EFFECT OF OXYGEN STORAGE COMPONENT (CeO_2) ON CATALYTIC PROPERTIES AND PERFORMANCE OF Co_3O_4/TiO_2 FOR THREE WAY CATALYTIC ACTIVITY UNDER REAL ENGINE OPERATING CONDITIONS

By

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APPROVAL SHEET

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Table of Contents

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

ICE	Internal combustion engine
A/F	Air to fuel ratio
CC	Catalytic converter
TWC	Three-way catalytic converter
EFI	Electronic fuel injection
OSC	Oxygen storage component
TiO_2	Titania
Co	Cobalt
Co_3O_4	Cobalt oxide
CO	Carbon monoxide
HCs	Hydrocarbons
uHC	Unburned hydrocarbons
NOx	Oxides of nitrogen
CO_2	Carbon dioxide
CH_4	Methane
CNG	Compressed natural gas
GHG	Greenhouse gases
VOC	Volatile organic carbon
XRD	X ray diffraction
SEM	Scanning electron microscopy
BET	Brunauer Emmett Teller
GHSV	Gas hourly space velocity

ABSTRACT

Three-way catalytic converter (TWC) is a primary emission control technology that allows simultaneous conversion of three major exhaust gas pollutants i.e.CO, unburned hydrocarbons (HC), and NOx into harmless compounds. Commercially available TWC's use ceria as a promotor and Oxygen storage component (OSC) along with noble metals as catalysts. Certain disadvantages are associated with these TWC's like noble metals based catalytic convertors are highly expensive and these metals like Platinum, Palladium and Rhodium are observed to be emitted from the catalytic convertors, thereby causing serious risk to environment. Here in this present research study, we have evaluated the effect of impact of ceria in terms of its characterization and it's TWC conversion efficiency in Co_3O_4-TiO_2 non-noble metal based catalytic convertor. Catalysts synthesis route has major impact on TWC conversion efficiency, so catalysts were synthesized by two methods. Incipient Wetness Impregnation (IWI and Precipitation method. Comparison of these two methods for its three way catalytic conversion efficiency was also performed. Three Ceria loadings were selected i.e.03%,06% and 09% and ceria was doped in 15wt.% Co_3O_4/TiO_2 catalysts. The Three way catalytic conversion efficiency was evaluated at four different RPM's i.e. 2000,4000,6000,8000 at idle conditions. Overall, results reveal strong impact of ceria loading as the conversion efficiency increases significantly with ceria doping. Catalyst synthesized by IWI method gave better conversion efficiency overall and its maximum efficiency for CO, HC and NOx was 92%, 83 % and 90%.

Chapter 1

INTRODUCTION

1.1 Air pollution problem

Air pollution historically termed as presence of one or greater contaminants, in our environment that could drive quick-or long-term harmful consequences to humans, animals, flora and to our surroundings. Air contamination generally known to have impacts over human wellbeing, ecology, buildings and structures, atmosphere and to environment (Kampa & Castanas, 2008).

In few cities of USA problematic smog, photochemical smogs became so frequent that quality of air became a significant concern of health. The vast production and usage of automobiles were the reason of photochemical smog as they consume petroleum and gasoline products, there had been exothermic reactions and their engines generated noxious byproducts (Twigg, 2007).

Generally, air pollution contaminants are arranged into primary and secondary pollutants. Primary pollutants are the ones which radiated straightforwardly into environment and secondary contaminations are those pollutants which are formed by combination of primary pollutants itself or by combining primary pollutants with different gaseous types of the air (Hickey et al., 2014).

As per the study conducted by WHO, 2018 found out that open air contamination is assessed to cause 4.2 million yearly deaths around the world. A portion of the air pollutants, for example, dark carbon, tropospheric ozone, and methane additionally have global warming potential. Due to aerosols concentrates, the radiation absorbed by the atmosphere is increased causing warming of the environment . Air pollutants cause severe health effects on a long- or short-term basis as some of them remain persistent in the environment and is inhaled regularly by humans that can be deposited in the lungs (Behera & Balasubramanian, 2016).

1.1.1 Automobile exhaust gases

An advance in industrial technology especially in the technology of internal combustion engine has its negative influences on the environment. Such effects include air pollution from exhausts from locomotive, stationary equipment and automobile.

Significant source of urban air pollutants has been figured out to be road transport. All the more explicitly, it is internal combustion engine (ICE) in different types of transport which contributed enormously to expanded issues of urban pollution (Sekmen & Topgu, 2009).

Major pollutants in exhaust stream from gasoline based automobiles are carbon monoxide, hydrocarbons (HC) and NOx (Twigg, 2007). Oxidation byproducts of gasoline in the engine are H_2O and CO_2 (equation 1) is not totally efficient, and because of this, the exhaust gas stream has huge concentrations of unexhausted hydrocarbons and partly burned byproducts as carboxylic acids, ketones and aldehydes, that are stated as hydrocarbon, along-with huge concentrations of CO. (equation 2)

$$\text{Gasoline (hydrocarbons)} + O_2 \rightarrow H_2O + CO_2 \quad \text{eq. (1)}$$

$$\text{Gasoline (hydrocarbons)} + O_2 \rightarrow H_2O + CO \quad \text{eq. (2)}$$

Further to this, high temperature attained in combustion chamber during the engine operation assists reaction among key composites of air, O_2 and N_2, to form NO (equation 3) .

$$N_2 + O_2 \rightarrow 2NO \quad \text{eq. (3)}$$

Nitric oxide is partly changed to NO_2 by O_2 in tailpipe of engine (equation 4), and because of this equilibrium, the assortment of NO + NO_2 is typically denoted as NOx.

$$NO + 1/2O_2 \leftrightarrow NO_2 \quad \text{eq. (4)}$$

Consequently, real endeavors are being made for the abatement of noxious discharges from mobile transport (Santos & Costa, 2008a). These efforts have been mainly attentive on incorporating vehicle innovation changes, blending natural reserves in fuel and refining fuel, advancement of urban movement administration and the most significant is the usage of more tightly discharge and stringent control measures.

1.2 Introduction to catalytic converter

The substantial actions to save the surroundings and public health from noxious compounds released from exhaust of automobiles have motivated the researchers and scientists to achieve and claim the increasingly stringent emission standards for the pollutants emitted from the exhaust streams.

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 via it and converted into relatively harmless gases. A two-way catalytic converter (oxidation catalyst) has one sort of the chemical system i.e. catalytic oxidation. In this level, HC’s and CO burn with enough quantity of oxygen. This technique consequences in oxidation of CO and HC to form CO_2 and H_2O. Latterly, this oxidation catalyst is replaced with the aid of three-way catalytic converter which has each oxidation and reduction of NOx (Tyagi & Ranjan, 2015). Commonly, a catalytic converter comprises of metal/stainless steel covered chamber, monolithic substrate (tubular walls) or wire mesh, normally alumina or titanium are used as wash coat on which we disperse catalyst having different ratios. Lambda-sensors regulate air to fuel ratio of engine and catalyst efficiency in order to get the best feasible transformation of the pollutants.

1.2.1 Three-way catalytic converter (TWC)

Emission stream of gasoline-based engines is treated with “Three way catalysts” (TWC) these days. The catalyst changes the exhaust stream components like HC , CO and NO_X into compounds like H_2O, N_2 and CO_2 by chemical reactions.

In response to issues related with handling of these gases present in exhaust streams, three-way catalyst has been extensively employed to decrease exhaust gas emissions from gasoline based automobiles (Zhao et al., 2010). Facing future regulations for the exhaust regulations of spark ignition based automobile engines needs the progress of efficient three way catalysts (Bickel et al., 2017).

Within the three-way catalytic converter, there exists two processes. i.e. catalytic reduction and catalytic oxidation. In ‘catalytic reduction’ oxide of the nitrogen affords its oxygen to generate pure nitrogen. Then the unfastened oxygen combines with CO to form CO_2 emissions. In catalytic oxidation, HC and CO burn under sufficient amount of O_2. This process aids in oxidation of CO and HC to form CO_2 and H_2O.

1.2.2 Components of catalytic converter

Current TWC has a characteristic design that has body of stainless-steel cylinder which includes a monolith honeycomb substrate that is made up of metal or ceramic. Wash-coat and active catalysts are coated on the monolith substrate which acts as the inert substrate coating. Wash-coat is a coating of layer that gives higher surface area, it may be a promotor or oxygen storage component like ceria in our case. For the preparation the monolith a layer of wash-coat initially is deposited on substrate before catalyst is being applied on the wash-coat. The coating can also be performed by dipping the monolith into a slurry containing wash-coat components and the metal oxide which is cobalt oxide Co_3O_4 in our scope of study. The surplus of the coated material (wash-coat) is removed using by applying a vacuum or by high-pressure air. Then the metallic monolithic substrate is calcined for attaining the desired and finished catalyst.

1.2.3 Monolithic reactor vs wire gauzes reactor

Geometrical features and characteristics of monolithic substrate plays a major part in achieving the distribution and diffusion of temperature, exhaust gas flow movement throughout the device and it ultimately reflects the efficiency of TWC. It should fulfil the need of providing low back pressure and permitting the exhaust gaseous stream to pass with high volumetric flow rates (Jodłowski et al., 2013).

In this work, keeping in view of above-mentioned benefits of wire mesh metal substrate having cell density of 100/ inch^2 was utilized to deposit a catalyst on substrate. The metal substrate coating is the method by which catalyst is deposited onto the substrate. In this way, it's critical to know the methods of coating. The geometric area of meshed wire network substrate is more than the substrate ceramic which will give the oxidation and reduction of exhaust gas pollutants likewise this will be useful to enhance converter execution and getting higher selectivity.

1.3 Requirements for application of TWC's

Application of TWC requires the following three factors/conditions:

- Electronic fuel injection (EFI) to provide a stoichiometric air/fuel (A/F) combination;
- Microprocessor manipulates a feedback loop. i.e. when the usage of oxygen sensors alerts determining the quantity of a gasoline to inject in a certain quantity to keep the fuel closer to the stoichiometric value.
- Sensor of oxygen within the exhaust

1.4 Oxygen storage capacity (OSC) in TWC's

Oxygen storage capacity (OSC) is a parameter that closely correlates to catalytic performance of TWCs. As the engines works under transient rich–lean Air/Fuel (A/F) conditions, release/storage of oxygen from oxygen storage components/materials can facilitate both oxidation and reduction reactions. The quantity of this property is called oxygen storage capacity (OSC).

Oxygen storage components are used to extend the conversion efficiency of noble metal catalysts for NOx, CO and unburned HC under cyclic operating conditions.

OSC material promotes CO oxidation and at the same time it accomplishes NO reduction. OSC material improve these reactions due to the fact that oxygen from the OSC material promotes oxidation reactions by offering oxygen, while NO reduction is possible due to adsorption of NO at reduced sites (Kolli et al., 2004).

1.4.1 Role of CeO_2 in three-way catalytic convertors

Ceria i.e. CeO_2, is the most renowned and widely used promotor with a well-known redox and catalytic properties. The prime basis of employing ceria is its attribute to possess oxygen storage capacity i.e. OSC. Ceria plays a significant role in refining the thermal stability of composite catalysts, enhancing the active metal dispersion and due to its ability to provide enough oxygen vacancies, it has been widely utilized in automotive three-way catalytic convertors (Hou et al., 2008). Doping and usage of ceria empowers the TWC to achieve high conversion efficiencies of noxious gases in automobiles exhaust under rapid and transient oxidation/reduction processes being confronted by TWC. The CeO_2 has been extensively added in modern TWC's and massive research and development has been made in this regard.

1.5 Background of study

Regarding the plan of thesis, major considerations have been carried out and it had been reviewed and outlined. In the manufacturing of catalytic convertor multiple factors need to be considered like selection of base metal and its precursor, selection of substrate, wire mesh module, cell density, length of threaded bar, number of wire meshes in threaded bar and its pretreatment, wash-coat material, engine selection i.e. whether 70 cc or 125 cc motorbike engine.

Then the selection of doping material i.e. the promoter. Due to vast advantages of ceria CeO_2 as an oxygen storage component (OSC) and still being used in conventional and modern TWC's we selected ceria as our promotor to be doped in cobalt oxide Co_3O_4 and titanium dioxide TiO_2 composite catalyst.

1.6 Objectives

The purpose of subjected research was aimed at examining the impact of ceria as a promotor in cobalt oxides Co_3O_4 i.e. tricobalt tetroxide and TiO_2 as a support for the catalytic reduction of three major noxious automobile exhaust pollutants, i.e. unburned HC, CO and NOx. These pollutants were considered due to their presence in exhaust gas streams from the automobiles and causing multiple environmental issues.

1. Comparison of synthesis routes of ceria doped Co_3O_4/TiO_2 based catalyst for three-way catalytic activity
2. Evaluate the effects of loading of ceria in terms of characterization and its TWC conversion efficiency

Chapter 2

LITERATURE REVIEW

2.1 Background

Diesel and gasoline automobiles are the key sources of harmful air contaminants in most of the cities worldwide. These are mainly the most significant reasons of exposure of public to these air pollutants . In Latin America, Africa and Asia 2-stroke motorbikes and three-wheel automobiles are two significant sources of respirable particulate matter (Twigg, 2007).

Gasoline based automobiles and their fuel injection setup is the key source of unburned hydrocarbons, carbon monoxide, lead, aerosol, VOC as well as NOx emissions. The emission streams include huge concentration of HC and CO with some amount of partly burned by-products such as carboxylic acids, aldehydes and ketones (Twigg, 2006). So, summarizing the above discussion, gasoline contribute significantly to toxic emissions to our ambient environment.

2.2 Causes of CO, unburned HC and NOx from automobile exhaust

Under several driving styles diverse amounts of pollutants are generated, but there are some typical conditions at some particular gaseous pollutants are emitted from gasoline exhaust. The three pollutants of consideration released from automobiles exhaust are NOx, CO and HC (Twigg, 2006).

