Effects of loading and particle size on Co supported TiO_2 catalysis for catalytic converter

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Dedicated to……….

My beloved parents & respected teachers without their support all this would not have been possible.

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List of Abbreviations

ICE	**Internal combustion engine**
A/F	**Air to fuel ratio**
CC	**Catalytic converter**
TWC	**Three way catalytic converter**
TiO_2	**Titania**
Co	**Cobalt**
Co_3O_4	**Cobalt oxide**
CO	**Carbon monoxide**
HCs	**Hydrocarbons**
NOx	**Oxides of nitrogen**
SOx	**Oxides of sulfur**
CO2	**Carbon dioxide**
CH4	**Methane**
CNG	**Compressed natural gas**
GHG	**Greenhouse gases**
O_3	**Ozone**
XRD	**X ray diffraction**
SEM	**Scanning electron microscope**
BET	**Brunauer Emmett Teller**
EPA	**Environmental Protection Agency**

Abstract

Carbon monoxide (CO) and hydrocarbons (HCs) are two of the major pollutants from vehicles affecting air quality in general and urban air quality in particular. Catalytic converter transforms these pollutants into less harmful products and are one the most widely used means of vehicular emission control. This study investigates the effect of loading and particle size of the cobalt oxide catalyst supported on titania using stainless steel wire mesh as substrate for the oxidation of HCs and CO from a real engine exhaust. Five different loadings of titania supported cobalt catalyst ranging from 6-21 wt. % have been prepared by the wet impregnation method. The catalysts have been characterized by using X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM) and (BET) surface area analyzer. By increasing the loading of Co, results showed increasing trend in conversion efficiency till the optimization occurred at 18 wt. %. The catalytic converter oxidized 93 and 96% CO and HCs emissions respectively.

Chapter 1

Introduction

The pollution from the air has a vital role in modern civilization. It interrupts the environment and human's life. The introduction of any material into the environment which has negative results on environment or people's health is understood as air pollution **(**Kampa and Castanas, 2008). The sources of air pollution are mobile and immobile. Exhaust industry, transportation and human actions like burning of fossil fuels are main issues of air pollution (Degobert, 1992).

The emissions produced by personal vehicle are normally less, compared to various other contaminant causes. However, more vehicles increase this pollution **(**Belcastro, 2012).

1.1 Problems identification

1.1.1 Global warming and climate change due to transportation

The disastrous storms, floods, dearth, frozen and snow are out of control today. The occurrence of these weather conditions are not simple response to the reality that the influence of universal warming is the reason. Ozone depletion layer which prevents ultra violet heat from the sun to earth. Information showed that the greenhouse gasses, (GHG) which is identified to reduce the ozone layer are contributed by the road pollution which has not better post combustion technology (Peter et al., 2010). Hence a knowledge of new fuel energy resources, catalysis and post combustion technology for automobiles are necessary to understand.

1.1.2 Limitation of Platinum Group metal

The platinum group metal (PGM) catalyst is a rare element and not a cheaper. Different studies have established the restriction of Platinum. Pt oxidizes easily in methane (CH_4). This drawback has put a limitation to its conversion efficiency. So, there is no study to connect PGM with metal oxide. Automakers and catalyst dealers are worry about the rising cost and stock availability of these conventional catalysts (Nassar, 2015).

Thus, researchers are finding alternative catalyst material for a good environment. Modern studies have set the possible way of some metal oxide catalyst. This study will provide the chance to use largely local available metal catalyst.

1.1.3 Metal Substrate and Its Challenges

The material on which catalysts are deposited may be ceramic or metal substrate. By using metal substrate, we can get low emissions of harmful gasses and minimum back pressure. Metal substrate is also a cheap material and locally available as compared to ceramic. This will give the better performance of catalytic converter. Many of the cars industry are using metal substrate like sports car and BMW (Capello et al., 2005).

In this study, a wire mesh metal substrate was used to replace the ceramic substrate. The challenge for metal substrate is how to deposit catalyst on substrate. So, it’s very important to know the techniques of coating. The geometric surface area of wire mesh substrate is higher than the ceramic substrate which will give the random movement of oxidation and reduction. Also this will be helpful to improve converter performance and getting higher conversion efficiency.

1.2 Exhaust pollutants

When fuel in the combustion chamber does not burn or partially burn then the hydrocarbon (HC) emissions are produced (Henein et al., 1995). These hydrocarbons after reacting with nitrogen oxide (NOx) form ground level ozone (O_3). The production of smog is also due to this HC. Ozone is the most prevented gas but this gas is unable to control the urban air pollution trouble. Hydrocarbons are toxic to health. The diseases from the hydrocarbons maybe lung damage, respiratory issues and eye irritation. Benzene (C_6H_6) and Toluene (C_7H_8) are the big examples of hydrocarbons which are creating diseases like blood cells problems and asthma (Herbert et al., 2006; Barbeau et al., 2004)

Oxides of nitrogen(NOx) are the results of high temperature in combustion chamber due to high temperature and pressure, oxygen reacts with atmospheric nitrogen and forms various types of NOx (Ban wises et al., 2008). Formation of acid rain and ozone is due to NOx. The primary element of smog is ozone. Therefore, NOx produces the similar brunt to the HCs. Its hazardous to environment and toxic to plants life. The major diseases from the NOx are lungs and respiratory infections (Belcastro, 2012).

Due to incomplete combustion carbon monoxide is created from an engine. CO is injurious to health. Respiration problem of a body may be from this CO. Also it is dangerous to heart and brain (Yavuz et al., 2013). The largest emission from an engine is carbon monoxide (CO). In history, it has not been measured an environmental problem and there was no legislation for it. But now a day's studies showed, this gas is a big problem for the environment**.**

1.3 Background of study

In combination to the plan of thesis. Limited criteria have been reviewed and outlined. First is to increase the capabilities of metal oxide catalyst as compared to the conventional catalyst. Second is to immerse the prepared catalyst onto stainless steel wire mesh. Third criteria is to maximize the conversion efficiency and reduce the back pressure by using this stainless steel wire mesh. Thus the concentration will be on catalysts i.e. cobalt oxide Co_2O_3 and titanium dioxide TiO_2. Theses catalysts are locally available and more efficient as compared to the platinum group metals (Pt, Pd, Ru). Coating of this wire mesh with prepared catalysis is necessary for making catalytic converter (Dignon, 1992). The Co_3O_4/TiO_2 catalysis are synthesized by the impregnation (wet or incipient) method.

1.4 Catalytic converter

Catalytic converter is a device used to reduce the harmful exhaust gases from an internal combustion engine. Catalytic converter is installed between engine manifold and exhaust tailpipe (closed couple catalytic converter) or at the end of the exhaust manifold. The pollutant gases from an engine pass through it and converted into comparatively harmless gases by undergoing chemical processes. A two way catalytic converter (oxidation catalyst) has one type of the chemical process i.e. catalytic oxidation. In this stage, HC and CO prolong to burn. Sufficient amount of oxygen is required for this process. This process results in oxidation of CO and HC to form CO_2 and H_2O. Latterly, this oxidation catalyst is replaced by three way catalytic converter which has both oxidation and reduction of NOx **(**Tyagi and Ranjan, 2015; Pontikakis et al., 2004). Usually, a catalytic converter comprises of steel cover plate or steel box, monolithic substrate (tubular walls) or wire mesh, normally alumina or titanium as washcoat on which we disperse catalyst material like Co_3O_4, Pt, Pd, Rh with different ratios. Besides these promoters,

CeO_2, or CeO_2-ZrO_2 are also deposited in the washcoat for the better performance of catalytic converter. Hence, the best and easiest way to reduce the exhaust pollutants is catalytic converter (Ozawa, 1998; Kaspar et al., 1999; Tyagi and Ravi, 2013).

Platinum group metals (PGMs) or the noble metals are usually known as conventional catalyst material. The PGMs consist the rare metals such as palladium (Pd), platinum (Pt), rhodium (Rh), ruthenium (Ru), iridium (Ir) and osmium (Os). All of these metals have same characteristics like static as regard biological reactions or less chemical reaction. But now days, studies demonstrate that these types of material have a large number of application and widely used in automobile exhaust catalyst, industry, anticancer drug and jewelers. These materials used as alloy in dentistry which cause their anthropogenic emission and swell in the surroundings. Platinum can be soluble into the water, sediments and finally to the food chain. The diseases from the PGMs are asthma, increased in hair fall and nausea and other seriously affected human health problems (Ravindra et al., 2004; Whiteley and Murray, 2003).

1.5 Components of catalytic converter

The primary components of the washcoat are titanium oxide and cobalt supported on titania catalysis. Titanium shows the high strength against the hydrothermal conditions of the exhaust gasses. TiO_2 is used for increasing the surface area. The manufacturing of catalytic converter comprises of little components, called converter chamber (hollow) and substrate. The chamber is made of mild iron.

Substrate: The pieces of wire mesh were coated with slurry before arranged onto a straight screw rod.

1.6 Chemical process in catalytic converter

From the exhaust port gases entered into TWC were considered as feed gases like hydrocarbon, carbon monoxide and oxides of nitrogen. In the catalytic converter two types of the chemical processes are happened i.e. catalytic reduction and catalytic oxidation. In the first process ‘catalytic reduction’ oxide of the nitrogen provides its oxygen to form pure nitrogen. Then the free oxygen combines with CO to form CO_2 emissions. In the second process which is catalytic oxidation, HC and CO prolong to burn. Sufficient amount of oxygen is required for this process. This process results in oxidation of CO and HC to form CO_2 and H_2O. Fig. 1.1

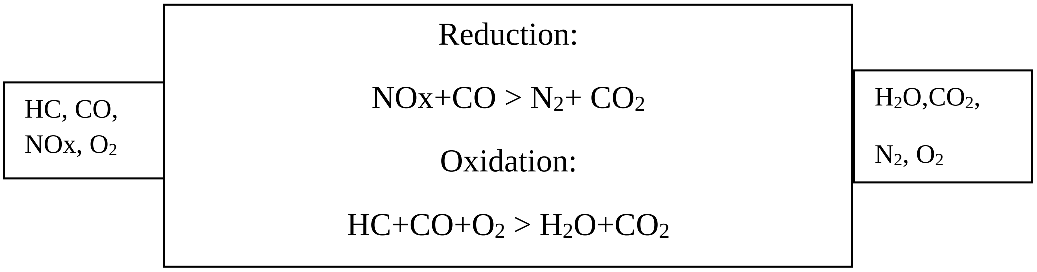


Fig.1.1. Oxidation and reduction process

1.7 Rationale of study

As it is explained earlier in problems identification, national and international issues have been highlighted. For improving air quality there is a need to find out the easiest and cheapest chemicals and more efficient coating technology for getting the maximum efficiency. This study will help the automobile industry in constructing a less price, well organized and successful catalytic converter. It will also increase the potentials of local automotive industries in trading with global problems.

