Building A Cheaper Catalyst for Automotive Exhaust Emission Control

By

Julie M Pardiwala

10MCHE14

DEPARTMENT OF CHEMICAL ENGINEERING

AHMEDABAD - 382481

May, 2012

Building A Cheaper Catalyst for Automotive Exhaust Emission Control

Major Project

Submitted in partial fulfillment of the requirements

For the Degree of
Master of Technology in Chemical Engineering

By
JULIE M PARDIWALA
(10MCHE14)

Guided By
Prof FEMINA J PATEL

DEPARTMENT OF CHEMICAL ENGINEERING
AHMEDABAD-382481

Declaration

This is to certify that

1. The thesis comprises my original work towards the degree of Master of Technology in Environment Process Design at Nirma University and has not been submitted elsewhere for a degree.
2. Due acknowledgement has been made in the text to all other material used.

Julie M Pardiwala

Undertaking for the Originality of the work

I, Julie Pardiwala, 10MCHE14, give undertaking that the major project entitled “Building a Cheaper Catalyst for Automotive Exhaust Emission Control” submitted by me, towards the partial fulfillment of the requirements for the degree of master of technology in Environment Process Design of Nirma University, Ahmedabad is the original work carried out by me and I give assurance that no attempt of plagiarism had been made. I understand, that in the event of any similarity found subsequently with any published work or any dissertation work elsewhere, it will result in severe disciplinary action.

Julie M Pardiwala
Signature of student
Date:
Place:

Endorsed by
Signature of Guide

Certificate

This is to certify that the Major Project entitled "**Building a Cheaper Catalyst for Automotive Exhaust Emission Control"** submitted by **Ms Julie M Pardiwala (10MCHE14)**, towards the partial fulfilment of the requirements for the degree of Master of Technology in Chemical Engineering of Nirma University of Science and Technology, Ahmedabad is the record of work carried out by her under my supervision and guidance. In my opinion, the submitted work has reached a level required for being accepted for examination. The results embodied in this major project, to the best of my knowledge, haven't been submitted to any other university or institution for award of any degree or diploma.

Prof Femina J Patel
Guide, Assistant Professor,
Department of Chemical Engineering,
Institute of Technology,
Nirma University, Ahmedabad.

Dr J P Ruparelia
Professor and PG Co-ordinator,
Department of Chemical Engineering,
Institute of Technology,
Nirma University, Ahmedabad

Dr S S Patel
Professor and Head,
Department of Chemical Engineering,
Institute of Technology,
Nirma University, Ahmedabad

Dr K Kotecha
Director,
Institute of Technology,
Nirma University, Ahmedabad

Examiners :

Abstract

The uses of automobiles increase exponentially day to day. With fast increasing vehicle population, enormous amount of obnoxious emission like CO, HC, NO_x and particulate matter are being emitted. These pollutants have hazardous effect on environment and human health. Thus, the use of catalysts for purifying exhaust gases is absolutely necessary and indispensable in every vehicle Automotive three way catalysts (TWCs) is use to reduce emission from internal combustion engine since last 25 years.

Efforts are being carried out for the replacement of supported noble metals in catalytic converter because of the drawbacks of noble metals in practical application including high cost, volatilization and sintering at high temperature. Perovskite have been considered as promising alternatives to precious metals acting as effective TWCs due to their low cost, high thermal stability and diverse physicochemical properties, promote noble metal dispersion, increase thermal stability of the alumina support, promote the water gas shift and the steam reforming reactions, store and release oxygen under conditions uctuating between oxidizing and reducing.

The project is to illustrate the technology for abatement of exhaust emissions by analysis the current understanding of TWCs, the specific role of the various components, the achievements and the limitations. It also discusses Perovskite catalyst, occurrence, various synthesis methods, their characterization, Catalytic activity, usage of perovskite in automobiles, advantages over conventional catalyst.

Keywords-Automotive three way catalytic convertor (TWCs) , Perovskite , synthesis methods , characterization, Catalytic activity.

Acknowledgements

My deepest thanks to my guide **Prof Femina J Patel,** Assistant Professor, Chemical Engineering Department, Institute of Technology, Nirma University for introducing me to the world of catalysis. It was only due to her valuable guidance, cheerful enthusiasm and ever friendly nature that I was able to do my research work in a respectable manner.

I take opportunity to express deep and sincere sence of gratitude towards **Dr Sanjay S Patel**, Head of Chemical Engineering Department, Institute of Technology, Nirma University.

My deep sense of gratitude to **Dr J P Ruparelia** , Professor and PG-Coordinator of Department of Chemical Enginering, Institute of Technology, Nirma University, Ahmedabad for an exceptional support and continual encouragement throughout part one of the Major project.

I would like to thanks **Dr K Kotecha**, Honourable Director, Institute of Technology, Nirma University, Ahmedabad for his unmentionable support, providing basic infrastructure and healthy research environment.

I would also thank my Institution, all my faculty members in Department of Chemical Engineering and my colleagues without whom this project would have been a distant reality. Last, but not the least, no words are enough to acknowledge constant support and sacrifices of my family members because of whom I am able to complete the rest part of my dissertation work successfully.

Julie M Pardiwala

10MCHE14

List of Figures

List of Tables

Contents

Chapter 1

Introduction

1.1 Introduction to Pollution

Vehical Emission and air pollution

Human activities generate three broad sources of air pollution: stationary or point, mobile, and indoor. Air pollution generated from mobile sources such as automobiles contributes major air quality problems in urban and industrialized areas. About 50 million cars are produced every year, and over 700 million cars are used worldwide. In developing countries especially in the rural area, indoor air pollution from using open fires for cooking and heating may be a serious problem. Industries, power plants etc. are the cause of stationary air pollution [1,2].

Although urban air quality in developed countries has been controlled to some extent during the past two decades, in most of the developing countries it is worsening and becoming a major threat to the health and welfare of people and the environment. In our modern society, quality of life is greatly measured by the amount of consumption of electricity or by the use of car. Electricity generation and operation of vehicles mostly use fossil fuel

The global vehicular population excluding motorcycles increased from about 250 million in 1960 to 671 million in the year 2000 [3].

Nitrogen oxides emissions from motor vehicles which cause acid rain and photochemical smog, leading to ecological damages and respiratory diseases has become one of the most important issues for environmental protection. Depletion of the ozone layer are also attributable in part to emissions from motor vehicle

The different air pollutants due to vehicles can have effects at all the three levels-local (e.g., smoke affecting visibility, ambient air, noise etc.), regional (such as smog, acidification) and global (i.e., global warming). The vehicles besides being the prominent source of air pollutants also account for a number of external effects, such as congestion, noise, accidents, road wear and tear, and ‘barrier effects’. According to the World Health Organization (WHO), 4 to 8 % of deaths that occur annually in the world are related to air pollution and of its constituents, the WHO has identified SPM as the most sinister in terms of its effect on health

The major pollutants emitted from gasoline fueled vehicles are CO, HC, NO_x[3].

Due to incomplete combustion in the engine, there are a number of incomplete combustion products. Typical exhaust gas composition at the normal engine operating conditions is carbon monoxide (CO, 0.5 vol. %); unburned hydrocarbons (HC, 350 vppm); nitrogen oxides (NO_x, 900 vppm); hydrogen (H_2, 0.17 vol. %); water (H_2O, 10 vol.%); carbon dioxide (CO_2,10 vol.%); oxygen (O_2, 0.5 vol.%). HC, CO and NO_x are the major exhaust pollutants. HC and CO occur because the combustion efficiency is <100 % due to incomplete mixing of the gases and the wall quenching effects of the colder cylinder walls. The NO_x is formed during the very high temperatures ($>1500\,^{\circ}$ C) of the combustion process resulting in thermal fixation of the nitrogen in the air which forms NO_x. Because of the large vehicle population, significant amounts of HC, CO and NO_x are emitted to the atmosphere. The formation of ground level ozone occurs as a result of a chemical reaction between HC and NO_x and sunlight. When stagnant air masses linger over urban areas, the pollutants are held in place for long periods of time. Sunlight interacts with these pollutants, transforming them into ground level ozone. Ozone is a major component of smog which damages vegetation and reduces atmospheric visibility

Volatile organic compounds (VOCs) are an important class of air pollutants, emitted from many industrial processes and transportation activities. Catalytic combustion is one of the most promising technology for the destruction of VOCs, due to its definitive character and save of energy. VOCs can be, in fact, oxidized over a catalyst at temperatures much lower than those of thermal oxidation [4,5,6,7,8].

1.2 Pollutant Emission from Motor Vehicles

After the spark ignites the compressed fuel air mixture, the flame propagates across the combustion chamber and burns the charge in engine cylinder. Nitric acid and carbon monoxide are formed in the bulk of burned gases during combustion reaction. Nitric oxide NO is formed in the high temp. burning gases inside the engine cylinder primarily through oxidation of nitrogen present in the inducted air. Nitrogen oxide contain mainly NO and small amount of nitrogen dioxide NO_2.

Partially in the SI engine. CO is due to deficiency of O_2in fuel air mixture that leads to incomplete oxidation of fuel. With decreases in the air to fuel ratio below the strochometry ratio formation of CO increase sharply During expansion stroke, piston travels downward rapidly cooling the combustion products by expansion, freezing the reaction that involves NO and CO formation [9,10,11].