In acceleration of engine, the amount of HC and CO enhances at once because of quite rich condition . As the speed of engine increases, combustion speed rises too, that results in increase of combustion temperature and production of NOx. When the engine deaccerlates, HC and CO rise because of erratic combustion and over rich mixture. The generation of NOx is lower at this stage. Typically, in idling and warm up conditions of engine as the blend is rich , automobile engines exhaust release higher amounts of HC and CO whereas the amount of NOx declines to least because of decrease in temperature of combustion. At lower speed condition A/F is slightly lean as compared to stoichiometric ratio so were generating lesser hydrocarbon and CO emissions but the content of NOx generation is higher. At increased accerlation mixture is richer, and the amount of HC and CO is elevated in exhaust gas streams. Two stroke gasoline engines in motorcycles and three wheel automobile emit higher gaseous pollutants as compared to four stroke automobile engines.

2.2.1 CO emissions

The biggest discharge from a motor is carbon monoxide (CO). The most significant engine parameter that impacts CO emission is air-fuel equivalence ratio. Because of fragmented and incomplete burning, carbon monoxide is released from exhaust chamber of a motor. Maximum CO is released when engine runs richer than stoichiometric level and fuel components do not find enough oxygen to react. This condition prevails when the engine transients such as start-up and rapid acceleration under load.

CO is a scentless, toxic gas that is colorless, and it is noteworthy result of the uneven burning of carbon and carbon-containing constituents. CO being discharged from engine exhaust, contributes an exceptionally huge measure of CO outflows in urban areas, especially in territories with heavy traffic blockage. Carbon monoxide is hazardous to people as breathing in even generally little measures of it can prompt, neurological harm, hypoxic damage and in extreme scenario it can be fatal for human health. When it enters the body, it joins with hemoglobin to shape carboxy hemoglobin. The ability of blood to carry oxygen that is essential for survival of human life is greatly reduced in such scenario. Carbon monoxide may damage nervous system and may provoke heart diseases if any human life is exposed for longer duration of time (Yavuz et al., 2013). Despite of its major impacts, it has not been categorized as a natural issue, but modern researches reveal that this gas is a major issue for nature and environmental sustainability.

2.2.2 HC emissions

The emissions of HC by gasoline engine become significantly increased in fuel rich mixture condition. Main causes of HC emissions from S.I engines are operation of engine at non-stoichiometric air-fuel ratio, incomplete combustion, and crevice volume, leakage past the exhaust valve, valve overlap, and deposits on combustion chamber walls and oil on combustion chamber walls. HC emissions also occurs when the air-fuel ratio is too lean, as the poorer combustion occurs, the extreme is total misfire at leaner air-fuel ratios. One misfire out of 1000 cycles gives exhaust emissions of 1gm/kg of fuel used. Hydrocarbon emissions from a single two-stroke motorbike can exceed those from three uncontrolled passenger cars and particulate matter emissions can exceed those from heavy-duty diesel truck (Mansha et al., 2012).

2.2.3 NOx emissions

Oxides of nitrogen (NOx) are the results of excessive temperature in combustion chamber because of high pressure and temperature, oxygen reacts with atmospheric nitrogen and thus releasing various types of NOx (Ban-Weiss et al., 2008). NO_x also assists in formation of acid rain and ground level ozone. The main element of smog is ozone therefore, NOx is dangerous to environment and poisonous to plant lifestyles. Some notable diseases from the NOx are lungs and respiration infections.

In S.I engines, maximum burned gas temperatures occur at equivalence ratio of 1.1, but at this equivalence ratio oxygen concentration is low however at slightly lean mixture condition i.e. at equivalence ratio of 0.9; NO emission level is at its peak.

Greater amount of NOx is released at low and minimum speeds conditions as the air-fuel ratio is bit leaner than theoretical air-fuel ratio. During acceleration due to very rich mixture condition and as the engine speed rises, the speed of combustion also increases, causing combustion temperature and NOx to rise. During deceleration lower amount of NOx is produced due to erratic combustion (Mansha et al., 2012).

2.3 Role of catalytic oxidation in controlling automobile exhaust gas emissions

In the early days of automobile industry advancement, gasoline oxidation in the engine to CO_2 and H_2O was far from completely efficient. Catalytic oxidation has long been employed to combat the problem of exhaust gas pollutants from being released into the environment (Twigg, 2006).

Catalytic oxidation was primarily linked with the early development of catalysis and it later became a part of many industrial processes, so it was not surprising to be used for removal of hydrocarbons and CO when it became necessary to control these emissions from cars. Levels of tailpipe pollutants from American cars in the mid-1960s were typically HC 15g/mile; CO 90 g/mile; and NOx 6g/mile. Engine modifications could not alone meet the demands of the 1970 Clean Air Act , so as a result, catalytic systems were introduced to control exhaust emissions (Twigg, 2006).

When it became obvious that catalytic oxidation could restrict some exhaust gas emissions from being released by automobiles, Pt-based catalysts were then utilized extensively in chemical plants and laboratories. It was then thought that their efficiency should be tested as catalysts for automobile exhaust gas pollutants.

The first cars with oxidation catalysts injected air into the rich exhaust gas to provide O_2 for oxidation of HC's and CO. A variety of base metal catalysts were also tested, but only those containing Pt and two of its allied metals, Rh and Pd, were effective in real-world applications (Twigg, 2006)

2.4 Noble metal based catalysts

Normally, the catalysts employed for this manner are noble metal based. However, the rarity and expensive nature of noble metals presents serious obstacle to the implementation of easy strength technologies on a worldwide scale (Vinodkumar et al., 2014).

Though, these noble metals were used for quite long period of time but due to mechanical as well as thermal pressures, these noble metals were detected to be released from catalytic convertors and remained present in ambient environment. These noble were observed to be present as air borne particulate matter, rivers, plants, soils etc. The excessive use of these noble metals caused its rise in concentration in environment which resulted in causing multiple health risks like allergic and mutagenic effects as well as associated with causing cancer (Ahmad et al., 2017). Subsequently, lowering the concentration of these noble metals or may be entire replacement of non-noble metals has extensively encouraged the researchers (Vinodkumar et al., 2014).

Commonly as a catalysts in auto catalysts, a combination of two metals Pt/Pd were utilized. For control of NOx from exhaust stream during rich conditions a mixture of Pt/Rh was also employed. Now a days, three-way catalysts generally comprises of Pd/Rh. Sometimes nowadays Pt/Rh catalysts are still employed as a catalyst on some cars but using all these three noble metals i.e. Pt/Rh/Pd have been largely reduced.

Carbon monoxide, unburned hydrocarbons as well NOx emissions were catalytically converted at the same time by using a catalyst comprising of two metals Pt/Rh in a three-way catalyst (TWC). Later Pt-based oxidation catalyst was used to reduce NOx by a catalyst constituting Pt/Rh in which air was injected after oxidation by Pt-based oxidation catalyst (Twigg, 2006).

2.5 Non-noble metal catalysts

Automotive industry is now the biggest consumer of platinum group metals (PGMs), due to which their cost raised. Therefore, since the beginning of 21^{st} century, non-noble metals fascinated the attentions of researchers as low-cost catalysts and feasible alternative for purification of exhaust gases. Almost 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 and Al etc. Base metals oxides were investigated individually or in combination for either oxidation of carbon monoxide or unburned hydrocarbons and nitrogen oxides reduction. 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 to check conversion efficiency of more than one pollutant in gas stream. So here we will report three-way catalytic conversion efficiency of all three major exhaust gas pollutants by non-noble metals i.e. Co_3O_4/TiO_2 composite.

2.5.1 CO Oxidation over non-noble metal based catalytic convertor

Due to the known negative and damaging impacts presented by CO, a major consideration has been centered on catalytic control of carbon monoxide (Vinodkumar et al., 2014).

Epling et al. (2003) and his co-workers investigated reaction and characterization studies of titania-supported Co/Pt, Pt and Co catalysts and revealed that among the tested catalysts Co/TiO_2 catalyst was most efficient regarding catalytic oxidation of carbon monoxide at elevated temperature (>100 ◦C) (Epling et al., 2003).

2.5.2 HC oxidation over non-noble metal based catalytic convertor

Several researchers examined cobalt oxide for oxidation of specific hydrocarbons ranging from methane to hexane and described excellent activity of nanocrystalline Co_3O_4 with formidable selectivity of end products to CO_2 and H_2O (Solsona et al., 2008) (Lojewska et al., 2008).

Cheng et al., (2010) investigated the HC emissions from spark-ignition engine process from fuel flow into the engine cylinder to burned gas flow into the exhaust system. He and his fellow workers described the oxidation of these unburned HC’s and discussed the reasons that how composites of gasoline are avoided during combustion at normal modes.

Complete conversion with high steadiness of different hydrocarbons was attained at about 200˚C by Co_3O_4 in its nanocrystalline form , which is lower light off temperature as compared to noble metals. The major disadvantage concerned with the usage of Co_3O_4 is its thermal stability. At temperatures of about 700˚C, Co_3O_4 changes into CoO which gives less catalytic activity than Co_3O_4 (Ahmad et al., 2017).

Ngamou & Bahlawane (2010) stated catalytic conversion of alcohols, aromatics and carbon monoxide into CO_2 by Co_3O_4 catalyst in its spinel shape placed over stainless steel mesh. Similarly, Tian et al. (2012 & 2013) inspected deep oxidation of propene and acetylene by Co_3O_4 catalyst with a spinel shape deposited over stainless steel mesh and testified that CO_2 was the only end product in the whole oxidation procedure. Moreover, the author also described insignificant role of stainless steel meshes in catalytic action (Tian et al., 2012) (Tian et al., 2013).

After having the catalyst decent enough to oxidize hydrocarbons with appreciable conversion efficiency and selectivity , additional problem with HC oxidizing broadly discussed in literature is of reactor's type. Catalytic oxidation of HC’s is done by process of diffusion which depicts that conversion is governed by the mass transfer between catalyst and flowing gas mixture (Ahmad et al., 2017)

2.5.3 NOx reduction over non-noble metal based catalytic convertor

Indeed, recent research emphasize the development of efficient after-treatment systems not only for the removal of NOx at low temperature but also for lean-burn applications, since noble metals exhibit a poor selectivity in the presence of an excess of oxygen (Granger & Parvulescu, 2011).

The low efficiency of TWC during the cold start engine also represents an important issue. Additional parameters have to be considered to model automotive post-treatment systems under realistic conditions.

2.6 Support elements in heterogeneous catalysis

Suitable metals are used as support in catalysis, few of them have been mentioned below.

2.6.1 Titanium Oxide (TiO$_2$) as support in heterogenous catalysis

Li, et al., (2014) examined various arrangements of TiO$_2$ structure as a support material for Co$_3$O$_4$ nano particles. He and his co-workers examined low temperature CO oxidation and reported that among various TiO$_2$ crystalline configurations, the highest activity was exhibited by anatase form with high stability and selectivity towards CO$_2$ (Li et al., 2014).

Yang et al., (2007) inspected the CO oxidation by TiO$_2$ supported Co$_3$O$_4$ and revealed the impact of calcination temperature. The catalysts were synthesized by incipient wetness impregnation (IWI) technique. The catalysts were calcined at 450˚C having 5 wt.% CoOx/TiO$_2$. The catalyst proved to be extremely efficient for oxidation of carbon monoxide (CO) at a temperature of 100˚C as compared to catalysts calcined at below and above temperatures of 450˚C.

In a similar study carried out by (Kalam & Hassan, 2011) they investigated the performance CoOx/TiO$_2$ catalysts synthesized via wet impregnation technique over an engine that was powered by natural gas and revealed higher activity of mentioned catalyst in conversion of CO, HC and NOx.

2.6.2 Co$_3$O$_4$ as oxidation catalyst in TWC

The transition metals in the periodic table and its oxides drew attention with an imperative class of materials with various structures and beneficial applications. These materials display many exciting physical, electronic, optical and synthetic properties. Oxides of these metals possess strong thermodynamic qualities, which can be interconverted by fluctuating the oxidation and reducing conditions.

Among these metal oxides, nanostructured tricobalt tetra oxide (Co$_3$O$_4$) has been drawing in much attractiveness in heterogeneous catalysis. Bulk cobalt oxide has been compared with other transition metals for special CO oxidation within the presence of hydrogen and has demonstrated the most elevated action. Both Co$_3$O$_4$ and CoO are stable oxides in cobalt oxide system and the depiction of high catalytic activity is credited to comparatively low ΔH of vaporization of O$_2$. (Tang et al., 2008)

Reduction of CO at low temperature have been widely discussed in recent four decades. The Co_3O_4 has shown amazing execution in the reactant oxidation of CO and hydrocarbons even under the extreme low-temperature conditions. It has been thoroughly investigated in different researches focusing on low temperature oxidation for CO and HC.

Lou et al., (2014) investigated carbon monoxide oxidation at low-temperature by Co_3O_4 and proclaimed that temperature at which 50% conversion is achieved/acquired can be as low as −54˚C.

Xie et al., (2009) that the Co_3O_4 nanorods can achieve catalytic oxidation of CO at a temperature even at −77˚C and CO transformation to CO_2 by 100% within the six hours can be achieved. Hence, as valuable and convenient competitor of noble metal-based catalysts, cobalt oxide catalysts have pulled in extensive considerations in view of not just its high activity for CO oxidation at low temperature but also for various applications like hydrocarbon oxidation.

