Application of Gamma Alumina (γ-Al_2O_3) as Washcoat for Non-Noble Metal based Catalytic Converter and its Performance Evaluation

By

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Furqan Sabir

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LIST OF ABBREVIATIONS

GHG	Greenhouse Gases
EPA	Environmental Protection Agency
PGM	Platinum Group Metal
GSA	Geometric Surface Area
CoO	Cobalt Oxide
TiO_2	Titanium Dioxides
C/H	ratio carbon to hydrogen
Pt/Pd/Rh	Platinum/Palladium/Rhodium
OEM	Original Equipment Manufacturer
LEV	Low Emissions Vehicle
SEM	Scanning Electron Microscope
TGA	Thermal Gravimetric Analysis
XRD	X-ray diffraction
SAE	Society of Automotive
BET	Brunauer, Emmett and Teller
TEM	Transmission Electron Microscope
IC-Engine	Internal Combustion Engine
CC	Catalytic Converter
TWC	Three-way Catalytic Converter

ABSTRACT

Due to excellent economy and durability, gasoline engines have been used widely in automobiles and other energy production machinery. On the other side, gasoline engines are major contributors towards air pollution. Exhaust from gasoline engines contain carbon monoxide (CO), unburnt hydrocarbons (HCs) and oxides of nitrogen (NO_x). More stringent regulations on automobile and other industries have made researchers to develop some technology for reduction of such pollutants from exhaust. In this work three-way catalytic converter is designed to treat the exhaust gases released from engine, for example, Hydrocarbons (HCs), Carbon Monoxide (CO) and Oxide of Nitrogen (NOx). Conventional catalytic converter with precious metal catalyst, Pt/Rd coated on ceramic substrate displays lower efficiency, high generation cost, constrained material supply and not environment friendly. Hence, an attempt to use metal oxide catalyst is researched. Titanium Dioxide (TiO_2) with Cobalt Oxide (Co_3O_4) was picked as the catalyst because of its points of interest in the raw material expense, locally accessible and suitable in manufacturing. The catalysts were coated onto treated wire mesh, SUS-304 where its surface was characterized by using SEM and XRD. Standard procedures were used to measure efficiency of developed catalytic converter. The outcomes revealed some suitability and limitations of the new catalytic converter. In this research work emission pollutants have been decreased such as carbon monoxide was reduced from 2.8 to 0.25 (V/V%) and hydrocarbons from 200ppm to 59ppm.

CHAPTER 1

Introduction

1.1 Background

Rise in air pollution have been brought about by rapid increase in number of vehicles from last 50 years in developing countries like Pakistan. Air pollution created from mobile sources is an issue of general interest. Emissions from automobiles have become a concern because of majority of engines are running by combustion of fuel derived from crude oil. Ideal burning of fuels should form water and carbon dioxide (CO2). But due to incomplete burning of fuels and higher temperatures in engine, formation of unburned hydrocarbons (HCs), carbon monoxide (CO) and oxides of nitrogen (NOx) takes place, which are harmful for human beings and environment as well (Kašpar, Fornasiero, & Hickey, 2003). First time in 1975, catalyst mounted automobiles were introduced. After experiencing the positive results in USA, first Japan and then Europe introduced catalyst containing vehicles in 1986. Thereafter, developing countries also realize the importance of use of catalyst to minimize emissions from automobiles (Shelef & McCabe, 2000). In the beginning, vehicle manufactures thought that deploying catalyst for emission reduction is just short term solution but now it's been more than 40 years that catalysts are serving as pollution abatement solution. At present catalyst is heart of emission control system (Farrauto & Heck, 1999).

There are two ways to deal with these harmful pollutants from internal combustion engine (IC Engine). One is about change in technology of IC-engine itself and other is treatment of exhaust gases after the combustion. Three way catalytic (TWC) converters are mounted in vehicles to convert harmful gases into less harm, it converts hydrocarbons (HCs), carbon mono oxide (CO) and nitrogen oxide (NO) into H2O, CO2 and N2 simultaneously (Ullah, Waldram, Bennett, & Truex, 1992).

Catalytic converter is core piece for effective reduction of emissions from automobiles. Automobile makers were unable to control emissions without installation of catalytic converters at the time of US Clean Air Act amendments came into play in 1970. In mid of 1970 first catalytic converter was installed on a car engine which was a two-way catalytic converter because of its ability to control CO and HC. It was installed on all types of automobiles since then with advancement towards threeway catalytic converter from a simple two-way oxidation catalyst. In current time catalyst industry is one of the significant engineering industry as it is the only way to meet strict regulations all over the world. Now catalytic converter is installed as integral part of engine in almost all kind of automobiles.

In late 1980s three-way catalytic converter was introduced with its ability to reduce NOx as well as oxidize CO and HC from engine emissions. A three-way catalytic converter contains a specific amount of catalytic material to oxidize CO and HC and reduce NOx at the same time without being consumed is mostly installed on gasoline engine. Catalytic converters are only recommendation for abatement of consequences of pollutants released from engine exhaust. So selection of effective catalyst for selective pollutant is major challenge. Control of one pollutant is not sufficient in this context. Selection of specific catalyst and determine its loading rate for conversion is very much important. Noble metals have been used in catalytic converter from many years. High cost of noble metals and due to high cost chances of being theft, make researchers to think about utilization of non-noble metals in this industry (Wang et al., 2015).

1.2 Objectives

1. Development and characterization of new Co_3O_4/TiO_2 based threeway catalytic converter for gasoline engine.

2. Coating of catalyst to metallic substrate by suitable method and use a testing method according to physical and chemical stability of material.
3. Effective use of metallic wire mesh to limit pressure drop to an acceptable limit.
4. Evaluate newly developed catalyst in terms of its conversion efficiency.

1.3 Scope of Study

1. Development of cheap catalyst and use it for treating exhaust from a gasoline engine.
2. Production of new alternative for post treatment technologies.
3. Introducing a new locally made catalytic converter.
4. Introducing a new metallic substrate by using wire mesh as a substrate.
5. Enlighten the use of metallic substrate.

CHAPTER 2

Literature Review

This chapter reviews different steps of technology advancement as required by enforcing regularities. Gasoline is commonly considered as perfect fuel and high efficient in energy production. Likewise, clarification of limitations of current platinum group metals (PGM) and development of many new metallic oxide catalyst as an alternative option, new substrate materials, different coating techniques to enhance performance efficiencies.

2.1 Air Pollution

Air pollution caused by mobile sources is a worry and an interest of the general public. These harmful gasses from burning of their by-product contributes 40% of total emissions. Combustion of fuel, mostly hydrocarbons (HCs) in a perfect world prompts the development of water and carbon dioxide. On the other hand, because of incomplete burning and the high temperature in the combustion chamber, the ousted exhaust contains a huge amount of toxic contaminants which should be converted to less toxic gas compounds. Essentially, the exhaust gas contains three primary pollutants. They are the unburned hydrocarbons (HCs), carbon monoxide (CO) and nitrogen oxides (NOx), for the most part NO, in addition to it some other compounds, for example, water, hydrogen, nitrogen, oxygen, and so on. Emission of unburned hydrocarbons results when fuel particles in the engine do not burn or partially burned. Hydrocarbon responds in the vicinity of nitrogen oxides and sunlight to shape ground-level ozone, a noteworthy segment of smog. It is our most broad and immovable urban air pollution issue. Various exhaust hydrocarbons are likewise dangerous, with the possibility to bring about cancer. Nitrogen oxides are the non-specific term for the group of highly reactive gasses, all of which contain nitrogen and oxygen in different zooms. A large portion of the nitrogen oxides is colorless and odorless. However, one regular toxin, nitrogen dioxide (NO_2) alongside particles noticeable in the air can frequently be seen as a reddish brown layer over numerous urban regions. As in burning procedure, oxides of nitrogen are formed when fuel burned at high temperatures. NOx causes a wide assortment of health and ecological effects in light of different compounds and their derivatives in the group of nitrogen oxides, including nitrogen dioxide, nitric acid, nitrous oxide, nitrates, and nitric oxide. It is the known contemplate for acid rain and global warming. Carbon monoxide is a colorless, odorless gas that is formed when carbon in fuel is not completely burned. A solitary introduction of CO at low levels may bring about pain in chest and decrease that an individual's capacity to work out; rehashed exposures may add to other cardiovascular impacts. It is a segment of engine, vehicle exhaust, which contributes around 60 percent of all CO emissions across the nation. More elevated amounts of CO for the most part happen in zones with substantial traffic congestion. Recently, the U.S. Environment Protection Agency (EPA) has begun to view carbon dioxide, a result of "complete" burning, as a contamination concern. Carbon dioxide (CO2) does not specifically weaken human health, but rather it is a "greenhouse gas" that traps the world's heat and adds to the potential for global warming.

2.1.1 Pollution from Mobile Sources

Rapid rise in air pollution is due to rapid increase in vehicle population. Asian region has highest concentration of automobiles. Motorcycles are thought to be most fuel economic way of transportation. Motorcycles are major contributors to hydrocarbons and carbon monoxide production, and its share is more than four wheeler vehicles (Bokde & Waghmare, 2013). Motorcycles have serious impact on energy and greenhouse effect over the world. It’s a general thought that automobiles used for transportation have used half of world’s oil. Energy consumption and carbon dioxide emissions due to transport grew by about a thrice in just one decade since the 1990s, with nearly half of this increase coming from the low-income countries (Issn & Online, 2007). Next-generation catalytic converters must possess the properties such as high activity and selectivity, very fast light-off (<20s), high thermal stability and high oxygen storage capacity (Kašpar et al., 2003).

2.1.2 Basics of IC-Engine

Engine is most commonly used as power source, where mechanical power takes place by expansion of burned gases. There are two types of engines, in first type power is generated by spark ignition and in second type compression is used. Gasoline engine or petrol engine is well known example of spark ignited engine where plug is used to initiate burning of air and fuel mixture. While in a diesel engine compression is used for auto ignition of fuel which is (air to fuel ratio of diesel engine 25:1) quite higher as compared to petrol engine (14.7:1). Higher compression ratio in diesel engine is used to create high temperature of around 700-900˚C which starts auto burning of fuel as air came into contact with fuel. Combustion process in petrol engine is very simple but limited compression ratio makes it less efficient as compared to diesel engine. All types of engines have their own exhaust system which is used to discharge exhaust gases of engine away from user. Both diesel and gasoline engine exhausts contains almost same gases with different compositions. CO, HC, PM and NOx are main pollutants of engine exhaust. Diesel engine is considered as most economic as compared to petrol engine because of it combustion takes place towards lean side but higher percentage of PM and NOx in exhaust are adverse for environmental concerns.

2.1.2.1 Combustion Reactions in IC-Engine

Incomplete burning happens when a fuel component is not totally oxidized during ignition. For instance, a hydrocarbon may not totally oxidize to carbon dioxide and water, but rather may shape partially oxidized compounds, for example, carbon monoxide, aldehydes, and ketones.

Incomplete combustion uses fuel wastefully, can be toxic as a result of carbon monoxide formation, and adds to air pollution. From literature, it's been clear that there are following reasons for incomplete combustion.

