

**Development and Performance Evaluation of a Non-Noble
Metal Based Catalytic Converter for Gasoline Engine**



By

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NUST201362271MSCEE652113F

A thesis submitted in partial fulfillment of the requirements for the degree of

Master of Science

In

Environmental Engineering

Institute of Environmental Sciences and Engineering (IESE)

School of Civil and Environmental Engineering (SCEE)

National University of Sciences and Technology (NUST)

Islamabad, Pakistan

2016

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ACKNOWLEDGEMENTS

This dissertation would not have been possible without the guidance and the help of several individuals who helped me throughout this research phase.

First and foremost, I would like to express my sincere gratitude to my thesis supervisor **Dr. M. Zeeshan Ali Khan** (IESE) for his continuous support throughout my thesis at IESE, for his patience, motivation, enthusiasm, and immense knowledge. His guidance helped me through my research and writing of this thesis. I could not have imagined having a better advisor and mentor for my MS research work.

Many thanks also go to **Dr Samiur Rahman Shah** (SMME) and **Dr. Faheem Khokhar** (IESE) for their guidance and support.

I am also very thankful to **Dr. Tayyaba Noor** (SCME) for his unfailing moral support as my external advisor.

I am also very grateful to several other individuals who assisted me during the data collection, processing and analysis stage and provided all the required technical support in a timely manner. Lastly, I would like to appreciate the endless support I received from all my friends.

“Waleed Ahmad”

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LIST OF ABBREVIATIONS

A/F	Air to Fuel Ratio
CH ₄	Methane
CNG	Compressed Natural Gas
CO	Carbon Monoxide
CO ₂	Carbon Dioxide
Co ₃ O ₄	Cobalt Oxide
CI	Compression Ignition
EDS	Energy Dispersive Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
FWHM	Full Width of a diffraction line at Half of Maximum intensity
GHGs	Greenhouse Gases
GPS	Global Positioning System
HC	Hydrocarbons
HCl	Hydrochloric Acid
HCCI	Homogeneous Charge Compression Ignition

IWI	Incipient Wetness Impregnation
JCPDS	Joint Committee on Powder Diffraction Standards
N ₂ O	Nitrous Oxide
NH ₃	Ammonia
NO ₂	Nitrogen Dioxide
NO _x	Nitrogen Oxides
OSC	Oxygen Storage Compounds
PGMs	Platinum Group Metals
SCR	Selective Catalytic Reduction
SO _x	Sulphur Oxides
SEM	Scanning Electron Microscopy
TiO ₂	Titanium Dioxide
WI	Wet Impregnation
XRD	X-Ray Diffraction

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ABSTRACT

With increase in urbanization and consequent growth in vehicular fleets, resulting air pollution is becoming serious problem for urban environment. One of the technological options to control vehicular emissions is catalytic converters. Conventionally, precious metals e.g. Pt, Pd and Rh, collectively named as Platinum group metals (PGMs) have been used as a catalyst in catalytic converters. However, increasing prices of PGMs and their adverse effects on human health and environment, necessitate the investigation of potential low priced alternatives such as $\text{Co}_3\text{O}_4/\text{TiO}_2$. Co_3O_4 supported over TiO_2 has been previously investigated for low temperature oxidation of CO in controlled laboratory environment, however, it has yet to be tested under real vehicular engine exhaust conditions. Here we report catalytic converter based on $\text{Co}_3\text{O}_4/\text{TiO}_2$ as catalyst with stainless steel wire mesh as a substrate. Catalyst was prepared by wet impregnation (WI) as well as incipient wetness impregnation (IWI) methods. Catalyst was deposited on wire mesh via dipping technique and tested for oxidation of CO and HC present in the tailpipe emissions of motorcycle in idle condition at different rpm ranging from low to high. The conversion efficiencies were superior in catalysts prepared with IWI method as compared to WI method. Then IWI catalyst was taken for testing in real driving conditions ranging from 15 km/h to 40 km/h on a 2 km patch of a road. Reduced efficiency of catalyst was observed in real driving conditions due to high load of pollutants in case of HC and in case of CO reduced efficiency was observed due to presence of NO_x

INTRODUCTION

1.1. Background

Air pollution historically defined in many ways generally it is defined as presence of one or more contaminants, in atmosphere which can cause short- or long-term deleterious effects to human, animal or plant life, or to environment. These contaminants are classified into primary and secondary pollutants. Primary pollutants are the ones which emitted directly into atmosphere and secondary pollutants which are formed in atmosphere by reaction of primary pollutants itself or primary pollutants with other gaseous species of the atmosphere (Neal Hickey, Ilan Boscarato, 2014). Air pollution with no doubt is a risk to environment and health. It was estimated that outdoor air pollution in both urban and rural settings caused 3.7 million premature deaths worldwide in 2012 (WHO, 2014). In source apportionment studies, road transport appears important source of pollutant emissions in urban areas(Feng et al., 2015; Franco et al., 2013). More specifically, it is internal combustion engine (ICE) in various forms of transport which contributed greatly to increased problems of pollution. Catalysts are being used to remove any kind of pollutant from air. Moreover, the phenomenon of catalysis is intricately woven into the fabric of chemistry, and the recognition of its nature and importance is relevant. Mostly used catalysts to alleviate air pollution are of heterogeneous type. Heterogeneous catalysis is simply defined as catalysis where the catalyst phase differs from the reactant phase.

1.1.1. Exhaust gases

Exhaust gases which forms due to combustion of fuel in internal combustion engine consist of many pollutants. The major pollutants from gasoline fueled engines are unburned or partially burned hydrocarbons (HCs), carbon monoxide and nitrogen oxides (NO_x), especially nitric oxide (Acres and Harrison, 2004; Alkemade and Schumann, 2006; Farrauto and Heck, 1999; Ronald M. Heck and Farrauto, 2001; Jankowski and McCluskey, 2014; Kašpar et al., 2003; König et al., 2001; Ramanathan et al., 2004; Shelef and McCabe, 2000; Twigg, 2011). Furthermore, sulphur oxides are also formed from the sulphur in the fuel. In addition to these, it mainly contains oxygen, hydrogen, nitrogen, water and carbon dioxide as combustion products. Typical composition of gasses in exhaust reported in literature are CO (0.5%), HCs (350ppm), NO_x (900ppm), H₂ (0.17%), O₂ (0.5%), H₂O (10%) and CO₂ (10%) at normal operation of an engine (Ronald M. Heck and Farrauto, 2001). The exact gas composition at any moment depends on many factors, among them majors are driving conditions (A/F ratio), engine type (2 stroke or 4 stroke, SI or CI), fuel type and quality (Jankowski and McCluskey, 2014). Air to fuel ratio is very important factor in all types of vehicles with respect to control of pollutants. For gasoline engine 14.7 is the stoichiometric A/F ratio at which amount of fuel becomes equal to amount of air and resultant A/F becomes equal to 1. If A/F ratio results in >1 this means, there is more air than fuel and this termed as leaner and if A/F results in <1 this indicates richer fuel mixture (Burch J. P.; Meunier, F. C., 2002; Busca et al., 1998; Fritz and Pitchon, 1997; Roy et al., 2009).

1.1.2. Legislation

Air pollution problem was started to experience in some urban areas by 1940s and 1950s but until then there was not any law to control air pollution. Then by 1970 clean air act was passed and first US federal standards were described to control pollution from vehicles. Initially CO and HCs were main pollutants to be reduced but then by substantial improvements in the standards, it became necessary to reduce oxides of nitrogen (NO_x) (Acres and Harrison, 2004; Busca et al., 1998; Epling et al., 2003; Garin, 2001; Jensen, 1995; Ravindra et al., 2004; Zhang et al., 2006). To reduce these emissions, catalytic converter was introduced in cars. Over the years standards became more stringent due to which after commercialization of catalytic converter in 1975 to up till now much of research and development work has been devoted in improvement of catalytic converter (Burch J. P.; Meunier, F. C., 2002; König et al., 2001; Pârvulescu et al., 1998; Shelef and McCabe, 2000; Tsai et al., 2000; Xiao et al., 2001).