The carbon monoxide oxidation over alone and composite cobalt oxide catalysts was attempted frequently to succeed noble metals in previous researches. Even though cobalt oxide (Co_3O_4) has shown excellent performance in oxidation of CO and HC, but its sensitivity to water vapor in any feed gas, decreases its catalytic performance to a major extent, thus limits its applicability to gas streams where there is certain percentage of water vapor (Hou et al., 2008). This has been a point of concern for the researchers. To overcome this drawback/limitation of Co_3O_4 and eying to further improve the performance literature recommends the technique of doping and utilizing the benefits of promoter. This technique has particularly been used when we intend to further increase the benefits of any main base metal by addition of certain other component.

With the intention to attain high catalytic performance by TWCs has been enhanced by the doping of various categories of promoters which may include rare earth or alkaline earths., including alkaline earth metals (Ba Ca, Mg), rare earths metals and transition metals. The doping of certain promoters encouraged the redox characteristics and attained the lesser light-off temperature especially at the cold start stage (Li et al., 2012).

2.7 Oxygen storage component (OSC)

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 components (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. Currently metallic monolith with higher surface area and less reactor volume are being used (Heck & Farrauto, 2001) (Twigg, 2011).

Hou et al. (2008) carried out the study regarding the CeO_2 doping impact on structure as well as on the catalytic performance of Co_3O_4. As similar to our case as far as synthesis procedure is concerned, impregnation method was adopted for synthesizing Co_3O_4/Ce_2O_3 composite catalyst and results show much improved resistance to poisoning by water vapor than the alone Co_3O_4. The characterization results of prepared catalyst reveal that it is mainly due to higher dispersion degree of CeO_2, larger S_{BET} thus resulting in smaller particles, and there exists a strong interaction between Co_3O_4 and doped CeO_2. Similarly, work carried out by Kang et al. (2003) also revealed excellent water resistance of Co_3O_4 and CeO_2 catalysts that were synthesized by technique of precipitation method. Wang et al. (2012) and his fellow scientists also evaluated the textural and structural properties of cobalt/ceria composite. They revealed that cobalt addition in ceria impacts the oxygen storage and release property of ceria and results in amplified catalytic efficiency of cobalt oxide.

Strictly speaking the definition of the OSC, i.e. capability to store and release oxygen, ignores a fundamental aspect of the OSC that is the nature of the oxidizing and reducing agents that may interact with the CeO_2 . There exists a redox behaviour of the CeO_2 containing promoters under the exhaust conditions, due to the presence of continuously changing reaction conditions and presence of a variety of oxidants/ reductants, e.g., H_2O, CO_2, CO, HC, H_2, that easily react within the pure redox process (Monte & Kašpar, 2004).

2.7.1 CeO_2 as an oxygen storage component (OSC) in TWC

By keeping in view different researches carried out it is anticipated that it will be a useful method to increase the three-way catalytic performance of Co_3O_4/TiO_2 based catalyst by tuning the amount of surface oxygen vacancy through the doping of ceria .

Ceria has well known redox and catalytic properties, and due to its ability to provide enough oxygen vacancies it has been widely utilized in automotive three-way catalytic convertors. Doping and usage of ceria empowers the TWC to achieve high conversion efficiencies of noxious gases in automobiles exhaust under rapid and transient oxidation/reduction processes being confronted by TWC.

CeO_2 and cerium oxide containing materials were closely examined as catalysts for heterogeneous catalytic reactions due to their electronic and structural and properties. Unquestionably there exists the presence of CeO_2, as a main constituent in three-way catalysts (TWC) for the catalytic conversion of exhaust gases being released from automobiles. Extensive research effort has been made in this regard by researchers and automobile concerned industrialists owing to the fact that it is technologically and economically feasible and its most important application is its usage in three-way catalysts (Trovarelli, 1996).

The CeO_2 and the CeO_2 composite materials in three-way catalytic convertor present the buffering capacity during the substantial fluctuations in A/F ratio. Due to the fact that it provides oxygen storage and release purpose and ensures that acceptable or enhanced catalytic performance by TWC (Zhao et al., 2010).

Cerium oxide (CeO_2) is extensively used in many areas of heterogeneous catalysis due to its capacity to oscillate between Ce^{+3} and Ce^{+4} oxidation states (Li et., 2010). It possesses a crystal structure of fluorite-type. In such type of configuration each Ce cation is enclosed by eight oxygen atoms. The coordination number of oxygen atoms is four. The release of atomic O_2 results in achieving high removal efficiency of pollutants especially CO.

Monte & Kašpar (2004) stated that general definition of OSC represents a quite restrictive view of this functionality of the TWCs . He and his co-workers described that consistently the efficiency of the TWCs in the real exhaust is related to the oxygen concentration, that in turn is regulated by a complex network of reactions. The capability of CeO_2 and its composite materials to offer oxygen at the sites where catalytic oxidation is sought is improved explanation of this OSC property. Annihilation of oxygen positions, spillover assets and various metal support interactions combine to promote the activity of the supported metal.

2.8 CO, HC oxidation and NOx reduction over ceria and ceria composites

2.8.1 CO oxidation over ceria/ceria composites

The catalytic oxidation of CO at low temperature has turned into an essential research subject throughout the years because of its numerous fields of applications.

The ability of ceria to decrease the concentration of carbon monoxide in feed gas is well documented. Initially ,the adsorption of carbon monoxide on ceria surface takes place and then it follows the decrease of surface oxygens of CeO_2, as oxygen vacancies are created (Trovarelli, 1996).

Hou et al. (2008) studied the consequence of doping of CeO_2 on catalytic activity of Co_3O_4 catalyst for the purpose of oxidation of carbon monoxide at low temperature. To synthesize Co_3O_4 catalyst, precipitation technique was utilized and the doped composite catalyst CeO_2/Co_3O_4 catalyst was synthesized by an impregnation technique. The catalytic activity results reveal that CeO_2/Co_3O_4 catalyst displays considerable improved resistance against water molecules poisoning than the alone Co_3O_4 catalyst within a continuous flowing microreactor. The Co_3O_4/CeO_2 composite catalyst can keep complete conversion of carbon monoxide for 8,400 minutes at 110˚C having 0.6% feed gas water vapor concentration. Contrary to that alone Co_3O_4 catalyst can sustain for only 100 minutes with the achievement of 100% efficiency.

The higher catalytic performance of ceria doped catalyst and other valuable features that were observed are credited to much improved degree of Co_3O_4 dispersion in Co_3O_4/CeO_2 composite catalyst, larger S_{BET} and hence smaller particles that were synthesized in ceria composite catalyst. The synergistic interaction was observed between Co_3O_4 and CeO_2. Due to these reasons CO oxidation at low temperature was achieved and composite catalysts exhibited excellent water resistance (Hou et al., 2008).

In a similar sort of study, carried out by Tang et al. (2008), the researchers synthesized series of ceria doped catalyst. The doping of ceria (CeO_2) was done in cobaltic oxide. The catalysts with multiple different loadings of ceria were synthesized by employing the impregnation method. The CO oxidation results revealed the appreciable increase of surface area of cobaltic oxide and the surface area was around 109 m^2/g. The activation energy required for oxidation of carbon monoxide was decreased due to the collective impact of ceria and cobaltic oxide. The catalysts having 20% cerium content displayed highest surface area and hence revealed the highest catalytic performance for CO oxidation with T_{50} being achieved at 88°C.

Río et al. (2016) and his co-workers improved the 1.5 wt% Au/TiO_2 by doping 5.4 wt% CeO_2 depositing on its surface. The catalysts synthesis and desired loading was achieved by IWI technique and catalysts were calcined at 673 K. The doping of ceria onto the surface of Au/TiO_2 WGC catalyst although without modification in the original particle size distribution, exhibited higher catalytic activity than the base 1.5 wt% Au/TiO_2 catalyst in the CO oxidation reaction. Doped catalysts displayed great enhancement of the stability against deactivation of gold nanoparticles and improved catalytic performance at high temperature that can be credited to the interaction between ceria and gold particles.

2.8.2 HC oxidation over ceria/ceria composites

The reaction and adsorption of hydrocarbons with multiple metal oxides have been under much consideration since majority of the catalytic reactions involve hydrocarbons. In automotive emissions control, control of HC is of significant importance. From the early days of catalytic control of unburned HC's, its adsorption and response with ceria and CeO_2 containing materials are examined. (Li et al., 1993) investigated the response of CeO_2 during its reaction with HC's and gave a detailed description regarding the impact of thermal treatment on the response and adsorption by CeO_2 against HC's. They have inspected the impact of heat treatment on the adsorption and response of light hydrocarbons with CeO_2 (Trovarelli, 1996).

2.8.3 NOx reduction over ceria/ceria composites

Nitrogen oxides (NOx), released through mobile and stationary sources have been stated to be a reason of many environmental issues like green-house effect, ozone layer destruction photochemical smog and acid rain. Many techniques for NOx abatement have been utilized like selective NOx recirculation, NOx storage and reduction and SCR (selective catalytic reduction).

In lean combustible engine, NOx is commonly made up of NO. So, the oxidation of NO into NO_2 can be a significant process for controlling NOx. Up-till now many catalytic setups are used for oxidation of NO. Those can be classified into the transition metal oxides and noble metal catalysts (Kim et al., 2010).

In catalyst of noble metals, supported platinum-based catalysts are significantly utilized. Oxidation activity of NO is stated to enhance with increasing the platinum's particle size. Based on higher through put conditions, (Schmitz et al., 2006) stated the relative order of significance of factors that played role in achieving the conversion efficiency. It was in following order support > pre-treatment> loading> calcinations atmosphere > calcinations temperature > precursor salt.

The system of catalysts based on oxides of transition metal is needed for platinum-based catalysts as platinum group metals are stated to be deactivated by few reasons. Up till now cobalt based systems are commonly stated to have very good activity for oxidation of NO.

Some comparison among supported cobalt oxides have been done systematically. Yung et al., 2007 did comparison of oxidation of NO in TiO_2/Co and ZrO_2/Co and stated that 10% Co/ZrO_2 synthesized by IWI i.e. incipient wetness impregnation method was most efficient.

Kim et al., 2010 investigated the NO oxidation carried over Co_3O_4 supported on different supports like, TiO_2, CeO_2, SiO_2 and ZrO_2. Cobalt oxides supported on ceria with a high surface area depicted the highest catalytic performance for NO oxidation. This catalyst showed superior catalytic activity as compared to unsupported Co_3O_4. Unsupported Co_3O_4 and 1wt% Pt/γ-Al_2O_3 were also experimented under the identical reaction condition. The greatest catalytic performance was exhibited by Co_3O_4/CeO_2(H), which had equivalent catalytic performance with a renowned noble metal catalyst, Pt/γ-Al_2O_3. For ceria supported Co_3O_4, the catalytic activity, the NO uptake at 298 K and the dispersion of Co_3O_4 increased with increasing the surface area of CeO_2.

2.9 Comparison of efficiency of ceramic and metallic substrate

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

2.10 Gas hourly space velocity (GHSV)

The space velocity is stated as the ratio of exhaust gas volume per hour to applied volume of catalyst (Yu, et al., 2009). By the knowledge from GHSV, we know that for the treatment of an equal exhaust volume with less active catalyst about twice as much catalyst is requisite/necessary with consequential increase in catalyst weight requirements and space.

Space Velocity = Exhaust Gas (Nm^3/H) **/** Catalyst Volume(m^3)

$$\text{Space Velocity} = \frac{Exhaust\ Gas\ (\frac{\text{Nm3}}{\text{H}})}{Catalyst\ Volume(m3)}$$

Among many other aspects of conversion efficiency of any catalyst, GHSV plays a pivotal role as there are specific active sites available at the interface of catalyst for the conversion of noxious gas to innocuous gas in the continuously passing exhaust gas stream. The conversion efficiency of any catalyst seems more authentic and reliable specifically if we mention the GHSV for that catalyst being used. Commonly in literature an optimum GHSV is revealed and its allied conditions that favor and induce the maximum catalytic activity.

In achieving the highest combustion efficiency, apart from many other factors like composition and concentration of exhaust gases, temperature of exhaust gases, capacity of catalyst material to oxidize/reduce the exhaust gas , gas hourly space velocity (GHSV) is of substantial significance. GHSV establish maximum and minimum limitations for the highest conversion efficiency that can be extracted from any catalyst material.

2.11 Selection of catalyst synthesis methods

Catalysts applied in many industrial processes can be sectioned into two broad categories.

- Unsupported catalysts
- Supported Catalyst

The synergistic properties of heterogeneous catalysts are clearly influenced by each step of the synthesis procedure adopted together with the nature of the precursor materials. The decision of a lab preparation/synthesis for setting up a given catalyst relies upon the chemical and physical properties, sought to have in the synthesized catalyst. It is well understood that the variety of ways of preparation methods and their arrangement can be considered, even for given or selected precursor (Perego & Villa, 1997).

The catalysts with advanced metal oxide can be regularly customized to control the catalyst activity. The reactant execution of catalyst emphatically relies upon the planning strategies including the decision of synthesizing and depositing active component, catalyst activity advancement by certain dopants, and oxidative and reductive mechanisms. In addition to that, the depositing active phase onto the support, altering the support material, and morphology of the surface can be changed by calcination and drying processes. In the past decade, multiple preparation methods were adopted to synthesize the catalysts such as Sol-gel method, hydrothermal method, emulsion technique, chemical vapor deposition (CVD) technique and flame spray method (Lee & Yoo, 2014).

Beside the above-mentioned synthesis procedures numerous other methods have also been reported for the preparation of catalyst i.e. impregnation method, solution combustion, urea gelation, precipitation deposition leaching and chelating, adsorption method and ion exchange etc.

There has been a lot of recent progress in the two synthesis techniques employed in industry as well by researchers. These two techniques are incipient wetness impregnation and precipitation method. Keeping in mind we have chosen these two methods and ceria doping have also been done via these two methods. In our study, we have compared the precipitation method and incipient wetness impregnation i.e. IWI.