1.8 Significance of the study

Some of the significant of this study is to maximize the use of Co_3O_4/TiO_2 as a cheaper and professional catalyst for gasoline engine. This study gives the good substitute to the vehicle industry with post combustion technology. Introduction of new stainless steel wire mesh catalytic converter for automobile industry. This thesis will also explain the metal coating method. The effective and cheaper catalytic converter will increase the use of non-noble metals (TiO_2 and CoO).

Chapter 2

Literature review

2.1 Air pollution from mobile sources and its measures

Air pollution engendered from the automobiles is a big threat to environment. Since the year 1940 the globe fleet vehicle has incremented from about 40 million vehicles to over 750 million. This digit is expected to increase to 980 million by the year 2018. The toxic gasses from the internal combustion engine are 40% of total air emission **(**Guibet and Faure, 1999). For the urban air pollution, automakers strive to inhibit and clean up the harmful gasses from exhaust stream. As engine technology has been modified over the years which emphasized to do major changes in post combustion engine technology. Also a new production of engine application has placed a lot of requirements on the exhaust strategies to reduce the harmful exhaust pollutants (Matsumoto, 2004).

In combustion chamber of an engine all fuel can never be burnt. Therefore, a huge amount of unburned hydrocarbons (HC) and carbon monoxide (CO) would be emitted (Kalam and Hassan, 2011). However, internal combustion engine which produces higher amount of gaseous pollutants can be oxidized by many ways like thermal system, exhaust gas recirculation and positive crankcase ventilation. But now days these types of approaches are not suitable for most of the applications. So, the best option is catalytic converter (Heywood, 1998; Amin et al., 2012).

2.2 Air to fuel ratio

Harmful exhaust gasses from vehicles depend on air to fuel ratio (A/F). when the fuel is in rich condition by consuming big quantity of fuel then the power will also be higher. On the other hand, when the temperature of combustion chamber will be low then the generation of NOx will also be low. This condition is known as fuel lean condition. CO emissions will be low under higher A/F ratio while HCs emissions will increase under this condition. So, for the better efficiencies of these pollutants there is a need to stoichiometric this A/F ratio and that is 14.5 on mass basis. In an engine this ratio is controlled by the oxygen sensor which is good for the operation of catalytic converter (Air, 2007).

2.3 Characteristics of catalytic converter

There are many characteristics of catalytic converter. Some of the characteristics are given below.

2.3.1 Light off temperature

It is defined as the temperature where the 50% conversion is occurred. Catalytic converter shows its best performance at light off temperature when conversion takes place from 0% to 100%. At the start of an engine due to cold condition there will be a lot of exhaust emissions. So for the maximum efficiency first need to warm up the engine up to a certain temperature (Kaspar et al., 2003).

2.3.2 Conversion

One of the main significant variable to calculate conversion of risky pollutants to harmless pollutant by using the catalyst. So the main purpose of catalyst is to decrease the emission and give the maximum conversion. In this condition for car or motorcycle, first test the exhaust gasses without catalytic converter and then put a converter in exhaust system and measure the conversion of these harmful pollutants.

2.4 Chemical reactions in catalytic converter

From the exhaust harbor gases penetrated into TWC were considered as feed gases like HC, CO and NOx. In the catalytic converter two types of the chemical processes are take place i.e. catalytic reduction and catalytic oxidation. In ‘catalytic reduction’ oxide of the nitrogen provides its oxygen to form pure nitrogen. Then the free oxygen combines with CO to form CO_2 emissions. In catalytic oxidation, HC and CO prolong to burn. Sufficient amount of oxygen is required for this process. This process results in oxidation of CO and HC to form CO_2 and H_2O.

2.5 Ageing mechanisms

With the passage of time the efficiency of automotive catalyst is decreased. This is known as ageing mechanism. This mechanism is divided into three areas, thermal, chemical and mechanical ageing which are given below.

2.5.1 Thermal ageing

Catalytic converters for vehicles use under high temperature for a long period of time which has a harmful effect on the movement of catalyst. One reason of this is the collision of the deposited particles, which decrease the number of active sites and the results in decrease the efficiency of catalyst (Fathali et al., 2013). The agglomeration is due to movement of atoms between two particles.

2.5.2 Chemical deactivation

The chemical deactivation of the catalyst is due to presence of poison atoms in fuel and engine oil. These poison atoms may be S, Ca, Mg, Zn and P (Winkler et al., 2010). These atoms will be bonded with active sites through chemisorption and changed all the characteristics by blocking all the catalyst activity. Some poisons adsorbed reversible with materials and some irreversible. This means if the catalyst is operated under certain conditions then poison atoms will be detaching and catalysts will have regained activity. In case of sulfur at high temperature the desulfurization from the catalyst is occurred. Chemical deactivation may also be occurred in porous block sites which may reduce the catalyst activity.

2.5.3 Mechanical ageing

The washcoat on a vehicle catalyst is used for increase the surface area of material. This form of composition makes them perceptive to fouling. Materials such as Zn, P and Mg as well as particles from the internal combustion engine and exhaust stream can jam pores and block active sites and thus decrease the efficiency of catalyst. This aspect can be condensed by reducing the quantity of problematic substances in the engine oils and by putting more durable materials in IC engine and exhaust system (Fatima et al., 2005).

2.6 The history of reducing tail pipe emissions

2.6.1 1970-1975: First standards

In 1970, the Clean Air Act enacted by the US congress which is known as first exhaust emissions standards. The gasses measured are volatile organic compounds (VOC), carbon monoxide (CO) and oxides of nitrogen (NOx). Later on in 1975, the new standards made for NOx, CO and hydrocarbons (HC) are 3.1, 15 and 1.5 grams per mile (gpm) respectively for light duty vehicles (Shen et al., 2011).

2.6.2 1977-1988: Tightening Standards for the first time

In 1977, Congress redresses the Clean Air Act and reduces these emission standards in two steps. In first step, the value of NOx became 2.0 gpm for cars between 1977 to 1979 and the rest pollutants i.e. HC and CO were same. Then in second step 1981, the NOx standard tightened to 1.0 gpm and HC and CO to 0.41 and 3.4 gpm respectively.

2.6.3 1990-1994: Tier 1

In 1990, Congress again revises the Clean Air Act, further fixing discharge principles. The NOx standard is set at 0.6 gpm for automobiles (CO, HC at 4.2 and 0.31 gpm individually), successful in 1994. The new standard called ‘Tier 1’is a 40 percent decrease for NOx from the 1981 standard. For light duty trucks, the new standard reaches from 0.6 to 1.53 gpm, depending upon the heaviness of the vehicle. The Clean Air Act Amendments of 1990 additionally oblige EPA to survey the air quality need, cost viability, and practicality of more tightly discharge levels for the 2004 model year and past.

2.6.4 Voluntary Agreement for Cleaner Cars

In 1998, the Clinton Administration with the automobile business and the Northeast states strike an inventive, intentional agreement to put cleaner autos out and about some time recently they could be ordered under the Clean Air Act. The new vehicles are called National Low Emanation Vehicles (NLEV). The main NLEV autos under the agreement achieve shoppers in New England in 1999 and will achieve whatever remains of the nation in 2001. NLEV cars work with a NOx standard of 0.3 gpm (CO, HC at 4.2 and 0.09 gpm, individually), a 50 percent decrease from Tier 1 measures for NOx and more than 70 percent for HC. In 1998, as mandatory by the Clean Air Act Amendments of 1990, EPA issues the Tier 2

2.6.5 1999: Tier 2

In 1999, EPA proposes ‘Tier 2’ tail pipe discharges guidelines starting in 2004 the first run through both autos and light-obligation trucks are responsible to the same national contamination control system. The new standard is 0.07 gpm for NOx (CO, HC at 4.2 and 0.09 gpm, individually). For NOx it is a 77-86 percent decrease for autos and a 92-95 percent decrease for trucks past the NLEV agreement. EPA additionally proposes a reduction in average sulfur levels to 30 parts per million (ppm) (maximum of 80 ppm) to achieve the full execution of vehicle discharge control innovations (Bertelsen, 2001).

2.7 Heat and mass transfer

The total reaction rates and catalyst studies are affected by the heat and mass transfer phenomena and different process in catalytic converter. Thus, actual catalyst is frequently studied with basis models, e.g. with particular crystals (Twigg, 1989; van Santen *et al.*, 1999). The heat exchange between substrate and exhaust gas in a catalytic converter is known as heat transfer mechanism. From the exhaust gas heat is created in exothermic reactions on the washcoat. Further, from the washcoat this heat radiation goes to surrounding walls at high temperature. Therefore, the heat offended from converter to the atmosphere occur by convection. (Koltsakis and Stamatelos, 1997). The concentration slopes among the exhaust gas flow and the reactive washcoat in monolith channel make the convective mass transfer mechanism. Dynamic components are distributed onto a big area, which facilitates the capable mass transfer between the washcoat and bulk gas for high conversion efficiency (Angove and Cant, 2000).

2.8 Sources of vehicle pollutants emissions

2.8.1 Evaporative emissions

Through the fuel evaporation hydrocarbon (HC) pollutants flee into the atmosphere. When the levels of ozone are highest during the hot days then evaporative losses might be a large part of the whole hydrocarbon pollution even under the efficient control of exhaust system.

2.8.2 Combustion process

Diesel and petrol fuels are the combinations of hydrocarbons, compounds that consist hydrogen and carbon atoms. In an ideal engine, oxygen will have oxidized the hydrogen into water and all the carbon in the fuel would be convert into carbon dioxide. Nitrogen would remain unchanged in air. The combustion process can't be perfect in realism and the vehicle engines produce different types of pollutants. In this manuscript, pollutants and pollutant control are considered for gasoline engine.

2.9 Typical engine combustion

Under stoichiometric condition the ratio of air to fuel will be ideal. The burning of fuel in air will progress to full achievement. Under perfect combustion the products will be carbon dioxide (CO_2), water (H_2O) and nitrogen (N_2). It can be seen by the chemical equation which is given below.