1 Inadequate air to fuel ratio

2 Deficient of air supply to the flame

3 Incomplete residence time of reactants to flame

4 Impingement of flame on a cold surface

5 Lowering the temperature of the flame

On conversely, in stoichiometric burning of a hydrocarbon fuel, fuel is responded with the accurate measure of oxygen required to oxidize all carbon, hydrogen, and sulfur in the fuel to CO_2, H_2O, and SO_2. Subsequently, exhaust gas from stoichiometric ignition hypothetically contains no incompletely oxidized fuel constituents and no non-responded oxygen (i.e., No carbon monoxide and no abundance air or oxygen). Table 1 shows expected concentrations of different pollutants at various operating conditions.

Table.1 Concentrations of Exhaust Gases at different Operating Modes

Operating Mode	Carbon Monoxide (CO)	Hydrocarbons (HCs)	Nitrogen Oxide (NOx)
Idling	Very High	High	Low
Deceleration	Very High	High	Very Low
Low Speed	Moderate	Moderate	Low
Acceleration	Low	Low	High
High Speed	Very Low	Very Low	Ver High
Uniform Speed	Minimum	Minimum	Minimum

2.1.3 Pollutants of Major Concern

The main primary pollutants from automotive exhaust are carbon monoxide (CO), unburned hydrocarbons (HCs) and oxides of nitrogen (NO_x) (Farrauto & Heck, 1999). In urban areas major source of carbon monoxide more than half is emissions from automobiles (Flachsbart et al., 2016). Estimates of developed countries have shown that major source of carbon monoxide (CO) is exhaust gases from automobiles (US Department of Health Education and Welfare, 1970). Lead (Pb), particulate matter (PM), nitrogen oxide (NOx), volatile organic compounds (VOCs), carbon monoxide (CO) and Sulphur dioxide are most unfavorable pollutants. Lead (Pb) and particulate matter (PM) are more toxic among all above mention pollutants. These compounds are considered to be the primary driver of the surplus mortality that was seen in London and New York smog scenes of the 1950s and 1960s. Particulate matter found at that time was generated from combustion of coal. Whenever humans are exposed to these particulate matters (PMs), they have faced serious adverse health effects. Worldwide, the fast development in engine vehicle activity has genuine energy security and climate change indication. Transport as of now expends almost 50% of the world's oil. Rapid utilization of energy and carbon dioxide releases because of transport developed by around a thrice in only one decade since the 1990s, with almost 50% of this build originating from developing countries (Issn & Online, 2007).

2.1.3.1 Carbon Monoxide (CO)

Carbon monoxide which is colorless and odorless gas shows much more harmony towards hemoglobin than that of oxygen. Carbon monoxide caused to chunk the supply of oxygen to tissues of body which results in suffocation that is why it is very lethal even concentration of some thousands ppm. Oxygen deficient conditions in internal combustion engine (IC-Engine) results in production of carbon monoxide. Therefore, during rich air-to-fuel ratio (A/F) of internal combustion engine (IC-Engine) produces carbon monoxide due to deficiency of air and when engine is operating at lean air-to-fuel (A/F) carbon monoxide (CO) is produced due to incomplete combustion. A solitary introduction to CO at low levels may bring about pain in chest and decrease that individual's capacity to work out; rehashed exposures may add to other cardiovascular impacts. It is a segment of engine vehicle exhaust, which contributes around 60 percent of all CO emissions across the nation. More elevated amounts of CO for the most part happen in zones with substantial traffic congestion. Recently, the U.S. Environment Protection Agency (EPA) has begun to view carbon dioxide, a result of "complete" burning, as a contamination concern. Carbon dioxide (CO_2) does not specifically weaken human health, but rather it is a "greenhouse gas" that traps the world's heat and adds to the potential for global warming.

2.1.3.2 Hydrocarbons (HCs)

Partially oxidized fuel compounds which consists of hydrogen and carbon are called hydrocarbons (HC). When engine is operating at rich air-to-fuel (A/F) hydrocarbons (HCs) produces due to excess of fuel quantity. Emission of hydrocarbon results when fuel particles in the engine do not burn or partially burned. Hydrocarbon responds in the vicinity of nitrogen oxides and sunlight to shape ground-level ozone, a noteworthy segment of smog. It is our most broad and immovable urban air pollution issue. Various exhaust hydrocarbons are likewise dangerous, with the possibility to bring about cancer. Major examples of hydrocarbons (HCs) are odorless alkanes and alkenes and alkynes with sweet smell while benzene is carcinogenic. Hydrocarbons (HCs) caused coughing and tiredness effects on humans. Hydrocarbons (HC) reacts with NOx and results in photochemical smog and tropospheric ozone which has very significant health effects on humans.

2.1.3.3 Oxides of Nitrogen (NOx)

A group of highly reactive gases that contain nitrogen and oxygen in varying amounts. Nitric oxide (NO), Nitrogen dioxide NO_2) and Nitrous oxide (N_2O) are major components of nitrogen oxides (NOx). 80% of nitrogen oxides emissions from gasoline engine are nitric oxide (NO) however nitric oxide (NO) and nitrogen dioxide both are major sources of photochemical smog and formations of acid rain. Nitrogen oxides are the non-specific term for the group of highly reactive gasses, all of which contain nitrogen and oxygen in different sums. A large portion of the nitrogen oxides are colorless and odorless. However, one regular toxin, nitrogen dioxide (NO_2) alongside particles noticeable in air can frequently be seen as a reddish brown layer over numerous urban regions. As in burning procedure, oxides of nitrogen are formed when fuel burned at high temperatures. NOx causes a wide assortment of health and ecological effects in light of different compounds and their derivatives in the group of nitrogen oxides, including nitrogen dioxide, nitric acid, nitrous oxide, nitrates, and nitric oxide. It is the known contemplated for acid rain and global warming.

2.2 Legislation

The introduction and manufacturing of catalytic converter is surely a major achievement in the automobile industry. Significant environment quality has prompted by reduction of pollutants particularly in urban territories. Then again, this exertion was obviously joined with significant expenses and investment and would have scarcely been made without savage authoritative action. In beginning the researchers were concentrating on improvement of fuel quality and electronic control systems of engine. But sooner they realized that catalytic converter is only solution to treat exhaust gases (Cook et al., 2006).

Low cost, low back pressure, low weight and better conversion efficiency, are basic needs of a good catalytic converter. Rajadurai et al, first time in 2006, used metallic wire of different mesh sizes to develop a selective catalytic redactor for diesel engine (Rajadurai et al., 2006). A Ghasemi et al in 2008, designed and fabricate a new model of catalytic converter (Ghasemi, 2010). According to him, when the exhaust gases enter the monolithic catalyst area flow of gases do not remain uniform, which effects its conversion. Cones were installed by him to make flow uniform, which in results give better conversion but temperature distribution was effected by this design. Oxygen level plays an important role in working efficiency of a three-way catalytic converter. A new model was introduced by Ammann et al in 2000 (Sun, Kolmanovsky, Cook, & Buckland, 2005).

The United States were the first to present extremely stringent limitations for exhaust gas segments as a reaction to the serious air contamination in urban regions. In Los Angeles for instance, the smog was more regrettable in 1955 than in Mexico City today (Bertelsen, 2001). As a result, Congress passed the Clean Air Act Amendments of 1970. Initially, a 90% decrease of HC, CO, and NOx emissions over uncontrolled levels was required inside of six years. Then again, these limitations ended up being excessively stringent for an execution in the given time allotment and the due dates must be delayed. At long last, all gasoline driven traveler autos in the U.S. needed to meet as far as possible by the model year 1983.

The general way towards a significant decrease of the emissions was being kept and improved constantly. With the Clean Air Act Amendments of 1970, the State of California was approved by Congress to present its own particular engine vehicle emission control program. After that, California led the pack in emission control enactment and worked in a route as a "demonstrating ground" for extremely stringent exhaust gas limits. After experiencing positive change in the U.S.A, Japan and Europe present the utilization of catalyst for automobiles, the recent in 1986 (Shelef & McCabe, 2000). European brought their standards in form of Euro-I, II, III, IV, V and VI in 1992, 1996, 2000, 2005, 2009, 2015 respectively.

In recent years, driving cycles have been made to developed repeatable and comparable results of emissions testing of automobiles. These driving cycles not only include the conditions of vehicle but also take into account ambient temperature and pressure. In U.S they use Federal Test Procedure (FTP) (Bauer, 1999). In Europe they use European driving cycles.

2.3 Catalytic Converter

These stringent emission standards portrayed above cannot be achieved by improvement of the combustion process in the engine alone. In a perfect world, i.e., with a complete burning, the exhaust gas only comprises of nitrogen, carbon dioxide, and water, when the air-to-fuel ratio is stoichiometric. Complete burning is never reached, i.e., the exhaust gas leaving the engine cylinder has not reached to chemical equilibrium. In this manner, a catalyst is utilized, which quickens this procedure such that the condition of the exhaust gas approaches the balance before being discharged to atmosphere. The most widely recognized after treatment gadget for gasoline fueled engine these days is the three-way catalytic system (TWC). Catalytic converters had across the board take off in the US business sector beginning in 1975 by the Engelhard Corporation. From that point forward they have turned into the standard in exhaust emissions control. Huge improvements in automobile exhaust systems have happened with three-way catalysts (TWCs) to be most promising of these advancements (Sideris, 1998).

2.3.1 Two-way Catalytic Converter

Two-way catalytic converter also known as oxidation catalytic converter. Two-way catalytic converter can oxidize carbon monoxide to carbon dioxide and unburned hydrocarbons to water and carbon dioxide. Two-way catalytic converters are usually installed to diesel engines, also on gasoline engines before 1981. Three-way catalytic converters have now replaced two-way because of his ability to reduce oxides of nitrogen to N_2 and O_2 along with oxidation of hydrocarbons and carbon monoxide at the same time (Sekhar, 2015).

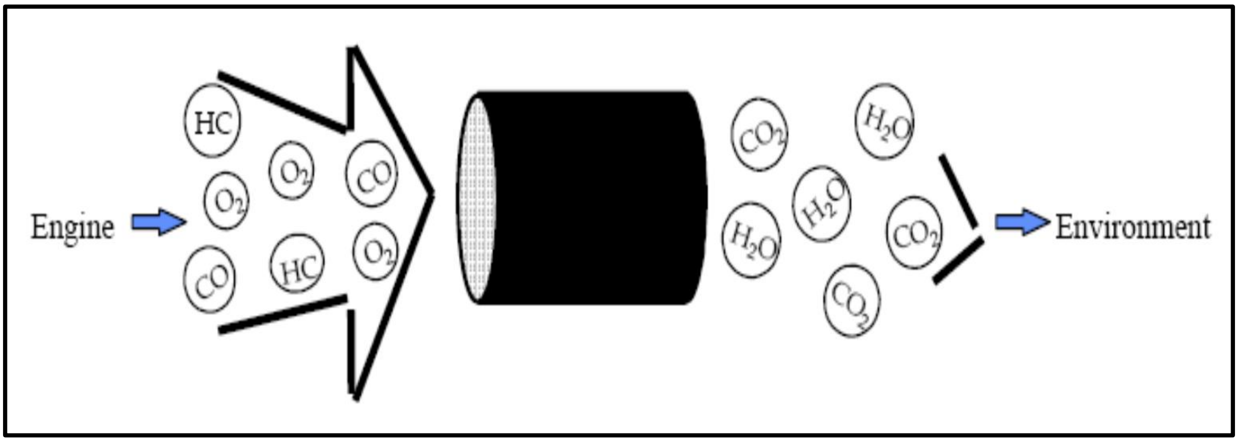

Figure 2.1: Two-way Catalytic Converter

2.3.2 Three-way Catalytic converter

The ability of three-way catalytic converter to reduce nitrogen oxides (NOx) and oxidize hydrocarbons and carbon monoxide at the same time makes it more prominent. Oxides of nitrogen in particular nitrous oxide have three hundred times more potential greenhouse gas than carbon dioxide, precursor to acid rain and also play major role in ozone depletion. Three-way catalytic converters have been used in gasoline engines in all over America and Canada. Three-way catalytic converter could contain oxidizing and reducing catalyst in same housing. This type of converter has three tasks to do, oxidize hydrocarbons and carbon monoxide and reduction of nitrogen oxide (Sekhar, 2015).