Current progresses of the synthesis techniques being employed by industry concerned to our study i.e. precipitation and impregnation, are highlighted. In both of these methods, a metal precursor, mostly an inorganic salt, is the preliminary point to deposit the active metal onto the support. In the precipitation method, supersaturation of the precursor solution is done for inducing metal particle growth, that results in growth and nucleation of metal particles. This can happen in aggregation with the development of the support (coprecipitation) or on an existing support (deposition precipitation) (Munnik et al., 2015).

With impregnation techniques, the support is contacted with a precursor solution. Low loadings, often for precious metals, are achieved by adsorption of the precursor molecules onto surface groups of the support (ion adsorption) or through the exchange of ions in, for example, zeolites (ion exchange), after which excess precursor is removed. When higher loadings are required, the washing step is not done, and the support is directly dried, so that all precursor ends up on the support (impregnation and drying) (Perego & Villa, 1997) (Munnik et al., 2015).

Further, two types of impregnation are examined which depend on the volume of solution. One is incipient wetness impregnation and other is 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 used is not in large amount. This volume is equal or slightly less than the pore capacity of support (Campanati, Fornasari, & Vaccari, 2003).

For both synthesis routes, the temperature was operational variable. The solubility and solution viscosity are controlled by the temperature. So, we can say that fine-tuning of any catalyst material by synthesizing the catalyst through innovative preparation techniques is of particular significance.

Lykaki et al. examined the effect of preparation parameters on solid state characteristics of CeO_2 materials. They prepared their catalysts by three separate preparation methods that were cost-effective and consumed less time. The methods were co-precipitation, thermal decomposition, and hydrothermal method of high and low sodium hydroxide NaOH concentration. $Ce(NO_3)_3.6H_2O$ as cerium precursor was employed in all cases. The ceria nanoparticles prepared by the hydrothermal technique exhibited the elevated surface area i.e. greater than >90 m^2/g, enhanced redox properties, and particles possessed a well-defined geometry of nanorods (Lykaki et al., 2017).

2.12 Disadvantages/concerns of catalytic converter

The following paragraphs will be detailing concerns regarding catalytic converters

2.12.1 Catalyst deactivation

Deactivation of catalyst is defined as the decrease of catalytic conversion efficiency over time. The five significant reasons which cause deactivation of a catalytic converter bed are:

- Fouling
- Thermal deactivation
- Poisoning
- Crushing

Poulopoulos and Philippopoulos (2004) investigated the impact of the gradual deactivation of a three-way catalytic converter exhaust emissions from an internal combustion engine. The exhaust gases were analyzed for CO, HC (i.e. total unburned organic compounds), MTBE, methane and ethylene, before and after their catalytic treatment, in a wide range of engine operating conditions. The thermal aging of the catalytic converter resulted in an increase in the required time for the start of its operation and loss of its efficiency. The catalytic efficiency was significantly decreased after each thermal aging step, especially at idle conditions. As a result, CO and especially HC emissions were increased, whereas ethylene and MTBE emissions were multiplied by a factor of 6–7 at 3.81 hp, in the case of the deactivated catalyst.

2.12.2 Ageing mechanisms

The thermal deactivation takes place because of ‘sintering’ process. Sintering is the loss of active surface area of the adsorbent, i.e. the catalyst. Sintering occurs due to agglomeration of small metal crystallites into larger ones. At high temperatures, extreme sintering leads to the transformation of the catalytic crystalline phase of the metal into a non-catalytic one. This phenomenon is called solid state transformation (Forzatti, 2002).

2.12.3 Cold start emissions

When a vehicular engine is started, the engine walls as well as the catalyst are at atmospheric temperatures. As the engine operates further, hot gases heat up and exhaust gases emitted from the engine start warming up catalyst gradually. The time required by a catalyst to get optimal conversion for specific pollutant is known as “Light-Off” period of that catalyst for that specific pollutant. Due to incapability of the catalyst to treat the cold start emissions (CSEs) during light-off period, the emissions that occur in this tenure are relatively elevated. About 70% of the overall

CO and unburned hydrocarbons (UHC) emissions occur during light-off period and these emissions are known as cold-start exhaust emissions.

In cold start-up of engine, in order to assist proper combustion of fuel and to increase cold engine operations, A:F mixture is intentionally placed many times richer than that in warmed-up engine operation, resulting in excessive discharge of pollutants, too called cold start emissions (Puértolas et al., 2014)

In cars a number of reasons of non-combusted hydrocarbons have been marked in cold start and warming up process of cold engines. Enriched air to fuel ratio and lower engine temperatures in cold start up, enhance generation of CO and HC whereas on the other side because of low operating temperatures at this specific time, the activity of catalytic converter to oxidize these pollutants is also extremely low. About 70-80% of total hydrocarbons emissions take place in initial some minutes of engine operation when converter is warming up (Sarshar et al., 2009).

Temperature above 150˚C is prerequisite to initiate catalytic activity at commercially available catalytic converters (Iliyas et al., 2007). At low temperatures, a catalytic converter is unable to treat emissions in exhaust stream passing through it. Here are some solutions for cold start emissions.

- Shortening the light-off Period
- Phase change material
- Electrical heating of catalyst
- Variable conductance insulation

2.12.4 Environmental impacts and high costs of catalysts

Catalytic converters are a major means in controlling the emissions of NOx, uHCs and CO, three harmful products emitted by gasoline combustion engines. Catalytic converters can reduce the emissions of CO and unburned hydrocarbons till 97% (Burch et al., 2010). However, the use of catalytic converters is not the very ultimate solution to the control of these harmful emissions. There are several limitations and disadvantages of proliferating the use of catalytic converters in automobiles.

As designated previous, the use of platinum, rhodium and palladium is done as catalysts in catalytic converters. These are precious metals and are thus expensive. In a typical TWC, the oxidation catalyst has a Pt/Pd mass ratio of 2:1 and the reduction catalyst has a Pt/Rh mass ratio of 5:1; this brings the overall Pt:Pd:Rh mass ratio of the three noble metals to 10:4:1. Because of the high cost of these noble metals, the overall price of a catalytic converter increases. Apart from noble metals, a TWC also requires the use of EFI which can regulate the A/F ratio in accordance with the signal from the λ-O_2 sensor. The cost of electronic fuel injection combined with the catalytic converter enhances the cost at whole of a conventional car by 10%, out of which the cost addition by the noble metals is of 28% (Degobert, 1995).

Furthermore, the extraction and mining of these noble metals from their ores have important effect on the ecological worth in the neighborhood of the mining area. Platinum mining, for example, has been proven to have undesirable effects on the marine bionetworks, sediment quality and water quality of the water bodies about the mining operation site (Gumede, 2012).

Chapter 3

MATERIALS AND METHOD

3.1 Materials selection/ methodology

All precursors utilized in order to carry out this study were of analytical grade. $Ce(NO_3)_2.6H_2O$ Cerium Nitrate (Sigma Aldrich) and $Co(NO_3)_2.6H_2O$ Cobalt nitrate hexahydrate (Sigma Aldrich) was used as a precursor for synthesis of CeO_2 and Co_3O_4 respectively. For binding the synthesized catalyst onto the wire mesh support/substrate, sodium silicate solution (Merck) and sodium metabisulfite (BDH) were used. De ionized water was used to wash all glassware's (Pyrex, Germany).

3.2 Experimental framework

Experimental framework has been illustrated in figure 1.

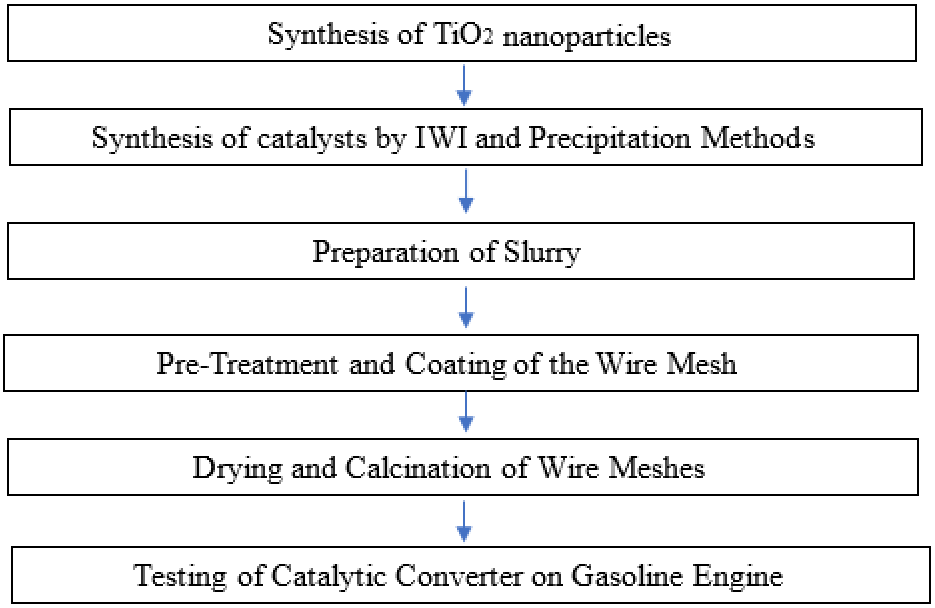

Figure 1: Experimental framework

3.3 Synthesis of titania nanoparticles

Titania nanoparticles were synthesized by means of titanium oxide TiO_2 (Sigma Aldrich) powder. Same preparation procedure of titania nano-particles was adopted as reported by (Ahmad et al., 2017). Briefly, 100 g of titanium oxide powder was added to 600 mL of distilled water in a 1 L beaker. The mixture was stirred for 10 h and then allowed to settle for 10 h. Settled material was dried in an oven at 105˚C for 12 h to remove moisture. The gained powder was then crushed using mortar and pestle and then exposed to calcination in the presence of air at 500˚C for 6 h in a muffle furnace with a heating rate of 15˚C/min.

3.4 Catalyst preparation

In our research study, the catalysts were synthesized by two techniques. The one method is incipient wetness impregnation (IWI) and other is precipitation (PPT). The brief description of how these catalysts were synthesized by these methods is given below.

3.4.1 Incipient wetness impregnation (IWI)

For the synthesizes of catalyst, stoichiometric amount of $Co(NO_3)_2.6H_2O$ was liquefied in water that is deionized and added droplet wise on TiO_2 nanoparticles with continuous stirring. The loading of cobalt oxide was 15 wt% on support of TiO_2. A stoichiometric amount of cerium nitrate hexahydrate was liquefied in water that is deionized. The solution of cerium nitrate was impregnated then onto the already impregnated cobalt oxide based TiO_2 support. A series of samples were prepared with cerium content of 03%,06% and 09%. wt%. Preparation of catalysts by IWI method has been illustrated in Fig. 2.

Figure 2: Pictorial view of synthesis of IWI (from left to right)

Summary of ceria loading and cobalt/titania ratio in IWI method has been mentioned in table 1.

Table 1:Summary of ceria loading and cobalt/titania ratio in IWI method

Catalyst	**Cerium oxide (%)**	**Cerium nitrate (g)**	**Cobalt nitrate (g)**	**TiO_2 (g)**	**Co_3O_4/TiO_2**
15% IW1	0 % CeO_2	0	19.35	10	15 wt.%
03-CE-IWI	03 % CeO_2	2.5	19.35	10	15 wt.%
06-CE-IWI	06 % CeO_2	4.10	19.35	10	15 wt.%
09-CE-IWI	09 % CeO_2	6.15	19.35	10	15 wt.%

3.4.2 Precipitation method

Out of two methods selected , the other series of catalysts were prepared by precipitation method.

1. Aqueous solutions of $Co.(NO_3)_2.6H_2O$, (Cobalt Nitrate) Titania nanoparticles (the amount of Co/TiO_2 is 15 wt.%), and Cerium oxide separately mixed. The summary of ceria loading in precipitation method is as mentioned below in table 2.

Table 2: Summary of ceria loading and cobalt/titania ratio in precipitation method

Catalyst	**Cerium oxide(%)**	**Cerium nitrate (g)**	**Cobalt nitrate (g)**	**TiO_2 (g)**	**Co_3O_4/TiO_2**
15% PPT	0 % CeO_2	0	19.35	10	15 wt.%
03-CE-PPT	03 % CeO_2	2.5	19.35	10	15 wt.%
06-CE-PPT	06 % CeO_2	4.10	19.35	10	15 wt.%
09-CE-PPT	09 % CeO_2	6.15	19.35	10	15 wt.%

2. The resulting solution heated to 80˚ C in a reflux flask equipped with a condenser.
3. Aqueous $(NH_4)_2CO_3$ (Ammonium Bicarbonate) was added drop wise to the mixed solution.

4. Continuous stirring was applied while the temperature was maintained at 80˚C until reaching pH=8±0.3
5. Then the aged precipitate (1 h) was filtered and washed with warm distilled water.
6. The precipitate was dried in an oven (120°C,10h) and subsequently calcined in a furnace at 450˚C to give the desired catalyst denoted as 15%PPT,03-CE-PPT, 06-CE-PPT and 09-CE-PPT.

3.5 Preparation of slurry

After synthesizing the catalysts by both techniques, catalysts were deposited on to wire meshes by preparing slurry which is obtained by mixing binder's solution with catalyst powder. The slurry was stirred for 12 hours and then applied to treated wire meshes.

3.6 Pre-treatment and coating of the wire mesh

The substrate that can be employed in exhaust systems of automobiles should have some favorable features like possessing high thermal stability, low cost, mechanical strength, and inertness within the operating conditions of the converter. As a substrate material austenitic type AISI 304 stainless steel wire mesh (number 10) was chosen.

Wire meshes were cut into round shape of 2.5-inch width and fitted on a 9-inch-long threaded bar, each wire mesh disconnected by a nut of 0.20 inch. In total, 26 wire meshes were placed on a single 8-inch bar which is threaded. To evaluate the catalytic activity of all samples, 8 such isolated modules (having four modules of each method) were arranged.