1.1.3. Catalytic Converter

Catalytic converter is a device used to detoxify the exhaust emissions from a vehicle. Its main components include substrate, washcoat and catalyst. Substrate is a material over which washcoat is deposited. It may be ceramic or metallic. Washcoat is act like a carrier for catalyst. It provides high surface area to catalyst which is responsible for conversion of pollutants (Alvarez et al., 2009; Chen et al., 2003; Gandhi, 2003; Holmgreen et al., 2007; Horng et al., 2004; Jia et al., 2006; Kašpar et al., 2003). Catalyst is dispersed over washcoat so that active sites can easily be accessible to pollutants in gas streams. Catalytic converter technology has been revolutionized over last four decades. Initially it can oxidize only CO and HCs. In exhaust stream secondary air was introduced to make overall oxidizing

conditions. Historically used catalysts for this converter were Pt and Pd and this converter was named as two way catalytic converter (Roy et al., 2009).

Furthermore, to meet stringent standards, a series of new catalysts experimented in laboratory and Rh was introduced as reduction catalyst. Therefore, it became possible to convert all three main pollutants simultaneously over a single bimetallic catalyst Pt/Rh or Pd/Rh provided air to fuel ratio near to stoichiometric (Li et al., 2010; Young, 2010). This process named as three-way catalyst. While focusing on NO_x reduction in diesel and natural gas engines, selective catalytic reduction (SCR) was introduced. In SCR a reductant was used to reduce selectively NO_x into nitrogen N₂. In gasoline engine CO act as a reducing agent but for diesel engine ammonia (NH₃) and HCs used as reducing agents. Selective catalytic reduction by ammonia (SCR- NH₃) is mostly used in stationary sources such as power plants because in mobile application handling ammonia is difficult and ammonia slip can also occur which is also a pollutant. In automobile usually urea is used to generate ammonia. Selective catalytic reduction by using HC (SCR-HC) is inexpensive and convenient option. Historically vanadia oxide (V₂O₅) supported over TiO₂ have been proved best catalyst for SCR application (Granger and Parvulescu, 2011; Imanaka and Masui, 2012; Kim and Kim, 2011; Kolodziej et al., 2012; Prati et al., 2011; Wang and Li, 2012). Many changes are continuously being introduced in various components of catalytic converters to increase their efficiencies. Major changes include introduction of electronic fuel injection system (EFI), oxygen storage components (OSC), stabilizers to withstand at high temperatures, metallic substrate with higher cell densities and dual bed or layered catalysts systems.

1.1.4. Monolithic reactor Vs Wire gauzes reactor

Virtually all automobiles now a days equipped with monolithic type substrate either metallic or ceramic. Monolithic reactor is composed of parallel straight channels. These parallel channels may be of different shape and thickness. Historically honeycomb like structure type monolithic reactors with 400 and 600 cell per square inch available in market(Franco et al., 2013; Huo et al., 2012; P. J. Jodłowski et al., 2013; Kaur and Kishore, 2013). Metallic substrates have higher surface area and open frontal area with thicker walls than ceramic and up to 1200 cells per square inch achievable by using metallic foils. Wire gauzes are basically wire meshes either woven or knitted and provide higher surface area than monolithic reactors. Although back pressure may exceed than monolithic reactors but wire gauzes provide turbulent flow which alternately resulted in good interaction with active sites of catalyst and remove mass transfer and heat transfer limitations. Furthermore, substantial decrease in reactor length can be achieved by using wire gauzes instead of monolithic. Coke formation in parallel channels of monolithic reactor is common phenomena due to which back pressure does increase on engine. But in wire meshes this effect is negligible and alternately long term better efficiency can be obtained(Jankowski and McCluskey, 2014; P.J. Jodłowski et al., 2013; Kelyp et al., 2013; Lee and Chen, 2013; Shahreen et al., 2013; Yu et al., 2013).

1.2 Objectives

- Development of catalytic converter using metallic wire mesh as substrate coated with $\text{Co}_3\text{O}_4/\text{TiO}_2$ catalyst prepared via two different routes
- Study the effect of preparation methods on performance of pollutant's conversion.

- Study performance of prepared catalysts on 125cc motorcycle at Idle and real driving conditions

1.3. Scope of study

- Development of a new and locally manufacture catalytic converter for motorcycles.
- Identification of a low cost alternative of PGMs and efficient catalyst for 4 stroke engine.
- Performance evaluation of catalytic converter in real driving conditions ranging from low to medium driving speeds.

REVIEW OF LITERATURE

2.1 Introduction

Air pollution with no doubt is a risk to environment and health. It was estimated that outdoor air pollution in both urban and rural settings caused 3.7 million premature deaths worldwide in 2012 (WHO, 2014). In source apportionment studies, road transport appears important source of pollutant emissions in urban areas (Feng et al., 2015; Franco et al., 2013; Neal Hickey, Ilan Boscarato, 2014). Asia is a largest consumer of motorcycles in the world as it is private transportation in urban areas to travel over short distances (Horng et al., 2004; Prati et al., 2011; Tsai et al., 2005). In Pakistan, total number of vehicles on road had increased rapidly over last two decades from 2.1 million (1991-92) to 10 million (2009-2010). Share of Motorcycles in total fleet of vehicles is 56 percent. (JICA, 2011). In coming decades, situation would be even worse.

History of air pollution problems dates back to early civilization of mankind. Air pollution from road transport was identified in first half of twentieth century and efforts to reduce were intensified in second half of twentieth century. These efforts have gone through various stages with different levels of success, among them major innovations were engine modifications, fuel alternatives and eventually catalytic control of exhaust gas emissions to reduce pollution from mobile sources. (Chen et al., 2015; Hirata, 2014; Lee and Yoo, 2014; Yao et al., 2014; Yazdani Boroujeni and Frey, 2014). The catalytic

converter is now so well established that it is almost part of the language. The technological achievement in producing an after-treatment system that can continue to destroy more than 90% of the emissions from an engine for more than 100,000 miles is quite outstanding (Chen et al., 2015; Hirata, 2014; Hu et al., 2015; Klyushina et al., 2015; Lee and Yoo, 2014; Liu et al., 2016; Yao et al., 2014; Yazdani Boroujeni and Frey, 2014; Zhang et al., 2015).

Catalytic converters are the biggest consumer of PGMs due to which the resources of these metals are getting reduced over the years and from last 3 decades researches are devoted towards low cost alternate. In literature virtually all metals have been tested as an alternate to PGMs. Here we confine ourselves to only researches related to non-noble metal based catalyst either single or bimetallic catalyst. It is well established fact that combination of various base metals performs better than single metal oxide. Very early researches over base metals do not give fruitful results but after having improved quality of fuels by abandoning lead content completely.