The concentration of NO and CO thus are frozen at much higher value then expected from the chemical equilibrium consideration. The fuel air mixture being rich during cold starting, engine warm up and transients like accelerations. The fuel air mixture being rich during cold starting, engine warm up and transients like acceleration, engine operation during these modes contributes significantly to CO emission

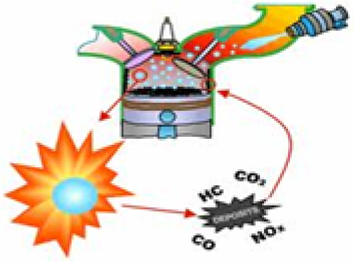


Figure 1.1: Formation of Pollutant in combustion engine

As the flame approcheas to cold combustion chamber wall it is quenched leaving a very thin layer of unburn fuel air mixture. The flame is unable to propogate in narrow passage called “CERVICES” in the combustion chamber. Therefore the mixture in the cervice b/w piston crown and cylinder wall, around spark plug and cylinder head gasket is left unburned. Adsorption of fuel vapor by the lubricating oil layer on the cylinder wall and combustion chamber deposits is another source of unburned fuel emission. Presence of liquid fuel in combustion chamber during cold start to contribute to unburn H/C emissions. As the pressure inside the engine cylinder decreases due to expansion, the unburn mixture from the cervices expand in the cylinder and some of get entrained by the bulk of gases. A large fraction of the unburn H/C that are re-entrained in the combustion chamber during the expansion stroke mixes with the burned gases and partially or completely oxidized before the exhaust gases leave the engine. Finally the exhaust valve open combustion product along with CO, NO_x and part of entrained H/C form quench layer and cervices leaves the engine and are exhausted. From the above it is seen that NO, CO are formed in the bulk gases and involve combustion chemistry and chemical kinetics. On the other hand, H/C emission result from flame quenching at the combustion chamber wall and cervices and form adsorption desorption in lubricating oil film and combustion chamber deposites that involves boundary layer aerodynamics, mixing and oxidation. Air-fuel ratio is one of the most imp parameter that influences the engine exhaust emission. Emission from vehicles especially automobiles contribute significantly two third of air pollution in the urban area [10,11,12,13].

1.3 Automotive Engine

What is an Engine?

The word Engine comes from the Latin word ingenium which means ’ability’. Engine is machinery.

Generally a combustion engine is defined as a machine that produces power (mechanical) by the combustion of substance like water or a fuel.

Engines are classified into various categories based on the type of cycle they use, the layout, the energy source used, the cooling mechanism employed or its use. Based on the layout, there are two types of Engines.

Internal Combustion Engine

An engine is called an Internal Combustion Engine, If the combustion of a fuel like petrol takes place inside it, in a chamber. The oxidizer used for combustion is usually air. The gases produced as a result of combustion are high temperature and pressure. These gases exert pressure on components such as a piston which moves over and produces energy (mechanical). E.g. Petrol Engine.

External Combustion Engine

An External Combustion engine is one in which the energy is externally applied on a non combustible fluid like pressurized/hot water, liquid sodium etc. Here these fluids are heated in an external chamber like boiler and steam is used to drive the engine. E.g. Steam Engine.

Based on the source of energy, internal combustion engines are classified as,

- Petrol Engines
- Diesel Engines

Petrol Engine is again categorized into,

- 2 Stroke Engine
- 4 Stroke Engine

Spark-ignition and Diesel engines are the two most common engines. Other types of engines are Rotary (Wankel) Engines, Gas-Turbine (Brayton) Engines, Steam (Rankine) Engines, Stirling Engines, Electric and Hybrid Vehicles

Two and Four Stroke Engines

- In any vehicle, the power plant is the engine.
- An engine converts the chemical energy of the fuel to mechanical energy.
- If the combustion of the fuel takes place inside the engine, it is called ‘Internal Combustion Engine’. If the combustion takes place outside the engine, it is called ‘External Combustion Engine’.
- In automobiles, Internal Combustion Engine is used.
- The movement of the piston from the TDC to BDC or vice-versa is defined as a stroke.
- If the process of combustion is completed in two strokes of the piston, it is called a 2-stroke engine. If completed in four strokes, it is called a 4-stroke engine [14,15].

1.3.1 Working of a Spark-Ignition (Petrol) Engine

As the name suggest the Four Stroke Petrol Engine uses a cycle of four strokes and petrol as the fuel. Each cycle includes 2 rotations of the crankshaft and four strokes, namely,

1. Intake Stroke
2. Compression Stroke
3. Combustion Stroke also called Power Stroke
4. Exhaust Stroke

For 4-stroke gasoline engine

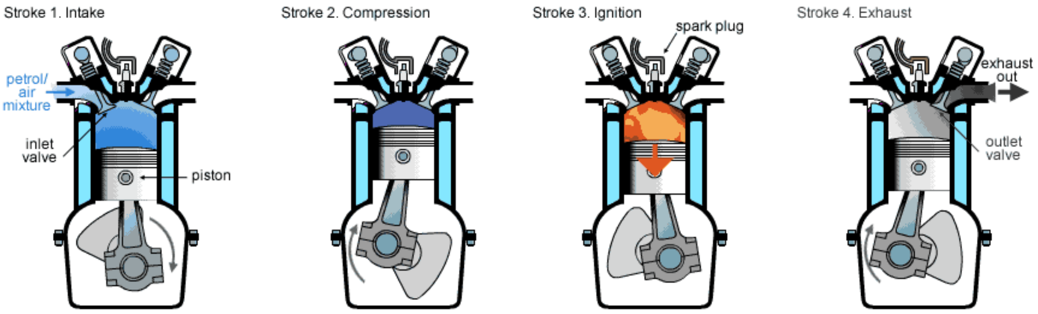


Figure 1.2: Intake stroke / Compression stroke / Combustion / Exhaust stroke /

1. Intake stroke

This is the first stroke. In this stroke, the piston moves from TDC towards BDC. Just before the commencing of this stroke, the inlet valve begins to open. Thereby, as the stroke begins, the valve is completely open. Due to the low pressure created in the cylinder, the fuel-air mixture flows in through the valve. Before this, the mixture is mixed in correct proportions in the carburetor. Now, a fuel-injector does the work of the carburetor, and with much precision.

2. Compression stroke

In this stroke, the air-fuel mixture is compressed by a piston-stroke. This compression occurs according to the compression ratio of the engine, which is the ratio of the volume of the mixture when piston is at BDC to when piston is at TDC. Compressing the mixture results in better mixing of the air and fuel. It also raises the temperature before reaction. Higher the compression ratio, better the performance of the engine. For gasoline engine, compression ratio varies between 6:1 to 9:1, and for diesel engine, it is 12:1 to 22:1.

3. Power stroke

Just after the compression stroke comes in the power stroke. In this stroke, the fuel-air mixture is ignited with the help of a well-timed spark. For this, we use a spark plug. As the mixture gets ignited, the reaction occurs with a blast. This blast forces the downward stroke of the piston. The piston is attaches to a crank-shaft. The chemical energy of the fuel gets converted to mechanical energy in this phase

4. Exhaust stroke

The fourth stroke is the exhaust stroke in which the piston moves from BDC to TDC. As a result, the exhaust present in the cylinder is forced out of the cylinder due to pressure increase. This exhaust is controlled using the exhaust valves [14,15].

1.4 Pollutants Emissions from Motor Vehicles

The different air pollutants due to vehicles can have effects at all the three levels local (e.g., smoke affecting visibility, ambient air, noise etc.), regional (such as smog, acidification) and global (i.e., global warming). The vehicles besides being the prominent source of air pollutants also account for a number of external effects, such as congestion, noise, accidents, road wear and tear, and 'barrier effects'. According to the World Health Organization (WHO), 4 to 8 % of deaths that occur annually in the world are related to air pollution and of its constituents, the WHO has identified SPM as the most sinister in terms of its effect on health. The major pollutants emitted from gasoline fueled vehicles are CO, HC, NO_x. Gasoline motor vehicles are a major source of O_3(GL) which is formed by the oxidation of VOCs in tailpipe emissions. Ground level ozone is a principal component of smog which damages vegetation and reduces atmospheric visibility. Emission from vehicles especially automobiles contribute significantly two third of air pollution in the urban area.

Main sources of emission from automobiles

The amount of pollutants that an automobile emits depends upon number of factors, including the design and operation (ideal, acceleration etc.) of the hydrocarbons emitted by a car with no controls, the exhaust gases accounts for roughly 65 %, evaporation from the fuel tank and carburetor for roughly 15% and blow by or crank case emission (gases that escape around the piston rings) for about 20 %. Carbon monoxide, nitrogen oxides and lead compounds are emitted almost exclusively in the exhaust gases.

The emission produced by a vehicle fall into three basic categories

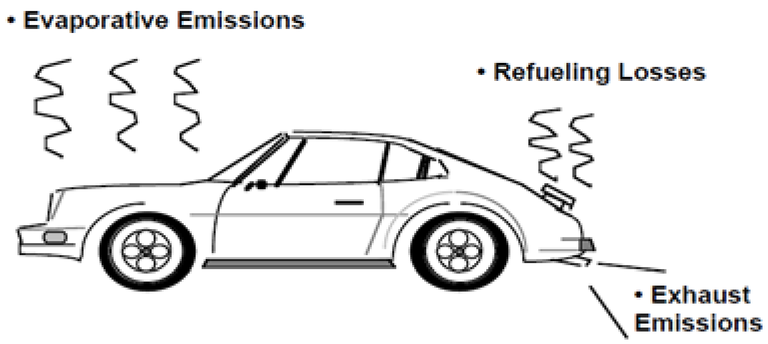


Figure 1.3: Pollutants Emissions from Motor Vehicles

1) Evaporative Emissions
2) Crankcase Emission (also called running loss emissions)
3) Exhaust Emission

1) Evaporative Emissions

Evaporative emissions are HC vapors lost constantly and directly to the atmosphere due to volatile nature of petrol, mainly from the fuel line's, fuel tank and carburetor depending upon fuel composition, engine operating temperature and ambient temperature. Volatile organic compounds (VOC) also escape into the air through fuel evaporation. Evaporative losses can account, on hot days, for a majority of the total VOC pollution.

Evaporative emissions occur in several ways:

Running Losses The hot engine and exhaust system can vaporize gasoline while the vehicle is running.