$CHy+(1+y/2)\ (O_2=3.76N_2) = CO_2+y/2H_2O+3.76(1+y/2)\ N_2$

In reality, however this happens. Instead, in the products there are unburned NOx and CO along with CO_2 and H_2O.

2.10 Catalyst

Catalyst Increase rate of reaction without being consumed. Phenomenon of catalysis is intricately woven into the fabric of chemistry.

2.10.1 Types of catalyst

(i) Homogeneous catalyst

Catalyst and reactants are molecularly dispersed in same phase (liquid or gaseous).

(ii) Heterogeneous catalyst

Different phases, usually catalysts are solids and reactants are liquid or gas.

2.10.2 Methods for the preparation of catalyst

There are several types of methods for the preparation of catalyst i.e. impregnation method, precipitation deposition, urea gelation, solution combustion, leaching and chelating, ion exchange and adsorption method etc. But in this study, the only impregnation method is used for the catalyst synthesis. In impregnation method, a definite amount of solution consisting the sign (precursor) of dynamic stage is linked with solid surface, and absorbed solvent is removed by drying in the following action. Further, two types of impregnation are examined which depend on the volume of solution. One is wet impregnation and other is incipient wetness impregnation. In first 'wet impregnation' a large amount of solution is used. Separation of the solid from the excess solvent is occurred after some time by drying. In second 'incipient wetness impregnation' the volume of solution is used is not in large amount. This volume is equal or slightly less than the pore capacity of support (Campanati et al., 2003). Temperature is operating variable for both methods. The solubility and solution viscosity is controlled by the temperature.

2.11 Automotive exhaust catalysis

Gandhi et al. (2003) stated that since 1960 the research in the field of automotive industry has been started and became commercial in 1970's mid. This study is continuing till now. These efforts are continuing for searching the efficient catalyst for the good environment and to decrease the air pollution from mobile sources. By using oxidation catalytic converter, they reduced the harmful HC and CO to CO_2 and H_2O vapors.

From the last 25 years' heterogeneous catalysis have a vital role in automobiles. Here in this review the history of vehicle catalysis is shortly review with respect to its current condition and future recommendation. According to them there is a need to improve the catalyst abilities in fuel cell automotive. Also research is continued in the field of exhaust emission treatment for gasoline or diesel engine (Shelef and McCabe, 2000).

2.12 Catalytic converters state of the art and perspective

Farrauto and Heck (1999) found some of emission control technology for the betterment of an environment. Like catalytic converter is a device which reduces the toxicity of an engine has been established since last 25 years. Catalytic converter is a one the utmost application of 20th century. However, new techniques for controlling the exhaust gasses are still being introduced for mobile source. This briefly review tells about how to improve the technology for emission control system and for better fuel economy.

2.13 Noble and non-noble metals

This study is carried out for the replacement of noble metals with non-noble metals. As from the mobile sources the emissions like hydrocarbon (HC), carbon monoxide (CO) and oxides of nitrogen (NOx) are big problem for health. Catalytic converter is a device which oxidizes these harmful exhaust gasses (HC, CO) to harmless gasses. There are different problems related with noble metals i.e. Pt, Pd. These metals are not locally available and have various types of diseases. These metals also operated at very high temperature. So, the catalytic converter which is based on these metals is not suitable now days. This paper tells about the characteristics and durability of the non-noble metals. The converter based on non-noble (copper, zinc and cobalt oxide etc.) metals is efficient for controlling the exhaust toxic gasses. These metals are easily available and less priced. Also this review is about to increase the catalytic converter temperature during cold start emissions (Amin et al., 2012).

2.14 Metallic substrate

Rajadurai et al., 2006 showed that effectiveness of metal substrate. After treatment of the gasses from an internal combustion engine the main requirements are low back pressure, better efficiency of catalytic converter and cost estimation. All of these properties represent the engine performance and the value of system. Wire mesh substrate with different geometrical design and different area of coating represent the various conversions. At maximum conversion efficiency they did not change further designs. So this is called optimization where the efficiency is not increasing further. This wire mesh substrate also works on high temperature. It also provides the different flow i.e. radial and longitudinal.

2.15 Comparison between engine manufacturing CC and CoO/TiO_2 CC

Kalam and Hassan (2011) described the characteristics of new catalytic converter used for natural gas fueled engine is studied. From the automotive vehicles the exhaust emissions carbon monoxide (CO), hydrocarbon (HC) and nitrogen Oxide (NOx) are the big problems of general interest. This paper presents the development of a new three way catalytic converter based on wire mesh substrate of stainless steel with CoO/TiO_2 catalysts for the oxidation and reduction of emissions from an engine. The harmful gasses HC and CO will have oxidized whereas NOx will be reduced. TiO_2 and CoO are inexpensive as compared to platinum group metal (PGM). Also there is a comparison between original engine manufacture catalytic converter and new catalytic converter which is based on CoO/TiO_2 with wire mesh substrate catalytic converter. The newly developed converter decreases the 24%, 41% and 40% higher NOx, CO and HC emissions as compared to the emissions with original engine manufacture catalytic converter. This catalytic converter is suitable due to low cost, domestically available and more efficient as compared to conventional catalytic converter.

2.16 Effect of TWC substrate cell density on the mass transfer and reaction resistance

There are three types of phenomenon which are necessary to find for the conversion of pollutants in three way catalytic converter. First one is fluid mechanics then heat and mass transfer and finally catalytic reactions. The quantification of the entire and relative significance of the properties (physical, chemical) concerned with major importance for the optimization of TWC. In this paper, they present the methods to find out the internal and external mass transfer resistance. The resistance quantification method is applied for checking the performance of TWC. Also they observed these resistances on two different substrate cell densities i.e. TWC 200cpsi and TWC 400cpsi (Santos and Costa, 2014).

2.17 Efficiency of ceramic and metallic substrate

Santos and Costa (2008) compared the efficiency of ceramic substrate and metallic substrate for three way catalytic converter under different vehicle operating condition. Both catalysts tested for same spark ignition engine on a chassis dynamometer under steady state condition for different engine rpm and loads. Also the temperature range is noted for both substrates. Finally, they concluded that the ceramic substrates work best at low space velocities as compared to metallic substrate due to low thermal conductivity. But at high space velocities metallic substrate presents the better efficiency due to large surface area. The limitation for metallic substrate is a mass transfer.

2.18 Effects of loading and synthesis methods for oxidation process

For the Fischer tropsch process Eschemann et al. (2014) prepared the cobalt supported titania catalysis with 4-24 wt.% Co. These catalysts have great interest from industrial and institutions. In this review, these catalysts are prepared by three different synthesis methods, incipient wetness impregnation (IWI), deposition precipitation using urea hydrolysis (DPU) and ammonia evaporation (DPA). Finally, they compared the results of all synthesis methods. Also the samples were analyzed by X-ray diffraction (XRD) and Transmission electron microscopy (TEM).

By the wet impregnation method there are five samples of Co-zn/SBA catalysts are prepared with different cobalt and zinc loading. These samples were examined to check out the conversion of synthesis gas. These prepared samples are also characterized by the XRD, SEM, N_2 adsorption surface area analyzer (BET) and thermo gravimetric analyzer (TGA) (Aida and Mustapa, 2012).

In another case by using ultrasound microwave assisted method the cobalt supported titania catalyst is synthesized. Different amount of cobalt is deposited on titania and tested the performances of all catalysts. Finally, they found that by increasing cobalt loading maximum efficiency occurred for oxidation of HC and CO. These samples also characterized by BET, SEM and XRD. Also they compared their results with the samples which were prepared by conventional radiation method (Khosravi et al., 2015).

2.19 Platinum effects on environment

Merget and Rosner (2001) presented the hazardous effects of platinum (Pt) on environment which is discharged from the automotive catalytic converters. A huge literature is discussed about the platinum characterization and its toxicity to humans' health. The emission of platinum is very small from catalytic converters. Hence the risk assessment from Pt is only respiratory problems. From recent work, in automotive catalyst the rhodium is also included. Pt is substituted by palladium (Pd) and iridium (Ir) based catalyst have currently developed. Although the record on these platinum group metals (PGMs) is relatively small. So, there is no facts that they create a nuisance to general population (Kielhorn et al., 2002).

2.20 Objectives of the study

Following are the objectives of this study,

1. To study the effect of cobalt loadings on titanium dioxide.
2. Characterization of the catalyst by X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM) and surface area analyzer (BET).
3. To study the effects of particle vs. powder of Co_3O_4/TiO_2 catalysis.
4. To evaluate the performance of this catalytic converter on the basis of conversion efficiency and pollutants conversion.

Chapter 3

Materials and Methodology

3.1 Materials selection for the catalyst

Four types of the chemicals collected for preparation of catalyst which are titanium (IV) oxide, TiO_2 (Panreac)**,** cobalt(II) nitrate, $Co(NO_3)_2.6H_2O$(EMSURE)**,** sodium silicate solution, Na_2O_3Si (Merck, KgaA) and sodium metabisulphite, $Na_2S_2O_5$ (BDH, ANALAR). There were also two sieves (75ɥm and 150ɥm) for getting the exact particle size of Co_3O_4/TiO_2 calcined sample between 75ɥm to 150ɥm.In this paper, the different cobalt ratios i.e. 6-18% were applied. TiO_2 and Co_3O_4 were known as a metal oxide catalyst. The pure titania and cobalt oxide are referred as oxidizing and reducing agents respectively. It's chemically inactive to sulphate formation.

3.1.1 Materials selection for the substrate

The material is stainless steel (SUS, 304), due to its physical and mechanical benefits and low priced the large number of the automobile industry used it extensively for the exhaust system (Bode et al., 1996). After cutting this stainless steel wire mesh into a circular shape and getting the diameter of 7.0 cm which is suitable for the coating of catalyst as can be seen from figure 3.1.

3.1.2 Fabrication of the catalytic converter

The manufacturing of catalytic converter comprises of little components, called converter chamber (hollow) and substrate. The chamber is made of mild iron. Fig. 3.2

Substrate: The pieces of wire mesh were coated with slurry before arranged onto a straight screw rod. The length of this screw rod was 18cm. The space between these wire mesh pieces was approximately 0.5cm each that was produced by placing the nuts of mild iron. The outer diameter of these nuts was 1.5cm and the inner diameter (hollow) was 1cm. The screw rod which was used as a support for the wire mesh with a diameter of 0.8cm. Figure 3.3 shows the sum of 27 pieces which was arranged on the screw bar.