2.2. Non-noble metal catalyst

Since the introduction of PGMs as a catalyst for exhaust gas treatment, a great deal of researches had been devoted towards increasing the efficiency of PGMs by introducing oxygen storage compounds (OSC), electronic fuel injection systems to maintain Lambda close to 1, and Phase change materials to reduce cold start emissions. Furthermore, to remove mass and heat transfer limitations at higher gas hourly space velocity (GHSV), reactor design improved a lot from packed bed reactor filled with catalytic beads or grains to ceramic monolith reactor and currently metallic monolith with higher surface area and less volume of reactor (Ronald M Heck and Farrauto, 2001; Twigg, 2011). Automotive

industry is now the biggest consumer of PGMs due to which their cost raised. Therefore, since the beginning of 21st century non-noble metals attracted the attentions of researchers as an alternative and low cost catalyst for purification of exhaust gases. Virtually all known base metals oxides have been tested as an alternate to PGMs but promising activity and selectivity was achieved by few base metals oxides mainly include Co, Fe, Cu, Ce, Ti, Al etc. Base metals oxides were investigated individually or in combination for either oxidation of CO or HC and reduction of NO_x. They have been tested under real automobile exhaust conditions rarely due to sintering effect in exposure to high temperature. Although much of experiments were conducted under conditions similar to fuel cell and homogeneous charge compression ignition (HCCI) engines (Yang et al., 2007). Mostly in literature non-noble metals catalyst were reported for conversion of single pollutant and very few researches have been conducted either to check efficiency of conversion for more than one pollutant in gas stream or effect on conversion of one pollutant on another. So here we will report first literature review of single pollutants removal and then on parametric and mechanistic studies of conversion of pollutants.

2.3. Carbon monoxide (CO) oxidation over non-noble metals

Carbon monoxide (CO) is a colorless, odorless, poisonous gas which is a major product of the incomplete combustion of carbon and carbon-containing compounds. It is a byproduct of vehicle exhausts, which contributes a very large amount of CO emissions in cities, particularly in areas with heavy traffic congestion. Carbon monoxide is dangerous and life threatening to humans and other forms of air-breathing life, as inhaling even relatively small amounts of it can lead to hypoxic injury, neurological damage, and possibly death. When it enters the body, it combines with haemoglobin to form carboxy

haemoglobin, reducing the oxygen-carrying ability of the blood. Long term exposure to low levels of carbon monoxide may result in heart disease and damage to the nervous system.

In context of reducing automotive emissions, CO oxidation at low temperature had become more important (Xie et al., 2009). Preferential oxidation of CO, in excess of hydrogen, by Co_3O_4 had also been studied extensively in literature. Low temperature oxidation of carbon monoxide in excess of oxygen has applications for improvement in air quality whereas preferential oxidation of carbon monoxide in presence of hydrogen is an application of purification of hydrogen streams to be used in PEM fuel cells (Yung et al., 2007).

In very early research, Yu Yao studied catalytic oxidation of CO and HCs over unsupported Co_3O_4 and Co_3O_4 supported on alumina. He studied reaction kinetics at low temperature oxidation of CO and HCs and his research findings concluded that specific catalytic activity of Co_3O_4 is highest among other metal oxides. He also reported retardation effect in oxidation of CO and C_2H_4 when they coexist in gas phase and inhibiting effect of NO in oxidation of CO present in gas stream at 200 °C without any reaction with CO.

Epling found Co/TiO_2 catalyst was effective for selective, catalytic oxidation of CO in H_2 containing streams at high temperatures (>100 °C) and reported retardation in activity by CO_2 and H_2O presence at low temperature. Wang et al. investigated CO oxidation over three supported cobalt oxide catalyst Co/SiO_2 , $\text{Co}/\text{Al}_2\text{O}_3$ and Co/TiO_2 . Author reported promising activity by Co/TiO_2 . Yang investigated the effect of calcination temperature on

low-temperature oxidation of CO over, cobalt oxide supported on TiO₂, catalysts and found 5 wt% CoO_x/TiO₂ catalyst calcined at 450°C highly active for CO oxidation at 100°C than calcined at higher and lower temperature of 450°C. Kim et al. (Kim and Kim, 2011) reported the effect of various parameters of reactions such as GHSV, temperature and CO concentration, and also studied the effect of guest molecules such as C₃H₈ and H₂O on deactivation of 5% Co₃O₄/TiO₂ catalyst prepared by incipient wetness impregnation method for oxidation of CO. Results of this extensive research concluded that the catalyst showed less deactivation at low GHSVs, low CO concentration and at high temperature.

To minimize effect of moisture content in gas stream on cobalt catalysts during low temperature oxidation of CO Xie et al. prepared nanorods of Co₃O₄ found no decrease in catalytic activity by presence of moisture in stream for oxidation of CO at -77°C and room temperature.

Li et al. investigated different forms of TiO₂ as a support material for Co₃O₄ in oxidation of CO at low temperature and reported among P25 degussa, anatase and rutile forms of TiO₂, the anatase form gives highest activity with stability and selectivity to CO₂.

2.4. Hydrocarbons (HCs) oxidation over non-noble metals

Similar to application of cobalt oxide (Co₃O₄) catalyst in low temperature oxidation of CO, it has been extensively studied over last two decades for HCs (individual hydrocarbon of different chain length and collectively in a gas stream) oxidation. Methane combustion over cobalt oxide catalyst supported on ZrO₂, Al₂O₃, MgO and TiO₂ supports studied by Xiao et al. (Xiao et al., 2001) and reported that oxidation starts at 600°C and 100 percent conversion achieved at 700°C over TiO₂ support. More recently Jodłowski et

al. (P.J. Jodłowski et al., 2013) investigated methane combustion by coating bimetallic catalyst ($\text{Co}_3\text{O}_4\text{-CeO}_2$) over wire gauzes, knitted and woven, and reported enhanced mass and heat transfer properties along with short length of reactor than conventional monolithic reactor. The best reactor design found according to studied condition was woven gauze reactor. In similar fashion Łojewska et al. (Łojewska et al., 2005) reported n hexane conversion over spinel type Co_3O_4 deposited over wire gauzes and found cobalt oxide is more active than $\text{Pt/Al}_2\text{O}_3$. Solsona et al. (Solsona et al., 2008, 2007) reported complete oxidation of propane and n butane over nanocrystalline cobalt oxide. In another study author (Łojewska et al., 2009) compared activity of spinel type cobalt oxide with Pt and Rh catalyst and reported 50% reduction in length of reactor by using wire gauzes as compared to monolithic reactors. Tian et al. (Tian et al., 2009) investigated oxidation of alkene and alkane hydrocarbons with carbon chain of C1-C4 over Co_3O_4 catalyst and reported 100 % selectivity of this catalyst towards end product of CO_2 with no byproducts of CO and methane as an intermediates, by using FTIR transmission spectra. In very early research, it was found Titania pretreated with NO_2 catalyze the partial oxidation of propene into oxygenates such as acetone and acrolein at around 623 K, while fresh TiO_2 produces only carbon oxides(Ueda et al., 1998).

In literature main disadvantage reported related to use of cobalt oxide is its thermal stability. At temperatures about 700°C , Co_3O_4 converts into CoO which is less active than Co_3O_4 (Li et al., 2010; Solsona et al., 2008). After having the catalyst good enough to oxidize HCs with high efficiency and selectivity there is another issue with HC oxidizing reported in literature extensively is of reactor's type. Monolithic reactors have been reported less effective for oxidation of HC because they composed of straight channels in

which flow becomes laminar (Kolodziej et al., 2012; Lojewska et al., 2009; Solsona et al., 2007). Catalytic oxidation of hydrocarbons is controlled by diffusion which means conversion is limited due to mass transfer between catalyst and flowing gas mixture as they present in very low concentration (<1%) in exhaust stream(Łojewska et al., 2008). Therefore researches over last decade had proposed wire mesh structure either woven or knitted for effective oxidation of HCs instead of monolithic reactor especially for automotive applications (Kolodziej et al., 2012). Co_3O_4 has proven to be a good catalyst for methane combustion, however, undergoes severe sintering from 550°C upwards which drastically decreases its catalytic performance. This sintering process might be avoided, or at least deterred, through the use of supports which lead to the stabilization of cobalt ions.(Chen et al., 2015).

2.5. NO_x reduction over non-noble metals

It has been well established by reviewing literature that cobalt oxide is good catalyst for oxidation of CO and HCs and its activity under some circumstances even better than precious metals. Furthermore, cobalt oxide performance for reduction of NO_x had also been studied extensively in literature. Mixture of NO and NO₂ collectively named as NO_x whereas in this mixture predominate amount is of NO 95% and 5% is of NO₂.