Hot soak (Cooling Down) (Losses from the carburetor) The engine remains hot for a period of time after the vehicle is turned off, and gasoline evaporation continues when the car is parked while cooling down.

Diurnal Emissions (Emissions while Parked and Engine is Cool) Even when the vehicle is parked for long periods of time, gasoline evaporation occurs as the temperature rises during the day.

Refueling - Gasoline vapors escape from the vehicle's fuel tank while the tank is being filled

2) Crankcase Emission (also called running loss emissions)

"Crankcase emissions" means substances emitted directly to the atmosphere from any opening leading to the crankcase of a motor vehicle engine. Crankcase emissions are unburnt or partially burned fuel components that, under pressure, escape from the combustion chamber, pass the pistons and enter the crankcase. This mixture is called blow-by. The main constituent of blow-by emission is HCs.

If uncontrolled, it may constitute 13-25 % of total emissions. Since, diesel engines compress only air, blow-by contain very low levels of pollutants

3) Exhaust Emission

The products of burning fuel in the vehicle's engine, emitted from the vehicle's exhaust system. It is tailpipe emission. Exhaust emissions occur during two modes:

Cold Start - Starting and driving a vehicle the first few minute's results in higher emissions because the emissions control equipment has not yet reached its optimal operating temperature.

Running Exhaust Emissions Pollutants are emitted from the vehicle's tailpipe during driving and idling after the vehicle is warmed up.

Automotive exhaust is the major source constituting about 60% of the total emission. Exhaust products are a result of combustion in the engine under high temperatures and pressure. The combustion process results in emission of wide range of pollutants from simple to carcinogenic substances such as

(1) Hydrocarbons (Unburnt)

(2) Carbon monoxide

(3) Oxides of nitrogen (NO$_x$)

(4) Lead oxides

(5) Particulate matters e.g. lead, carbon, alkaline earth compounds, iron oxide, tar, oil, mist

(6) Traces of aldehydes, esters, ethers, sulphur dioxide, peroxides, ketones benzene (C_6H_6), 1, 3 butadine, Poly Aromatic Hydrocarbons (PAH), metal dust, asbestos fibre, dioxin, furon, ammonia, organic acids , chlorofluorocarbons (CFCs) etc. which are released from the tail pipe while a vehicle is operating.These emissions vary with: the fuel ratio, spark timings, and engine operating conditions

Emissions from Spark-Ignition (Petrol) Engine Vehicles

Gasoline has two problems when burned in car engines. The first problem has to do with smog and ozone in big cities. The second problem has to do with carbon and greenhouse gases. The internal combustion engine is not perfect. In the process of burning the gasoline, it also produces. Carbon monoxide - a poisonous gas, Nitrogen oxides-the main source of urban smog .Unburned hydrocarbons, the main source of urban ozone

Gasoline-powered engines are of two types 4 strokes and 2 strokes. The exhaust consists of CO, HC, NO_x, SO_2 and partial oxides of aldehydes, besides particulate matter, lead salts account for the larger chunk of all pollution from gasoline-run vehicles [14].

Table 1.1: Emission from Gasoline Vehicles

Source	**Amount of Emissions (%)**		**Remarks**
	4-Stroke	**2-Stroke**	
Crankcase blow by	20	0	Carbureted air-fuel mixture & combustion fuel under pressure escape combustion chamber past engine piston and ring and enter crank base to be discharged into atmosphere through vents
Evaporative Emissions	20	3	Fuel vapors lost to the atmosphere from tanks and carburetor
Exhaust Emissions	60	97	Exhaust gases emitted with pollutants through the tailpipe

Table 1.2: Emission norms for passenger cars

Gasoline	CO	HC	HC + NO_x	NO_x	Reference
1991	14.3-27.1	2.0-2.9	-	-	-
1996	8.68-12.4	-	3.00-4.36	-	-
1998	4.34-6.20	-	1.50-2.18	-	-
2000	2.72-6.90	-	0.97-1.70	-	Euro-1
2005	2.2-5.0	-	0.5-0.7	-	Euro-2
2010	2.3, 4.17, 5.22	0.20, 0.25, 0.29	-	0.15, 0.18, 0.21	Euro-3
	1.0, 1.81, 2.27	0.1, 0.13, 0.16	-	0.08, 0.10, 0.11	Euro-4
	2.2	-	0.5	-	Bharat stage-II
	2.3	-	0.35(combined)	-	Bharat stage-III
	1.0	-	0.18(combined)	-	Bharat stage-IV

1.5 Control Technology For Gasoline-Fuled Vehicle (SI Engine)

The emission control techniques can be broadly grouped into the following types:

- Engine design parameters
- Engine add-ons enable reduction formation or burning pollutants within the engine
- Operations factors
- Exhaust treatment

1.5.1 Engine design parameters

These emissions are influences by such factors as gasoline formulation, engine emission ratio, combustion chamber size and shape, crevice volume, spark timing, fuel-air equivalence ratio, fuel system design and engine temperature control.

1.5.1.1 Air/Fuel ratio, mixture preparation engine compression ratio

CO emissions are almost totally dependent on the air/fuel ratio while HC and NO_x emissions are depending on other engine design parameters. CO and HC emissions can be reduced by increasing the air/fuel ratio. HC emissions reduced until flame speed becomes so low that pockets of unburned fuel are exhausted before full combustion occurs or in extreme cases if misfire occurs. Conversely NO_x emissions increases as air/fuel mixtures are enleaned up to the point of maximum or peak thermal efficiency. Beyond this point, further enleanment can result in lower NO_x emissions rates

1.5.1.2 Engine compression ratio

Use of a lower compression ratio was expected to reduce HC emissions due to decrease in surface/volume ratio of the combustion chamber and a proportionately lower crevice volume. Lower engine compression ratio also results in higher exhaust gas temperature that promotes oxidation of both the CO and unburned HC in the exhaust system. Another advantage of low compression ratio is lowering of the peak combustion temperature resulting in a lower formation of NO_x. The disadvantage of lower compression ratio is reduction in engine efficiency and increase in CO_2 emissions.

1.5.1.3 Cylinder size and combustion chamber shape

Larger cylinders have a lower surface to volume ratio. The ratio of crevice to cylinder volume is also lower for the larger cylinder when other design parameters remain unchanged. These would reduce HC emissions. The pent-roof types of combustion chambers are commonly used in the modern automotive spark ignition engines.

1.5.1.4 Fuelling system

Fuel injection systems have ability to control air-fuel ratio more precisely than the carburetors. With the use of fuel injection systems, precise control of air-fuel ratio using feedback exhaust oxygen sensor, improved fuel atomization and mixture distribution among the cylinder is achieved. A better dynamic response of fuel injection system to fuel demand during transient operation compared to carburetor is another advantage.

1.5.1.5 Variable valve timing and lift

In the current production of engines, 4 valves per cylinder have become almost a norm. This not only provides a large area of valve ports but also make central location of the spark plug possible when compared to the 2 valves per cylinder configuration. It results in improved combustion and performance of the engine.

1.5.1.6 Variable swept timing

Engine could be operated at reduced swept volume and consequently at higher mean effective pressures, fuel economy and emission benefits would be obtained. To obtain variable swept volume by varying piston stroke requires complicated mechanical design. However, the variable and effective engine swept volume could be obtained by deactivating the valve operation of one or more cylinders.

1.5.1.7 Ignition timing

As ignition timing is delayed (retarded), peak combustion temperatures tend to be reduced thereby lowering NO_x and peak thermal efficiency. By allowing combustion to continue after the exhaust port is (resulting in higher exhaust temperatures), oxidation of unburned hydrocarbons is greater and overll hydrocarbon emissions are reduced. The HC emissions generally decreases as the spark is retarded at constant power.

1.5.1.8 Combustion chamber deposits

HC exhaust emissions are significantly enhanced with accumulation of chamber deposits. The quantity of deposits affects the CR of the engine by lowering exhaust temperatures and reducing clearances volume and exhaust emission increases. Uniform distribution of deposits is likely to provide more void space for the absorption of unburned HC during combustion thereby raising exhaust emission level.

1.5.2 Engine add-ons to enable reduction in formation or burning of pollutants within the engine

Tighter emissions standards have required that more specific attention be given to the treatment of vehicle exhaust emissions. Commonly used technologies to control exhaust emissions include recirculation of exhaust gases, electronic control of engine performance, exhaust after treatment devices and advanced combustion technique.

1.5.2.1 Positive Crankcase Ventilation

The purpose of the positive crankcase ventilation (PCV) system is to circulate blow by gas (unburned hydrocarbon vapor) in the crankcase back to the air-fuel mixture entering the cylinder. Blow by gas is the air-fuel mixture that leaks between the pistons and the cylinder walls during engine operation. Due to pollution concerns, blow by gases containing unburned HC can no longer be vented to the air. A PCV valve is located between the crankcase and the intake manifold. As pressure from the blow by gases builds in the crankcase, the PCV valve is pushed open. Vacuum in the intake then draws the blow by gases into the intake manifold where they are mixed with air entering the cylinders. The PCV system is needed to keep pressure from blow by gases from building to dangerous levels in the crankcase. Fresh air to replace the blow by gases that are drawn into the intake manifold is supplied through the air cleaner. Excessive blow by gases in the crankcase can cause the engine oil to break down, thereby damaging the moving parts in the engine that are not properly lubricated.

1.5.2.2 Evaporative Emission Control

There are two main sources of evaporative emissions via the fuel tank and the carburetor. Insulation of the fuel tank to reduce temperature, sealed and pressurized fuel systems and vapour collection systems have been explored to reduce tank emissions. The fuel tank is fitted to the vapour liquid separator which is in form of a chamber on the fuel tank. Vapour from the fuel tank goes to the top of the separator where the liquid gasoline is separated and sent back to the fuel tank through the fuel return pipe. A vent hole is connected by a tube to the canister. Fuel vapours from the float chamber flow through the vent hole and the tube to the canister. The canister adsorbs the fuel vapors and stores them. Hydrocarbons are left in the canister due to the process of adsorption and air leaves from the canister into atmosphere.