Fig.3.1. Wire meshes of stainless steel

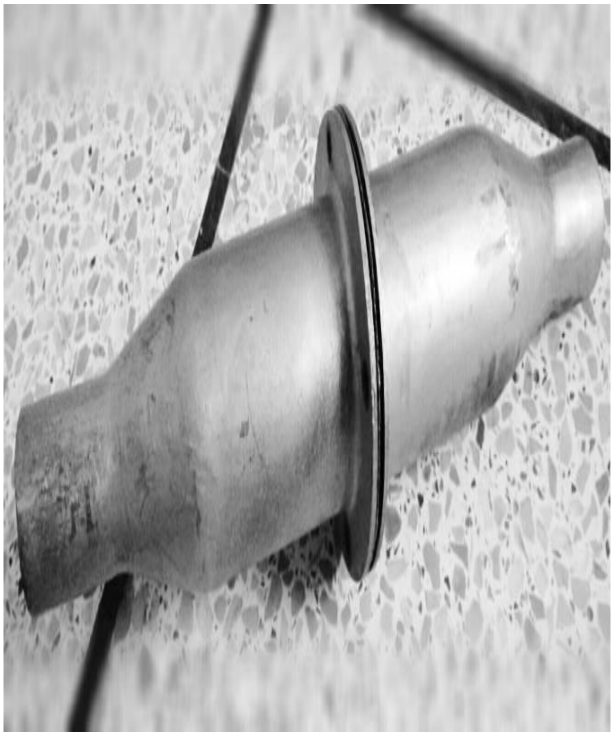
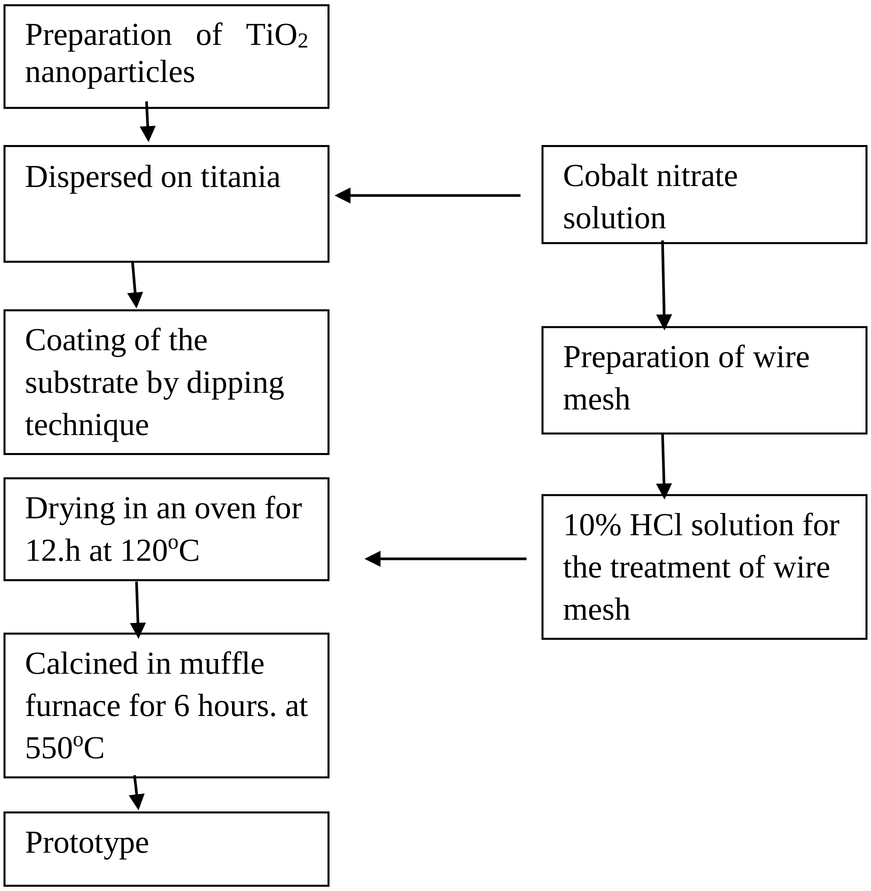


Fig 3.2. Converter chamber

Fig.3.3. Pieces of wire mesh arranged on screw bar

3.2 Methodology

3.3 Experimental frame work



3.3.1 Synthesis of titania nanoparticles by liquid impregnation method

50g TiO_2 were taken in 300 ml distill water and magnetic stirred for 24 hours at 300rpm.After that settled it for 24 h. Then dried in oven for 12 hours at 105°C and after being dried crushed and mixed it in mortar and pestle. Finally calcined in muffle furnace at 400°C for 6 hours (Younas et al., 2014).

3.2.2 Preparation of slurry

In this preparation, 35 grams of titania nanoparticles and 21.75 grams cobalt nitrate were taken in two different china dishes. Added 5ml distilled water in 21.75g cobalt nitrate (Haber, 1991). After that this solution is deposited on 35g titania nanoparticles by the help of pipette. This is known as 'wet impregnation' which can be seen from figure 3.4. Then dried this sample in an oven at 120°C for 12 hours. After being dried this sample is heated in muffle furnace at 550°C for 5 to 6 hours which is known as 'calcined sample' Fig. 3.5. By the calcination process 21.75g cobalt nitrate is converted into 5g cobalt oxide. So the calcined sample is grinded manually in mortal and pestle for 10 minutes. On the other hand, 315 grams sodium silicate and 3 grams sodium metabisulphite which work as a binder to increase the coating strength to surface of wire mesh are mixed in the beaker for 4 to 5 h at 450rpm. Then after that the calcined sample (black powder) is poured into the binders and magnetic stirred for 24 hours to make slurry **(**Nijhuis et al., 2001; Avila et al., 2005). Fig. 3.6. But this slurry is prepared for 6% cobalt loading (IW1). In this lab work, six slurries are prepared for the six converters with different cobalt loading and particle size named as IW1 to IW6. But rest of the chemicals (titania, binders) and operational parameters were kept same for all converters. Table 1 shows the prepared catalyst slurries for catalytic converter.

Fig.3.4. Wet impregnated sample of Co/TiO_2

Fig.3.5. Calcined sample of Co_3O_4/TiO_2

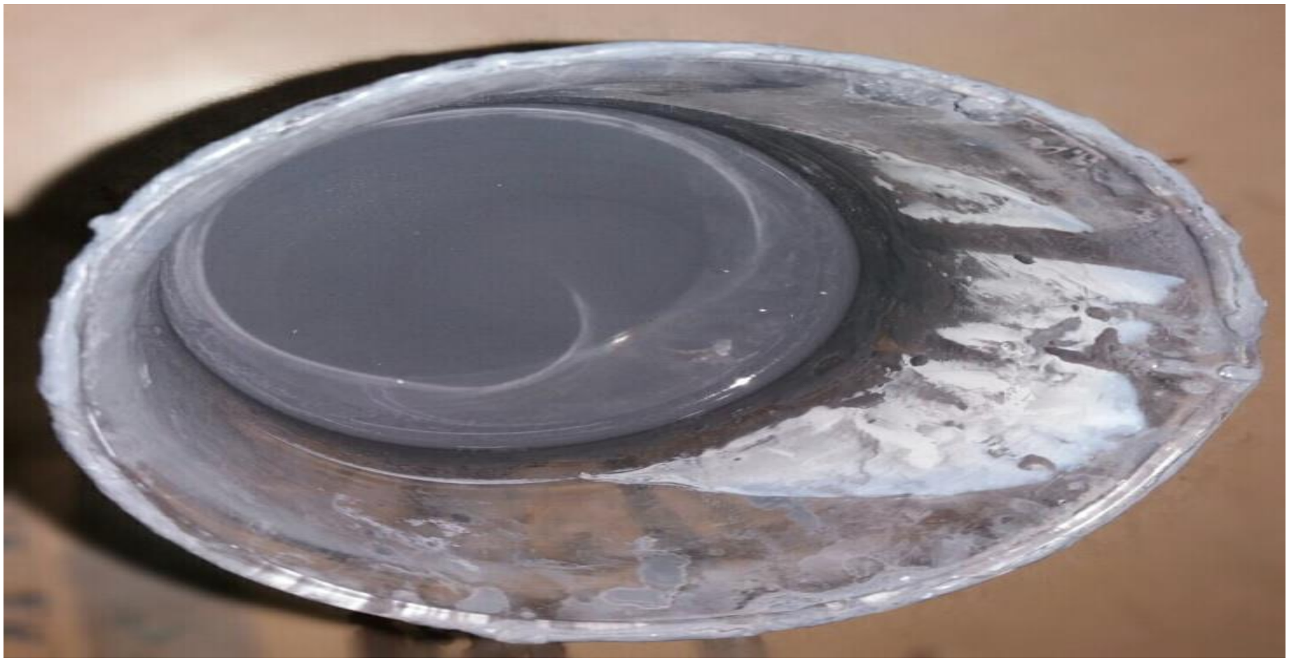


Fig.3.6. Catalyst slurry

Table 1. Summary of loading[a] composition and forming[b]operation

Catalyst composition w.r.t cobalt loading	Amount of titania (g)	Amount of cobalt nitrate (g)	Sodium silicate solution (g)	Sodium metabisulphite (g)	Forming operation
6% (IW1)	35	21.75	315	3	Powder
12% (IW2)	35	43.5	315	3	Powder
12% (IW3)	35	43.5	315	3	Granules (75-150um)
15% (IW4)	35	54.37	315	3	Powder
18% (IW5)	35	65.25	315	3	Powder
21% (IW6)	35	76.30	315	3	Powder

a: In loading the amount of cobalt deposited over titania is varied

b: Particle vs. powder is observed for the same loading

3.2.3 Treatment of the wire meshes

10% HCl solution is prepared for the removal of all dirtiness on wire mesh substrate. These wire meshes were submerged into the HCl solution for half an hour. After that these substrates were washed by distill water and put into the oven at 105°C for 1.5 h before the process of coating.