Pretreatment of wire meshes was considered essential to eliminate impurities that may have been present on the surface of wire mesh and also to make it coarser for enhanced catalyst adhesion. The HCL pretreatment has been considered in the past to wash and clean the metallic substrate surfaces Cutted wire meshes with matched specification were pre-treated with 15% HCL before applying slurry containing catalyst powder and binding agents. The wire meshes were immersed in HCL solution for 25 min, rinsed with distilled water and dried for two hours in an oven for appropriate drying.

Various methods exist and employed in catalysis research and development for depositing a catalyst on structured surfaces. For depositing the synthesized catalysts onto the wire mesh stainless steel substrate, dip coating method was adopted. Dip coating was performed 3 times to attain uniform coating of catalyst. 15 per cent inorganic binder solution with the synthesized catalyst was used to prepare slurry. To achieve proper homogenization of slurry and added catalysts, slurry was constantly stirred overnight for 12 hours before being applied to pre-treated wire mesh substrate. The stainless-steel wire meshes were immersed in catalyst slurry for 10 minutes and then placed onto a threaded bar of 8 inch and having each wire mesh separated by 0.20 inch nut as mentioned above. To remove any residual catalyst, the sieves were blow dried in air at a flow rate of 1 litre/minute.

3.7 Drying and calcination of wire meshes

Drying and heating procedure was same as adopted by (Ahmad et al., 2017). The calcination of wire meshes at 450˚C with a heating rate of 15˚ C and holding time of 3 hours was essential to remove unwanted compounds such as adsorbed volatile compounds, hydrated and carbonates.

3.8 Catalytic activity test

In this study, a real gasoline engine was used to investigate the catalytic activity of synthesized catalysts. The catalytic converter consists of casing, coated wire mesh module and an insulation. To check the inertness of wire meshes, initially non-coated wire meshes were installed/placed, which gave no catalytic conversion at all.

The catalytic convertor was positioned and installed on exhaust of a 70cc motorcycle (Honda CG 70). Ranges of engine rpm were nominated to gauge efficiency of catalyst at low, moderate and high engine rpm values. Motorcycle engine was run at 2000, 4000, 6000 and 8000 rpm in idle condition and concentrations of HCs and CO were measured before and after the catalytic converter by using Crypton 700 series emission analyzer. The Crypton 700 series emission gas analyzer is an integrated gas and smoke analyzer with state-of-the-art digital technology. This device was calibrated by relating its readings with a calibrated new analyzer. NOx emissions were measured by BTU 4500-N, portable flue gas analyzer (E instruments international USA).

Concentration of all three major exhaust gas pollutants i.e. CO, HCs and NOx, under consideration were analyzed at the inlet and at outlet. Gas concentrations variance at inlet and outlet of catalytic converter revealed the conversion efficiency of each individual catalyst. Considering the real engine being used for tests, it was more feasible to monitor temperatures of exhaust gas than temperatures of catalyst itself. Since both can be considered as surrogates for each other at steady state conditions.

Thermocouple of K-type was installed in the exhaust of motorcycle and used to monitor temperature of exhaust gas and attached with Arduino data logger to record readings. Temperature of exhaust gas was monitored by K-type thermocouple installed in close proximity to exhaust manifold at two different points. The one point being just at the inlet of exhaust gas into the exhaust manifold, and other thermocouple was installed at the outlet of exhaust into the ambient air. The averages of the data taken for each steady state operating condition were used. The method of installing and mounting metallic substrate in the metal housing remained same through-out the testing and only catalyst coated wire meshes were replaced to assess the relative conversion efficiency of synthesized catalysts which was the core focus of this investigative study.

3.9 Characterization

All the synthesized catalysts (ceria doped and undoped Co_3O_4/TiO_2) and of pure titania support were characterized by X-ray powder diffraction (XRD, JEOL JDX-II). X-ray powder diffraction (XRD, JEOL JDX-II) was performed with a target of Cu-Kα radiation operated at voltage of 40 kV and current of 20 mA. Samples were scanned from a 2θ value of 20˚ to 80˚ at a scanning rate of 2˚/min. The average crystalline size was calculated by using Scherrer equation.

Cobaltic oxide microstructures and ceria doped cobalt titania composite were characterized using Tescan VEGA3 Scanning electron microscope (SEM). It was employed to perceive morphology of synthesized catalyst powders. The catalyst powder sample materials were deposited onto an undercoat of a holey carbon film having a standard Cu grid as reported by (Hou et al., 2008). Quantitative as well as qualitative analysis of the samples were analyzed with microscope furnished with modern Oxford energy dispersive X-Ray detector.

Surface areas analysis i.e. (Brunauer–Emmett–Teller (BET)) of doped and undoped catalysts were calculated by N_2 adsorption. Analysis was done at -196˚C by micromeritics tristar 3000 sorptometer. Before the investigation, all the catalysts were degassed at 200˚C at vacuum conditions for three hours. BET equation was used for assessing the surface area.

Chapter 4

RESULTS AND DISCUSSION

4.1 Characterization results

4.1.1 Scanning electron microscopy (SEM)

Scanning electron microscope (SEM) is a commonly used technique which provides us the high resolution and three-D pictures of materials. Through SEM analysis we can extract the valuable information like morphology, topography and determine crystalline or amorphous nature of our materials.

The SEM results of IWI technique are depicted in Fig 3. Comparing all the images of fig.3 (a,b,c,d) reveals that there is no clear difference between the undoped 15% IWI catalyst and ceria doped catalysts i.e.03-CE-IWI,06-CE-IWI and 09-CE-IWI. Densely packed spherical shaped nanoparticles with a smooth structure were observed which illustrates uniform distribution of cobalt oxide on our support i.e. titania nanoparticles. The boundaries of catalyst particles in all synthesized catalyst particles are distinct and clearly visible.

Due to high degree of dispersion of cobalt oxide particles onto the support material ,the pollutants in the exhaust stream can easily be countered and catalytically converted. One of main reason of high degree of dispersion of cobalt oxide in the composite catalysts is the doping of ceria .The same effect of ceria on alone Co_3O_4 particles has been described by (Hou et al., 2008). Due to ceria doping, as described earlier the dispersion of cobalt oxide increases and the particle size decreases and hence surface area increases as confirmed by BET analysis described in the subsequent section.

The highly dispersion of ceria in ceria doped composite catalysts reveals the effective oxygen storage in the IWI catalysts and it is associated with a higher catalytic performance than precipitation method against considered exhaust gas pollutants.

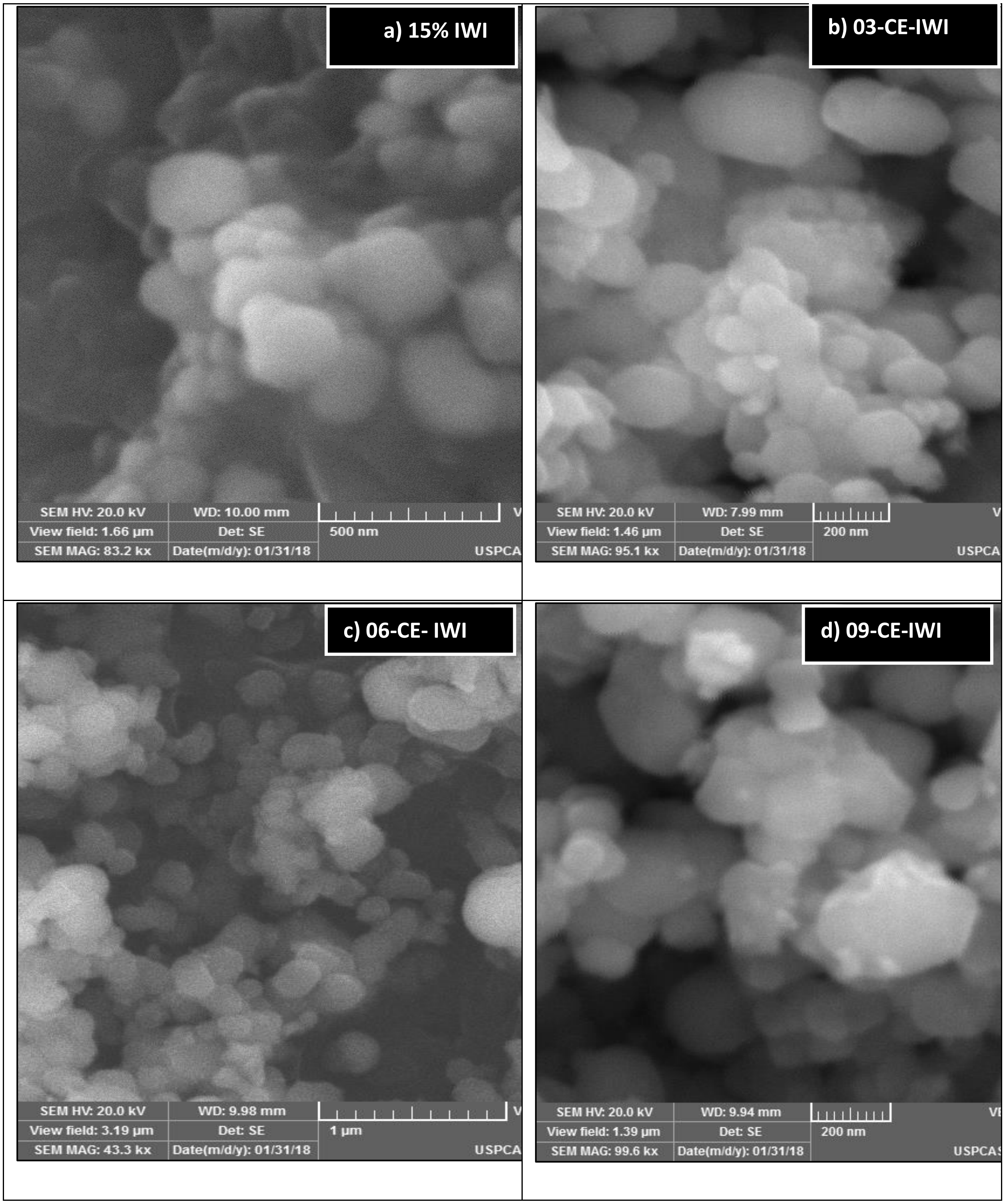

Figure 3: SEM image of catalysts synthesized with IWI method (a-15% IWI, b- 03-CE-IWI, c- 06-CE-IWI, d- 09-CE-IWI)

The SEM images of precipitation technique are depicted in Fig 4. Comparing all the images of catalyst synthesized by precipitation images of Fig 4. (a,b,c,d) illustrates that there exists no clear difference between the undoped 15% PPT catalyst and ceria doped catalysts i.e.03-CE-PPT,06-CE-PPT and 09-CE-PPT. The catalyst synthesized by precipitation method also depict densely packed spherical shaped nanoparticles with a smooth structure which illustrates uniform distribution and dispersion of cobalt oxide on our support i.e. titania nanoparticles.

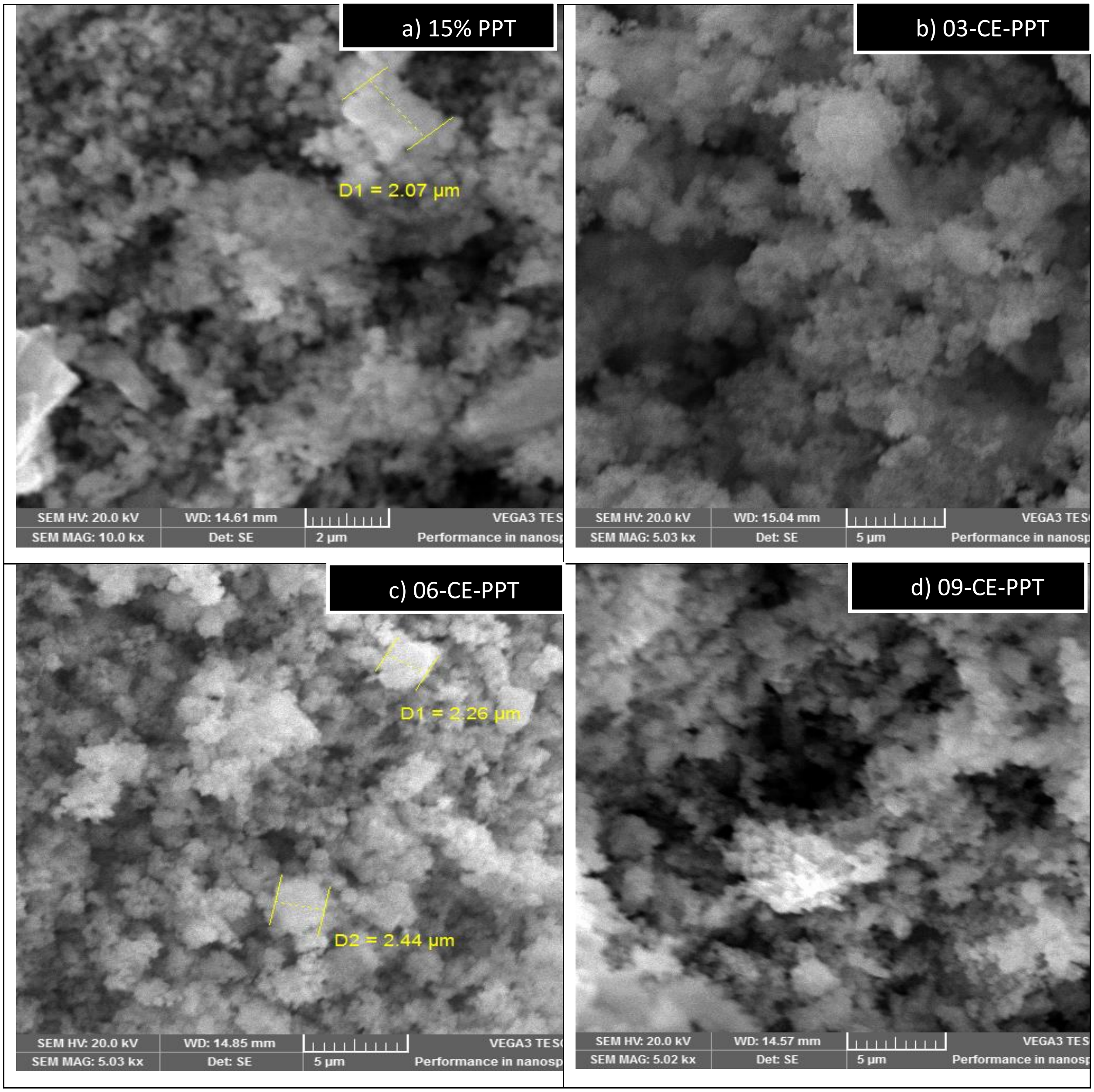

Figure 4: SEM images of catalysts synthesized with precipitation method (a-15% PPT, b-03-CE- PPT, c- 06-CE- PPT, d- 09-CE- PPT)

4.1.2 X-Ray powder diffraction

The JADE 6.5 software was used to analyze the diffraction patterns. All phases were recognized by corresponding to experimental patterns as listed in JCPDS powder diffraction file.