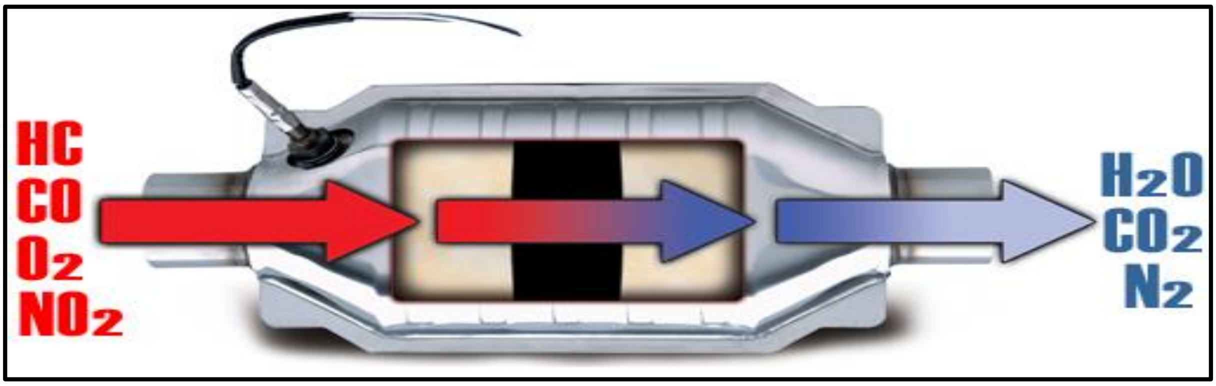

Figure 2.2: Three-way Catalytic Converter

2.4 Developments in Early Stages

There were series of hurdles to overcome before installation of catalytic converter on automobiles at early stages of catalyst development. Selection of active metals, temperature stability of exhaust gases and to provide enough oxygen to oxidize hydrocarbons and carbon monoxide, were such issues which had taken so long to be resolved. To begin business in this technology the cost of catalytic converter was main concern. The overall perception of consumers and business community was that they would be charged excessive cost than that of actual price, because actual cost was not clear. The most prominent concerns were weather catalyst would be sufficient to treat exhaust of automotive and enough availability of precious metals in case other metal oxide failed to overcome. Application of stringent laws make researcher to work doubles and find out solutions to all these problems. Lead was eliminated from fuel because it incompatibility with catalytic converter. With the passage of time list of elements were cut down to noble metals for being used as active metals which gives initiate mining of most refined metals. Recycling of active metals from removed catalytic converters was attractive option. Almost every innovation in this regard had faced many failures. At present the reliability of converters could be assessed from government regulation of its working ability up to hundred thousand miles (100 000 miles). To avoid back pressure, high flow rates and ability of compactness led to adoption monolithic substrate. It is multi channeled and exhaust gases flow through these walls where catalyst was coated. At present monolith is most widely used not only in automotive industry but also in many other industries. Catalytic converter at early times were only used for oxidation of CO and HCs, air pump was installed in conjunction with it which supplied enough oxygen to make sure that oxidation takes place. By late 1980s, tighter NOx emission standards ushered in three-way catalytic converter which have its ability to reduce oxides of nitrogen along with oxidation of CO and HCs. It’s been noted that oxidation of CO and HCs takes place in excess air condition while better reduction of NOx required excess fuel. To use oxidation and reduction in conjunction air to fuel ratio (A/F) must be restricted to stoichiometric.

2.4.1 First Generation Catalytic Converter (1976-79)

At first, catalysts were required only for oxidations of hydrocarbons (HCs) and carbon monoxide (CO). NOx standards was not introduced at that time. Engine manufacturers introduced exhaust gas recirculation (EGR), which recirculate exhaust gas which results in lower NOx emissions (Zeldovich, 1946). Engines were also operated at rich air to fuel ratio which further reduce NOx formation in engine exhaust. In some of engine exhaust systems air was introduced which enhance the oxidation process. In that era, many catalysts were explored. Noble metals were found best for oxidation of exhaust gases. But high cost and availability of precious metals make researchers to investigate base metals (Cu, Ni, Mn and Cr), which were readily available and cheaper than noble metals (Yoa, 1975). It was found that larger reactors are required to base metals, which does not suit to engine exhaust system (Evaluation & Calorimeter, 1974). Therefore, noble metals were introduced in first generation catalytic converters.

2.4.2 Second Generation Catalytic Converter (1979-2000)

Second generation catalytic converters include the reduction of NOx along the oxidation of HCs and CO. But the issue was that oxidation of CO and HCs requires oxygen and NOx reduction requires oxygen deficient condition. Reduction catalyst was introduced before air injection system in exhaust system. Ru was first catalyst material used for NOx reduction. Rh was also one of catalysts which shows excellent reduction of NOx (States & Office, 1964). Ideally if engine operated near to stoichiometric conditions, conversion of all three pollutants could occur at same time and same location. Whenever engine went towards rich air to fuel ratio CO and HCs formation will be more which requires more oxygen to oxidize them. While in other case, if engine operates on lean air to fuel ration, more NOx will be produced which requires less oxygen to reduce NOx. It was concluded to fix air to fuel ratio within a limit, which make introduction of oxygen sensors (Wang, 1993). Threeway catalytic converter was introduced in 1979, which have the ability to oxidize and reduce all three pollutants at the same time.

2.4.3 Third Generation Catalytic Converter (2000 and Post)

Standards have become more stringent with the time being as the world have recognized the importance of clean air and their confidence over catalytic materials. Moreover, the life span of catalytic converter has also been increase to 100,000 miles which was 50,000 miles before 1997. These standards are becoming more stringent with time. To meet these stringent regulations more investigation over design and catalytic material is required. Some of patents during the span of 1995-2000, which define the future of three-way catalytic converter. Modern catalytic converters include washcoat which provides high surface area, high porosity and more thermal stability. Materials like titanium dioxide, alumina and zirconia have been used as washcoating materials in three-way catalytic converter. Catalyst material which actively converts exhaust pollutants, platinum, palladium and rhodium metals area mostly used as catalyst material. Thirdly, oxygen storage materials called promoters have now incorporated to store and release oxygen whenever required.

2.5 Materials used in Catalytic Converters

A catalytic converter for an internal combustion engine comprises in general three main elements:

1. The ceramic or metallic support (Substrates)
2. The alumina washcoat (usually stabilized gamma alumina γ-Al_2O_3)

3. The noble metal (Catalyst)

The three-way catalyst compositions in 70% cordierite substrate ($MgAl_2O_4$) and the washcoat (*Book Review*, 2007):

- 20-25% γ-Al_2O_3 (or α-Al_2O_3, ZrO_2)
- <10% CeO_2, BaO, etc. (oxygen storage, stabilizer)
- 0.2 – 0.6% Pt, Pd (CO, HC conversion)
- 0.04 – 0.06% Rh (NO_x activity)

Single or double washcoat may be applied. Double coats are used to enhance specific reactions and improve durability by separating components of the catalyst. The coated substrate is air dried and calcined (drying at high temperature, typically 300 - 800˚C, either in air or in a synthetic gas mixture) to ensure good adhesion. Washcoat thickness, which ranges from 20-60 µm, is engineered for minimal diffusional resistance, so gases readily reach the catalytically active sites. It is also configured for maximum resistance to contaminants, many of which deposit in the outer 10 to 15 µm of the washcoat. The washcoat is 5-15% of the converter weight and has a surface area of 100-200 m^2/g.

The noble metals are impregnated into the highly porous alumina washcoat. Active catalytic converters contain about 0.1 to 0.15% noble metals. The most commonly catalytic materials used in the automotive industry are Platinum (Pt), Rhodium (Rh), Palladium (Pd) and Ruthenium (Ru), which become efficient for temperatures over 140˚C. The quantity of noble metals contained in a catalytic converter is 2-3 grams.

Recent trends in improvement of the catalyst relevant properties of the fuels available in the U.S.A. and Europe, along with the wide application of advanced engine management systems with a capability for much tighter air/fuel control close to stoichiometry (air/fuel ratio = 14.6), lead to the use of tri-metal catalysts (Pt, Rh, Pd).

Other materials used are common metals like Nickel (Ni), Chromium (Cr) and Copper (Cu). The disadvantage of these metals is that they become efficient at temperatures over 400˚C. In addition to the noble metals, the alumina washcoat of a three-way catalytic converter also contains other components like La_2O_3 and/or BaO, which function as catalytic promoters or stabilizers against aging. La_2O_3 and BaO consist 1 to 2% of the washcoat. Cerium is normally present in high quantities in the washcoat in the form of CeO_2 (10 to 20%) and has multiple functions: stabilization of the washcoat layer and improvement of thermal resistance, enhancement of noble metal catalytic activity, promotion of the water gas shift reaction and an oxygen storage component. Iridium has remarkable activity for NO_x reduction under net oxidizing conditions but it tends to form volatile oxides. Ruthenium and Nickel have catalytic properties for NO_x reduction, as already mentioned, and nickel is also capable of suppressing H_2S formation.

A typical monolith has square cross section channels with inside dimensions of the order of 1mm separated by thin (0.1-0.15 mm) porous walls. The number of channels per cm^2 varies between 60 and 100, although even higher cell densities of the order of 200 channels per cm^2 have been demonstrated for metallic honeycombs. In case of ceramic monolith, a resilient mat is also provided between the housing and the substrate in order to protect the substrate from being damaged from vibrations or shocks.

2.5.1 Metallic or Ceramic Substrate

The substrate in a combustion catalyst system is usually a ceramic or metal honeycomb monolith. This type of monolith is generally made up of parallel channels, with the catalytic material deposited on the channel walls. Other configurations, such as crosswise corrugated (herringbone) structures are also possible, and may present advantages in combustions applications. Monolith reactors provide a substrate with high geometric surface area and low pressure drop (high throughput).

Ceramic substrates made of cordierite ($2MgO. 5SiO_2. 2Al_2O_3$) or mullite ($3Al_2O_3. 2SiO_2$), are capable of withstanding the high combustor ceramics such as silicon carbide, silicon nitride and aluminium titanate are stable up to 1600-1800˚C. The principal disadvantage of ceramic monoliths in gas turbine applications is their relatively low resistance to thermal shock. Most ceramics will fracture during the very rapid temperature drop that occurs after a turbine trip, when the turbine load is suddenly lost.

New types of ceramic composites with high thermal shock resistance have recently been developed that show some promise for gas turbine application. These composites consist of a ceramic matrix reinforced by ceramic fibers or platelets inside the matrix. The fibers pull out of the matrix during fracture to resist crack propagation.