3.2.4 Coating of the substrate

In this process, by dipping technique the wire mesh was coated with slurry. The figure 3.7 shows this process. The stainless steel was submerged into the beaker of equipped slurry. The immersion time was 3 minutes. Then the substrate was escaped from the beaker. Figure 3.8 shows with the help of blower the unnecessary residual slurry was evaded from exterior of wire mesh coat and also blocked holes of wire mesh was cleared. The speed of blower was $1m^3$/min. Then arranged all the wire mesh on a straight screw rod and dried it horizontally in static air. After that put this arranged substrate in oven for 12 h at 120^oC. After the procedure of drying these wire mesh pieces were coated again two times for proper coating with same slurry. Then again dried completely and calcined this substrate in muffle furnace at 550^oC for 5 hours. Figure 3.9 shows the coated wire meshes that are calcined. By the calcination the material is heated to a high temperature without fusing, so that carbonates, hydrates or other compounds are deceased and volatile material is barred. Now this substrate is ready to use for catalytic converter.

Fig.3.7. Manually dipping

Fig.3.8. Bloworing process

Fig.3.9. Coated wire meshes in partially closed catalytic converter

3.3 Testing on gasoline engine (CD-70)

For the measurement of exhaust pollutants, a CD-70 motorcycle (Euro-II) is observed. In this procedure, first removed the silencer of bike and warmed up the engine and then measured the amount of exhaust gases (CO, HCs) at 2000 to 6000 rpm on idle condition. The figure 3.10 represents the testing of pollutants without catalytic converter. After that assembled a silencer bend with bike engine and put a catalytic converter between this bend and exhaust pipe which is known as closed coupled converter. Finally, from figure 3.11 it can be seen the measurement of gases with catalytic converter on same conditions and calculated the conversion efficiency of this converter. Repeated this procedure for all converters.

Fig.3.10. Testing without catalytic converter

Fig.3.11. Testing with catalytic converter

Chapter 4

Characterization of catalyst

4.1 Brunauer, Emmett Teller (BET)

By using the Brunauer, Emmett-Teller (BET) method (Table 2). Pore size and the surface areas of the samples were calculated by nitrogen adsorption at low temperature. Degas time and temperature were 3 h and 150^{o}C respectively for 1.5 gram of each sample. The pressure was 760.00 mmHg.

Table 2. BET Surface area of catalysts

Catalysts	**BET Surface area (m^2/g)**	**Pore volume (cm^3/g)**	**Pore size (A^0)**
6%Co_3O_4/TiO_2 (IW1)	48	0.24	20.59
12% Co_3O_4/TiO_2 (IW2)	42	0.22	20.53
12% Co_3O_4/TiO_2 (IW3)	39	0.21	20.50
15% Co_3O_4/TiO_2 (IW4)	37	0.19	20.45

It can be seen in table that with the increase in amount of cobalt the surface area of catalysts decreases significantly whereas surface area of IW2 is greater than IW3 because of powder while having same cobalt loading. As these samples are prepared by the ultrasound and microwave radiation method. So, these samples show a higher BET surface area than the samples which is synthesized by conventional radiation method **(**Khosravi et al., 2015; Li et al., 2002).

4.2 X-ray diffraction (XRD)

The calcined catalysts of Co_3O_4/TiO_2 were characterized by X-ray diffraction(XRD) using STOE powder diffraction system with Cu kα radiation (k=1.54060) at 20kV and 5 mA with a step size of 2°/minute in 2θ range with 20°-80°. Diffraction peaks of (Co_3O_4, TiO_2) were recognized. The anatase phases of TiO_2 were identified. These phases were accepted by the JCPDS files. The figure 4.1 (a, b, c, d) shows that by increasing the loading of cobalt the intensity peaks increase (Tang et al., 2009; Huang et al., 2009; Alanis et al., 2010).

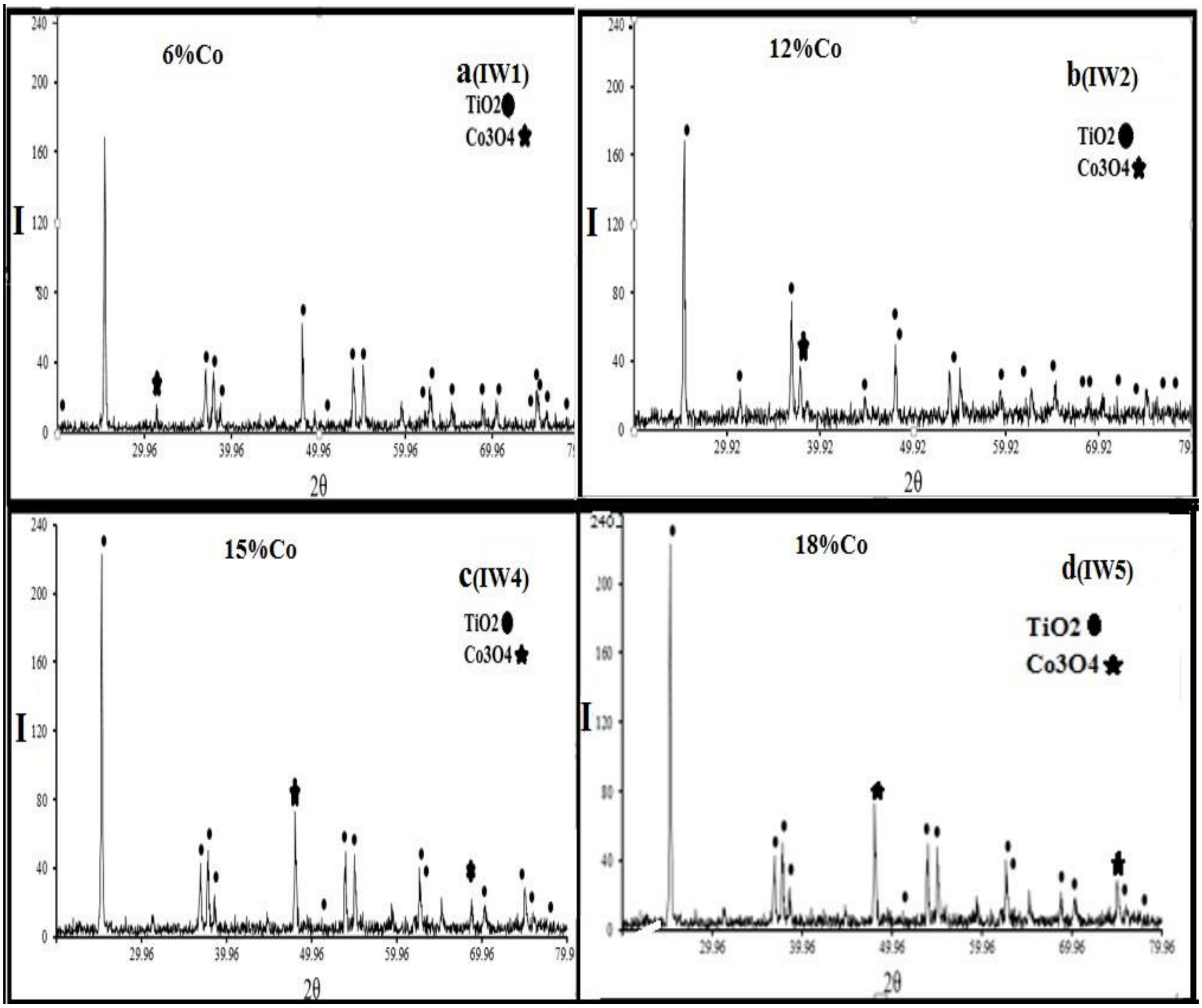


Fig 4.1. XRD of catalysts, a)6% cobalt loading, b)12% cobalt loading, c) 15% cobalt loading, d) 18% cobalt loading

4.3 Scanning electron microscope (SEM)

Scanning electron microscope (SEM) is a powerful technique which uses a focused beam of electrons to obtain largely magnified picture. The high resolution, three dimensional images produced by SEM provide information like;

- Topography
- Morphology
- Chemistry
- Crystallography

The results are shown in fig 4.2. By comparing all figures 4.2 (a,b,c,d) it is observed that, there was no big difference between all Co_3O_4/TiO_2 samples. This is because all the samples have prepared by the same method. However, figure 4.2(d) shows the uniform distribution of Co_3O_4 over titania due to 18 wt. % Co loading. Fig 4.2 (c, d) also show the larger particles and less pore size (Li et al., 2002; Mei et al., 2016).