XRD pattern of TiO_2 support is shown in Fig.5 along with its characteristic's peaks. The major peak of anatase phase TiO_2 was noticed at 2 theta value of 25.28˚ along with its subsequent peaks exhibited at 37.8˚, 48.04˚, 53.89˚, 55.05˚ and 68.76 º. The peak at 27.44˚ correspond to rutile TiO_2.

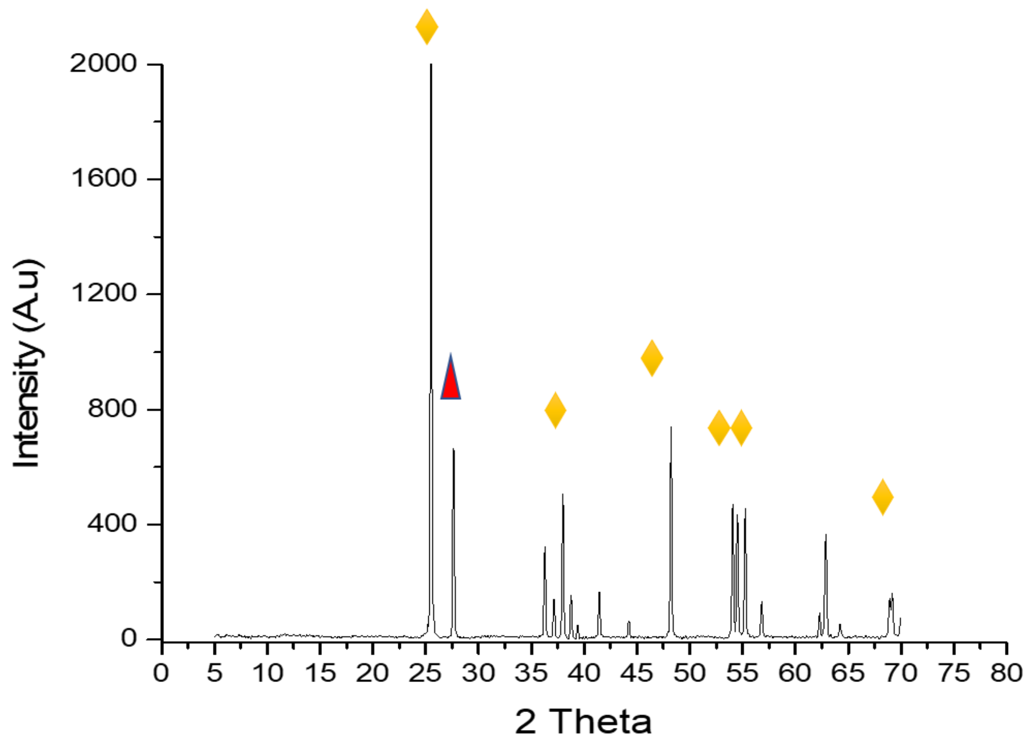

Figure 5: XRD pattern of pure TiO_2 nano particles

XRD pattern of 15% IWI is illustrated in Fig.6(a) along with its characteristic's peaks. In 15% IWI sample, cobalt oxide phase with spinal structure was recognized and that was the only pure cobalt oxide phase detected. Major peak of cobalt oxide was evident at 2 theta value of 36.84˚ in addition to minor peaks at 44˚, 59.36˚ and 65.2˚. No peak of CoO was detected as coincided with the work of (Ahmad et al., 2017). The elementary reason being is that CoO is formed at higher calcination particularly above 700˚ C and the peak at 2 theta value of 31.5˚ corresponded to $Co(OH)_2$.

Major peak of anatase phase in 15% IWI sample, was noticed at 2 theta value of 25.28˚.The subsequent peaks of anatase phase exhibited at 37.82˚, 48.04˚, 53.88˚, 55.04˚, 62.68˚ and at 68.76˚. Crystallite size of pure TiO_2 was evaluated as per Scherrer equation was 52 nm.

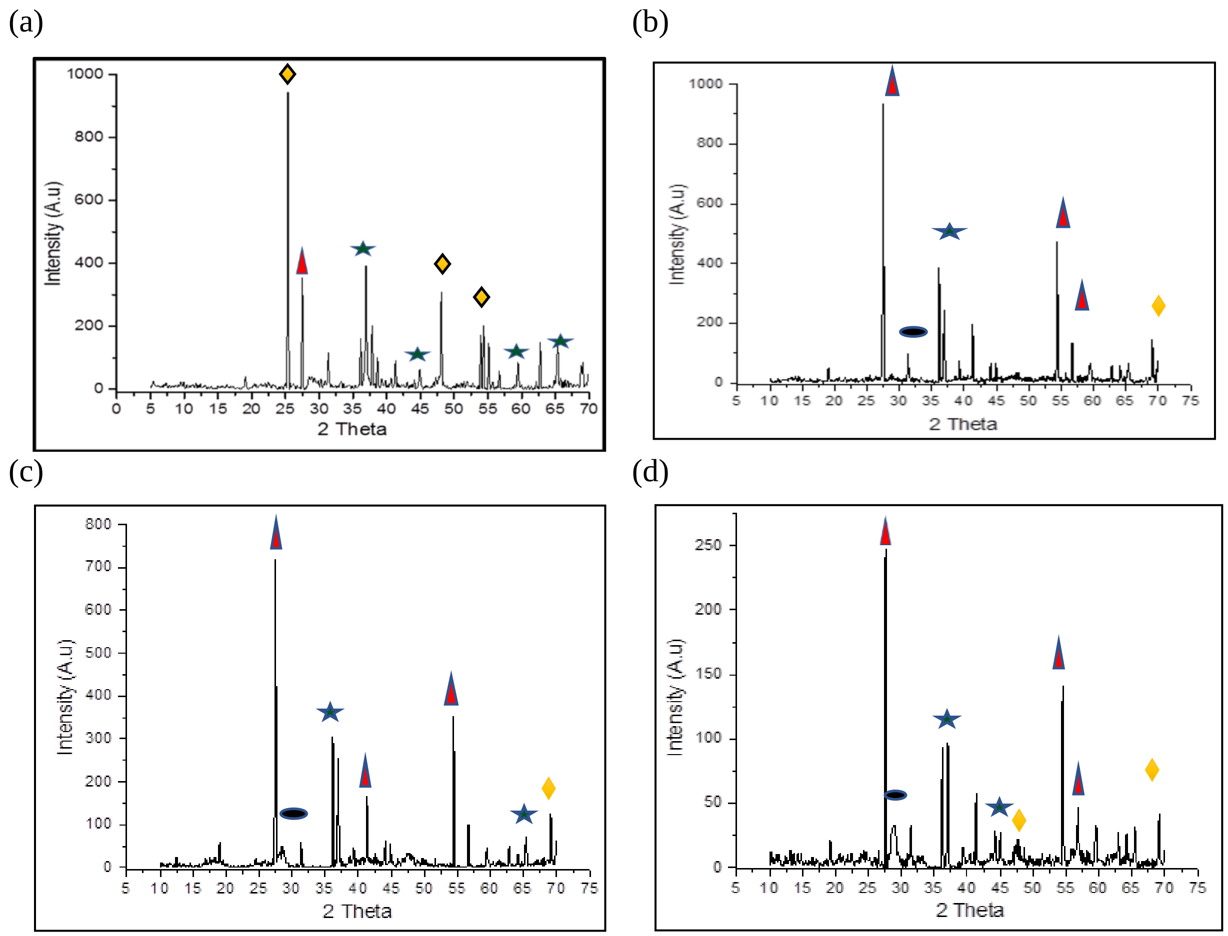

Figure 6: XRD patterns of IWI method (a) 15% IWI, (b) 03-CE-IWI, (c) 06-CE-IWI and (d) 09-CE-IWI

The subsequent discussion is about the XRD diffraction pattern analysis of ceria doped samples. XRD pattern of ceria doped samples via IWI method is illustrated in Fig.6 (b-d). In 03-Ce-IWI the predominant peak is at 2 Theta value of 27.43˚, which is attributed to rutile TiO_2 along with its subsequent peaks at 41.22˚, 54.35˚ and 56.58˚. The peak at 36.94˚ and at 69.0˚ are indexed to Co_3O_4.

For XRD diffraction pattern of 06-CE-IWI, the peaks were identified at 2 theta values of 27.43˚, 28.55˚, 36.08˚, 36.84˚, 41.22˚, 54.31˚ and at 65.21˚. Out of these, peaks at 27.43˚, 36.08˚, 41.22˚ ,54.31˚ correspond to rutile TiO_2 while peaks at 36.84˚ and 65.21˚ correspond to spinal Co_3O_4. It was observed that peaks shift to slightly higher 2 theta value as amount of ceria doping increases from 03% to 06%. The minor peak at 2 theta value of 28˚, designates the presence of ceria which is more projecting and intense as compared to with 03-CE-IWI catalyst which contains less cerium oxide than 06-CE-IWI.

In XRD pattern of 09-CE-IWI catalyst having 09% cerium doping, the diffraction peaks were observed at 2 theta value of 27.43˚, 28.55˚, 36.08˚, 36.84˚, 44.82˚, 48.05˚, 54.31˚ and at 69˚. The peak at 28.02˚ becomes even more intense and projected as compared to less ceria doped catalysts, i.e. 03% and 06%. The peaks at 2 theta value of 27.43˚, 36.08˚ and at 54.31˚ correspond to rutile TiO_2. The peaks at 2 theta value of 36.84˚ correspond to Co_3O_4 while one peak of anatase TiO_2 is also detected at 48.05˚. Some diffraction peaks shift to even higher values of 2 theta, as compared to 06-CE-IWI as was case earlier when ceria doping amplified from three percent to six percent.

Generally, from the XRD patterns of catalysts synthesized by IWI method , all the peaks of ceria can be indexed to ceria with a cubic phase fluorite structure. As coherent with the research work carried out by (Hou et al., 2008), it was revealed from width of diffraction patterns that doped samples have exhibited negligible change in their crystallite size. CeO_2 peaks are not prominently observed in the XRD diffraction patterns of ceria doped samples but minor peaks of ceria especially in 06-CE-IWI and 09-CE-IWI can be observed at 28.55˚ value of 2 theta. This behaviour specifies that CeO_2 exists in composite catalyst in a highly dispersed state . The same observation has been cited by (Hou et al., 2008) in which CeO_2 peaks are not apparent in Co_3O_4/CeO_2 composite catalyst. Characteristic spinal Co_3O_4 is exhibited at 2 Theta value of 36.12˚ in all IWI samples. It is not amazing that Co_3O_4 is detected rather than CoO due to high thermodynamic stability of Co_3O_4 both under ambient conditions and at higher temperatures. It is likely possibility that octahedral Co^{+3} sites are the active sites for oxidation of CO.

Due to small particles exhibiting size in nanometer range, the particles exhibited high surface area which is evident from BET analysis results. Overall, it has been observed from previous researches that dropping the particle size of a catalyst results in increasing the surface area apart from modifying its morphology. With an increase in surface area, the reactive edge sites increase. When the particle size is decreased below 100 nm the particles become nano-phasic.