1.5.2.3 Exhaust Emission Control

The exhaust recirculation systems utilize up to 15 % of the exhaust stream to recycle into the intake manifold with the fresh air-fuel mixture. The exhaust gases (diluents) dilute the fresh charge and lower the peak combustion temperature by slowing flame speed and absorbing some combustion heat and NO_x formation. The exhaust gas recirculation (EGR) system is designed to reduce the amount of oxides of nitrogen (NO_x) created by the engine during operating periods that usually result in high combustion temperatures. NO_x is formed in high concentrations whenever combustion temperature exceed aboot 2500 °F.

The EGR system reduces NO_x production by recirculating small amounts of exhaust gases into the intake manifold where it mixes with the incoming air/fuel charge. By diluting the air/fuel mixture under these conditions, peak combustion temperature and pressure are reduce resulting in an overall reduction of NO_xoutput.

EGR flow should match the following operating conditions: High EGR is required when combustion temperature are typically very high. Low EGR is required when low speed and light load conditions. NO EGR flow should occur during conditions when EGR operation could adversely affect engine operating efficiency or vehicle driveability [14,15,16].

The function of each system is shown in this table

Table 1.3: Control System and its Function

Sr. no.	System	Function
1	Positive Crankcase Ventilation	Reduces HC
2	Evaporative Emission Control	Reduces evaporated HC
3	Exhaust Gas Recirculation	Reduces NO_x

1.6 Sources and Effects of Common Air Pollutants

According to the World Health Organization (WHO), 4 to 8 % of deaths that occur annually in the world are related to air pollution and of its constituents, the WHO has identified SPM as the most sinister in terms of its effect on health.

The major pollutants emitted from gasoline fueled vehicles are CO, HC, NO_x and SO_2 while pollutants from diesel-fueled vehicles are particulate matter (including smoke), NO_x, SO_2, PAH [16,17].

Table 1.4: Pollutant and its Health and Environment Effect

Pollutant	Anthropogenic Sources	Health Effects	Environmental Effects
Nitrogen Oxides (NO_x)	Burning of gasoline, natural gas, coal, oil. (Cars are a major source of NO_x)	Lung damage, respiratory illnesses, ozone (smog) effects.	Ozone (smog) effects; precursor of acid rain which damages trees, lakes, and soil; aerosols can reduce visibility. Acid rain also causes buildings, statues, and monuments to deteriorate.
Carbon Monoxide (CO)	Burning of gasoline, natural gas, coal, oil.	Reduces ability of blood to bring oxygen to body cells and tissues.	Health Effects
Sulfur Dioxide (SO_2)	Burning of coal and oil, especially high-sulfur coal; industrial processes (paper manufacturing, metal smelting).	Respiratory illness, breathing problems, may cause permanent damage to lungs.	Precursor of acid rain, which can damage trees, lakes, and soil; aerosols can reduce visibility. Acid rain also causes buildings, statues, and monuments to deteriorate.

1.7 Catalytic Convertor

Catalytic converter :The current technology to convert simultaneously all three pollutants into innocuous materials is referred to as three way catalysis . The important role of automotive catalysts in catalytic converter contain precious metals palladium (Pd), platinum (Pt) and rhodium (Rh) is widely recognized for the conversion of three pollutant-emissions, such as carbon monoxide (CO) into CO_2, nitrogen oxides (NO_x) to nitrogen and unburned hydrocarbons (HC) into CO_2 and water in engine exhaust gases (Car's tail pipe) . The basic function of the catalyst in a catalytic converter is to perform the following reaction in the automobile exhaust at lower temperature than a thermal processes [18,19,20].

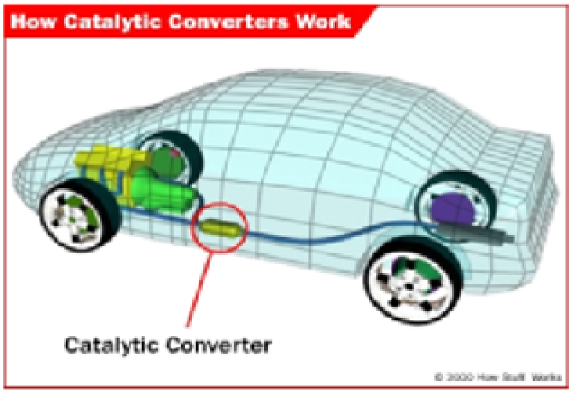


Figure 1.4: Catalytic Convertor

Oxidation: (Pt, Pd) : Oxidation catalytic converter:
$HC + O_2 \rightarrow CO_2 + H_2O$
$2CO + O_2 \rightarrow 2CO_2$
Reduction: (Pt, Rh): Reduction catalytic converter:
$2NO \rightarrow N_2 + O_2$

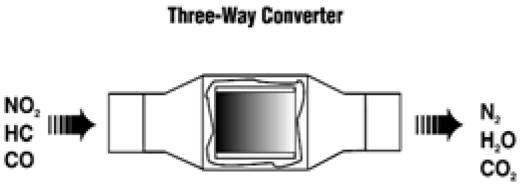


Figure 1.5: Three way Catalytic Convertor

Limitation of Catalytic Convertor

In the harsh conditions experienced in the exhaust stream with temperatures up to 1000 °C the metal in the catalyst is prone to deactivation by sintering, leading to a reduction in surface area and hence catalytic activity. The conventional means to meet tightening legislative emissions control targets is simply to increase the amount of PGM in the auto catalyst. The need to guarantee catalyst performance over the typical vehicle lifetime of 80,000 km also means that excess metal must be added, since the performance of the catalyst drops off over time. In addition rising PGM demand and costs are incentives towards achieving lower metal loadings and higher activity. The compounds of the PGM are generally considered highly toxic while the Pd and Rh are carcinogenic in nature. Due to the fact that the PGM are produced due to the abrasion of automotive catalyst washcoat. That is why the road traffic is responsible for metallic and organic pollutant-emissions which contaminate the environment.The catalytic converters in the exhaust system become deteriorated by several mechanisms e.g. thermal deterioration and poisoning. Thermal deterioration occurs as a result of exposure of the catalyst to high temperature conditions. This cause sintering of the PGM, loss of support surface area and phase transformation. Poison also cause loss of activity mainly by blocking the pores leading to active sites or even by direct blockage of the active sites themselves [20].

Achievements of Catalytic Convertor

Today's automobiles are meeting emission standards that require reductions of up to 99 percent for HC, CO and NO_x compared to the uncontrolled levels of automobiles sold in the 1960s. Catalytic converters have also been developed for use on trucks, buses and motorcycles as well as on construction equipment lawn and garden equipment marine engines and other non-road engines. Catalytic converters are also used to reduce emissions from alternative fuel vehicles powered by natural gas, methanol, ethanol and propane. To date more than 500 million vehicles equipped with catalytic converters have been sold worldwide. In 2005, 100 percent of new cars sold in the U.S. were equipped with a catalytic converter, and worldwide over 90 percent of new cars sold had a catalyst. Car and Driver magazine called the catalytic converter one of the century's 10 best automotive breakthroughs and the Society of Automotive Engineers selected the catalytic converter as one of the automobile industry's 10 greatest achievements over the past 100 years.

In the harsh conditions experienced in the exhaust stream with temperatures up to 1000 ºC, the metal in the catalyst is prone to deactivation by sintering, leading to a reduction in surface area and hence catalytic activity. The conventional means to meet tightening legislative emissions control targets is simply to increase the amount of pgm in the auto catalyst. The need to guarantee catalyst performance over the typical vehicle lifetime of 80,000 km also means that excess metal must be added, since the performance of the catalyst drops off over time. In addition, rising PGM demand and costs are incentives towards achieving lower metal loadings and higher activity [19,20,21,22].

Chapter 2

Literature Survey

2.1 Pervoskite

A perovskite is any material with the same type of crystal structure as calcium titanium oxide ($CaTiO_3$ Chemical compound and Mineral species), known as the perovskite structure. The general chemical formula for perovskite compounds is ABX_3 or ABO_3 where 'A' and 'B' are two cations of very different sizes, and X or O is an anion that bonds to both.The 'A' atoms are larger than the 'B' atoms. The ideal cubic-symmetry structure has the B cation in 6-fold coordination surrounded by an octahedron of anions (B surrounded by six oxygens in octahedral coordination) and the A cation in 12-fold cuboctahedral coordination (A coordinated by 12 oxygen). A ion can be rare earth, alkaline earth, alkali and other large ions such as Pb^{+2} ,Bi^{+} The B ion can be 3d, 4d and 5d transition metal ions, which occupy the octahedral sites (surrounded by six oxygen atoms in octahedral coordination). Large classes of perovskite-like materials are comprised of layers such as alkaline earth oxides. Perovskite compounds can also tolerate significant partial substitution (A and/or B with metals (A', B' correspondingly) of different oxidation states) and non-stoichiometry while still maintaining the perovskite structure. Metal ions having different valence can replace both A and B ions. This may generate a non-integral number of oxygen atoms. Because of their varied structure and composition, perovskites have been considered as prototype material for fundamental areas of solid state chemistry (redox reactions), physics, catalysis, solid oxide fuel cells, oxygen separation membranes, chemical sensors for the detection of humidity alcohol and gases such as oxygen, hydrocarbon and nitric oxide [23].

The red spheres are oxygen atoms, the deep blue are smaller (Ti^{+4}) metal cations (B-site) and the green(blue) are the larger (Ca^{+2}) metal cations (A-site) [23].