Historically Pt/Rh or Pd/Rh catalyst supported on alumina washcoat have been used for reduction of NO_x in catalytic converters of automobiles where CO act as a reducing agent (Busca, G., 1998). In literature, vanadia oxide supported on TiO₂ have been proved best catalyst for NO_x reduction via NH₃. Moreover, anatase phase of TiO₂ is more active than rutile phase (Hu et al., 2015; Imanaka and Masui, 2012; Pârvulescu et al., 1998; Roy et al., 2009).

Nitrogen oxides (NO_x) are emitted primarily from transportation and other industrial sources and contribute largely to a variety of environmental problems: the formation of acid rain and the resultant acidification of aquatic systems, ground-level ozone (smog), and general atmospheric visibility degradation. For these reasons, NO_x emissions are controlled (Burch J. P.; Meunier, F. C., 2002; Fritz and Pitchon, 1997; Gomez-Garcia et al., 2005; Granger and Parvulescu, 2011; Gu et al., 2015; Hu et al., 2015; Imanaka and Masui, 2012; Pârvulescu et al., 1998; Roy et al., 2009; Shahreen et al., 2013). In respect of the severe regulations imposed, the motor car manufacturers have had to decrease considerably the NO_x emissions from their vehicles. Initially, this was achieved either through action upon the nitrogen contents of the oil or by a modification of the engine's combustion chamber.

Practically two catalytic processes are applied for NO_x reduction. First is three-way catalyst for gasoline engine and other one is selective catalytic reduction which uses a reductant either ammonia, HC or CO. NO_x reduction by using unburnt HCs (HC-SCR) present in exhaust gas is relatively inexpensive process. In literature many publications highlighted use of different hydrocarbons such as methane ethane and propane etc. for reduction of NO_x by using different catalyst (Ohtsuka et al., 1997). Initially, better catalytic reduction of NO_x over oxides of Cu, Co and Fe was reported among other base metals. Recently, enhanced NO_x reduction was reported over cobalt oxide CoO/TiO_2 catalyst, tested on an engine fueled by natural gas (Kalam and Hassan, 2011).

MATERIALS AND METHODS

3.1 Methodology

All the chemicals used in this research were of analytical grade. Titanium oxide TiO_2 (Panreac) was used to synthesize titania nanoparticles. Sodium metabisulfite (BDH) and Sodium Silicate solution (Merck) both were used as binding agents. Cobalt nitrate hexahydrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Panreac) was used as a precursor for preparation of cobalt oxide Co_3O_4 . All glasswares (Pyrex, Germany) were used after washing with de ionized water.

3.2 Synthesis of titania nanoparticles

50 g of titanium oxide powder was added to 300 mL of distilled water in a 500 mL beaker. The Mixture was stirred for 24 h and then allowed to settle for 24 hours. Settled material was dried in oven at 105°C for 12 h to remove moisture. The obtained powder was then crushed using mortar and pestle and then subjected to calcination in presence of air at 500°C for 6 h in a muffle furnace (NEY-525 SRIESII) with heating rate of $10^\circ\text{C}/\text{min}$.

3.3 Preparation of Catalyst

3.3.1 Wet impregnation Method

Cobalt nitrate hexahydrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, (21.75g) was mixed in deionized water and then Titanium oxide nanoparticles (30g) were added, whole solution stirred vigorously

at 500 rpm for 2 hrs. Then sodium metabisulfite (3g) and sodium silicate (270g) was added. Resulting slurry was ball milled at 1400 rpm for 2 hrs.



Figure 3.1. Pictorial view of synthesis from left to right

3.3.2 Incipient wetness impregnation

Cobalt nitrate hexahydrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ added drop wise in TiO_2 while it was stirring at 500 rpm. The resulting product shifted into china dish dried for 12 hrs at 105°C and calcined at 550°C for 5 hrs with heating gradient of $10^\circ\text{C}/\text{min}$. Then calcined powder was mixed with Sodium silicate and sodium metabisulfite and stirred for 12 h at 500 rpm.



Figure 3.2. Pictorial view of synthesis from left to right

3.3.3 Pretreatment of wire mesh

Before applying powder catalyst to wire meshes they were treated with 10 % HCl. The wire meshes were dipped in HCl solution for 30 min, washed with distilled water and dried in oven for an hour as shown in Fig 3.3. This pretreatment was carried out to remove impurities from the wire mesh surface and make it rough for better catalyst adhesion.



Figure 3.3. Wiremesh immersed in 10% HCl

3.3.4 Washcoating of wire mesh

To deposit the catalysts on substrate, slurry was prepared by mixing 10% inorganic binder's solution with catalyst powder. The slurry was stirred for 12 h and then applied to treated wire meshes by dip-coating method. Coated wire meshes were heated for 6 h in furnace in presence of air at 550°C with heating rate of 10°C/min and then cooled down in desiccator to room temperature. Prepared wire mesh modules have been show in Fig 3.4.

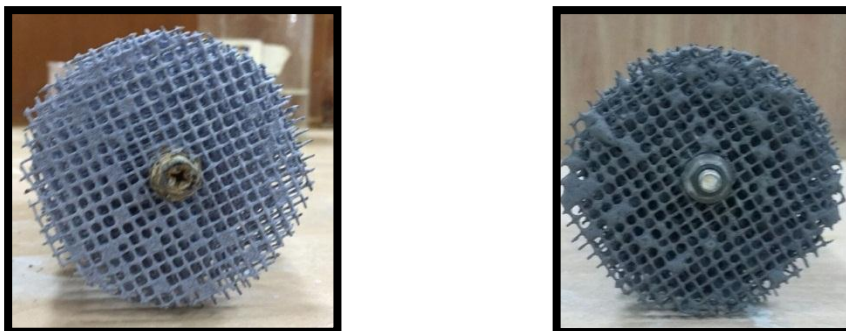


Figure 3.4. WI left and IWI right

Dip coating and heat treatment was performed three times to achieve uniform coating of catalyst. Both, WIC and IWIC catalysts were deposited on wire meshes by same procedure.

3.4 Wire mesh composition and specification

AISI 304 grade stainless steel was used as the substitute of the expensive and difficult to mechanize ferritic steel FeCrAlloy.

Table 3.1 Composition and specification of AISI 304 Stainless Steel Wire Mesh

Metal	Percentage (%)	Parameter	Value
Fe	70.40	Mesh	64 cells/in ²
Cr	18.40	Opening size	0.097 inches
Ni	8.11	Thickness	0.056 inches
C	0.06	Wire diameter	0.028 inches
Al	Nil	Opening area percentage	60 %
Mn	1.45	Weight	2.05 kg/m ²

3.5 Wire mesh Module

Two wire mesh modules were prepared with 22 no of coated sieves. Pictures of prepared modules have been shown in Fig 3.5 and some specifications has been mentioned in Table 2.

Table 3.2 Wire mesh module specifications

Parameter	Value
Diameter of wire mesh	2.5 inch
Length of rod	6 inch
Nut width	0.2 inch
No of meshes on rod	22

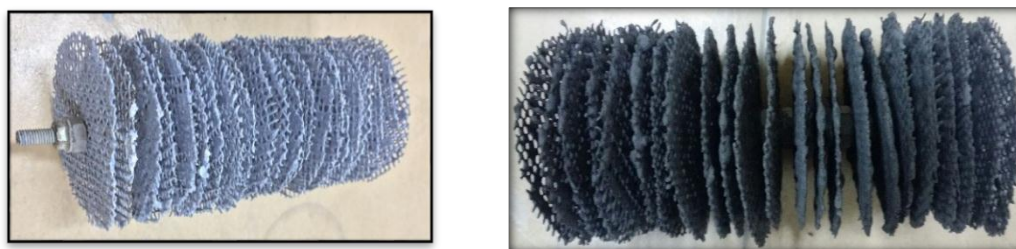


Figure 3.5 Wire Mesh Module WI on left and IWI on right

3.6 Characterization

3.6.1 X-Ray Diffraction (XRD)

XRD analysis of pure TiO₂, wet impregnation catalyst (WIC) and incipient wetness impregnation catalyst (IWIC) was carried out using JEOL JDX-II, X-ray diffractometer. The analysis was done by using Cu K α radiation at a voltage of 40 kV and 30 mA of current. The scanning was done between 10° to 80° at a rate of 2° per minute.