Monoliths made of metal foils can also be used as substrates in combustion catalysts. The metal is generally an iron or nickel based steel containing small amounts of aluminium. The aluminium layer gives the alloy high oxidation resistance and is essentially self-healing as it arises from diffusion from the bulk material. It also provides good adhesion for the alumina washcoat.

Metal monoliths have a number of advantages compared to ceramics. They are more robust than ceramic monoliths and have excellent resistance to thermal shock, provided that the metal is not oxidized at high temperatures. The foil sheet that is used to manufacture the walls of the metal monolith is much thinner than the walls in a ceramic monolith (typically 0.05mm in the metal versus 0.25mm in the ceramic). The thinner walls give a larger surface to volume ration which produced a smaller pressure drop for a given mass transfer limited performance

2.5.2 Alumina Washcoat

The substrate is coated with a high surface area material, known as washcoat, which acts as a support for the active components. The support must be able to maintain its surface area under the operating conditions for the catalyst. However, most oxide supports sinter rapidly above 1200˚C and transform into low surface area materials. In particular, neither silica nor alumina, the traditional support materials, has the high temperature stability required for catalytic combustion. Alumina undergoes a phase change above 1000˚C from the high surface area γ-phase to the low surface area α-phase. Other oxides, such as Titania and zirconia, also undergo phase changes to low surface phases at relatively low temperatures. The washcoat should also have low volatility at the catalyst operating temperature. Many oxides have significant vapor pressures above 1200˚C, however, leading to loss of washcoat over time. Computer models give the percentage loss over time as a function of washcoat vapor pressure. These models show that for a catalyst operating at 1300˚C, 10 bar pressure and typical gas velocities present in a gas turbine combustor, 50% of a silica washcoat would be lost in 5h, whereas only 0.1% of an alumina washcoat would be lost in 1000h (*Book Review*, 2007).

The washcoat technology has become more and more sophisticated. Deploying the noble metals in different washcoat layers, or even on different support phases within the same layer, has contributed not only to the prevention of undesirable deactivation effects, but also to the optimization of the catalyst. Accordingly, layered washcoating is a common practice in current TWC technology. Preparation methods allowing control of the axial distribution of components have also been developed. Such is the case of the zone coating technology, currently used for segregating the different noble metals along the monolith channels. In this way, deactivation effects due to alloying phenomena are prevented (“Introduction_to_Three-Way_Catalytic_Conv,” n.d.).

2.5.3 Noble Metals

The catalyst should have high activity for the oxidation of methane and other hydrocarbons in natural gas in order to obtain ignition at temperatures close to the compressor outlet temperature. At the same time the catalyst should maintain high surface area at the operating temperature. The noble metals, particularly platinum and palladium, are the most active catalysts for methane combustion. Perovskites such as $LaCoO_3$ and Sr-doped $LaCoO_3$ have been investigated extensively as combustion catalysts but these oxides sinter rapidly at 1000˚C giving low surface area materials with a low activity on per gram basis.

2.6 Catalysis

The major objective to use catalyst is its working capability in most threating environment created at exhaust of automobiles. We have seen far reaching developments in the field of catalysis such as use of ceramic and metallic substrate to make washcoat more readily available to react, which gives higher surface area with lower weight drop and high resistance to temperature. γ- Alumina is most commonly used as washcoat, whereas at higher temperatures gamma alumina converter to its most stable form that is alpha-alumina which caused sintering effect. To avoid sintering effect some stabilizers like Si, La, Ba and many others are used to maintain high surface area even at high temperatures. The colossal achievement of catalysis technology is it's used in different applications to clean environment from exhaust pollutants. Today we are using catalyst to treat exhaust of power plants, eateries, business engines and many small plants. It was discovered in late 1970s that certain proportion of noble metals like Pt and Rh with suitable amount of washcoat and stabilizers gives better conversion efficiency of engine exhaust at stoichiometric. The key to advancement towards TWC innovation is to maintain air to fuel ratio in narrow window around stoichiometric. Now lambda or O_2 sensors are installed before catalyst to measure air to fuel ratio. In 1979 TWC technology was installed first time on vehicles. TWC contains 0.1±0.15% of precious metals (PT, Rh) and CeO_2 admixed with $\gamma -Al_2O_3$ (washcoat) to develop a high surface area, which is then applied to ceramic or metallic substrate (Rusu & Dumitriu, 2003).

Catalysis plays major role in our daily life. The importance of catalysis can be seen by its involvement in all four major sectors of world economy; petroleum industry, food industry, chemical industry and pollution control industry. In automobile industry catalyst are used for oxidation of hydrocarbons and carbon monoxide and also used in reduction of oxides of nitrogen. Catalysts are used in more than 90% industrial processes (Carberry, 2001). We are using catalysis from so many years. Catalyst technology was used first time in 1875 for production of sulfuric acid. Whole scenario was changed with the development of catalytic cracking somewhere in 1935-1940. Use of catalyst for emission reduction during 1970-1980 was major development in automobile industry (Yadav & Thathagar, 2002). Noble metals catalysts were deployed in automobiles for emission control. That chemical reaction in which addition of small amount of chemical substance increases the rate of reaction without being any chemical change to that substance is known as catalytic reaction and that substance which increases the rate of reaction is called catalyst (Farrauto & Heck, 1999).

Catalytic reactions are divided into two major types.

1. Homogeneous
2. Heterogeneous

2.6.1 Homogeneous

Chemical reaction in which reactants and catalyst both are in same phase is called as homogeneous catalytic reaction. In homogeneous catalytic reaction both reactants and catalyst will be present either in liquid or gas form. Most of industrial process involves liquid phase during chemical reactions. Major examples are enzyme catalyzed reactions and hydrolysis of ester.

2.6.2 Heterogeneous

That chemical reaction in which catalyst and reactants both are in different phases. For example, if reactants are in liquid or gas phase the catalyst will be in solid form. Production of sulfuric acid is major example of heterogeneous reaction where sulfur dioxide passes over solid vanadium oxide.

2.7 Alternative Materials

Cerium oxide was found to play a major role in automotive catalyst industry. Bera and Hegde et al in 2000, found its excellent redox abilities (Bera, Patil, Jayaram, Subbanna, & Hegde, 2000). They proposed to use cerium and titanium along noble metals. Ervan et al in 2015, use manganese coated copper to reduce carbon monoxide emission form a gasoline fueled engine. Alumina and silica containing zeolites were used to oxidize exhaust emissions, it gives around 55% reduction of carbon monoxide and hydrocarbons (Bandyopadhyay, Das, & Banerjee, 1999). Kalam et al, in 2009 developed cobalt coated titanium oxide catalyst for natural fueled engine (Kalam & Hassan, 2011). He compared newly made and original catalytic converter. According to his findings cobalt coated titanium oxide gives very good result. Ramesh et al, used copper nickel and chromium as a catalyst and get very satisfactory results for copper catalyst (Poola, Nagalingam, & Gopalakrishnan, 1994). In short all metal oxides such as Cu, Ni, Cr, Mn, Co and titanium oxides were tried to get best combination of non-noble metal based catalyst.

2.8 Exhaust Emission and Catalyst Technology Development

First time in 1974, a car equipped with catalyst was introduced in USA. It takes 9-10 years to be appeared on European roads until in 1993 they set emission standards. With the start of new century, more stringent emission standards were the reason to introduce platinum group metals in automobiles. This catalyst technology includes thermally stable catalyst, light off catalyst, electrically heated catalyst, selective catalyst and diesel particulate filters. This large amount of catalysts availability makes easier to meet emissions standards. Such advanced catalyst system along with suitable engine management can play major role in meeting tighter emission standards in future (Bosteels & Searles, 2005).

2.8.1 Exhaust Emissions and its Control

Hydrocarbons are produced in exhaust when fuel do not burn or burn partially. Hydrocarbons are major source of ground level ozone as they react with nitrogen oxides in presence of sunlight. Ozone results in eye irritation, damage lungs and dangerous for our lungs also. Moreover, hydrocarbons are considered major source for cancer. Incomplete burning of fuel results in production of carbon monoxide which is extremely dangerous to humans as it decreases the flow of oxygen. Higher temperature and pressure in engine results in production of oxides of nitrogen which are precursors for production of ground level ozone and also contribute to ozone. Automobiles are backbone of our transportation system. Automobiles population is increasing day by day along with human’s population. It is also seen a huge increase in number of two wheelers on roads which are contributing very much in air pollution. Unburnt hydrocarbon (HCs), carbon monoxide (CO) and oxides of nitrogen (NOx) are main pollutants present in automobiles exhaust system. In spite of a lot of efforts have been made to reduce emissions from automobiles, it been observed that alternatives are far behind. That is why further improvement in engine technologies and in catalysis are the only way to reduce emissions from automobiles (Sharaf, Engineering, & Academy, 2013).

2.8.2 Cold Start Problem

Cold start emissions are considered major source of pollutant. The other problem associated with cold start emissions is its duration, due to very complex chemical reactions and change in ambient temperature it is very difficult to find out exact duration. Literature shows that emissions had been reduced in large amount but cold start emissions are still a big problem for catalytic converter developers. Engine and catalytic converter mostly takes 3-4 minutes to be warmed up and remain warmed after turn off up to 40-45 minutes depending upon ambient temperature. One solution to cold start emissions is electrically heated catalyst which required large batteries to be deployed in automobiles. Startup of engine even after soak period of three minutes' results in 10 % more emissions than per mile emissions (Palander, 2016).

2.9 Design Criteria of Catalytic Converter

Future exhaust emission legislation can be met through substantial improvement in effectiveness of the exhaust gas after treatment systems and engine management systems. For catalytic converter it is necessary to differentiate between cold start and effective at operating temperatures. The greater potential of emissions reduction depends upon cold start emissions which are more than 80% within operating cycle. Designing of catalytic converter depends upon following factors; heat capacity, surface area, cell density, wall thickness, catalyst diameter, coating and catalyst length (Bruk, 1995).

2.9.1 Heat Capacity

The heat capacity of a catalytic converter support is essentially determined by the construction material (ceramic, metal), cell density (catalytic surface area) and structural wall thickness. To get higher efficiencies heating with maximum effectiveness and utilization of exhaust energy, the lowest possible thermal capacity is required.

2.9.2 Diameter of Catalytic Converter

The diameter of catalytic converter similarly influences the light-off behavior and flow distribution. With decreasing diameter, the heat capacity of the front surface, and thus zone where the catalytic activity begins. Hence the smaller the diameter of the catalytic converter more quickly it will heat up.

2.9.3 Length of Catalytic Converter

The length of catalytic converter exerts direct influence upon flow distribution. The noticeably more uniform flow in the longer support is a result of back pressure. The back pressure increases in the channel increases in proportion to the catalyst length and flow velocity. It’s been concluded that catalyst length influence the flow distribution.

2.9.4 Substrate

We have seen far reaching developments in the field of catalysis such as use of ceramic and metallic substrate to make washcoat more readily available to react, which gives higher surface area with lower weight drop and high resistance to temperature.

2.9.5 Coating

The coating influence both heating up behavior of the catalyst by increasing the heat capacity, as well as the light off behavior through light off temperature specific to coating.

2.10 Hypothesis

The objective of this study was to develop a low cost catalytic converter. That is why metal oxides such as titanium dioxide (TiO_2) and cobalt oxide (Co_3O_4) along with aluminum oxide washcoat were selected. Both catalyst materials are not very much expensive and easily available also as compared to noble metals. It was found from literature review that titanium oxide has the capacity to oxidize hydrocarbons and carbon monoxide and cobalt was selected as reducing agent. Gamma alumina was selected as washcoat to enhance the surface area.