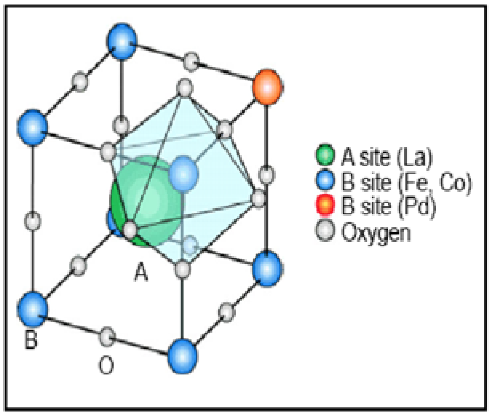


Figure 2.1: Perovskite structure ABO_3

Adsorption properties

The identification of the nature and structure of the exposed sites on the perovskite surfaces as well as the possible involvement of these sites in catalytic reactions have frequently been studied by the adsorption of suitable probe molecules. Both the equilibrium and the kinetics of adsorption and in some cases, the desorption of molecules from the surface were analyzed [23].

Specific Surface and Porosity

The chemical and physical properties of a catalyst and consistently its reactivity are strongly influenced by the synthetic procedure. Many different methods have been used in the preparation of perovskite oxides; the choice of a particular one basically depends on the expected application of these oxides. The application of perovskite oxides in the field of heterogeneous catalysis requires materials with a well-developed porous network. Classical methods of the preparation of perovskite oxides include: (i) equimolecular oxide mixing synthesis and (ii) decomposition synthesis. Type i method requires a high calcination temperature (1300-1500 K) for the solid state reaction to occur and often results in the formation of coarse aggregation. The grain size of the powder obtained by this method is relatively large and the specific area is too small, making it unsuitable for catalytic applications. Another major drawback of this method is that the purity of the product is not high. Type ii method, however, requires lower synthesis temperatures, usually below 1100 K thus high purity and homogeneity of the product are attainable [24].

Thermal stability

Perovskite has a good thermal stability at high temperature. The thermal stability of perovskites is determined by the cations at position A and also at position B showed that the extent of H_2 reduction of cobalt in $LnCoO_3$ (Ln = lanthanide) increased from Ln = La to Ln = Eu, i.e., with decreasing ionic radius of the lanthanide element.These later also reported a direct relationship between the reducibility and the sum of the energies of the Ln-O and Co-O bonds; i.e. the ease of reduction increases with decreasing metal oxygen bond energy. On the other hand, the stability in hydrogen of $LaFeO_3$ and $LaRhO_3$ was found to be higher than that of the corresponding perovskites.

The thermal stability of perovskite oxides was found to depend also on the type of cation at the B position studied the structural changes of a series of $LaBO_3$ (B = V, Cr, Mn, Fe, Co, Ni) oxides induced by H_2 reduction at 1273 K as a function of the oxygen partial pressure. Among the crystalline products produced by reduction, the dismutation La_2MO_4 phases were detected, with the exception of La_2MnO_4 which is unstable at temperatures above 1200 K. Other possible intermediate reduced mixed oxides such as $La_2Co_2O_5$, $La_2Ni_2O_5$ and $LaNiO_2$ phases were not observed because they are unstable.

Acid-Base Redox Property

Two important properties of perovskite type oxides directly related to catalytic performance such as acid-base and redox are examined briefly. Since the surface of perovskites may be primarily related to their catalytic properties, the nature and concentration of the surface sites can be evaluated by analysis of the interactions of suitable probe molecules and the surfaces of these oxides. Acid sites in perovskite-type oxides have been investigated by adsorption of a basic molecule such as pyridine, whereas basic sites have been evaluated by adsorption of acid molecules such as carbon dioxide. Furthermore, the reduction of perovskites and the oxygen adsorption-reaction on their surfaces play a central role in the catalytic activity of oxygen mediated reactions. The CO_2 coverage follows the order $LaCrO_3 > LaFeO_3 > LaCoO_3$. Activated adsorption was found to occur at temperatures above 420 K on $LaCrO_3$ and $LaCoO_3$.

However, the extent of CO_2 adsorption on $LaFeO_3$ decreased continuously with increasing temperature. CO_2 temperature-programmed desorption (TPD) measurements were also used to evaluate surface basicity in perovskites. TPD profiles after CO_2 adsorption on $LaBO_3$ oxides revealed two major peaks at 340-425 K and 540-920 K. The peak at 340-425 K originates from the decomposition of a monodentate carbonate, the least stable CO_2 adsorbed species.The CO_2 desorption peak at 540-920 K probably arises from the decomposition of bidentate and/or bridged carbonates whose presence was also revealed by infrared spectroscopy. The reduction and oxygen adsorption properties of several $LaBO_3$ (B = first-row transition element) perovskite oxides conclusively demonstrated that these parameters are directly involved in the catalytic activity of these oxides for oxidation reactions. It was observed that the more easily reducible perovskite oxides ($LaNiO_3$, $LaCoO_3$ and $LaMnO_3$) resulted in better catalysts for oxidation reactions than the less reducible one ($LaCrO_3$) [23,24,25].

2.2 Use of perovskites in Automobile

1. As long ago as 1952, perovskites were being used as catalytic materials for CO oxidation.

2. A plasma assisted reactor for the removal of carbonaceous combustion products or for simultaneous removal of carbonaceous products and nitrogen oxides from the exhaust emissions from an internal combustion engine wherein the reactor includes a gas permeable bed made at least primarily of active materials comprising perovskite

3. Perovskites catalysts convert synthesis gas to oxygenated organic chemicals. Several of these perovskites have been found to provide moderate to high selectivities to oxygenated organics particularly methanol and C_2O_x (acetic acid, acetaldehyde, and ethanol)

4. Perovskite materials have been evaluated for their applications in regeneration of diesel particulate filter (DPF) and also as diesel catalytic converter (DCC) It carried out oxidation of carbon/soot at lower temperature. The DCC shows 10-25 percentage reduction in smoke density depending on engine conditions. The perovskite-type catalyst appears to follow a redox mecha- nism for soot oxidation through oxygen removal and replenishment, while hydrocarbons adsorbed on soot particles may also help in oxidation of the carbonaceous part. The oxygen absorption and desorption properties of perovskites can play a crucial role for the low-temperature oxidation of soot-particulate

5. It improves Oxygen storage capacity (OSC) Ceria compounds can regulate oxygen storage and release properties, which is the most important and remarkable feature of the three-way catalyst. It is well known that, for the control of CO, HC and NO_x emissions, a three-way catalyst works under atmospheres with fluctuating air to fuel ratios (A/F) because the average A/F is maintained close to the stoichiometric value. An oxygen storage material is necessary to store excess of oxygen in an oxidative atmosphere and release oxygen in a reductive atmosphere. Through oxygen storage and release, a buffer is achieved between the lean- rich swings in exhaust gas composition during vehicle operation in order to maintain a stoichiometric atmosphere, in which NO_x, CO and HC are efficiently converted. Earlier, CeO_2 was recognized as a promising material, because it keeps a cubic crystal structure even during the alternate storage and release of oxygen and its volume change is small. However, OSC and thermal durability of CeO_2 were both insufficient for automotive use. Addition of lanthanum or zirconium ions into CeO_2 improves OSC by increasing the number of oxygen defects under reductive conditions

6. Self regeneration of a Perovskite catalyst (Cleaning up catalyst). The conventional catalysts disperse fine particles of precious metal on highly porous ceramic-support materials (alumina, ceria and zirconia). To ensure immediate action when the car is started, converters are placed closed to the hottest part of the car engine. Over time, heat exposure causes the tiny particles of precious metal to agglomerate and also growth of metal particles, thus reducing the catalyst's overall surface area and hence its activity. conventional catalytic converters are loaded with an excess of precious metal, ensuring that performance targets are met for vehicle use over the expected range, usually 80000 km. automotive gasoline engine is operated close to the stoichiometric air-to fuel ratio to convert the pollutant-emissions, accompanying with redox (reduction and oxidation) fluctuations in exhaust gas composition by adjusting the air-to-fuel ratio. A perovskite based catalyst has maintained its high activity with high dispersion of precious metals. Excess metal loading is not needed if the perovskite is used as the catalyst. This material investigated for catalytic converter applications in the 1970s [25,26,27].

2.3 Literature Survey for Pervoskite Catalyst

The table below shows the literature survey of different catalyst with citrate and co-precipetation method. All the possible temperature conditions , its pollutants, experimental conditions, with different auther with different result is shown in the table .

I have prepared the catalyst with the help of these references of Literature survey of Pervoskite by citrare method and co-precipetation method with the charactarization result XRD as temperature increases of calcination more phases are obtain the pure phases was obtain with good partical size calculated by scheerer equation and in BET in 600 ºC more surface area was obtain then in 800 ºC calcination temperature and activity in Lab-scale atmospheric gas /solid catalytic reactor with the space velocity of 32000 $Ncm^3g^{-3}h^{-1}$ and adjusting the flow rate of the simulated gas which is (1% CO , 98% N_2,1% O_2) composition of gas made for the experiment. $LaCoO_3$ catalyst with and without substitution at 800 ºC and 600 ºC gave the best result in citrate method with 100% selectivity of CO Conversion to CO_2 complete reaction was achieved in the reactor [28-32].

Table 2.1: Literature Survey of Pervoskite Catalyst

Sr no	Catalyst	Pollutants	Method of catalyst preparation	Exp. condition	Result	Ref.
1	$AMnO_3$ (A=La, Nd, Sm) Sm_{1-x} $SrxMnO_3$ (x = 0.1,0.3,0.5) XRD TPR ICP BET Redox	CH_4	Citrate Tc: 5 h at 1073K. SA=13–20 m^2 g^{-1}	space velocity 40000 Ncm^3 g^{-3} h^{-1}, CH_4 4% v/v, O_2 10% v/v.	100% CH_4 conversion selectivity to CO_2 below 1023 K	28

Preparation method

$LaMnO_3$, $NdMnO_3$ and $Sm_{-x}Sr_xMnO_3$ (x=0.0, 0.1, 0.3, 0.5) catalysts were prepared a concentrated solution of metal nitrates was mixed with an aqueous solution of citric acid. The molar ratio of citric acid to total metal cations was fixed at unity. Water was evaporated from the mixed solution at 343K and the sol was further dehydrated to yield a solid amorphous citrate precursor. The product was ground and fired at 573K for 1 h, then reground and calcined for 5 h at 823 K. The final calcination, after regrinding, was performed for 5 h at 1073 K.