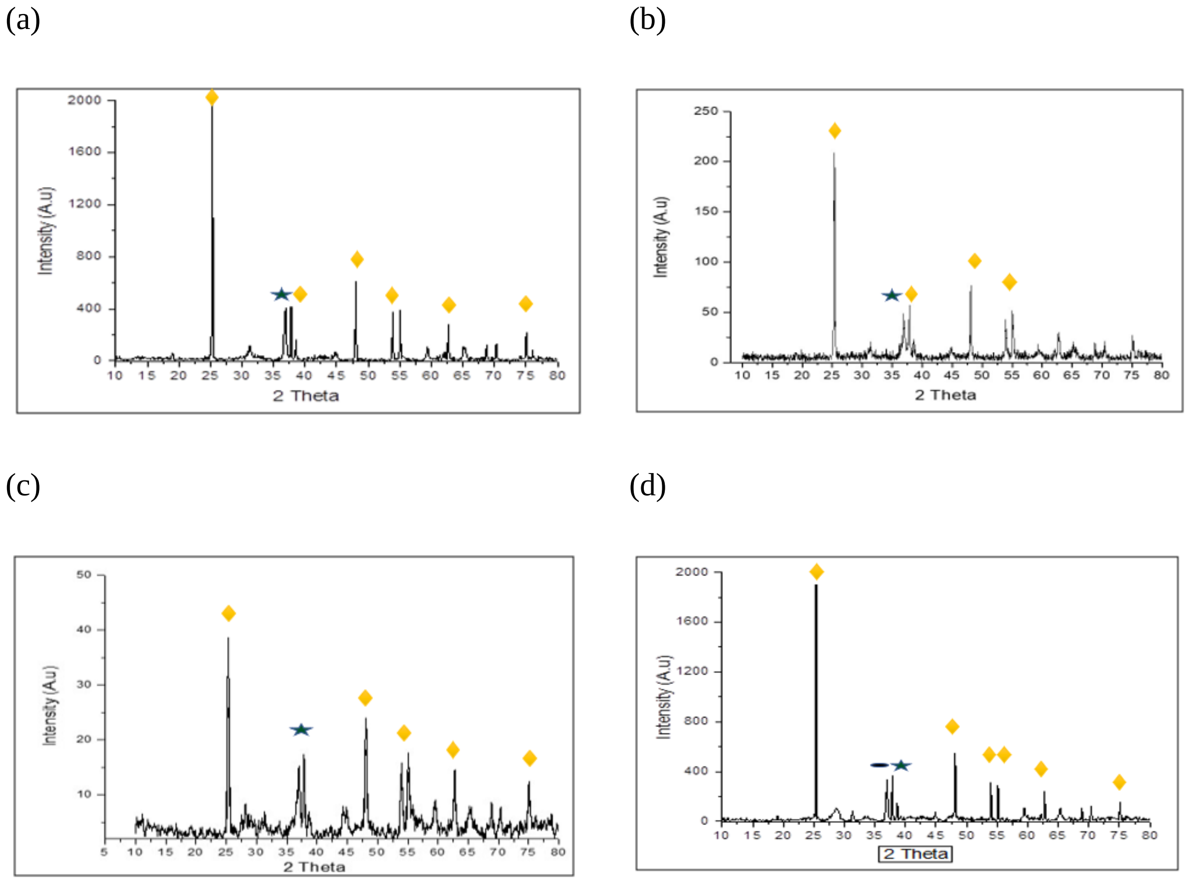

Figure 7: XRD patterns of precipitation method (a) 15% PPT, (b) 03-CE-PPT, (c) 06-CE-PPT and (d) 09-CE-PPT

XRD patterns of catalysts synthesized by precipitation method has been shown in figure 7 (a,b,c,d). The 15% PPT and 03-CE-PPT catalysts exhibit only TiO_2 and Co_3O_4 patterns, moreover, the anatase TiO_2 pattern has stronger reflection peaks in these catalysts than obtained from the IWI synthesized catalysts. In 15% PPT predominant peaks of anatase TiO_2 and Co_3O_4 are at 2 Theta value of 25.20˚ and 36.84˚ while for 03-CE-PPT these peaks are at 24.28˚ and 36.84˚ respectively. The diffraction patterns of pure CeO_2 have peaks at 2 theta values 28˚, 47˚ and 57˚ and normally reveal a face centered cubic fluorite type structure.

Mostly anatase form TiO_2 is detected for 06-CE-PPT and 09-CE-PPT catalysts and major peaks for TiO_2 in these catalysts are at 2 Theta value of 25.0˚ and 25.2˚ respectively. The Co_3O_4 peaks in both these samples are detected at 36.84˚. The cerium peak in 09-CE-PPT detected at 36.72˚ is the only peak of CeO_2 among precipitation method catalysts which might be the reason for its high catalyst activity among precipitation-based catalysts as described in later section.

Overall, if we conclude the XRD Diffraction analysis of all undoped and doped prepared by IWI and PPT methods we can say that the XRD patterns of the IWI and PPT catalysts include CeO_2, anatase TiO_2 , rutile TiO_2 and Co_3O_4 patterns. It was also figured out that ceria phase is highly dispersed on the cobalt oxide and TiO_2 support. Moreover, the Co_3O_4 pattern has stronger reflection peaks in catalysts synthesized by both IWI and PPT techniques.

4.1.3 Brunauer -Emmet -Teller (BET)

The pore volume was evaluated and analyzed by nitrogen adsorption/desorption. Porosity and surface area of catalyst are major factors that should be considered while synthesizing the catalyst. These parameters reveal its permeability, adsorption properties, mechanical strength under specific reaction conditions. The S_{BET} is calculated for the calcined catalyst by nitrogen adsorption of undoped Co_3O_4/TiO_2 and samples doped with ceria.

Table 2: BET surface area of IWI catalysts

Catalysts	BET Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (A^0)
15% IWI	18	0.021	32.3
03-CE-IWI	19.5	0.024	31.2
06-CE-IWI	21.6	0.026	30.7
09-CE-IWI	23.8	0.030	28.0

Surface area of catalysts synthesized by IWI method has been shown in table 2. The S_{BET} of 15% IWI was 18 m^2/g possessing pore volume 0.021 cm^3/g. As anticipated/expected, the surface area was increased considerably after doping of ceria in Co_3O_4/TiO_2 catalyst. Doping of minor amount of ceria, can significantly increase the thermal strength of Co_3O_4/TiO_2 composite catalyst. The ceria doped catalysts (03,06,09 % cerium content) exhibited surface area of 19.5 m^2/g having pore volume of 0.024 cm³/g, for 06-CE-IWI it was 21.6 m²/g with a pore volume of 0.026 cm³/g, for 09-CE-IWI it was 23.88 m²/g having pore volume 0.030 cm³/g correspondingly.

The surface area of pure Co_3O_4 was 46 m²/g but when the cobalt catalyst was loaded onto the TiO_2 support, the reduction in surface area was found. The main reason behind this is that due to cobalt metal loading onto the TiO_2 support, the pores are blocked by the cobalt metal particles. The other reason is the pore crystallinity encouraged by cobalt particles as evident by XRD. Increasing of surface area by the doping of ceria is credited to higher dispersion degree of Co_3O_4.

The surface area of 15% IWI synthesized catalysts was lower as compared to ceria doped catalysts as ceria increases cobalt oxide dispersion onto the support material. When the Co_3O_4/TiO_2 catalyst has been modified with ceria , not only the cobalt oxide dispersion increases onto the support but the it also decreases the internal diameter of composite catalyst as confirmed by BET analysis. The appreciable impact of higher surface area catalysts was also found on catalytic activity performance.

Comparison of XRD and BET results of doped and undoped ceria samples emphasize that ceria loading onto the Co_3O_4/TiO_2 based composite catalyst can increase the surface area of catalysts due to better and high degree of dispersion aided by ceria which ultimately increases the catalytic activity performance. The higher dispersion also demonstrates that greater number of oxygen atoms are available onto the catalyst surface which also promote the catalytic activity.

Surface area of catalysts synthesized by precipitation method has been shown in table 3.

Table 3: BET surface area of precipitation method catalysts

Catalysts	BET Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (A^0)
15% PPT	26.57	0.03	21.5
03-CE-PPT	28.4	0.12	20.9
06-CE-PPT	30.5	0.14	20.50
09-CE-PPT	33	0.2	19

The SBET of 15% PPT was 26.57 m²/g possessing pore volume of 0.03 cm³/g. The surface area was increased after doping of ceria in Co_3O_4/TiO_2 catalyst. The ceria doped catalysts in case of precipitation method (03,06,09 % cerium content) exhibited surface area of 28.4 m²/g for 03-CE-PPT having pore volume of 0.12 cm³/g, for 06-CE-PPT it was 30.5 m²/g with a pore volume of 0.14 cm³/g, for 09-CE-PPT it was 33.0 m²/g having pore volume 0.20 cm³/g correspondingly.

4.2 Catalytic activity performance

Wire meshes that were not coated with catalysts gave almost zero conversion efficiency at all operated rpm, which exposed no catalytic role of wire mesh substrate. Commonly, the exhaust temperature in the engine rises as the load and engine revolutions increase. In our study, average recorded temperatures were 105˚C , 150˚C, 213˚C and 261˚C at 2000, 4000, 6000 and 8000 rpm respectively. Due to proper insulation and sealing of catalytic convertor casing, the temperature nearly remained consistent at inlet, middle and just at the outlet of module. A minor decrease of 5-10˚C was observed from inlet to outlet of module and it seems understandable since some heat has been dissipated in heating the catalyst or wire meshes.

As the experiment was carried out , it was observed that inlet value slightly differs among all the conducted experiments .There are multiple reasons for this slight difference at inlet value e.g. engine condition/tuning, fuel quality, ambient environmental conditions etc. In case of CO the inlet value deviation was ± 0.01- 0.2 % CO , for HC it was ± 5-10 ppm and for NOx it was ± 3-5 ppm. The average of all the inlet values obtained at specific rpm's were taken and used as reference inlet value for that specific rpm. Catalytic activity performance of all catalysts has been described below.

4.2.1 IWI method

The average inlet values for CO was 2.9%, 3.27%, 3.75% and 3.88 % for 2000,4000,6000 and at 8000 rpm respectively. Figure.8 demonstrates the CO conversion efficiency(%) versus engine speed from 2000 rpm to 8000 rpm.

The conversion efficiency increased by increasing the ceria doping and highest conversion efficiency was achieved by 09-CE-IWI. Efficiency increased with increasing rpm till 6000 due to increase in temperature. After 6000 rpm efficiency decreased at 8000, which shows that although temperature was higher than lower rpm's, but flow rates of exhaust stream are much higher for the catalyst bed to convert the pollutant under the continuous exhaust stream. There were not enough active sites on catalyst surface to efficiently convert all the CO molecules with the passing exhaust gas stream. Maximum efficiency for carbon monoxide was 92% achieved at 6000 rpm.

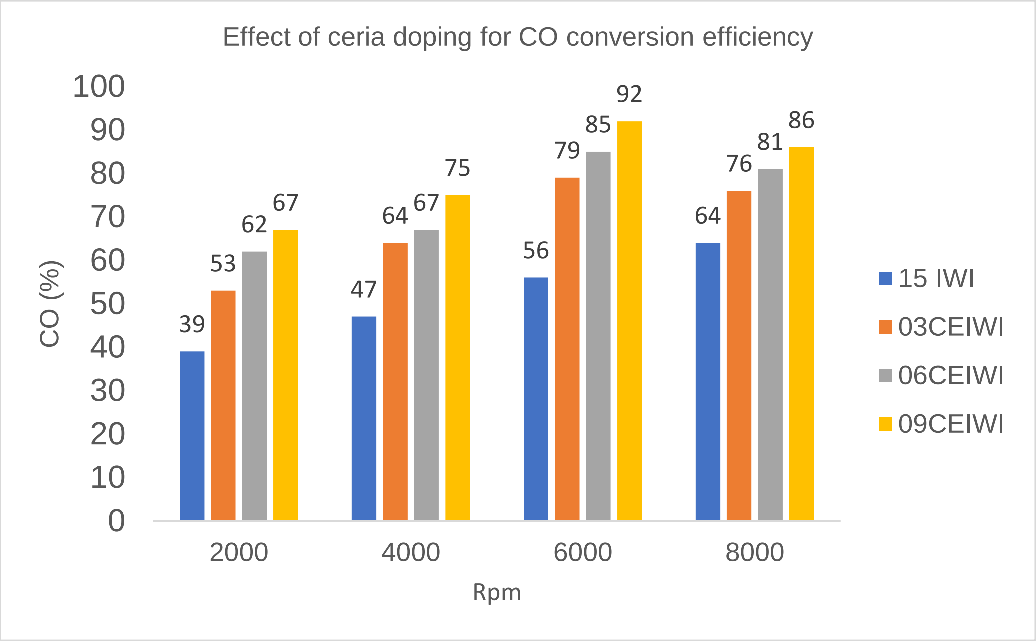

Figure 8: Conversion efficiency for carbon monoxide by IWI method

The same trend of conversion efficiency was observed in case of HC’s, but maximum efficiency was relatively lower than CO which predicts that catalyst is more active in oxidizing CO instead of HCs. This is well established in literature that HCs required higher activation energy to get oxidized by catalyst than CO.

The average inlet values for HC was 391, 545, 492 and 408 ppm for 2000,4000,6000 and at 8000 rpm respectively. Figure.9 demonstrates the HC (%) emissions versus engine speed from 2000 rpm to 8000 rpm.

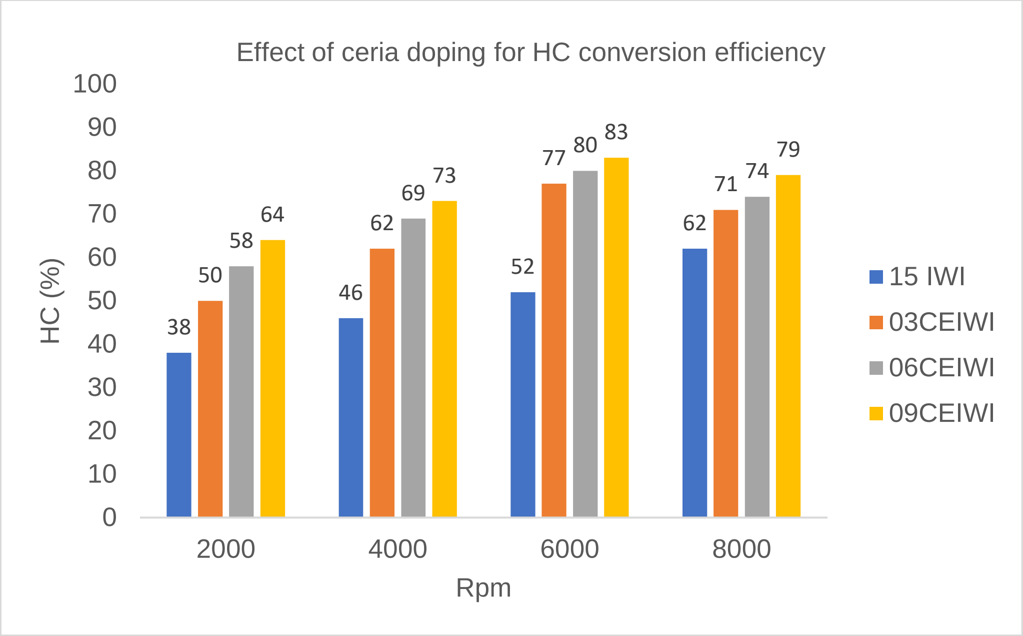

Figure 9: Conversion efficiency for hydrocarbons by IWI method

The average inlet values for NOx was 83, 71, 36 and 79 ppm for 2000, 4000, 6000 and at 8000 rpm respectively. Figure.10 demonstrates the NOx (%) conversion efficiency for IWI based samples versus engine speed from 2000 rpm to 8000 rpm.