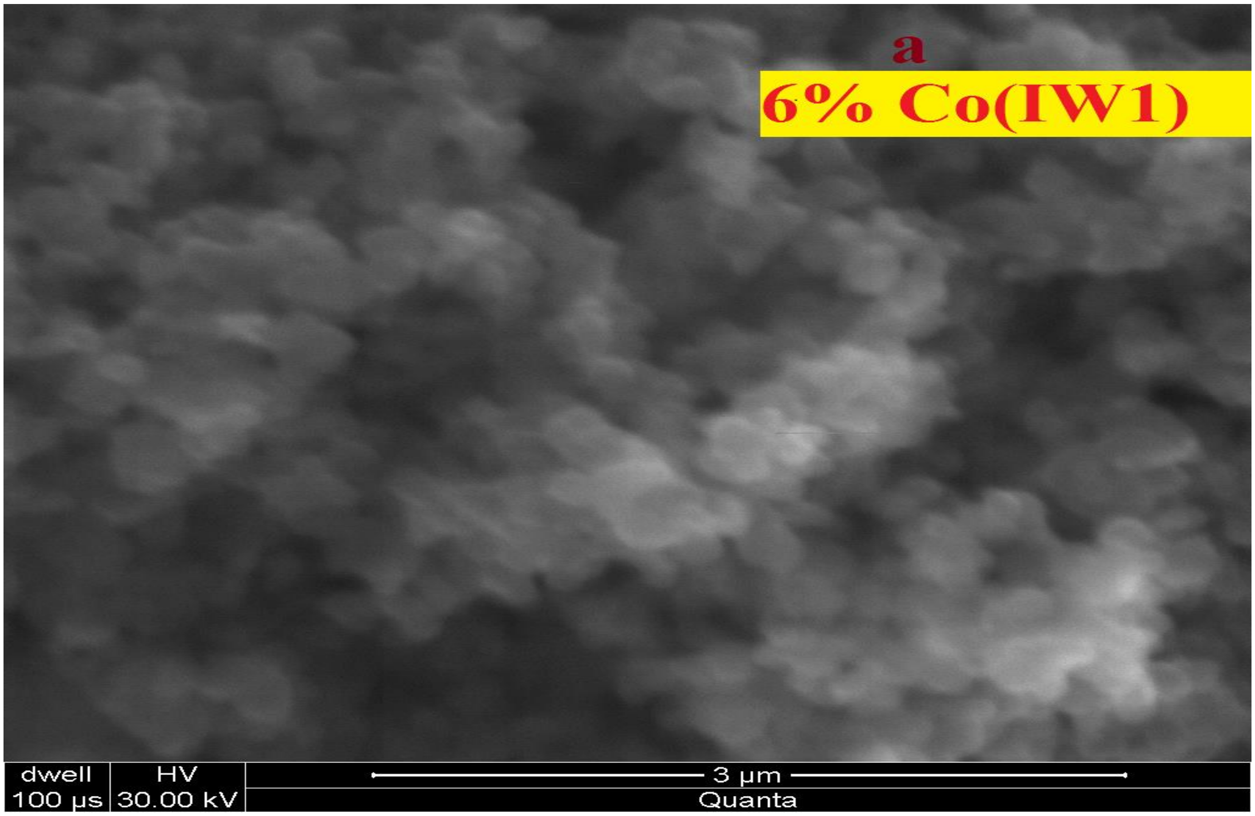


Fig 4.2(a). SEM of catalyst with 6% cobalt loading

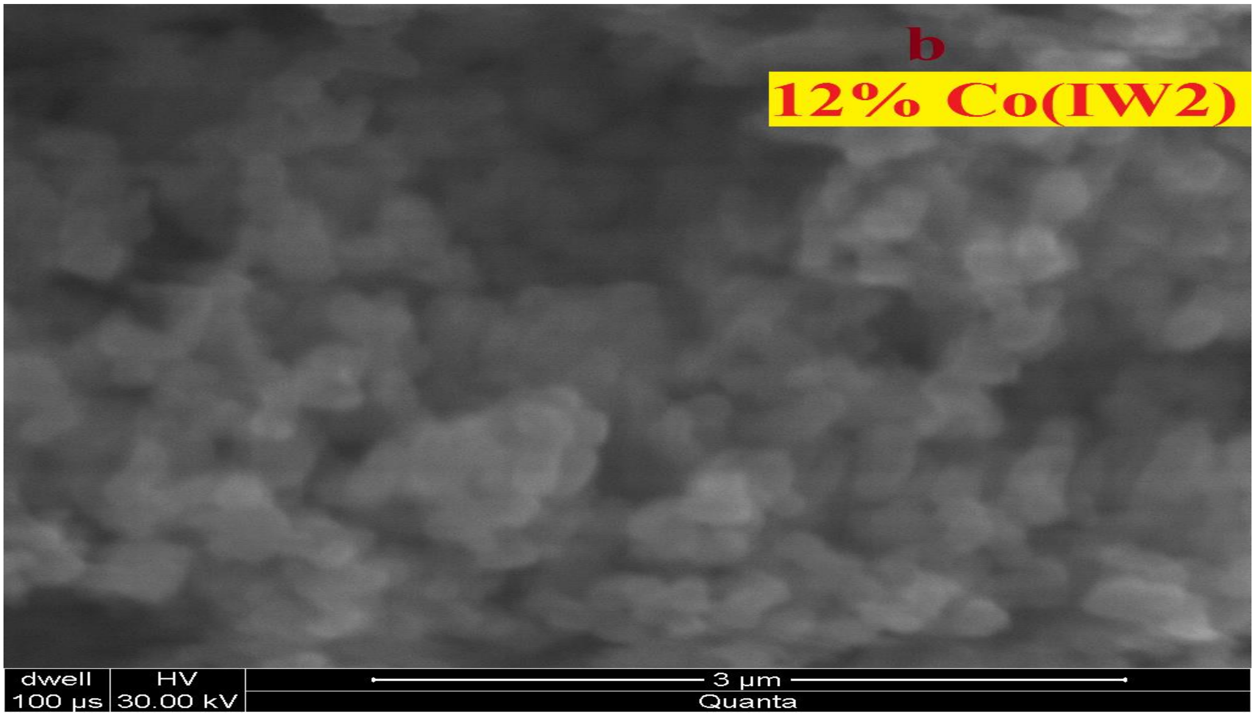


Fig 4.2(b). SEM of catalyst with 12% cobalt loading

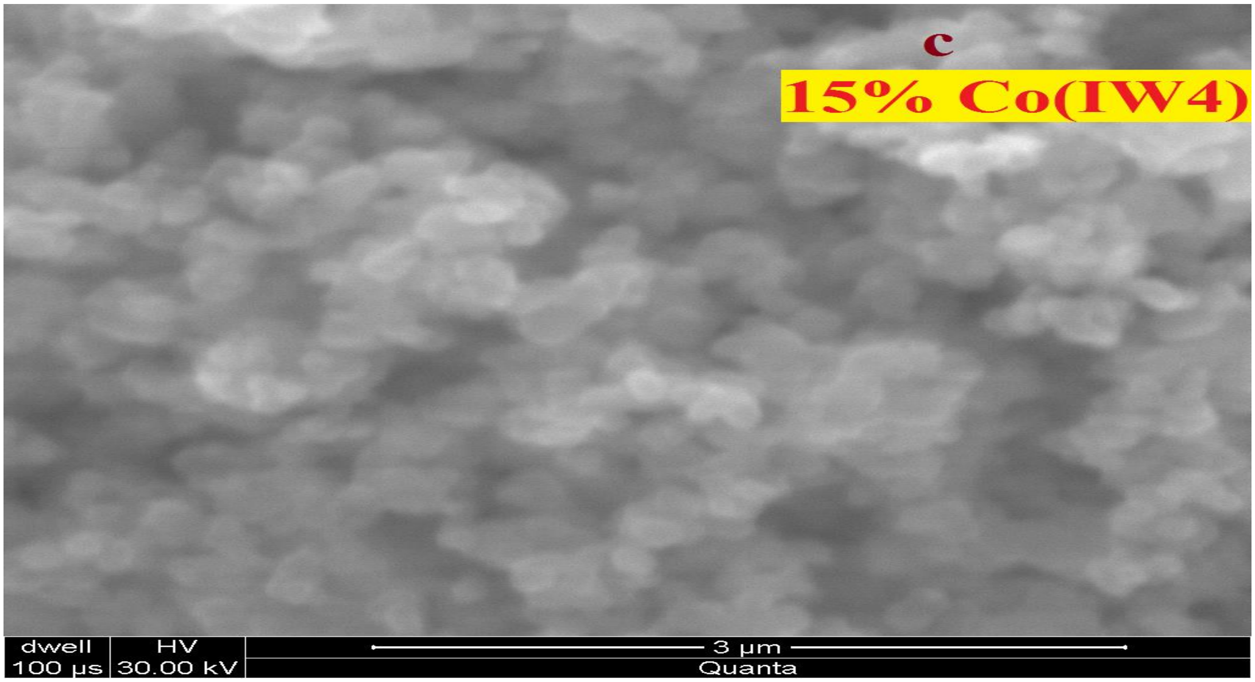


Fig 4.2(c). SEM of catalyst with 15% cobalt loading

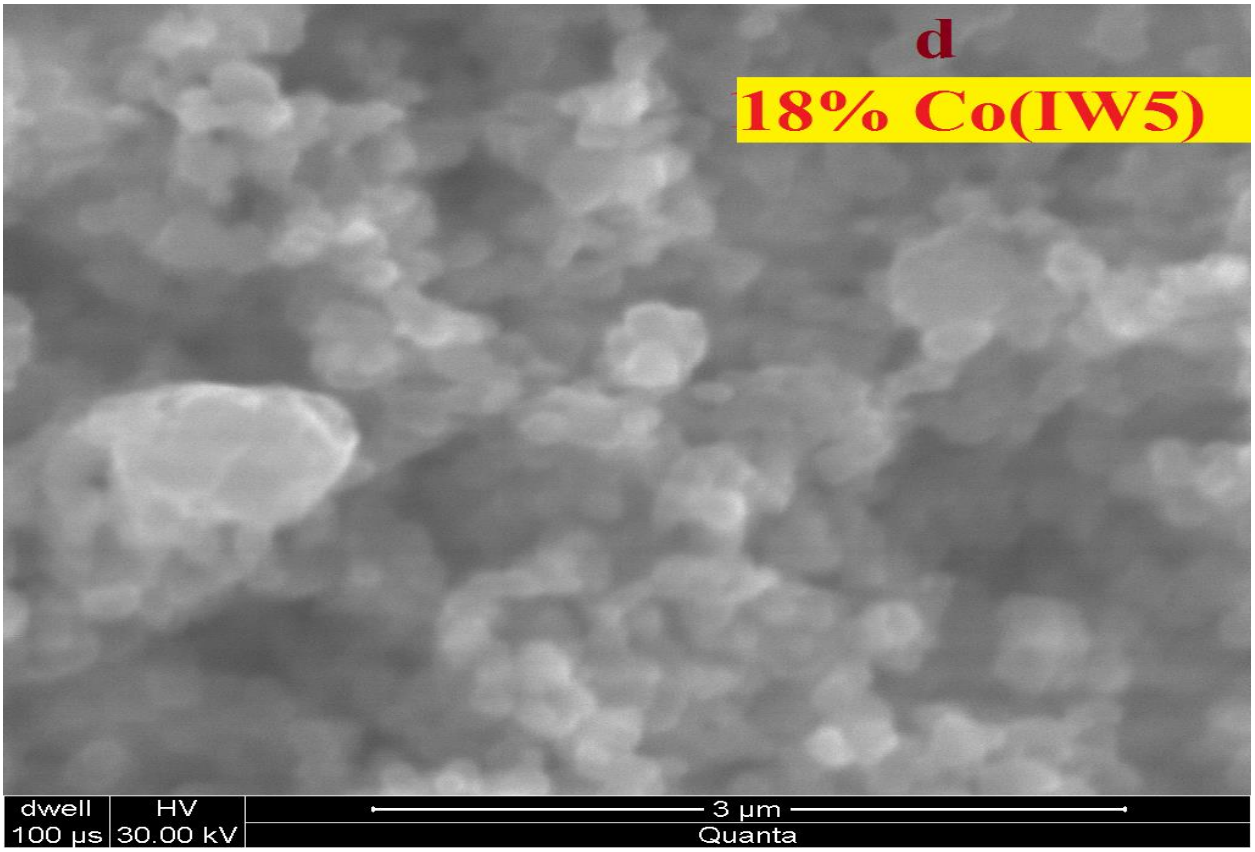


Fig 4.2(d). SEM of catalyst with 18% cobalt loading

Chapter 5

Results and discussion

5.1 Carbon monoxide vs Engine speed

Table 3 consists the data of CO emissions. Various figures are made with respect to the data. Figure.5.1 demonstrates the CO (%) emissions versus engine speed from 2000 rpm to 6000 rpm with and without catalytic converter. With catalytic converter the higher conversion efficiency is occurred. This conversion is due to Co_3O_4/TiO_2 catalyst and by increasing the Co loading i.e. 6 to 21% on titanium. This is also due to higher metallic substrate area and by increasing the length of substrate (Fuad et al., 2007).