2	$LaFe_{1-x}Co_xO_3$ x = 0.4–0.6 FT-IR, BET (XPS) (XRD), TPR (ICP)	CH_4	citrate sol-gel Tc :24 h calcined at 700 °C for 5 h.	CH_4/CO_2 = 1 CO_2 reforming $CH_4/CO_2/O_2$ = 4/1/2 Argon used 750–850 °C, 24 L h^{-1} g^{-1}hr S V : H_2 flow (20 ml/min, T = 700 °C, 8 h).	obtain highly crystalline, homogeneous and pure solids	29

Preparation Method

The mixed-oxide $LaFeO_3$, $LaFe_{0.8}Co_{0.2}O_3$, $LaFe_{0.6}Co_{0.4}O_3$, $LaFe_{0.4}Co=_{0.6}O_3$, $LaFe_{0.2}Co_{0.8}O_3$ & $LaCoO_3$ were synthesized by fine chemical using a modification of the citrate sol-gel method Adequate amounts of the precursor of the cation at B-position were dissolved under vigorous stirring in a solution of citric acid with an excess of ethylene glycol as the organic polydentate ligand. The citric acid/B-cation molar ratio was 4, while it was 1.38 for ethylene glycol/citric acid. The mixture was kept at 50-60 °C with mild continuous stirring until a clear solution was obtained. At this point, a stoichiometric quantity of the precursor of cation A, $La(NO_3)3.5H_2O$, was added while keeping the mixture at 60 °C. The evaporating process proceeded for 2 days until a viscous resin was formed. The resin was dried at 150 °C for 24 h and calcined in air at 700 °C for 5 h.

3	$La_{1-x}Ca_xFeO_3$ (x = 0.1, 0.2, 0.3, 0.4, 0.5) (XRD) (SA) BET Redox TPR	CH_4	citrate method Tc: 1073 K, 5h SA= 3-6m^2 g^{-1} (x= 0.4)	SA is 0.7m^2 g^{-1} for the specimen with x = 0.5	intrinsic activity in CH_4 combustion with activation energy, Ea, of about 23 kcal mol^{-1}	30

Preparation method

Samples with nominal composition $La_{1-x}Ca_xFeO_3$ (x = 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5) were prepared starting from nitrate solutions of the metals in the appropriate molar ratio. A solution of citric acid with the same amount of equivalents was added and the final mixture was slowly evaporated at about 340 K. The slurry was dried at 383 K for 15 h and then, after grinding, calcined at different temperatures, 623, 773, 923 and 1073 K, for 5 h .

4	$LaCoO_3$ XRD BET TEM	CH_4	Citrate method calcination at 600 °C,	SA$<$5 m^2/gW =F ¼ 7600 kgper s/mol	The results revealed that after calcination at 600 °C,highly dispersed $LaCoO_3$ perovskite was formed within the pore channels of the mesoporous host.	31

Preparation method

The amorphous La-Co citrate complex precursor solution was prepared 2.15 g of lanthanum nitrate, $La(NO_3)_3$. $6H_2O$, and 1.45 g of cobalt nitrate, $Co(NO_3)2$. $6H_2O$, (atomic Co/La = 1) were dissolved in 100 g of water containing 1.92 g citric acid. The molar ratio of citric acid to total La & Co cations was fixed to one. The clear mixture was stirred for 24 h at room temperature and finally corrected for loss of water during stirring. In a typical preparation of La-Co perovskite loaded catalysts, 2.2 g of the calcined mesoporous precursor was first dried in vacuum at 60 °C for several hours and then impregnated with 20 ml of the La-Co citrate complex precursor solution prepared above (corresponding to 10 wt.%). The citrate complexes are well soluble in water but the solution becomes viscous at high La-Co citrate complex concentrations. Therefore for high levels of La-Co loading, the impregnation-drying cycle was repeated for several times. After drying at about 80 °C, the catalysts were calcined at 600 °C for 8 h in air. Finally, the series of mesoporous silica supported $LaCoO_3$ perovskite catalysts having up to 50 wt.% $LaCoO_3$, was characterized and tested as catalysts in methane complete oxidation reaction.

5	$LaCoO_3$, $LaCo_{0.8}Cu_{0.2}O_3$, $La_{0.8}Sr_{0.2}Co_{0.8}Cu_{0.2}O_3$ $La_{0.8}M_{0.2}FeO_3$ (M= Ce and Sr) SEM nitrogen adsorption (BET) XRF XRD	CO	Co-Pre.	100 °C overnight and calcined at 700 °C	All samples gave complete methane conversion with 100% selectivity to CO_2	32

Preparation method

A certain amount of nitrate salts containing the following cations were dissolved in distilled water. NH_4OH (28%) was quickly added to the precursors under vigorous stirring until pH

10. The obtained precipitate was filtered and washed with distilled water until a pH of 7 is reached. The compound was then dried at 100 ºC overnight and calcined at 700 ºC under air atmosphere (5 h, ramp = 3 ºC/min).

6	$LaCo_{1-y}Fe_yO_3\pm$ lembda y = 0.1, 0.3, 0.5 X-ray (XRD) BET (SSA) X-ray (XPS) (TPR)	combustion of ethanol and propane	citrate method calcined Temp 700 °C for 2 h.	SSAs than ours, 4 m^2 g^{-1} for $LaCoO_3$ and 9 m^2 g^{-1} for $LaFeO_3$.	Due to substituting cation in the B-site we get good conversion	33

Preparation method

$LaCo_{1-y}Fe_yO_3$ (y = 0.1, 0.3, 0.5) prepared by citrate $La(NO_3)3.6H_2O$, $Co(NO_3)2.6H_2O$, $Fe(NO_3)3.9H_2O$, citric acid were used as reagents. An aqueous solution of citric acid with a 10% excess over the number of ionic equivalents of cations was prepared. The aqueous solutions of the metal nitrates were added to that of citric acid, and they were agitated for 15 min. The resulting solution was concentrated by slowly evaporating water under vacuum in a Rota vapor at 75 °C until a gel was obtained. This gel was dried in an oven, with the temperature increased slowly up to 200 °C and maintained there overnight, to produce a solid amorphous citrate precursor. The resulting precursor was milled and then calcined in air at 700 °C for 2 hr

7	$LaCoO_3$XRD, BET, TEM	CH_4	Citrate method calcination at 600 °C,	specific surface areas,gen erally <5 m^2/gW =F ¼ 7600 kg per s/mol	after calcination at 600 °C,highly dispersed $LaCoO_3$ perovskite was formed within the pore channels of the mesoporous host.	34

Preparation method

The amorphous La-Co citrate complex precursor solution was prepared 2.15 g of lanthanum nitrate, $La(NO_3)$.$6H_2O$, and 1.45 g of cobalt nitrate, $Co(NO_3)2.6H_2O$, (atomic Co/La = 1) were dissolved in 100 g of water containing 1.92 g citric acid. The molar ratio of citric acid to total La & Co cations was fixed to one. The clear mixture was stirred for 24 h at room temperature and finally corrected for loss of water during stirring. In a typical preparation of

La-Co perovskite loaded catalysts, 2.2 g of the calcined mesoporous precursor was first dried in vacuum at 60 °C for several hours and then impregnated with 20 ml of the La–Co citrate complex precursor solution prepared above (corresponding to 10 wt.%). The citrate complexes are well soluble in water but the solution becomes viscous at high La-Co citrate complex concentrations. Therefore for high levels of La-Co loading, the impregnation-drying cycle was repeated for several times. After drying at about 80 °C, the catalysts were calcined at 600 °C for 8 h in air. Finally, the series of mesoporous silica supported $LaCoO_3$ perovskite catalysts having up to 50 wt.% $LaCoO_3$, was characterized and tested as catalysts in methane complete oxidation reaction.

8	$AFeO_3$ (A D La, Nd, Sm) and $LaFe_{1-x}Mg_xO_3$ (x = 0:1, 0.2, 0.3, 0.4, 0.5) XRD BET TPR	CO	Citrate	S V : 40,000 Ncm^3 g^{-1} h^{-1} calcined temperature 1073K for 5 h.	CO complete conversion with 100% selectivity to CO_2 below 973 and 773 K	35

Preparation method

$AFeO_3$ (ADLa, Nd, Sm) and $LaFe_{1-x}Mg_xO_3$ (D= 0:1, 0.2, 0.3, 0.4, 0.5) perovskite catalysts were prepared according to the citrate method, which allows a very homogeneous dispersion of the precursor salts and in turn lowers the calcination temperature needed to form the perovskite structure, thus avoiding sintering phenomena and producing higher surface areas (SA). A concentrated solution of metal nitrates was mixed with an aqueous solution of citric acid. The molar ratio of citric acid to total metal cations was fixed at unity. Water was evaporated from the mixed solution at 353K until a viscous gel was obtained. The gel was then heated overnight at 383K to yield a brown glassy material which was ground, fired at 423K for 1 h and then slowly calcined to attain the temperature of 1073K for 5 h.