CHAPTER 3

Materials and Methodology

3.1 Introduction

In this chapter, all the chemicals used and synthesis methods have been explained along their references.

3.2 Chemicals used in this Synthesis

In this research work, many chemicals were used in different molar weight and molar ratios. Titanium dioxide (TiO_2, 99% pure, Panreac) and cobalt nitrate ($Co(NO_3)_2 . 6H_2O$, 98% pure, Panreac) was as a precursor to obtain pure cobalt oxide (Ganesh et al., 2012). Gamma alumina (γ-alumina) was used as a wash-coat material, which was obtained by heating of aluminum sulfate ($Al_2O_3 (SO_4)_3 . 18H_2O$, 99.4% pure, BDH) at 900°C (Hosseini, Niaei, & Salari, 2011). Sodium silicate solution (Na_2O_3Si, extra pure, Merck) and sodium metabisulphite ($Na_2S_2O_5$) was used as a binding material (Kalam & Hassan, 2011). Table 2, reviews list of used chemicals.

3.3 Synthesis

3.3.1 Preparation of Titanium dioxide (TiO_2) Nano-Particles

300 ml of distilled water was taken in a 500ml glass beaker. 300 gm of titanium dioxide (TiO_2) was weighed on an electrical weighing balance. This 300grams of titanium dioxide (TiO_2) was added gradually to 500ml beaker where 300ml of distilled water is already stirring at 450rpm on a magnetic stirrer, let it stirred for 24 hours at room temperature. After 24 hours, magnetic stirrer was stopped and beaker was placed at room temperature for settling for next 24 hours.

Then, this settled solution was placed in an oven at 105°C for 12 hours. After 12 hours, when the water was completely vaporized, all the powder was poured in a mortar and pestle. This powder was crushed and mixed with mortar and pestle for 5 minutes. Then, this crushed powder was transferred to a china dish, which was placed in a muffle furnace at 400°C for 6 hours. After calcination, china dish was placed in a desiccator to cool down its temperature to room temperature. These Nano-particles were then saved at room temperature for further usage as shown in figure 3.1.

Figure 3.1Preperation of Titania Nanoparticles

3.3.2 Preparation of 10% HCL Solution

The Hydrochloric acid (HCL, 35.4 % pure, Merck), available in wastewater laboratory was 35.4 % pure. Dilution formula ($C_1V_1 = C_2V_2$) was used to measure the amount of acid required to make 500ml of 10% pure HCL. After calculations, 28.24ml of water was taken in a 1000ml glass beaker and beaker was filled up to 500ml with distilled water.

3.3.3 Preparation of Washcoat

Gamma alumina (*γ*-alumina) was synthesized from aluminum sulfate ($Al_2O_3\ (SO_4)_3$. $18H_2O$, 99.4% pure, BDH). Aluminum sulfate was taken in a china dish and dried at 105°C for 12 hours, then calcined in an electrical muffle furnace for 2 hours at 900°C. Confirmation of gamma alumina (*γ*-alumina) was done by different characterization techniques (Hosseini et al., 2011).

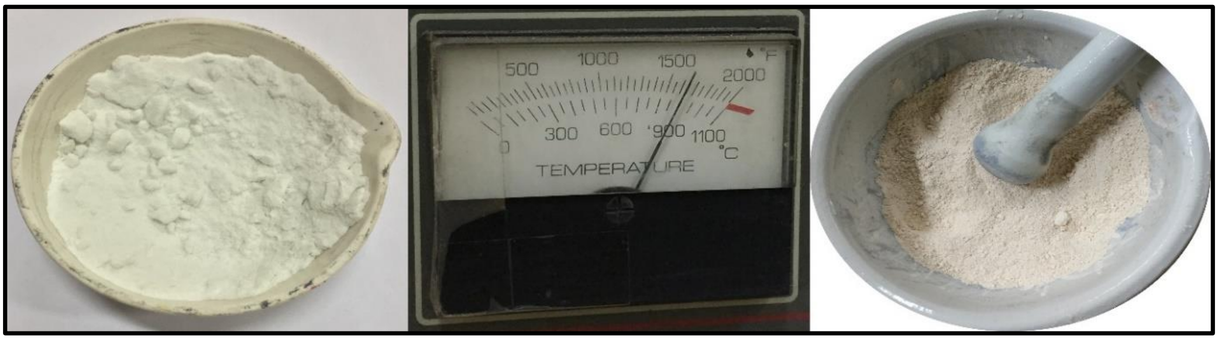

Figure 3.2 Preparation of Gamma Alumina

3.4Pre-treatment of Substrate

Metallic substrate woven wire mesh was cleaned manually and then was dipped in 10 % HCL solution for 30 minutes. And after rinsing them with deionized water they were dried in oven at 105'C for 2 hours.

3.5Preparation of Slurry

270grams of sodium silicate solution was taken in a 1000ml glass beaker and put it on magnetic stirrer at 450rm at room temperature. 3grams of sodium metabisulphate was weighed on an electrical weighing balance and added in already stirring beaker. 5, 10 and 15grams of gamma alumina powder was added to three different beakers, then slurry was stirred at 500rpm for 12 hours at room temperature. 21.75 grams of cobalt nitrate were taken in a china dish. Deionized water was used to make a solution of cobalt nitrate, which was then impregnated to 30grams of titanium dioxide nano-particles powder. Which was dried for 12 hours in oven at 105°C. Then it was calcined for 4 hours at 550°C in a muffle furnace. That is how Co_3O_4/TiO_2 powder was obtained. This black powder was added gradually into beaker where binding materials with washcoat were already mixing. This slurry was then stirred for 2 hours at 550rpm as shown

Figure 3.3 Preparation of Slurry

Figure 3.4Preparation of Slurry

3.6 Dipping of Wire Mesh

Each and every circular shaped wire mesh was dipped into slurry for 5 minutes. The excess amount of catalyst was removed with a blower. Then, these circular shaped and catalyst coated wire meshes were placed in oven at 105°C for 12 hours to evaporate water. After 12 hours, these wire meshes were transferred to muffle furnace at 550°C for 4 hours. After calcination process, wire meshes were placed in desiccator. After cooling, wire meshes were fixed on a metallic rod and encapsulated in casing of catalytic converter.

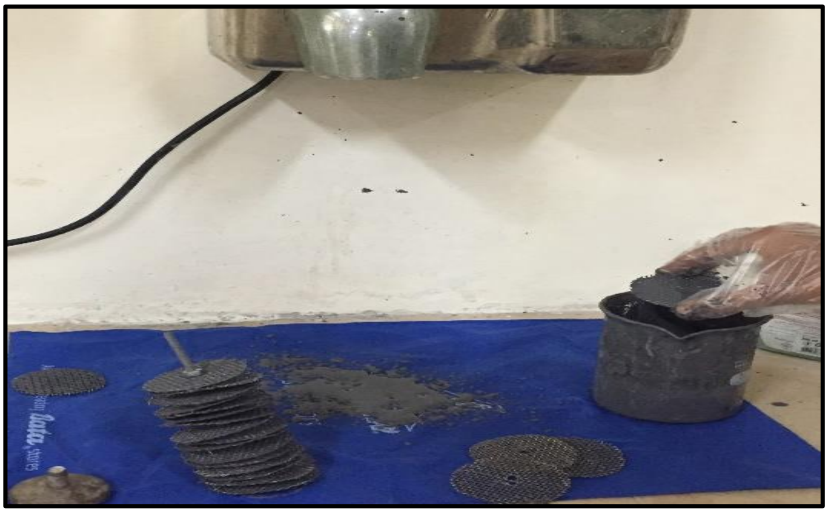

Figure 3.5Dipping of wire mesh

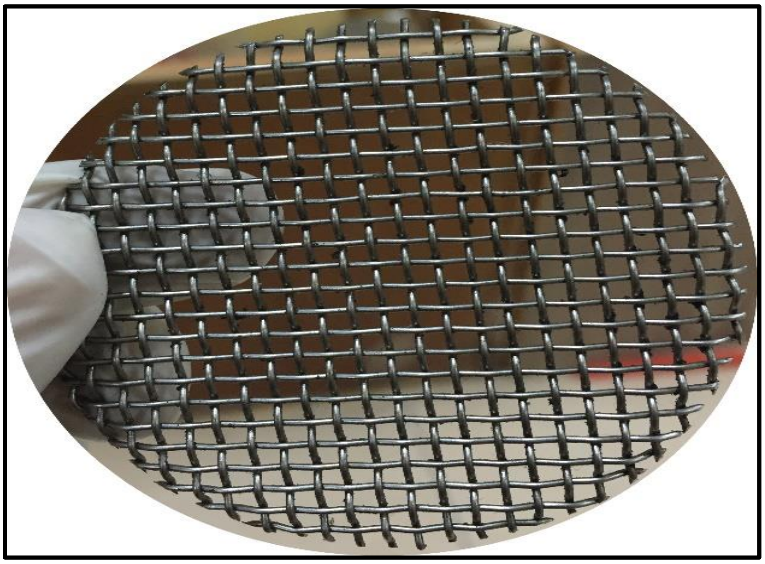

Figure 3.6 Wire mesh before dipping

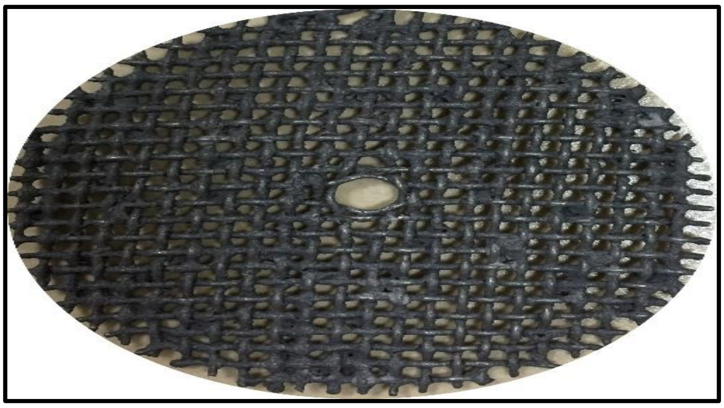

Figure 3.7Dipped wire mesh

Table 2 List of chemicals

Sr #	Chemical Name	Chemical Formula	Percent Purity	Company Name
1	Tinanium (IV) Oxide	TiO_2	99 %	Panreac
2	Cobalt (II) Nitrate 6-hydrate	$Co(NO_3)_2.6H_2O$	98%	Panreac
3	Aluminium Sulphate 18-hydrate	$Al_2(SO_4)_3.18H_2O$	99.4 %	BDH
4	Sodium Silicate Solution	Na_2O_3Si	Extra pure	Merck
5	Sodium meta bisulphare	$Na_2S_2O_5$	98 %	BDH

3.7 Catalytic Converter Fabrication

3.7.1 Catalytic Converter Chamber

To avoid the danger of rust to catalytic converter chamber Sus-304 material was selected to manufacture catalytic converter. Sus-304 sheet was going under folding, cutting, grinding and welding to be a catalytic converter chamber. A catalytic converter chamber of length 6 inches and diameter of 2.5 inches was developed with a flung in the middle, which we can use to open the chamber whenever needed as shown in figure 3.8.