Table 3. Summary of CO (%) emissions

Engine speed (rpm)	**Without Catalytic converter(cc)**	**IW1**	**IW2**	**IW3**	**IW4**	**IW5**	**IW6**
2000	3.581	1.253	0.572	0.859	0.421	0.380	0.470
4000	2.802	0.896	0.504	0.562	0.196	0.171	0.201
6000	3.240	0.955	0.388	0.550	0.162	0.130	0.143
Average of total rpm	3.207	1.034	0.488	0.657	0.259	0.227	0.271

Average Conversion efficiency of catalytic Converters		67.75%	84.78%	79.51%	91.92%	93.03%	91.53%	

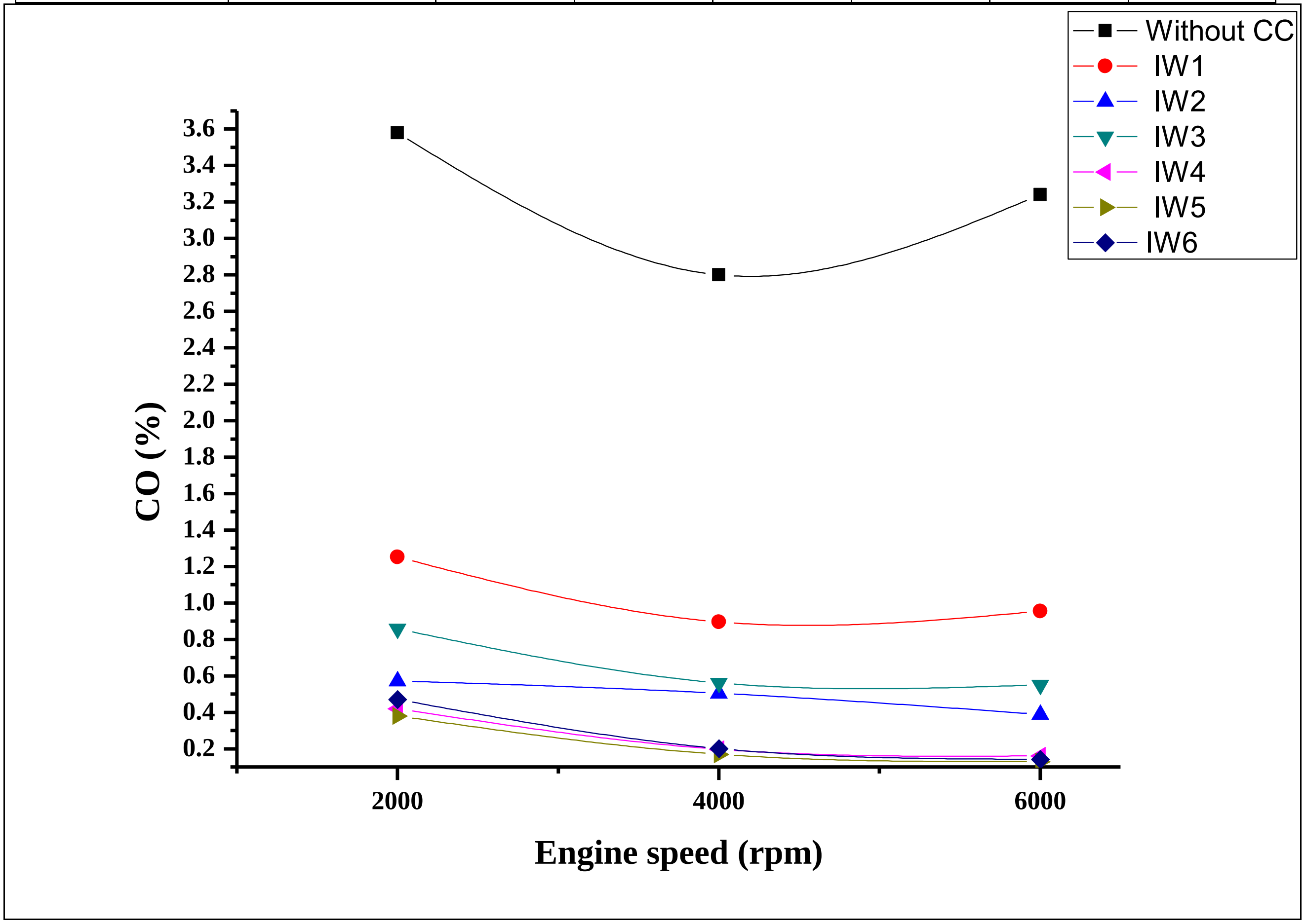


Fig 5.1. CO emissions versus engine speed with and without catalytic converters

5.2 Hydrocarbons vs Engine speed

Following from the table 4 the emissions of HCs are presented. In this regard figure 5.2 is made for HC (ppm) emissions versus engine speed from 2000 rpm to 6000 rpm.

Table 4. Summary of HC (ppm) emissions

Engine speed(rpm)	**Without catalytic converter(cc)**	**IW1**	**IW2**	**IW3**	**IW4**	**IW5**	**IW6**
2000	599	203.66	65.89	107.82	32	29.95	35
4000	403	128.95	60.45	80.66	22.15	16.52	20.1
6000	390	97.60	58.50	78	17	14	11.23
Average of total rpm	464	143.40	61.61	88.80	23.70	20.15	22.11
Average Conversion efficiency of catalytic Converters		69.66%	86.33%	80.66%	94.88%	95.77%	95.23%

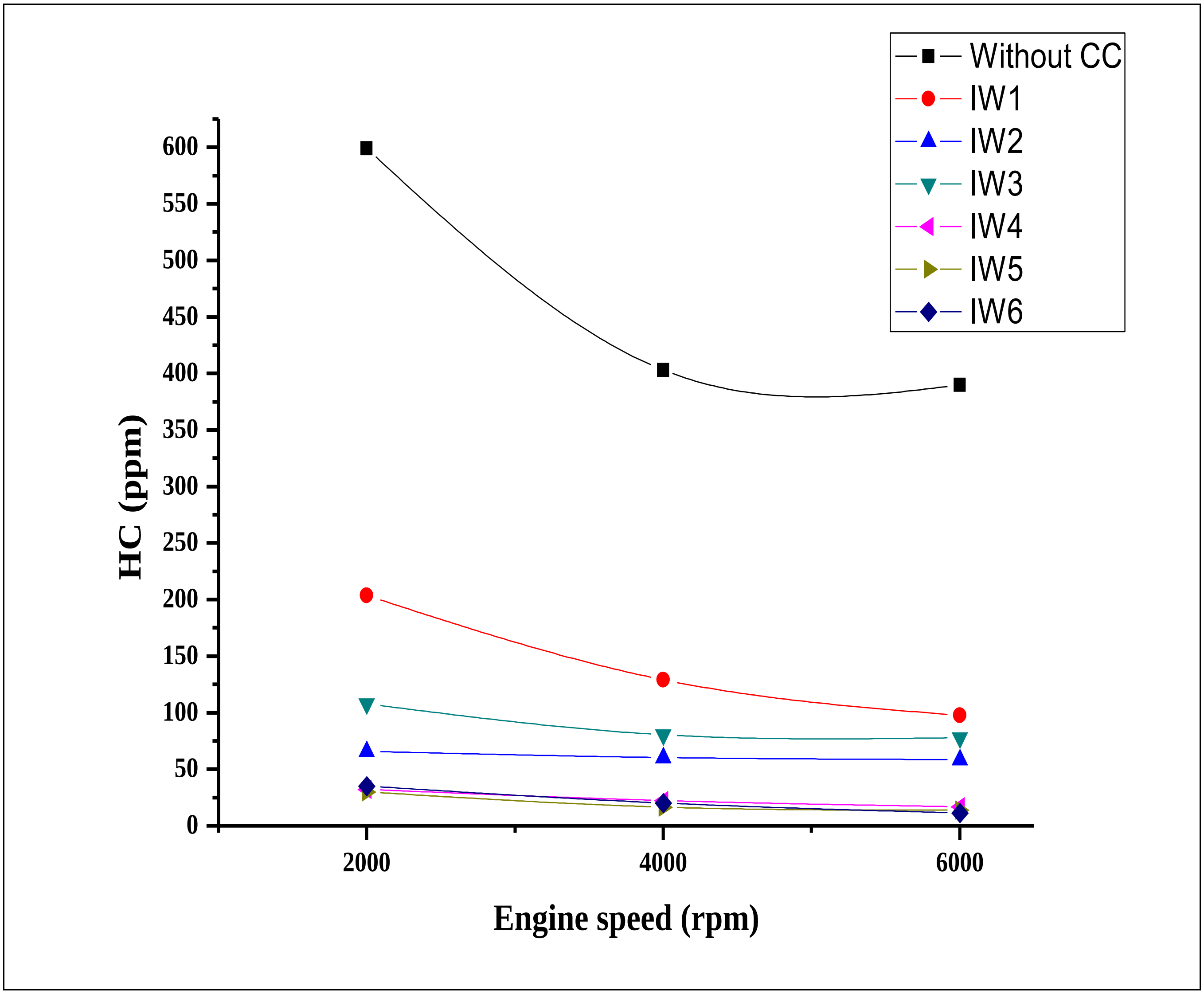


Fig 5.2. HC emissions versus engine speed with and without catalytic converter

5.3 Effects of Cobalt loading on conversion efficiency

From the following figure 5.3 it is shown that by increasing the cobalt loading the efficiency is also increased step wise from IW1 to IW5 and then decreased **(**Xiong et al., 2004; Das and Deo, 2012; Aida and Mustapa, 2012). This graph showed there is no significant difference between the efficiency of IW4, IW5 and IW6 which means optimization occurred at 18 wt.% and further no need to increase the cobalt loading**.**