9	$AMnO_3$ (ADLa, Nd, Sm) and $Sm_{1-x}Sr_xMnO_3$ (x=0.1, 0.3, 0.5) XRD BET TPR	CH_4	citrate	fixed bed reactor at T=623-1023 K, space velocity =40,000 Ncm^3 g^{-1} h^{-1}, CH_4 concentration=0.4% v/v	methane complete conversion with 100% selectivity to CO_2 below1023 K.	36

Preparation method

$LaMnO_3$, $NdMnO_3$ & $Sm_{1-x}Sr_xMnO_3$ (x=0.0, 0.1, 0.3, 0.5) catalysts were prepared according to the citrate method. A concentrated solution of metal nitrates was mixed with an aqueous solution of citric acid. The molar ratio of citric acid to total metal cations was fixed at unity. Water was evaporated from the mixed solution at 343K and the sol was further dehydrated to yield a solid amorphous citrate precursor. The product was ground and fired at 573K for 1 h, then reground and calcined for 5 h at 823 K. The final calcination, after regrinding, was performed for 5 h at 1073 K.

10	$LaFe_{1-x}Co_xO_3$ perovskites XRD BET SEM TEM	NO, CO	Citrate	Calcination temperature :550 C for 3 h and 800 ºC for 5 h	$LaFeO_3$ perovskite was substantially more active in the reduction of NO to N_2 with CO and oxidation of the last compound to CO_2	37

Preparation method

$LaFe_{1-x}Co_xO_3$(x = 0 or 0.4) perovskites were prepared by the citrate method using salts of $La(NO_3)3.6H_2O$, $Co(NO_3)2.6H_2O$ and $Fe(NO_3)3.9H_2O$ as inorganic precursors. In this conventional preparation, stoichiometric amounts of the nitrate salts were mixed and dissolved in deionised water. Then, equimolar amounts of citric acid and ethylene glycol were added and the solution stirred at room temperature for 5 min. The excess of water in the mixture was evaporated in an oven at 60 ºC for 20 h. The resulting powder was grounded and then calcined under air flow in two heating steps: 550 ºC for 3 h and 800 ºC for 5 h (heating rate of 4 C min^{-1}).

2.4 Synthesis Method for Perovskite

Perovskite can be prepared by following Method

1. Citrate Method
2. Co-Precipitation
3. Sol-Gel
4. Combustion Synthesis Method
5. Reactive Grinding method

[1] : Theory of Citrate Method

The starting solution is a mixture of metallic salts and a hydroxy acid such as citric, malic, tartaric, lactic, or glycolic acid. The metals are preferably in the form of nitrates or ammonium salts, which will not leave any residues on thermal decomposition at a later stage and the decomposition of the nitrate and ammonium ions promotes surface area and porosity, due to the large amount of gas the decomposition evolves. Typical concentrations are 1 g equivalent organic acid per equivalent of total metal content. The solution is concentrated by rapid evaporation under vacuum, for instance in a Rotavapor, until its viscosity exceeds 500 CP at ambient temperature. A very stable syrup is obtained in this way. It can be dehydrated under vacuum at about 350 K to a rigid-foam (meringue) precursor, which is amorphous to X-rays, hygroscopic, and exhibits the color of the metallic ions present. The amorphous precursor appears to be some sort of a three-dimensional polymer in which the multifunctional organic acids are linked to two or more cations. The thermal decomposition of the amorphous mass may proceed more or less continuously or in two distinct steps at 350-370 K and 520-670 K. Because of the danger of violent reactions, this decomposition step is to be carried out very carefully, taking all necessary precautions. The preparation of oxides containing metallic ions highly active in oxidation needs very stringent precautions and is generally not advisable. The mechanisms of reactions occurring during preparation of mixed oxides by the citrate methods have been outlined in some detail. In the dehydration under vacuum, extensive loss of nitrate ions (in the form of various nitrogen oxides and ammonium nitrate) occur together with the loss of water. Although easier in the presence of citric acid, the decomposition of nitrate does not involve extensive reaction with the latter below 380 K. The semi decomposed precursor obtained around 410 K is essentially a dehydrated, amorphous, highly porous mixed citrate. The higher temperature decomposition stage, mainly between 500 and 670 K, consists of the burning of citric acid by oxygen. It is facilitated because of the presence of nitrate ions in the initial precursor. As indicated above, this stage is catalyzed by the presence of metals whose oxides are oxidation catalysts [33,34,35].

[2] : Theory of Co-Precipitation Method

The objective of this method is to precipitate the catalyst precursor in the form of a hydroxide or carbonate in the pores and on the surface of the carrier by adjusting the pH of the metal salt solution-support slurry through addition of a base such as NaOH, NH_4OH or Na_2CO. Base and metal salt are carefully chosen to avoid the presence of species in the final catalyst that might later act as poisons, such as $Na^+$and SO_4 for hydrogenation processes. The precipitation of the hydroxides can be performed either starting from an alkaline solution which is acidified, or from acidic solutions by raising the pH

In the first case, the formation of the solid product proceeds via polyanionic species. However, most hydroxides for technical applications are precipitated from acidic solutions by the addition of a precipitating agent. Usually ammonia or sodium carbonate are used as the precipitating agent. If other ions do not adversely influence the catalytic performance, $Ca(OH)_2$ or NaOH can be used. Depending on the metal ion and the precipitating agent, either the hydroxides, carbonates or hydroxycarbonates precipitate. Precipitation from acidic solutions mostly proceeds via polycations and as in the basic case by olation or oxolation reactions [36,37,38,39].

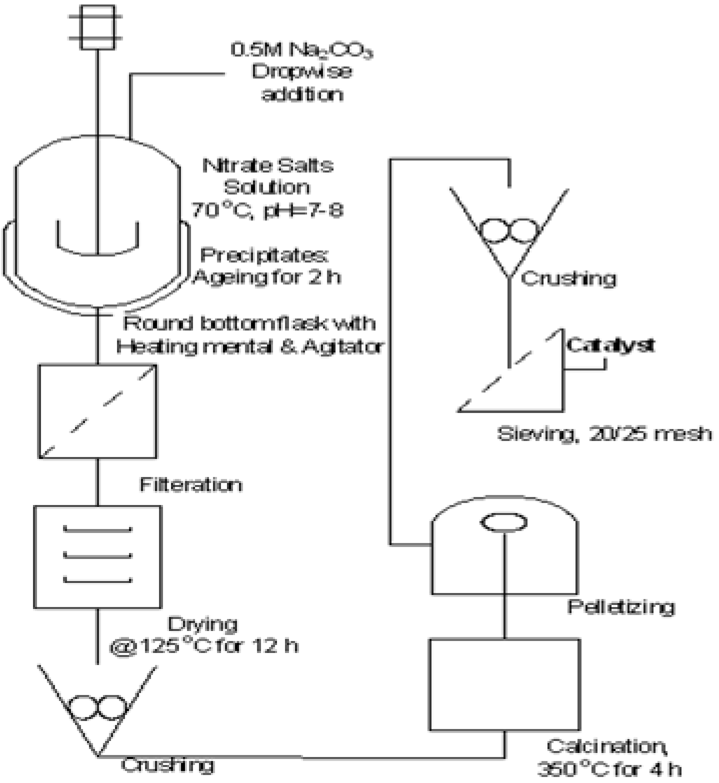


Figure 2.2: Flow Chart of Co-Precipitation

[3] : Theory of Sol-gel Method

The sol-gel process involves first the formation of a sol followed by that of a gel. A sol, which is a liquid suspension of solid particles ranging in size from 1 nm to 1 micron, can be obtained by the hydrolysis and partial condensation of a precursor such as an inorganic salt or a metal alkoxide. The further condensation of sol particles into a three-dimensional network produces a gel, which is a diphasic material with a solid encapsulating a solvent [40,41,42,43,44].

[4] : Theory of Combustion Synthesis Method

The combustion synthesis method takes advantage of exothermic, fast and self-sustaining chemical reactions between metal salts and a suitable organic fuel. Since most of the heat required for the synthesis is supplied by the reaction itself, the mixture of the reactants only needs heating up to a temperature that is significantly lower than the actual phase formation temperature. The energetic expense involved is therefore limited. In recent years this technique has been used to produce homogeneous, very fine, crystalline powders, without the intermediate decomposition and/or calcining steps which other conventional synthesis routes would require [44,45].

[5] : Theory of Reactive Grinding Method

A ball mill, a type of grinder, is a cylindrical device used in grinding (or mixing) materials like ores, chemicals, ceramic raw materials and paints. Ball mills rotate around a horizontal axis, partially filled with the material to be ground plus the grinding medium.Different materials are used as media, including ceramic balls, flint pebbles and stainless steel balls. An internal cascading effect reduces the material to a fine powder. Industrial ball mills can operate continuously fed at one end and discharged at the other end. Large to medium-sized ball mills are mechanically rotated on their axis, but small ones normally consist of a cylindrical capped container that sits on two drive shafts (pulleys and belts are used to transmit rotary motion). A rock tumbler functions on the same principle. Ball mills are also used in pyrotechnics and the manufacture of black powder, but cannot be used in the preparation of some pyrotechnic mixtures such as flash powder because of their sensitivity to impact. High-quality ball mills are potentially expensive and can grind mixture particles to as small as 5 nm, enormously increasing surface area and reaction rates. The grinding works on principle of critical speed. The critical speed can be understood as that speed after which the steel balls (which are responsible for the grinding of particles) start rotating along the direction of the cylindrical device; thus causing no further grinding [46,47]

2.5 Catalyst Characterization Techniques:

- Chemical composition of the bulk and surface of the solid
- Bulk and solid structure, crystallite size and size distribution, crystallite morphology, porosity (micro, meso, and macro), and surface area.
- Surface chemical properties such as valence state, acidity, reactivity with different molecules, surface energy and surface electronic states.
- Aggregate properties such as particle size, magnetic properties, density, mechanical strength and attrition resistance.
- Catalytic properties, i.e. activity, selectivity, and activity stability .

Objectives of Catalyst Characterization :

There are several important reasons for measuring the characteristics of solid catalysts:

- Understanding relationships among physical, chemical, and catalytic properties
- Elucidating causes of deactivation, designing procedures for regeneration
- Determining physical and chemical properties (e.g. composition, pore size, surface area, particle size and strength).
- Ensuring quality control in catalyst manufacturing [48,49]

Table 2.2: Catalyst Characteristics and its Methods .