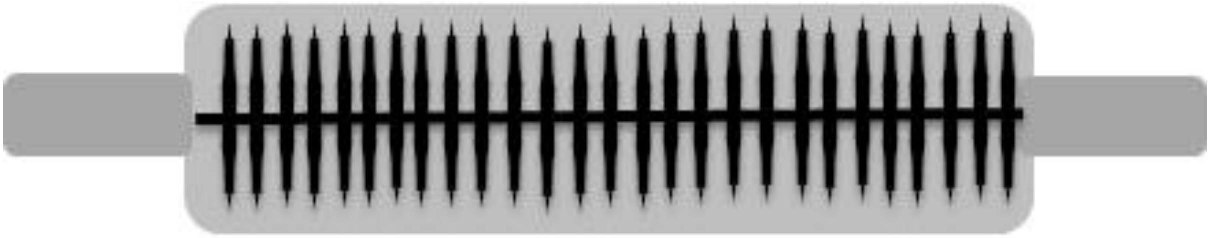

Figure 3.8Catalytic converter chamber

3.7.2 Substrate

Metallic wire mesh of mesh size 10 of Sus-304 grade was used. Mesh size 10 gives 100 number of holes per square inch. First of all, metallic wire mesh cut into round shape of 2.5 inches' diameter.

3.8Test Vehicle

The newly developed three-way catalytic converter (TWC) was tested on Honda CG 125 bike. The specifications of the engine are mentioned in table 3.

Table 3 Specifications of Engine

Engine	4-Stroke OHV cooled by air
Bore	56.5 x 49.5 mm
Dimension (Length x width x height)	1911 x 732 x 1016 mm
Starting	Kick start
Petrol Capacity	9.2 Liter
Final Driver	Roller Chain
Dry Weight	99KG

3.9 Experimental Method for Emission and Performance Evaluation

3.9.1 Catalytic Converter Testing on Engine

Coating of wire meshes and all the fabrication work was complete in air and noise lab IESE, NUST, Islamabad. The test vehicle was 4 stroke Honda CG 125 bike, which gasoline fueled. A few modifications were done with exhaust silencer of bike for emission evaluation. Silencer was cut from half of its length, a connector was welded with argon welding, so that catalytic converter could be mounted on exhaust pipe.

3.9.2 Emission Test Laboratory and Equipment

Newly developed catalytic converter was tested in a commercial car repairing workshop at sector G-10, Islamabad.

3.9.3 Testing Conditions

Gasoline fueled test engine was operated at 2000, 4000, 6000 and 8000 rpms, same time analyzers detection probe was inserted in exhaust pipe. Different concentrations of carbon monoxide (CO) and hydrocarbons (HCs) was recorded without and with installation of catalytic converter. Setup flow diagrams with and without catalytic converter are shown in figure 3.9 and figure 3.10.

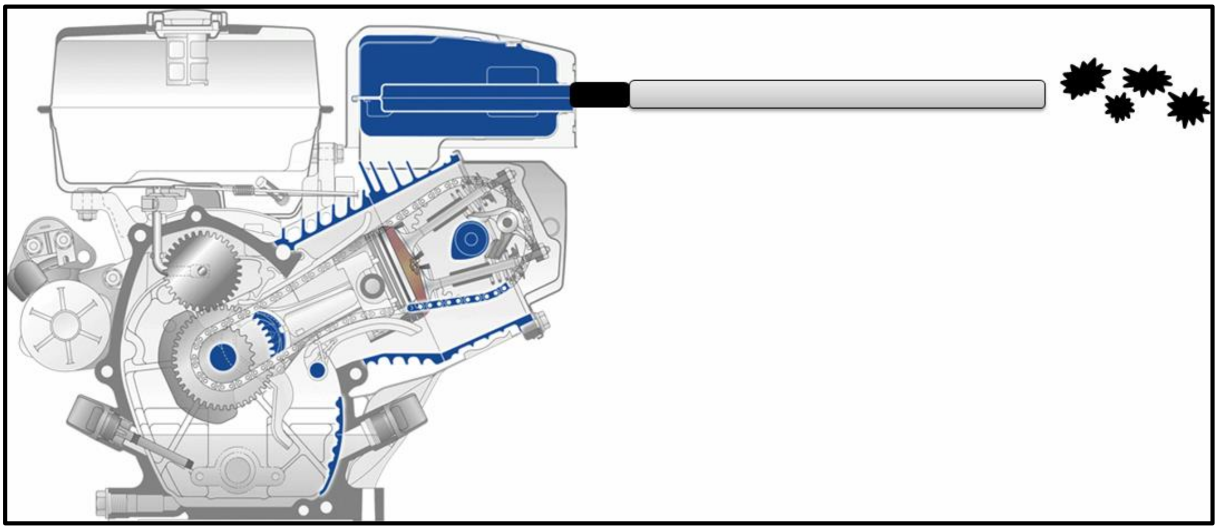

Figure 3.9Setup flow diagram without CC

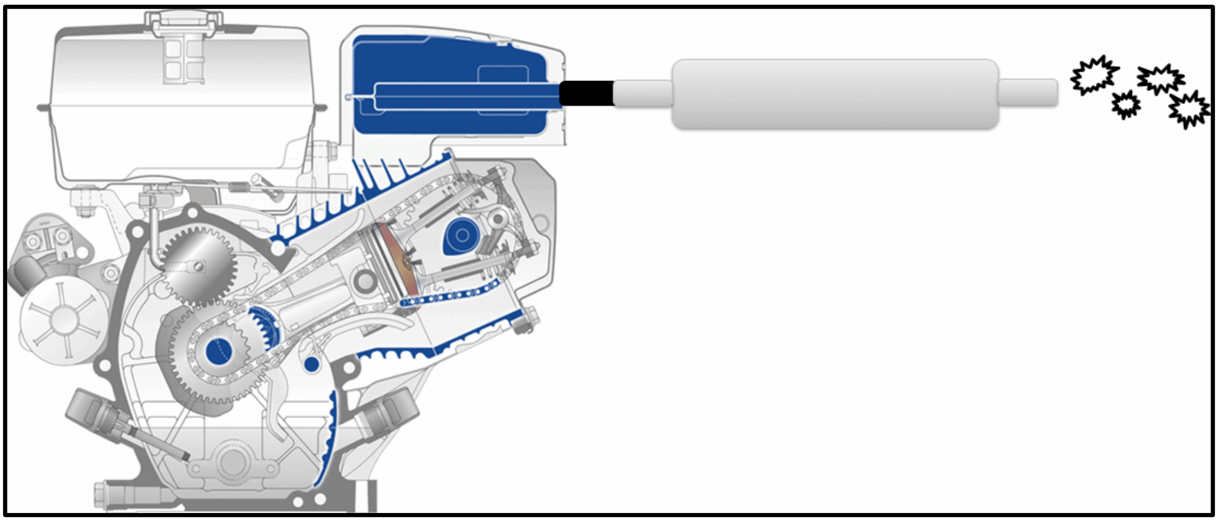

Figure 3.10 Setup flow diagram with CC

CHAPTER 4

Results and Discussion

4.1 **Characterization**

4.1.1 X-ray Diffraction (XRD)

XRD technique was also used to identify the presence of Co_3O_4 and TiO_2. The results obtained from XRD are shown in figure 4.1 and figure 4.2. X-pert High score software was used to interpret the XRD results and to identify crystalline phases. The XRD patterns confirmed the formation of pure γ-alumina, Co_3O_4 and TiO_2. Literature shows occurrence of main peaks of γ-alumina are at 31.9º, 37.7º, 39.4º, 45.8º, 50.2º, 57º, 60.8º, 66.8º, 70.3º, 71.5º, 76º, 79.4º and TiO_2 are at 25.2º, 36.9º, 37.7º, 38.57º, 48º, 51.9º, 53.8º, 55.1º, 62.1º, 62.6º, 68.7º, 70.2º, 74º, 75º, 76º, 78.6º which were in accordance with the sample results, presented in figure 7 (Hamadanian & Majedi, 2010). Major peaks of Co_3O_4 were also identified at 31.26º, 36.84º, 44.80º and 65.22º, which confirms the presence of anatase form of Co_3O_4 and TiO_2 (Yang, Hyeon, & Ham, 2007). The results were found in line with literature. By using Scherrer equation crystalline sizes were measures which were 22nm, 39nm and 54nm for γ-alumina, Co_3O_4, TiO_2 respectively. The dots have been placed over identified peaks which are matched with peaks in literature (figure 4.1, 4.2).