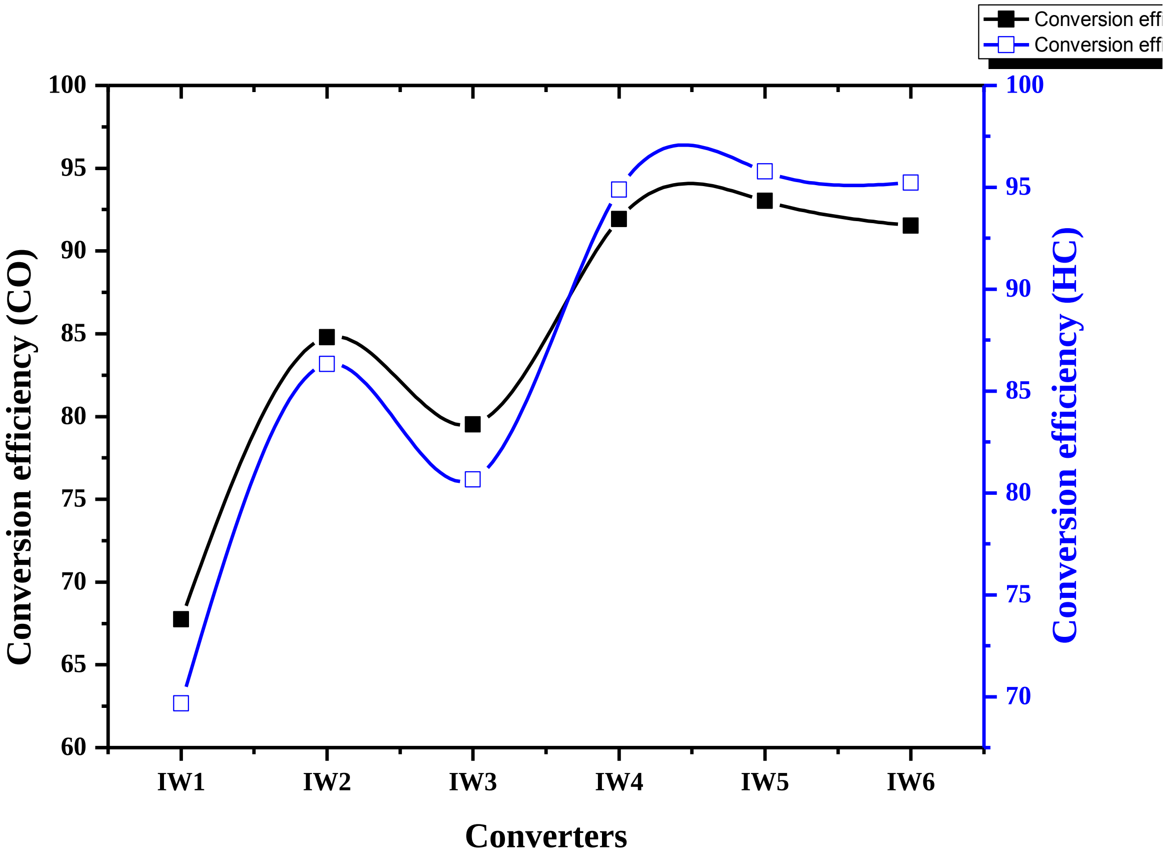


Fig 5.3. CO (%) and HC(ppm) conversion efficiency of all converter

5.4 Comparison between particle and powder

Besides increasing the Co loading on titania. There is another case i.e. 'particle vs. powder' is studied. For 12% cobalt loading two converters (IW2 and IW3) are prepared with different particle size. From table 3 and 4 the values of IW2 (With powder) and IW3 (with particle size i.e. 75 to 150um) are explained. The results of these converter showed that the conversion efficiency of IW2 is greater than IW3 due to large surface area. Fig 5.4 and 5.5 explained the CO and HC emissions respectively of these converter with respect to the engine speed.

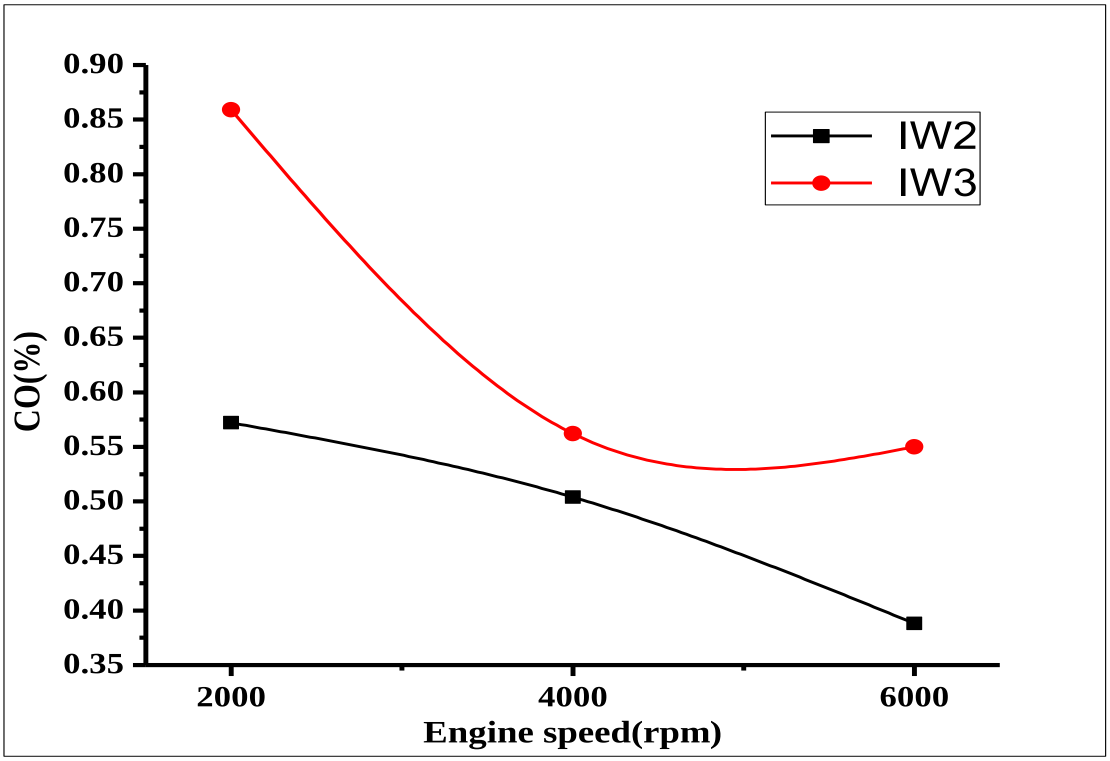


Fig 5.4. CO (%) Comparison of IW2 and IW3

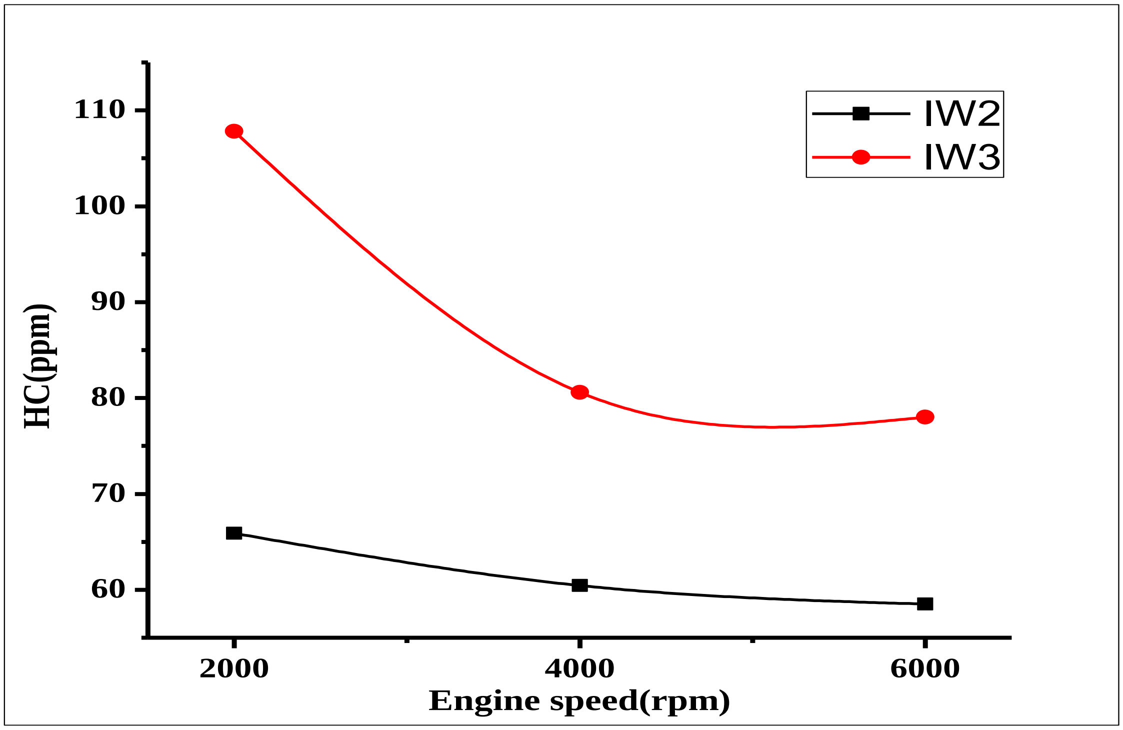


Fig 5.5. HC (ppm) Comparison of IW2 and IW3

Chapter 6

Conclusions and Recommendations

6.1 Conclusions

Following are some conclusions from this research,

1. The development of catalytic converter based on wire mesh substrate of stainless steel with Co_3O_4/TiO_2 catalysis has been successfully achieved.
2. Maximum conversion efficiencies of CO and HC are 93% and 96% respectively.
3. At high space velocity this converter presents the better conversion as compared to the conventional converter due to large surface area.
4. By increasing the cobalt loading i.e. 6-21 wt. % Co, maximum conversion achieved till optimization which means no need to increase cobalt loading further.
5. On same cobalt loading but different particle size IW2 is more effective than IW3 due to small particle size and having large surface area.
6. Hence, titania supported cobalt catalyst with wire mesh is successful for eliminating the harmful pollutants from gasoline engine.

6.2 Recommendations

Following are some recommendations for future work,

1. Different coating techniques can be used for coating of substrate.
2. Different methods for the synthesis of catalysis can be used.
3. Different geometric shapes of substrate can be tested to find out optimum substrate for better conversion.
4. The conversion efficiency of catalytic converter could be tested on the basis of exhaust temperature.
5. The evaluation of catalytic converter could be tested on the basis of pressure drop.

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