The crystal size is determined usually by XRD analysis using Scherer equation

$$L = \frac{k\lambda}{\beta \cos\theta}$$

Where,

$K = 0.9$, a shape factor for spherical particles

$\lambda = 0.15405$ nm, $\text{CuK}\alpha_1$ wavelength

β = Full width of a diffraction line at one half of maximum intensity (FWHM) radian

θ = The diffraction angle of crystal phase

3.6.2 Scanning Electron Microscope (SEM)

Scanning Electron Microscope provides images of high resolution. The focused beam of electrons produces images which provide us information like appearance, form, size, elemental composition of specimen. The Nova NanoSEM 450 scanning electron microscope (SEM) was used to observe morphology of prepared catalyst powders. Qualitative and quantitative compositional analysis of the samples were carried with microscope equipped with highly precise Oxford Energy Dispersive X-ray (EDX) detector.

3.7 Catalytic Activity Test

3.7.1 Testing at Idle condition

Prepared wire mesh modules loaded into catalytic converter casing and then installed on 125 cc motorcycle. Motorcycle was then operated at 4000, 6000 and 8000 rpm. Exhaust gasses concentrations were measured at inlet and outlet of catalytic converter by using

Crypton 295 gas analyzer and engine rpm were measured by using tachometer. Motorcycle with newly installed catalytic converter has been shown in Fig 3.6.



Figure 3.6. Catalytic converter installed at 125 cc Motorcycle

3.7.2 Testing under real driving conditions

After testing catalysts at idle conditions they have been tested under real driving conditions to check their stability under real scenario. A path of 2 km was selected on Kashmir highway as shown in Fig 3.7. Motorcycle was driven at different speeds ranging from 15 km/h to 20 km/h with and without catalytic converter. GPS (DG 200) was used to track path and speed of motorcycle. Motorcycle was heated up at every speed before taking readings by driving it at the same speed which is going to be tested. Motorcycle was driven at each described speed over 2 km path to take representable and stable reading. Motorcycle

was driven in 2nd gear for speeds of 15 to 30 km/h, with and without catalytic converter and it was driven in 3rd gear for speeds of 30 to 40 km/h. Pollutant gas concentrations were measure by using portable Kane Auto5-1 gas analyzer.



Figure 3.7. Path followed during real driving condition

RESULTS AND DISCUSSION

4.1 X-ray powder diffraction (XRD)

All phases were identified by matching experimental patterns to the JCPDS powder diffraction file. The only pure TiO₂ phase identified was the anatase with JCPDS card no 21-1272. No diffraction peaks related to rutile phase were identified.

XRD pattern of pure TiO₂ is shown in Fig.4.1 along with its characteristics peaks. The XRD pattern showed a predominant peak at 2 theta value of 25.24° along with subsequent peaks at 36.90°, 37.72°, 38.53°, 47.99°, 53.82°, 54.97°, 62.04°, 62.60°, 68.75°, 70.27°, and 74.96° which confirm the presence of pure anatase structure of TiO₂. Average particle size of pure TiO₂ calculated as per Scherrer equation was found to be 48 nm.

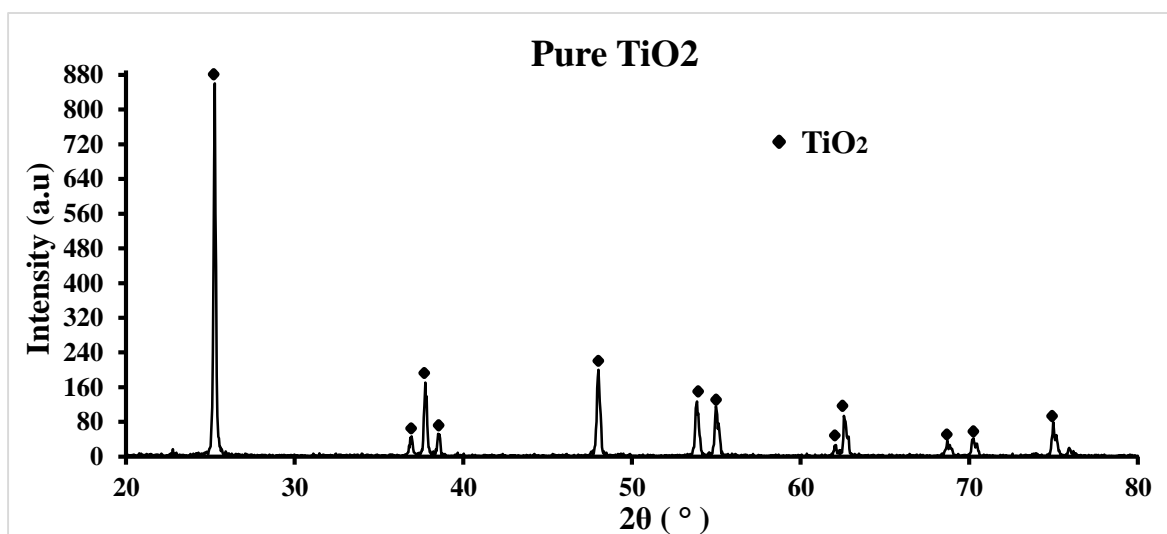


Figure 4.1. XRD patterns of Pure TiO₂

Table 4.1 X-ray Diffractometer Results of Pure TiO₂

Sr. No.	Peak Angle	d-spacing	FWHM
1	25.23	3.52	0.15
2	37.73	2.38	0.19
3	47.99	1.89	0.23
4	53.82	1.70	0.19

In XRD pattern of catalyst prepared by IWI method, the only pure cobalt phase identified was the spinel structured Co₃O₄ (JCPDS: 42-1467). No diffraction peaks related to a CoO phase were detected. Cobalt oxide (Co₃O₄) and TiO₂ were mainly detected in XRD pattern. In addition to TiO₂ peaks there were 6 peaks of cobalt oxide at 2θ values of 31.26°, 36.84°, 38.54°, 44.80°, 65.22° and 68.62°. Predominant peak of cobalt oxide was observed at 36.84° (Fig. 4.2a).

Table 4.2 X-ray Diffractometer Results of Co₃O₄

Sr. No.	Peak Angle	d-spacing	FWHM
1	31.22	2.86	0.19
2	36.84	2.43	0.27
3	38.54	2.33	0.23
4	44.80	2.02	0.31
5	68.62	1.3	0.31

Particles size of cobalt oxide was 31nm based on its intense peak at $2\theta = 36.84^\circ$. This was observed in XRD pattern that the diffraction peaks of spinel cobalt oxide was possibly overlapped with peaks of anatase. Weak XRD pattern for cobalt oxide in XRD pattern of IWI confirms its good dispersion over TiO_2 support.

