen releasing capacity of the catalyst in atmospheric conditions.

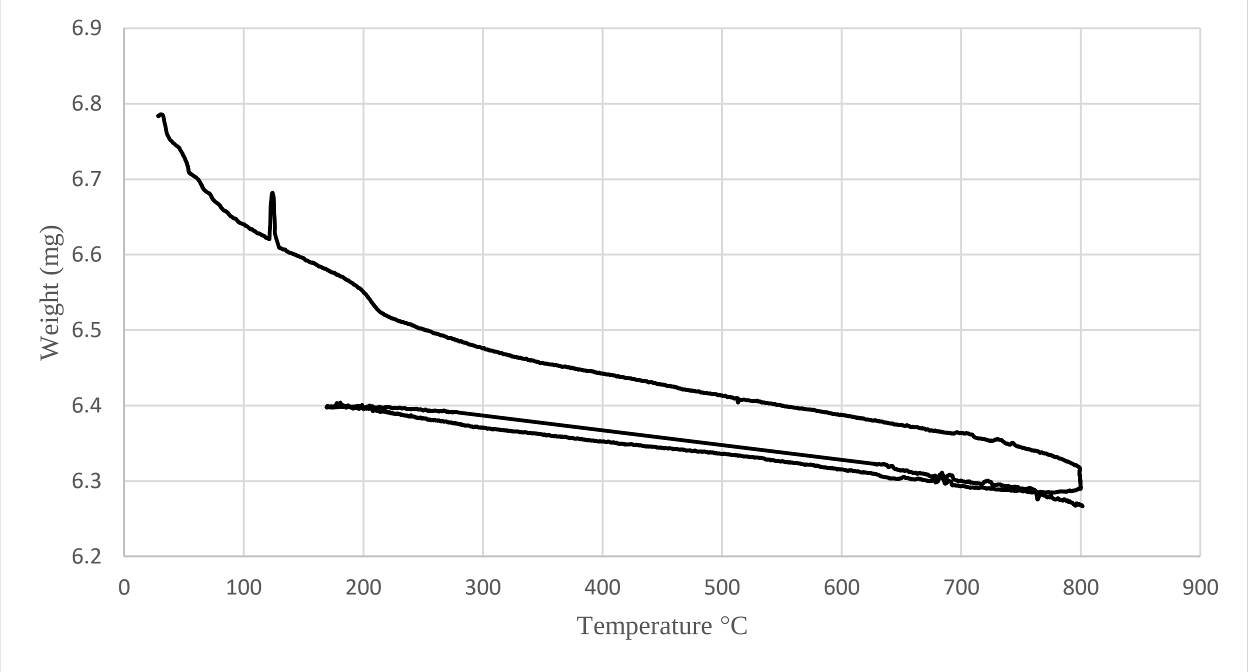


Figure 23: Graphical representation between weight of catalyst and temperature

3.4 Catalytic activity

The RPMs of the engine shaft were increased manually from 1500 to 6000 with the interval of 1500. Temperature of the exhaust gases also increased giving values 121°C, 257°C, 284°C and 391°C with respect to RPMs of 1500, 3000, 4500 and 6000. In case of NO_X the maximum conversion efficiency was noticed at 1500 RPMs as shown in figure 3 which was 71.4% for simple catalyst but Zirconia promoted catalyst showed higher efficiency of 75% for NO_X reduction shown in figure 4. At this point the exhaust gas temperature was minimum and NO_X amount in the gas stream was minimum in its range proving that NO_X are produced at higher temperature as mentioned in literature. While lambda value at this point was 1.323 which showed that the compression ratio inside the combustion chamber of motorcycle was 19.5:1 and the air fuel mixture was lean. In case of CO, maximum conversion efficiency was noticed at 1500 RPMs which was 78.15% for simple catalyst and slightly higher 78.65% for zirconia promoted catalyst as shown in figure 6. At this point CO amount in exhaust gas was maximum in its range which decreases drastically with temperature increment from 1500 to 6000 RPMs. The inlet lambda value was noticed to be same 1.323 thus the compression ratio of 19.5:1. Higher compression ratio indicating that air fuel mixture is lean thus oxidation reactions are more favorable. The outlet lambda value was recorded as 6.02 which means that catalyst is working properly. Hydrocarbons conversion efficiency was noticed as 82.5% for simple catalyst at 4500 RPMs as shown in figure 7 but in case of promoted catalyst HC conversion decreased and gave highest value of 69%. With increasing RPMs temperature also increased but the ppm of hydrocarbons decreased. Thus confirming that amount of CO, NOx and HCs producing inside combustion chamber depend on the temperature inside.