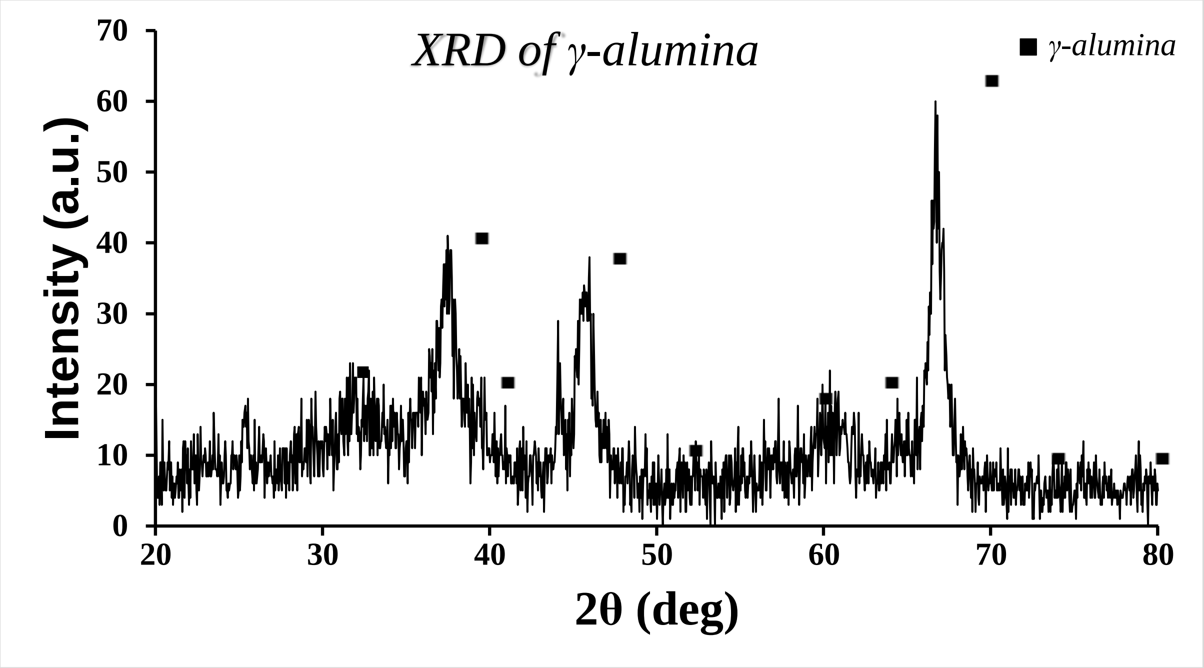

Figure 11 XRD graph of gamma alumina

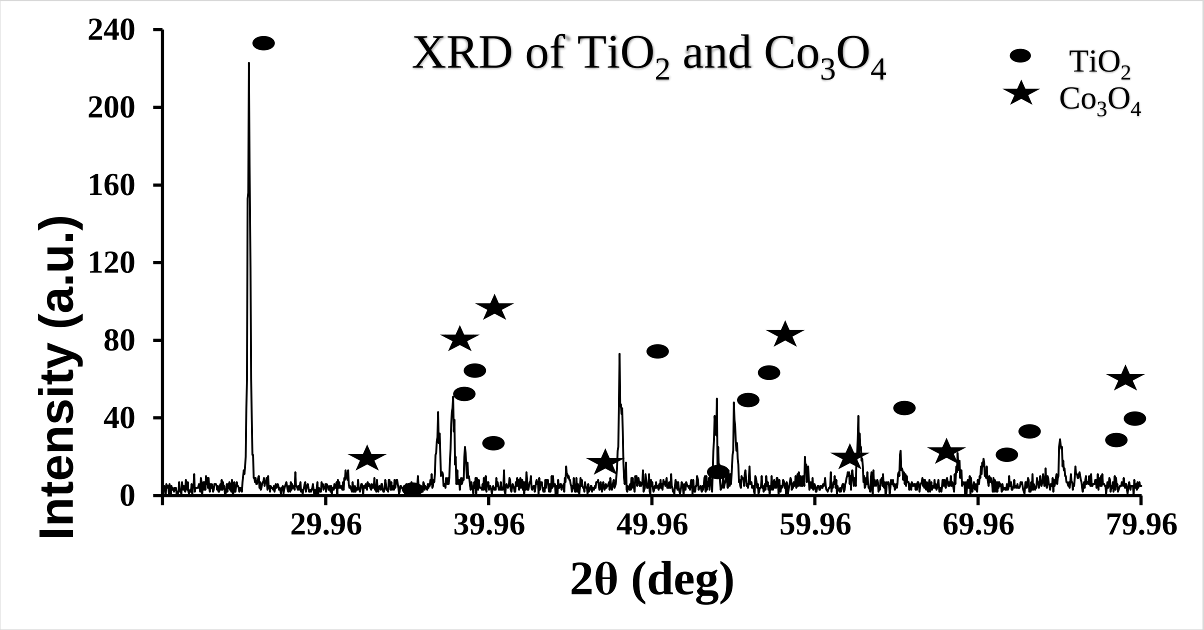

Figure 12 XRD graph of Titania & Cobalt

4.1.2 Scanning Electron Microscopy (SEM)

SEM images of γ-alumina and Co_3O_4/TiO_2 added catalyst are presented in figure 8. Figure 8a, shows porous structure of γ-alumina which depicts its larger surface area. In figure 8b, 8c and

8d, SEM images of alumina (27%, 42% and 53% respectively) added to Co_3O_4/TiO_2 are presented. There is no significant difference seen in the SEM images in Fig. 8b, 8c and 8d. However, the morphology revealed by SEM show uniform distribution of washcoat material along with catalyst matrix.

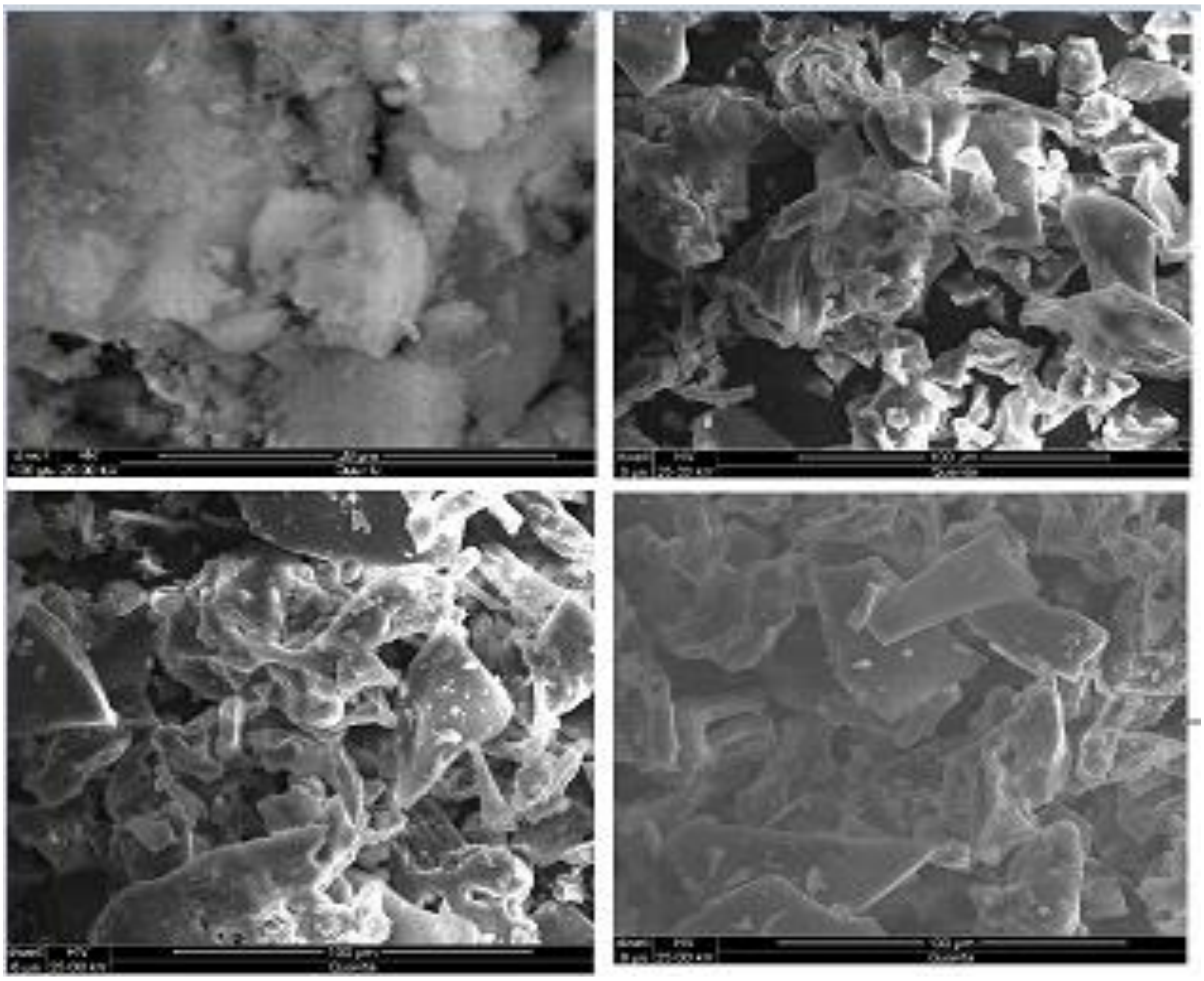

Figure 13 SEM images of Gamma alumina and catalyst (a-Gamma alumina, b- 25% washcoat Co_3O_4/TiO_2, c- 40% washcoat Co_3O_4/TiO_2, d- 55% washcoat Co_3O_4/TiO_2)

4.1.3 BET Surface Area Analysis

The table shows BET results of pure alumina sample and three Co_3O_4/TiO_2 samples with varying γ-alumina loadings. The samples were heated in a nitrogen atmosphere at rate of 10°C, from 10-600°C. Nitrogen adsorption and desorption isotherm data following Quantachrome Autosorb Automated Gas Sorption Method was used to estimate surface area and pore volume. The pore volume was determined at a relative pressure (P/P_0) of 2. The prepared samples were degaussed at 150°C for 3 hours before measurements. The pore size distributions in a prepared sample were verified by a BJH (Barett Joyner-Halenda) model from the adsorption branch of the nitrogen isotherms (Potdar, Jun, Bae, Kim, & Lee, 2007), (Akarmazyan, Panagiotopoulou, Kambolis, Papadopoulou, & Kondarides, 2014). BET results as shown in table 4 the formation of γ-alumina and also an increase in surface area of catalyst with washcoat amount.

Table 4 BET Surface area

Sample	**Average pore Diameter (A^o)**	**Average pore Volume (cm^3/g)**	**BET Surface Area (m^2/g)**
15g Al_2O_3 + $Co_3O/_4TiO_2$	21.622	0.064277	156.9963
10g Al_2O_3 + Co_3O_4/TiO_2	21.538	0.090708	147.1406
5g Al_2O_3 + Co_3O_4/TiO_2	22.098	0.091775	143.6403
Al_2O_3	21.099	0.117085	192.2297

4.2 **Results and Discussion**

Figure 4.4 shows CO (%) emissions vs engine speed (rpm) from 2000 to 8000 rpm with and without catalytic converter. Initially, data was collected with catalytic converter attached and then without catalytic converter. In figure 4.4, it is clear that initially at 2000rpm and 4000rpm, the catalytic converter without washcoat gives better conversion efficiency. But at higher rpms of 6000rpm and 8000rpm the converter containing washcoat works better. Trends were found similar in both CO and HCs (figure 4.5) conversion. It can be attributed to the fact that at higher rpms, temperature of exhaust gases rises up and at the same point, due to high surface area of γ-alumina washcoated catalyst, active metals are more exposed to exhaust. Results show that newly developed non noble metal based catalytic converter reduces up to 90% CO and 70% of HCs from the exhaust. It is clear from the results that with the increase in washcoat quantity, a significant increase in conversion efficiency has been observed as compared to pure catalyst. Catalytic converter based on pure catalyst works better at lower rpms (lower temperature) but at higher rpms the washcoat containing catalytic converter gives better results. The Co_3O_4/TiO_2 catalyst was a major contributor towards conversion efficiency. But with the increase in washcoat amount the lesser amount of catalyst was also capable of better conversion.