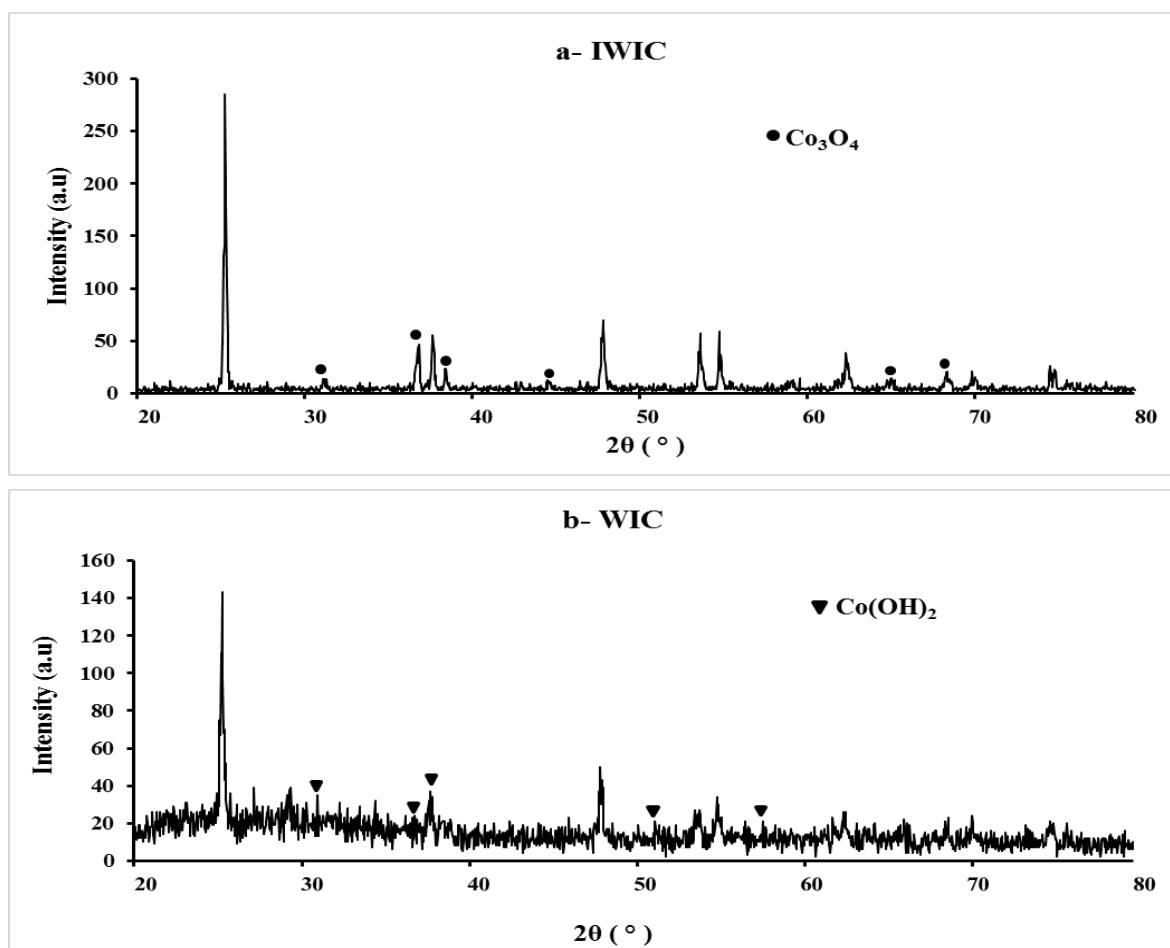


Figure 4.2. XRD patterns of a) IWIC catalyst and b) WIC catalyst

In XRD pattern of WIC catalyst a high quantity of cobalt hydroxide $\text{Co}(\text{OH})_2$ and very low amount of cobalt oxide (Co_3O_4) was detected. This was the main reason due to which WIC catalyst did not give promising conversion efficiency even at high rpm as discussed in the later part of this paper. Moreover, in addition to TiO_2 peaks, 5 peaks of cobalt hydroxide ($\text{Co}(\text{OH})_2$) were observed at 32.42° , 37.88° , 38.67° , 51.32° and 57.84° .

Strongest peak was observed at 2θ of 37.88° . Very weak peaks of Co_3O_4 were observed at 36.50° , 44.40° , 58.80° and 64.60° (Fig. 4.2b). Crystal size of Co_3O_4 particles calculated on basis of its intense peak at 36.50° was 102 nm.

4.2 Scanning Electron Microscopy (SEM)

Representative images of IWIC catalyst and WIC catalyst after calcination at 550°C are shown in Fig. 4.3.

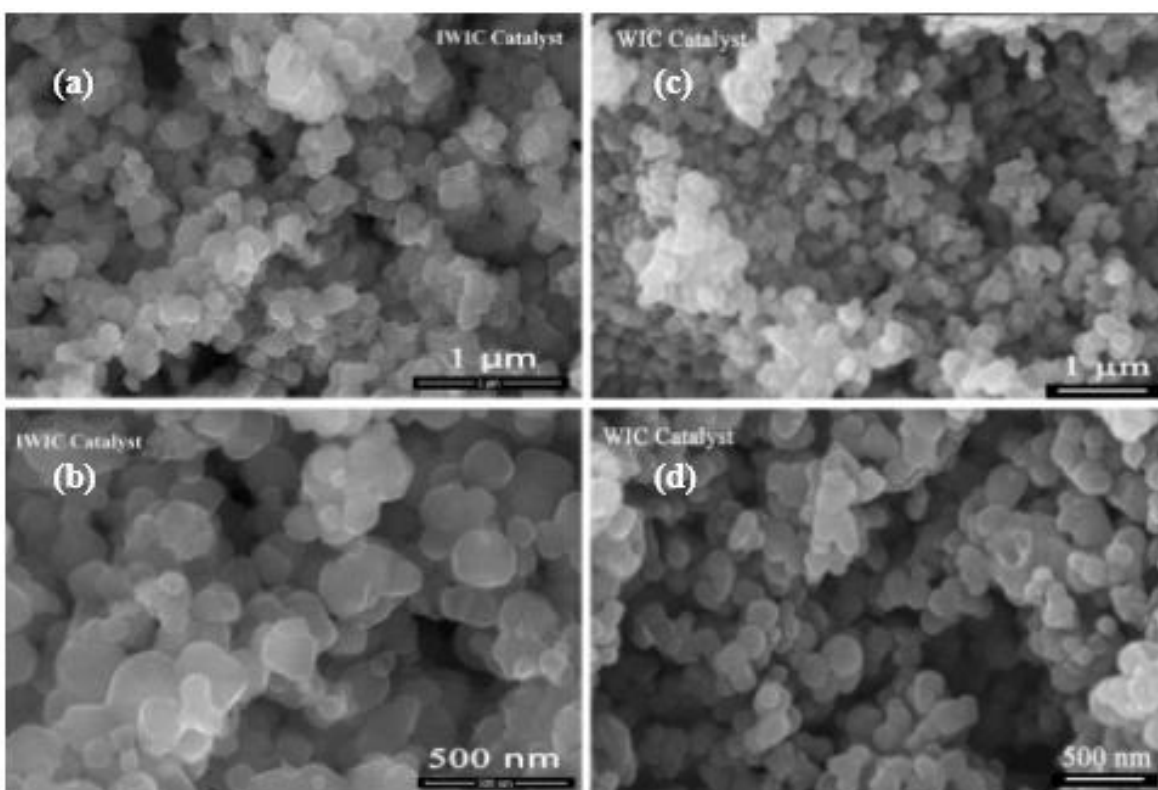


Figure 4.3. SEM images of IWIC catalyst a) 1 μm b) 500nm and WIC catalyst c) 1 μm d) 500nm

The micrograph images show formation of densely packed catalyst nanoparticles with uniform distribution of cobalt on the titania support. The particle size distribution from these images was judged visually in a range of about 100-300 nm for WIC and 50-150 nm

for IWIC. SEM images of WIC appears to be comprised of agglomerated nanoparticles whereas in IWIC SEM images shows distinct smooth structure is clear and boundaries are well defined. Therefore well dispersed particles of cobalt oxide can easily be accessed by pollutants in gas streams and this was also a reason of giving high efficiency of IWIC catalyst as discussed in later part of this thesis.