Our NOx conversion efficiency behaviour was found linear with the inlet concentration of NOx which also reveals that our catalyst bed has further capacity to reduce higher concentration of NOx. NOx conversion efficiency is highest at 2000 rpm and it decreased till 6000 rpm. At 8000 rpm, its conversion efficiency again increased due to high temperature and high inlet NOx concentration which provided the catalyst a greater chance to reduce greater amount/concentration of NOx thus enabling it higher conversion efficiency at 8000 rpm.

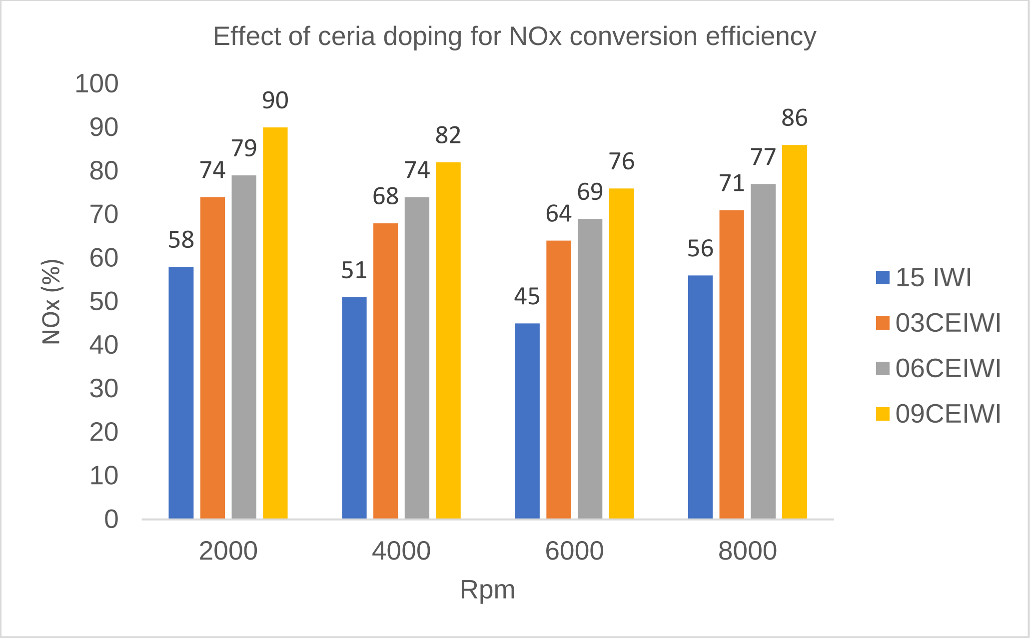

Figure 10: Conversion efficiency for NOx by IWI method

4.2.2 Precipitation method

Catalyst synthesized by precipitation method also converted the CO from engine exhaust, but efficiency was low as compared to incipient wetness impregnation (IWI) method. Still the same behaviour was observed as was in the case of IWI method that with increase in ceria doping the conversion efficiency increased and 09-CE-PPT gave highest conversion .

Overall it was observed that both of catalysts were oxidizing more carbon monoxide than hydrocarbons regardless of their preparation methods. The average inlet values for CO was 2.9%, 3.27%, 3.75% and 3.88 % for 2000,4000,6000 and at 8000 rpm respectively.

Figure.11 demonstrates the CO (%) conversion efficiency for precipitation-based samples versus engine speed from 2000 rpm to 8000 rpm.

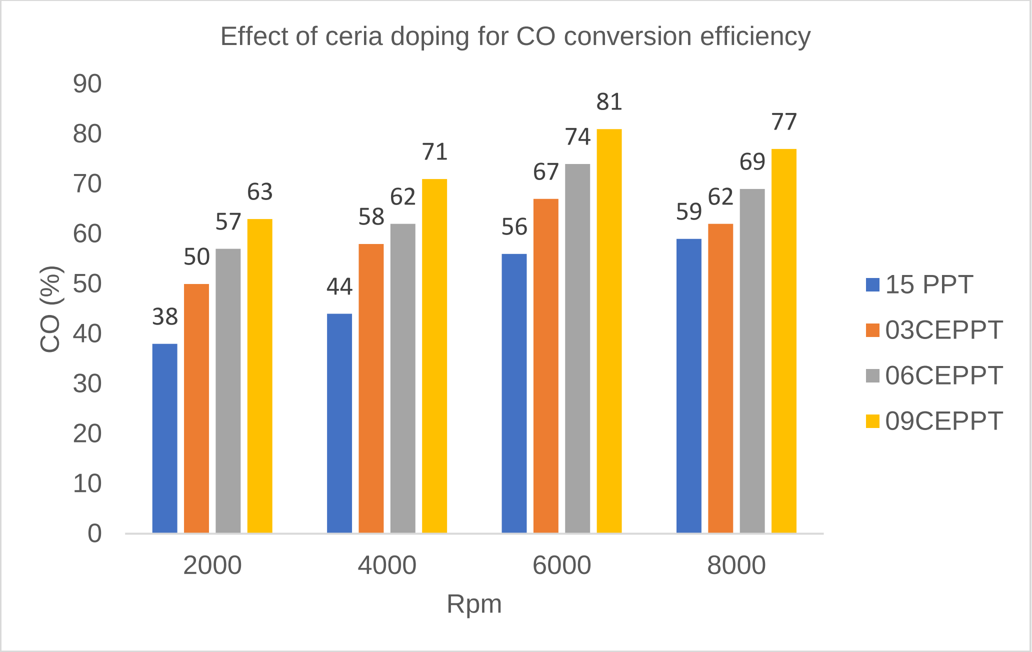

Figure 11: Conversion efficiency for CO by precipitation method

The catalysts synthesized by precipitation method gave lower HC conversion as compared to catalysts synthesized by IWI method. Overall conversion was increased with the doping of ceria and max. conversion efficiency was achieved by 09-CE-PPT at 6000 rpm.

The average inlet values for HC was 391, 545, 492 and 408 for 2000,4000,6000 and at 8000 rpm respectively . The reduction values i.e. Inlet – Outlet values were calculated for all samples and as shown in this graph.

Figure.12 demonstrates the HC (%) conversion efficiency for precipitation-based samples versus engine speed from 2000 rpm to 8000 rpm.

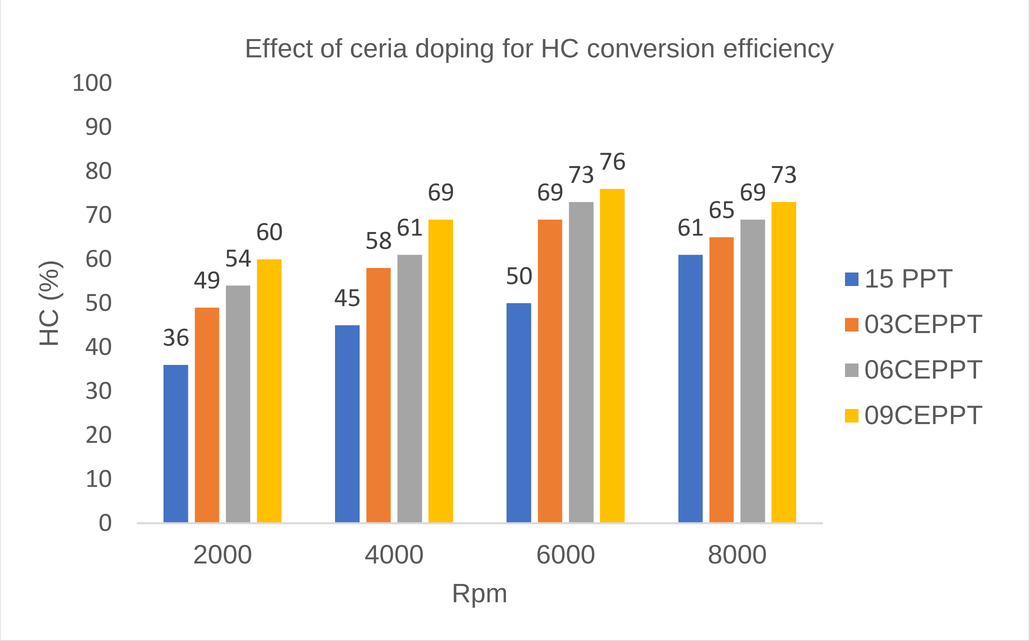

Figure 12: Conversion efficiency for HC by precipitation method

The same NOx behaviour was observed for samples synthesized by precipitation method as was the case for IWI. NOx conversion efficiency is highest at 2000 rpm and it decreased till 6000 rpm. At 8000 rpm, its conversion efficiency increased due to high inlet NOx concentration which provided the catalyst a greater chance to reduce greater amount/concentration of NOx thus enabling them higher conversion efficiency at 8000 rpm

The average inlet values for NOx was 83 ppm, 71 ppm, 56 ppm and 79 ppm for 2000, 4000, 6000 and at 8000 rpm respectively. Figure.13 demonstrates the NOx (%) conversion efficiency for precipitation-based samples versus engine speed from 2000 rpm to 8000 rpm.

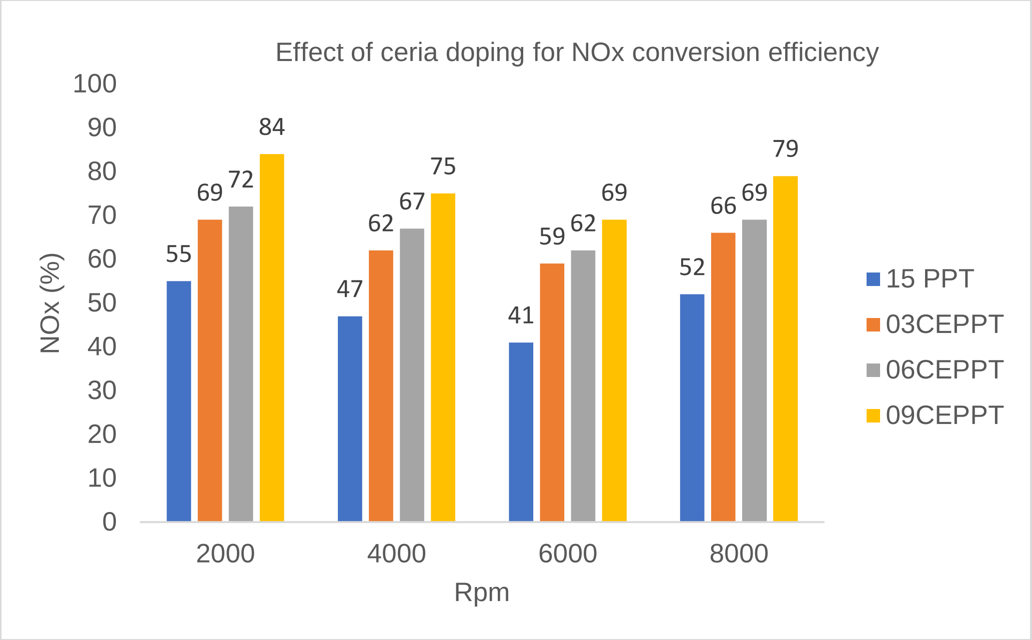

Figure 13: Conversion efficiency for NOx by precipitation method

Catalytic activity was markedly enhanced by doping of a small amount of cerium as promoter. For gasoline engines, various parameters/factors are linked to certain characteristics of engine.

Like load and engine revolutions affect the intake air flow rate, amount of fuel consumption, and primarily to our concern the exhaust gas type and its temperature. Exhaust gas concentrations can alter rapidly due to small fluctuations of above-mentioned factors even under steady state conditions. In real time scenario, the exhaust gas composition from gasoline engine constitutes minor quantities of several components besides unburned hydrocarbons, CO, NO_2, NO, and H_2O and CO_2 in state/case of complete combustion. Thus, in catalyst research and development there exists minor deviations between the experimental results attained under laboratory conditions by feeding mixture of gases and actual emission results of engine in running condition or by operating engine at idle conditions.

Chapter 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Following conclusions were drawn from the research study conducted.

- Significant impact of catalyst synthesis route was found on catalytic conversion efficiency and crystalline/ textural properties of synthesized catalysts.
- IWI synthesis technique exhibited overall better three-way catalytic activity than precipitation method due to highly dispersed ceria that easily undergoes redox and strongly interacts with cobalt oxide.
- Max. three-way catalytic conversion efficiencies for IWI, in case of CO, HC and NOx are 92%, 83% and 90% respectively.
- Increasing the cerium oxide (CeO_2) loading, increases the conversion efficiency in all scenarios.
- 09-CE-IWI revealed highest conversion efficiency due to larger surface area among IWI catalysts.
- At high space velocity 6000 rpm, this converter presents the highest conversion for CO and HC, while NOx conversion efficiency is highest at 2000 rpm i.e. Low space velocity.

5.2 Recommendations

- Optimization of cerium oxide loading in Co_3O_4/TiO_2 catalyst under real engine operating conditions.
- Long-term stability of the catalyst systems needs to be evaluated.
- Optimization in 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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