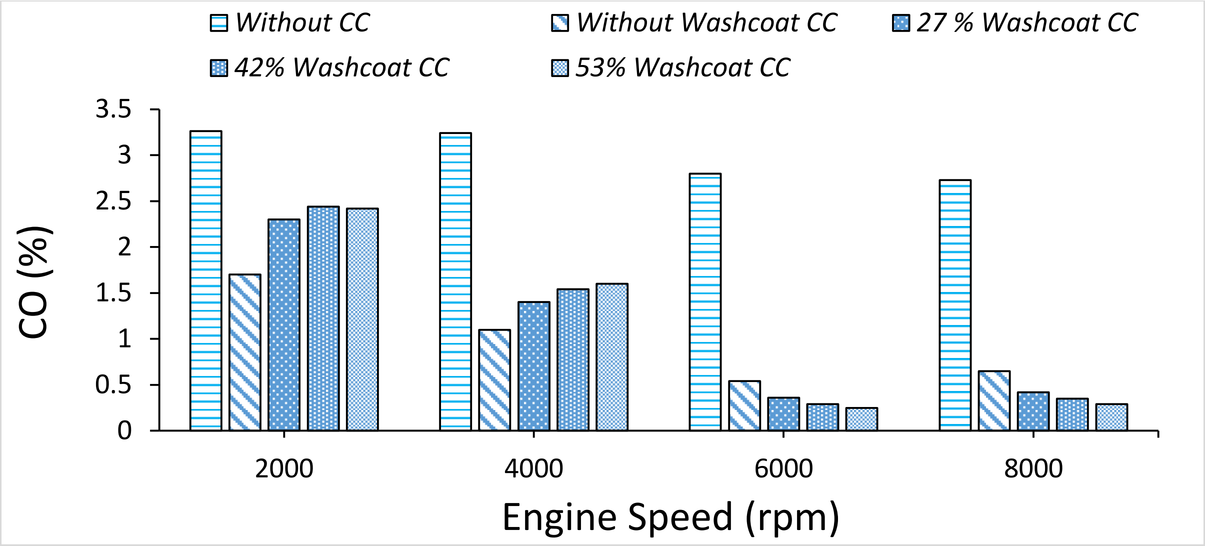

Figure 14 CO vs Engine speed graph

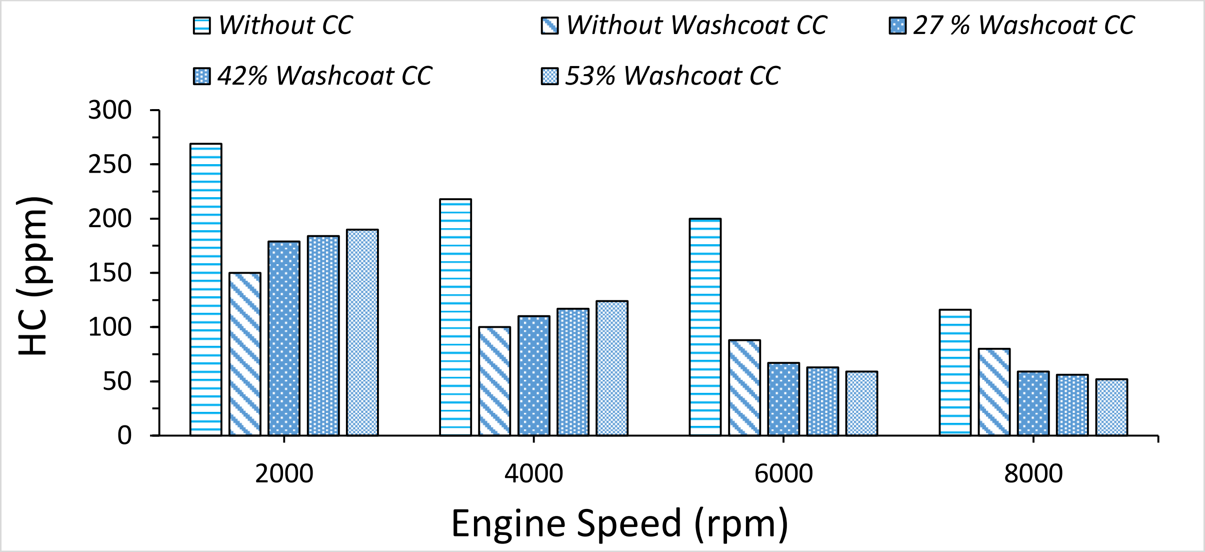

Figure 15 HC vs Engine speed graph

CHAPTER 5

Conclusion and Recommendations

5.1 Conclusions

This study was carried out to investigate the effect of washcoat loading over conversion efficiency of Co_3O_4 /TiO_2 based catalytic converter. Characterization of the catalyst showed that gamma alumina plays significant role in changing surface area of material which resulted in better conversion efficiencies. However, different techniques could be used for washcoat coating over the substrate. The washcoat properties strongly depend upon its synthesis and its coating techniques. Gamma alumina gives excellent adhesion over metallic substrate. Its thermal stability was also found satisfactory. The best application of this type of catalytic converter is smaller gasoline fueled engine, in which temperature does not rise too high to be favorable for excessive NOx production. However, the addition of some stabilizer is proposed to be investigated so that it can also be capable of being mounted over bigger engines and work as TWC.

5.2 Recommendations

1. Different coating techniques can be used for coating of substrate so that loading could be varied.
2. Different compositions of catalyst can be tested to find out optimum catalyst for better conversions.
3. The conversion efficiency of catalytic converter could be tested on the basis of exhaust temperature.

4. The application of this catalytic converter to higher rpm engine could also possibly gives better results.

REFERENCES

Akarmazyan, S. S., Panagiotopoulou, P., Kambolis, A., Papadopoulou, C., & Kondarides, D. I. (2014). Applied Catalysis B : Environmental Methanol dehydration to dimethylether over Al 2 O 3 catalysts. *"Applied Catalysis B, Environmental," 145*, 136–148.

Bandyopadhyay, U., Das, D., & Banerjee, R. K. (1999). Reactive oxygen species : Oxidative damage and pathogenesis. *Current Science*, *77*(5).

Bera, P., Patil, K. C., Jayaram, V., Subbanna, G. N., & Hegde, M. S. (2000). Ionic Dispersion of Pt and Pd on CeO 2 by Combustion Method : Effect of Metal – Ceria Interaction on Catalytic Activities for NO Reduction and CO and Hydrocarbon Oxidation. *Journal of Catalysis*, *301*, 293–301.

Bertelsen, B. B. I. (2001). The U . S . Motor Vehicle Emission Control Programme. *Platinum Metals Review*, (2), 50–59.

Bokde, K. K., & Waghmare, A. V. (2013). Cold Start Performance Enhancement of Motorcycle Catalytic Convertor by Latent Heat Storage System. *International Journal of Innovative Research in Science, Engineering and Technology*, *2*(2), 372–377.

Book Review. (2007). http://doi.org/10.1002/aoc.1247

Bosteels, B. D., & Searles, R. A. (2005). Exhaust Emission Catalyst Technology. *Platinum Metals Review*, (I), 27–36.

Brück, R., Diewald, R., Hirth, P., & Kaiser, F. W. (1995). Design criteria for metallic substrates for catalytic converters (No. 950789). *SAE Technical Paper.*

Carberry, J. J. (2001). Chemical and catalytic reaction engineering. *Courier Corporation*.

Cook, J. A., Sun, J., Buckland, J. H., Kolmanovsky, I. V, Peng, H., & Grizzle, J. W. (2006). Automotive Powertrain Control — A Survey. *Asian Journal of Control*, *8*(3), 237–260.

Evaluation, R., & Calorimeter, S. (1974). Rapid Evaluation, *13*(1), 45–47.

Farrauto, R. J., & Heck, R. M. (1999). Catalytic converters : state of the art and perspectives. *Catalysis Today*, *51*, 351–360.

Flachsbart, P. G., Howes, J. E., Mack, G. A., Rodes, C. E., Flachsbart, P. G., Howes, J. E., … Mack, G. A. (2016). Carbon Monoxide Exposures of Washington Commuters Carbon Monoxide Exposures of Washington Commuters. *Air & Waste Management Association*, *0630*(August).

Ganesh, I., Gupta, A. K., Kumar, P. P., Sekhar, P. S. C., Radha, K., Padmanabham, G., & Sundararajan, G. (2012). Preparation and characterization of Co-doped TiO 2 materials for solar light induced current and photocatalytic applications. *Materials Chemistry and Physics*, *135*(1), 220–234.

Ghasemi, A. (2010). Archive of SID A New Approach for Inlet Diffuser of Automotive Catalytic Converter Considering Conversion Effi- ciency of Pollutants. *The Journal of Engine Research*, *18*, 42–50.

Hamadanian, M., & Majedi, A. (2010). Iranian Chemical Society Sol-Gel Preparation and Characterization of Co / TiO 2 Nanoparticles : Application to the Degradation of Methyl Orange. *Journal of Iranian Chemical Society*, *7*(July), 52–58.

H. Bauer. *Kraftfahrtechnisches Taschenbuch (in German), Robert Bosch GmbH*. Vieweg, Brauschweig, 23rd edition, 1999.

Hosseini, S. A., Niaei, A., & Salari, D. (2011). Production of γ -Al 2 O 3 from Kaolin. *Open Journal of Physical Chemistry*, *2011*(August), 23–27.

Introduction_to_Three-Way_Catalytic_Conv. (n.d.).

Issn, J., & Online, F. A. (2007). A Review of Transport and Urban Air Pollution in Pakistan. *Journal of Applied Science, Environment and Management*.

Kalam, A., & Hassan, M. H. (2011). Design , Modification and Testing of a Catalytic Converter for Natural Gas Fueled Engines. *Arab Journal of Science and Engineering*, 677–688.

Kašpar, J., Fornasiero, P., & Hickey, N. (2003). Automotive catalytic converters : current status and some perspectives. *Catalysis Today, 77*, 419–449.

Palander, T. (2016). Environmental benefits from improving transportation efficiency in wood procurement systems. *Transportation Research Part D, 44*(August), 211–218.

Poola, R. B., Nagalingam, B., & Gopalakrishnan, K. V. (1994). Devices to improve the performance of.

Potdar, H. S., Jun, K., Bae, J. W., Kim, S., & Lee, Y. (2007). Synthesis of nano-sized porous g -alumina powder via a precipitation / digestion route. *Applied Catalysis A: General*, *321*, 109–116.

Rajadurai, S., Jacob, S., Serrell, C., Morin, R., Kircanski, Z., & Industries, A. C. S. (2006). Wiremesh Substrates for Oxidation , TWC and SCR Converters, *2*, 97–105.

Rusu, A. O., & Dumitriu, E. (2003). Destruction of Volatile Organic Compounds by Catalytic Oxidation. *Environmental Engineering & Management Journal (EEMJ)*, *2*(4), 273–302.

Sekhar, R. C. (2015). Design and Fabrication of Rechargeable Catalytic Converter for IC Engine. *International Journal & Magazine of Engineering, Technology, Management and Research, 2*(July), 113–119.

Sharaf, J., Engineering, M. T. A., & Academy, B. S. F. (2013). Exhaust Emissions and Its

Control Technology for an Internal Combustion Engine, *3*(4), 947–960.

Shelef, M., & McCabe, R. W. (2000). Twenty-five years after introduction of automotive catalysts: what next? *Catalysis Today*, *62*(1), 35–50.

Sideris, M. 1998. Methods for Monitoring and Diagnosing the Efficiency of Catalytic Converters: *A Patent-Oriented Survey*, 260–263. New York: Elsevier Science BV.

States, U., & Office, P. (1964). than "?, 1–4.

Sun, J., Kolmanovsky, I., Cook, J. A., & Buckland, J. H. (2005). Modeling and Control of Automotive Powertrain Systems : A Tutorial. *American Control Conference*, 3271–3283.

Ullah, U., Waldram, S. P., Bennett, C. J., & Truex, T. (1992). Monolithic reactors: mass transfer measurements under reacting conditions. *Chemical Engineering Science*, *47*(9-11), 2413–2418.

Wang, H., Chen, C., Zhang, Y., Peng, L., Yang, T., Guo, H., … Zhang, J. (2015). catalysts for hydrocarbon combustion. *Nature Communications*, *6*, 1–6.

Wang, T., Soltis, R. E., Logothetis, E. M., Cook, J. A., & Hamburg, D. R. (1993). Static characteristics of ZrO2 exhaust gas oxygen sensors (No. 930352). *SAE Technical Paper*.

Yadav, G. D., & Thathagar, M. B. (2002). E sterification of maleic acid with ethanol over cation-exchange resin catalysts. *Reactive & Functional Polymers*, *52*, 99–110.

Yang, W., Hyeon, M., & Ham, S. (2007). Effect of calcination temperature on the low-temperature oxidation of CO over CoO x / TiO 2 catalysts. *Catalysis Today*, *123*, 94–103.

Yao, Y. F. Y. (1974). The oxidation of hydrocarbons and CO over metal oxides: III. Co3O4. *Journal of Catalysis*, *33*(1), 108-122.

Zeldovich, Y. B. (1946). The oxidation of nitrogen in combustion and explosions. *Acta Physicochim. URSS*, *21*(4), 577-628.