4.3 Catalytic activity

4.3.1 Tested at idle rpm

Non coated wire meshes gave no conversion at all operated rpm because concentrations of both gases were same at inlet and outlet of non-coated wire meshes. Furthermore, concentrations of CO and HCs, at inlet of catalytic converter, were approximately same in case of both coated wire meshes (i.e. coated with WIC and IWIC catalyst). Average recorded temperatures were 120°C, 196°C and 235°C at 4000, 6000 and 8000 rpm respectively. Therefore, it is clear increase in rpm result in increased temperature of exhaust gas. Activity results of both catalysts have been shown in Fig.4.4.

IWIC performed better than WIC in reducing both, unburned hydrocarbons and carbon monoxide. Maximum efficiency of IWIC achieved for carbon monoxide and unburnt hydrocarbons was 89% and 78% respectively. WIC catalyst also converted the pollutant from engine exhaust but efficiency was too low at low rpm and relatively lower at high rpm as well (47% for CO and 34% for HC). Overall it was observed that both of catalysts were oxidizing more carbon monoxide than hydrocarbons regardless of their preparation methods.

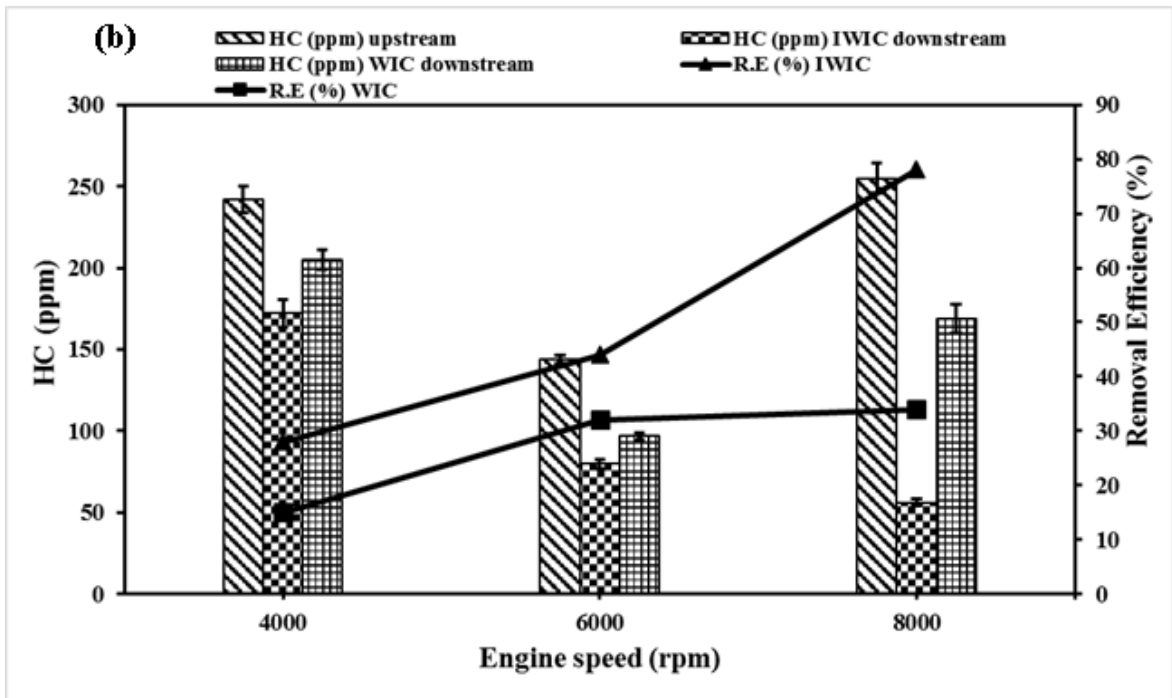
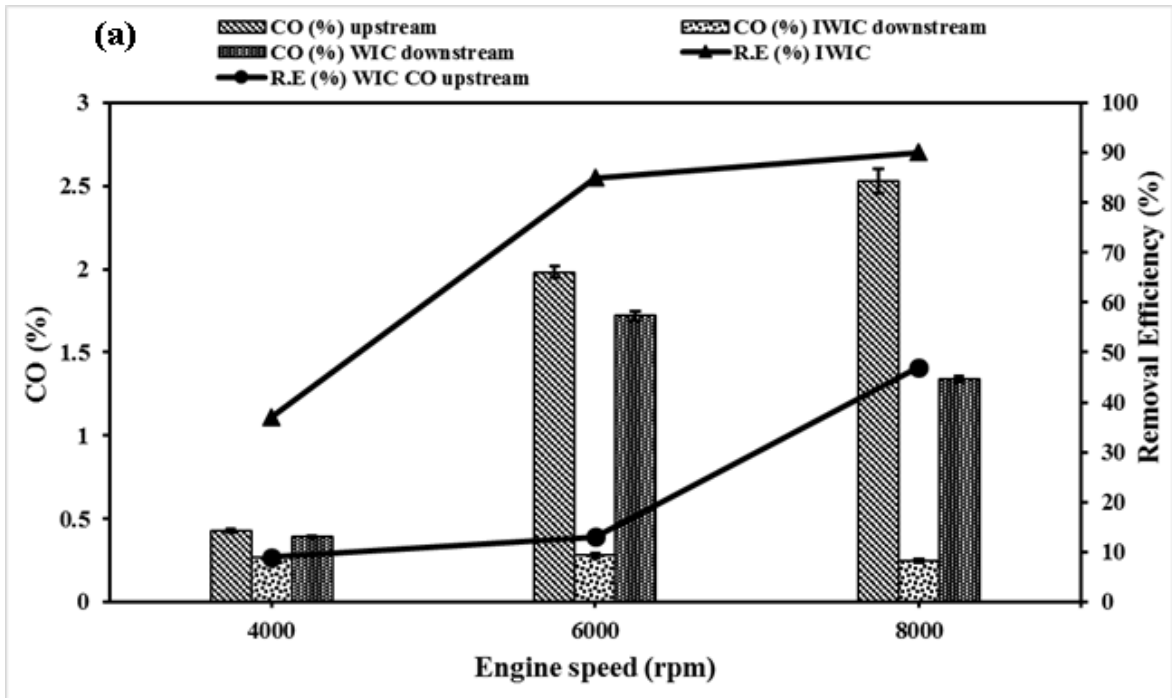
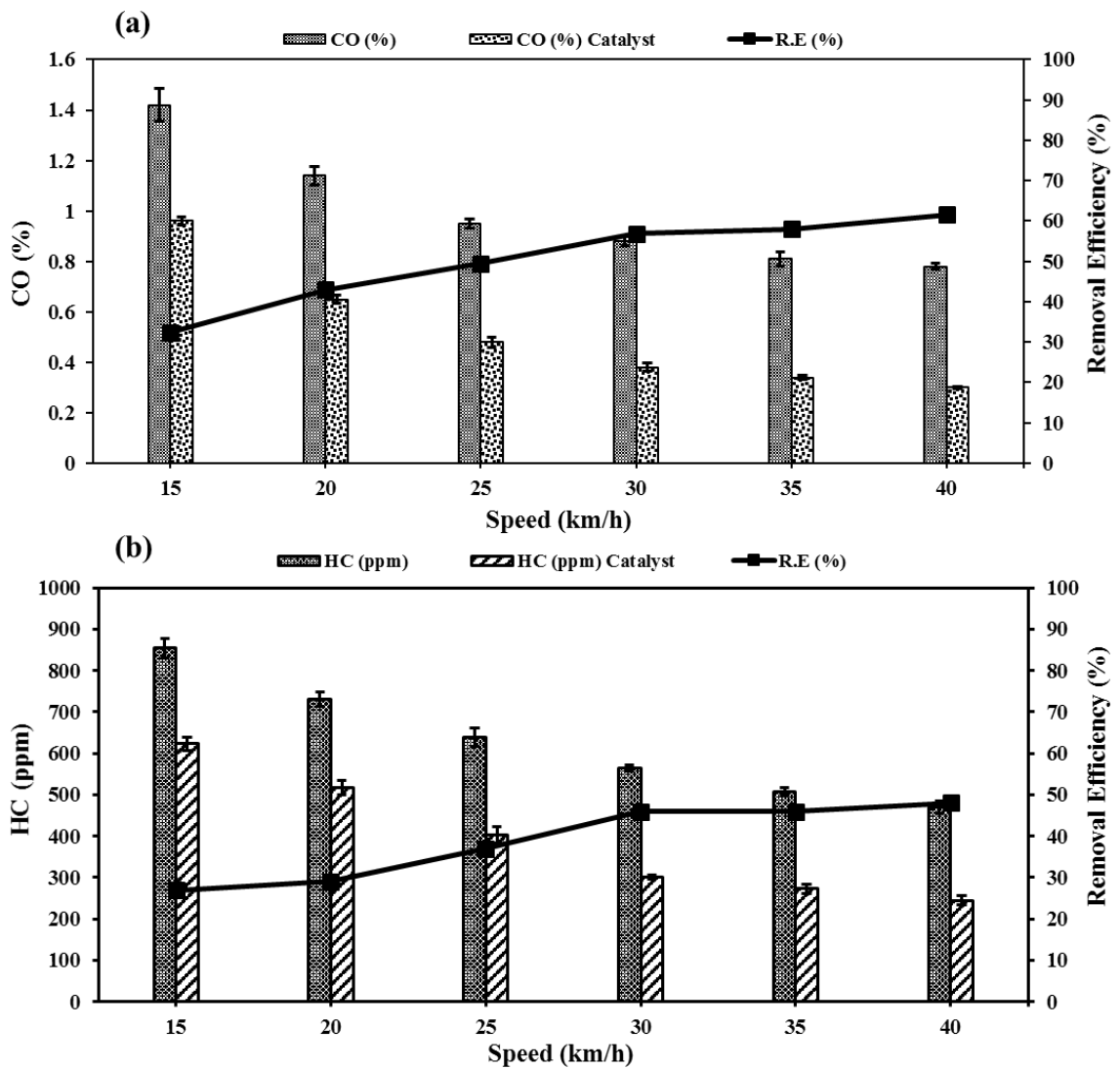