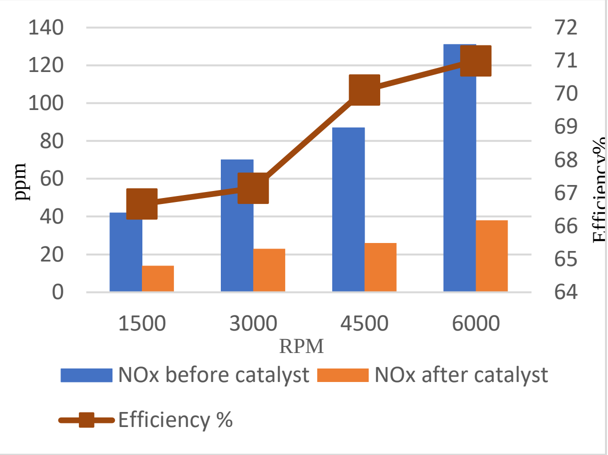


Figure 24: Conversion of NOx with Co_3O_4/TiO_2

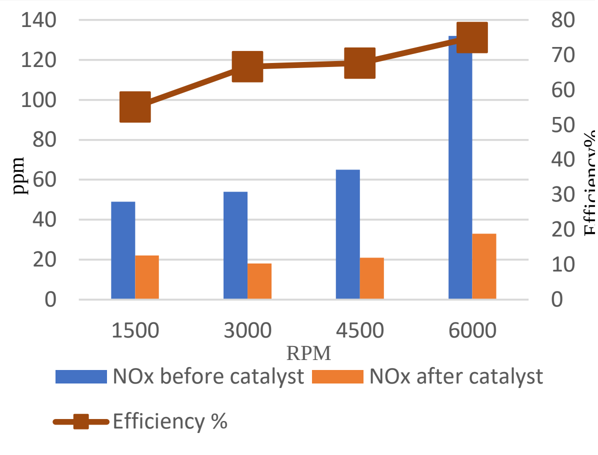


Figure 25: Conversion of NO_X with 8 wt. % ZrO_2-Co_3O_4/TiO_2

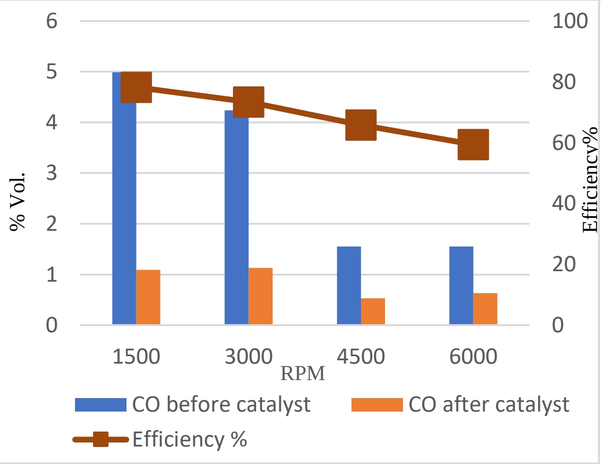


Figure 26: Conversion of CO with Co_3O_4/TiO_2

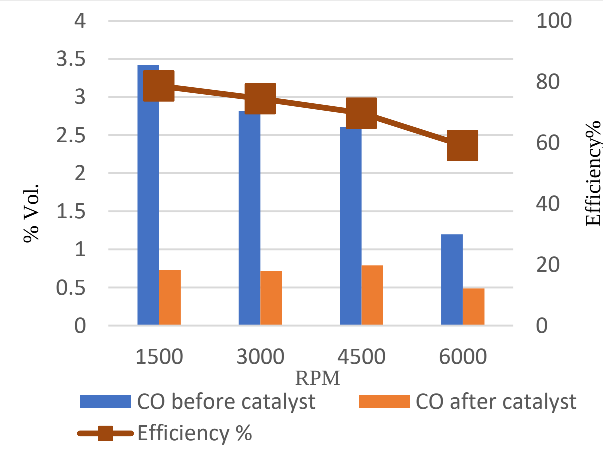


Figure 27: Conversion of CO with 8 wt. % ZrO_2-Co_3O_4/TiO_2

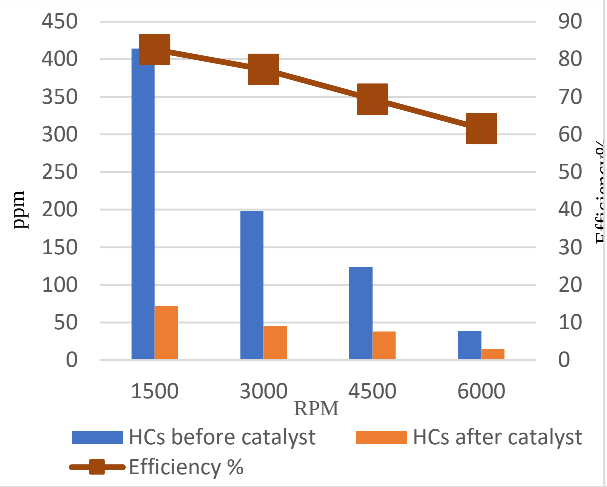


Figure 28: HC Conversions with Co_3O_4/TiO_2

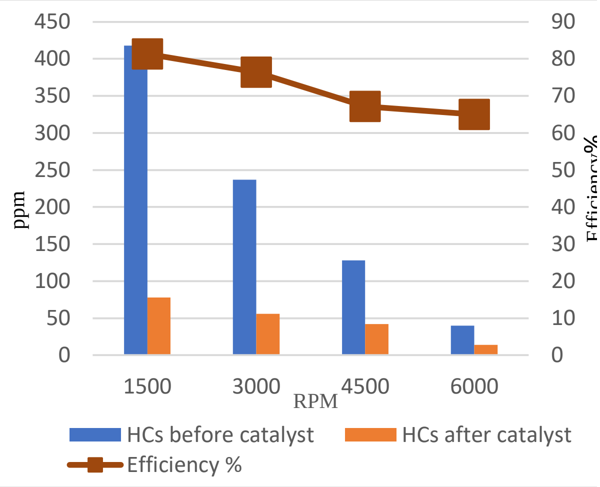


Figure 29: HC conversions with 8 wt. % ZrO_2-Co_3O_4/TiO_2

4. Conclusion

- Two alternative catalysts Co_3O_4/TiO_2 and 8% wt. ZrO_2 -Co_3O_4/TiO_2 have been found very active for CO, HC and NO_X conversions.
- Zirconia promoted catalyst showed more promising results towards NO_X and CO conversion.
- Lower efficiency of zirconia promoted catalyst towards HCs is due to the non-availability of the vacancies of oxygen for oxidation.
- Both the catalyst showed selectivity towards CO, NO_X and HC.
- Results revealed that addition of zirconia played a positive role in stability and oxygen storage capacity of the catalyst.

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