Figure 4.4. Conversion efficiency of WIC and IWIC for a) Carbon monoxide and b) Hydrocarbons

4.3.2 Testing under real driving conditions

Figure 4.5. illustrates the catalyst activity against different speeds of motorcycles for three main pollutants HC, CO and NO_x. As seen from Fig.4.5(a) maximum CO conversion efficiency obtained was 61% at 40 km/h which is indicating as speed is increasing efficiency gets better this can be even more greater if we drive motorcycle at higher speeds.



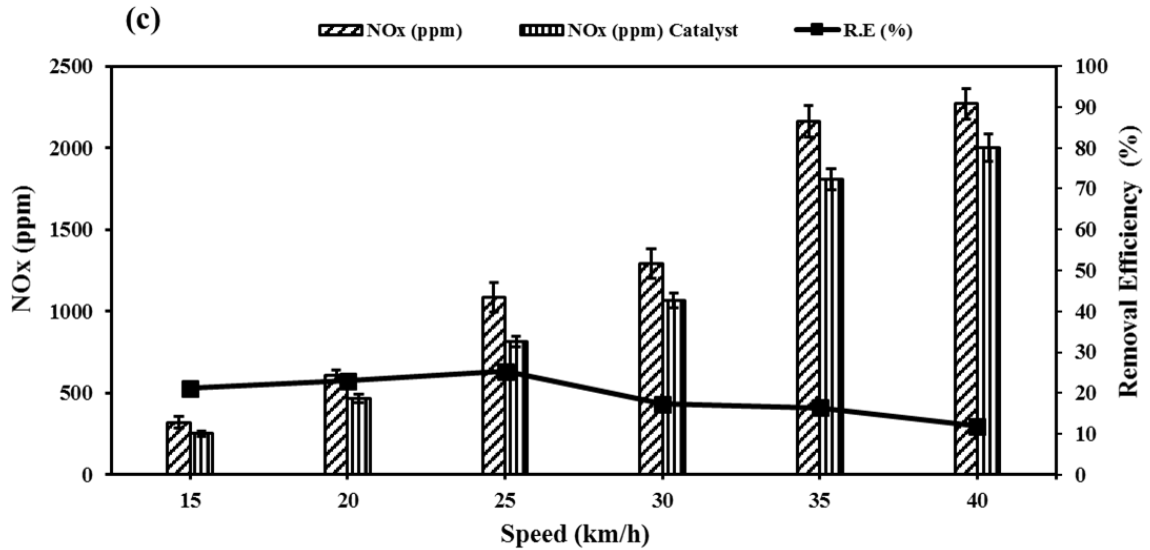


Figure 4.5. Conversion efficiency under real driving conditions a) CO b) HCs c) NOx

This same trend was observed in case of HCs but maximum efficiency was relatively lower than CO which predicting that catalyst is more active in oxidizing CO instead of HCs. This is well established in literature that HCs required higher temperature to get oxidized by catalyst than CO.

NOx conversion behaviour was not linear with speed as NOx conversion requires low temperature and its conversion decreases as space velocity increases (Kašpar et al., 2003). Its conversion efficiency increased upto 25 km/h and even maximum efficiency was not considerable. This reveals that catalyst needs to be optimized for NOx conversion either by adding some reducing agent in exhaust stream or by making dual bed catalyst.

CONCLUSIONS & RECOMMENDATIONS

5.1 Conclusions

Following are the conclusions.

1. A cost effective, non precious metal based $\text{Co}_3\text{O}_4/\text{TiO}_2$ catalyst have been screened and found active for the catalytic conversion of HC and CO by using two preparation routes.
2. Results revealed strong impact of preparation method on performance of catalyst. Preparation method determines the presence of different species of active metals from its precursor.
3. IWIC catalyst is more active than WIC catalyst due to formation of nanosize crystals of spinel type Co_3O_4 which was mainly responsible for oxidation of CO and HC.
4. IWIC catalyst showed higher activity and selectivity for oxidation of CO than HC. Efficiency increases as rpm does increase because of high temperature and less inhibition in activity by water.
5. WIC catalyst showed very low activity in oxidation of CO at 4000 and 6000 rpm whereas at 8000 rpm oxidation is 34%. While selectivity behaviour of WIC catalyst was observed same as of IWIC catalyst, CO oxidized more than HCs at all engine speeds. IWIC catalyst oxidized 43% and 44% more CO and HCs respectively than WIC catalyst.

6. Results of testing under real driving conditions revealed excellent performance of catalyst for oxidation of CO and relatively lower efficiency for HCs oxidation. CO oxidation does increase with engine speed because water vapors effect gets minimized.
7. Lower efficiency of HCs depict that catalyst needs higher temperatures than CO to effectively oxidize HCs.
8. Overall catalyst is not selective in reducing NO_x at any speed of motorcycle. At higher speeds of motorcycle NO_x may be influence catalyst oxidizing efficiency as this may act as a guest molecule.

5.2 Recommendations

Research level suggestions for future work in this area include:

- Long-term stability of the catalyst systems needs to be evaluated.
- Optimization in cobalt content loading and dimensions of catalytic converter is needed.
- Influence of substrate's cell density needs to be further evaluated.
- Development of regional driving cycle is needed to make baseline for testing of catalysts.

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