Characteristics	Methods
Surface area ,pore volume and size	BET
Pore size distribution	BJH (Barret,Joyner and Halenda)
Elemental composition of catalyst	Metal trace analyzer/atomic absorption spectroscopy
Phase present and cristanellity	XRD
Morphology	Scanning electron microscopy
Catalyst reducibility	Temperature programmed reduction
Dispersion SA and particle size of active metal	CO Chemesorption and TEM
Acidic basic side strength	NH_3TPD.CO_2 TPD
Surface and bulk composition	XPS
Coke measurement	Thermo gravimetric analysis TPO

[1] : **X-Ray Diffraction (XRD)**

Elemental Analysis: Energy-dispersive analysis can be used to perform spot analysis within a catalyst. The electron beam can be focused on a particle or area whose analysis is desired, and the X-ray characteristics of the elements present are measured. This is a common method for poison analysis in a selected area of the catalyst. It should not be a substitute for a total analysis since only a small area is analyzed.

Phase Analysis by X-Ray Diffraction: Provided that a material is sufficiently crystalline to diffract X-rays and present in an amount greater than 1%, X-ray diffraction (XRD) can be used for qualitative and quantitative analysis [50,51].

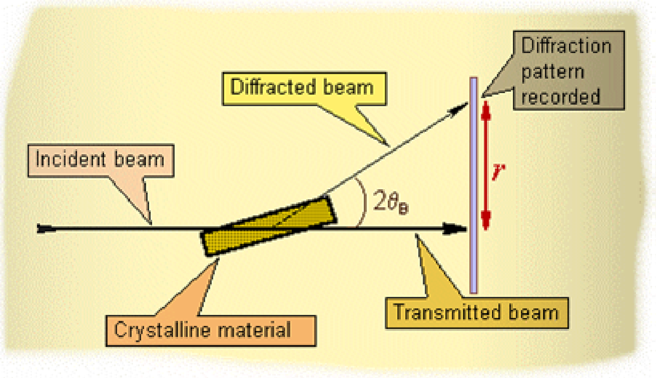


Figure 2.3: X-ray Diffraction

Applications of XRD

- XRD is a nondestructive technique
- To identify crystalline phases and orientation
- To determine structural properties :

Lattice parameters (10-4 Angstrom), strain, grain size , phase composition, preferred orientation order-disorder transformation, thermal expansion

- To measure thickness of thin films and multi-layers
- To determine atomic arrangement

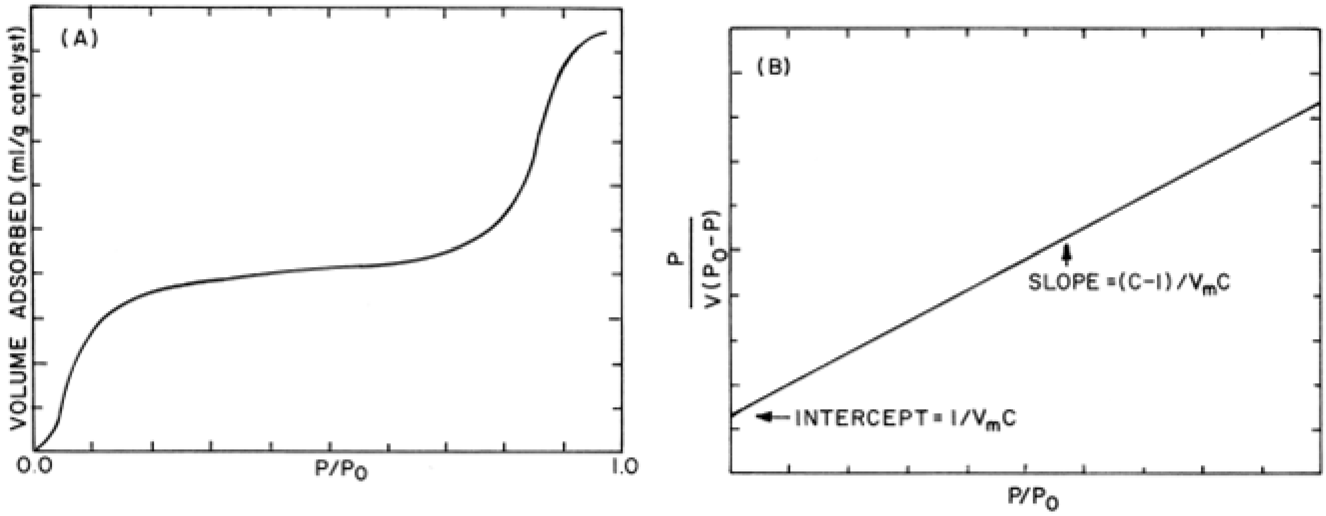
[2] : Brunauer , Emmett , Teller (BET)

Physical properties of catalyst: surface area and pore size

The same equipment as that for measuring surface area can be used to determine the pore size distribution of porous materials with diameters of 20 to 500 Angstrom except that high relative pressures are used to condense N_2 in the catalyst pores. The procedure involves measuring the volume adsorbed in either the ascending or the descending branch of the BET plot at relative pressures close to 1. Capillary condensation occurs in the pores in accordance with the Kelvin equation

Gas Adsorption: Pore Size

Hysteresis in the adsorption-desorption isotherms is a common observation for supports with a large fraction of small pores. It results from desorption from the meniscus at the end of a filled pore. The vapor pressure above the liquid at the pore mouth defines the pore radius in the Kelvin equation. Therefore, it is the desorption branch of the isotherm that is preferred in calculations of pore size distributions.



Measurement of surface area by the BET gas adsorption method. (A) Typical adsorption isotherm with a relatively flat curve in the region of monolayer adsorption. (B) Plot of the linear form of the BET equation between p/po = 0.05 and 0.3 used to calculate the monolayer coverage Vm [50,51].

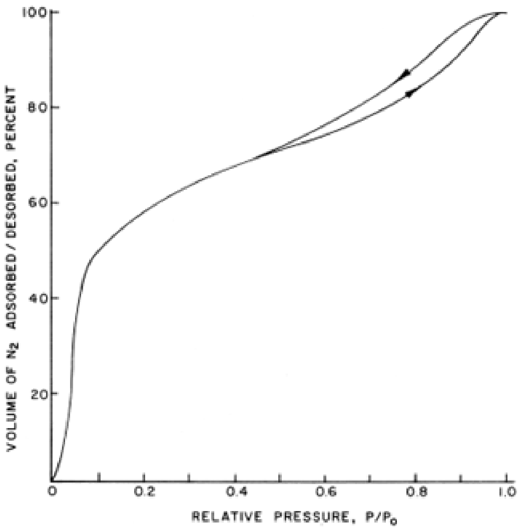


Figure 2.4: Nitrogen adsorption and desorption isotherms at 78 K. Pore size distributions in micropore range are calculated from isotherms using the Kelvin equation

[3] : Scanning Electron Microscopy SEM

Scanning Electron Microscopy (SEM) is a powerful method for the investigation of surface structures of mollicutes. This technique provides a large depth of field, which means, the area of the sample that can be viewed in focus at the same time is actually quite large. SEM has also the advantage that the range of magnification is relatively wide allowing the investigator to easily focus in on an area of interest on a specimen that was initially scanned at a lower magnification. Furthermore, the three-dimensional appearing images may be more appealing to the human eye than the two-dimensional images obtained with a transmission electron microscope. Therefore, an investigator may find it easier to interpret SEM images. The number of steps involved for preparing specimens for SEM investigation is lower and thus the entire process is less time consuming than the preparation of samples for investigation with a transmission electron microscope. SEM specimen preparation harbours various risk factors that can easily distort the integrity and ultrastructure of the mollicutes [52].

[4] : Transmission Electron Microscopy (TEM)

The first TEM was built by Max Knoll and Ernst Ruska in 1931, with this group developing the first TEM with resolving power greater than that of light in 1933 and the first commercial TEM in 1939. As opposed to a light microscope, the wavelength of illumination that is produced by an energized beam of electrons in TEM increases greatly the resolving capabilities. So, the main use of this technique is to examine the specimen structure, composition or properties in submicroscopic details so that this microscopy technique is significantly involved in numerous fields such as biological components, chemistry, materials science or electronics. Transmission electron microscopy (TEM) is a microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film or to be detected by a sensor such as a CCD camera. TEM forms a major analysis method in a range of scientific fields, in both physical and biological sciences. TEMs find application in cancer research, virology, materials science as well as pollution, nanotechnology and semiconductor research.

Components of transmission electron microscope

1. High tension cable
2. Electron emitter
3. Stepper motors for centering the electron beam
4. Condenser
5. Aperture controls
6. Specimen holder
7. Objective lens
8. Projector lens
9. Optical binoculars
10. Fluorescent screen
11. Vacuum pump leads
12. Goniometer
13. Vacuum and magnification control
14. Focusing control

[5] : Temperature Programmed Reduction (SEM)

Temperature-programmed reduction (TPR) is a technique for the characterization of solid materials and is often used in the field of heterogeneous catalysis to find the most efficient reduction conditions, an oxidized catalyst precursor is submitted to a programmed temperature rise while a reducing gas mixture is flowed over it. A simple container (U-tube) is filled with a solid or catalyst.

This sample vessel is positioned in a furnace with temperature control equipment. A thermocouple is placed in the solid for temperature measurement. To remove the present air the container is filled with an inert gas (nitrogen, argon). Flow controllers are used to add hydrogen (for example, 10 Vol % hydrogen in nitrogen). The composition of the gaseous mixture is measured at the exit of the sample container with appropriate detectors (thermal conductivity detector, mass spectrometer). Now, the sample in the oven is heated up on predefined values.

Heating values are usually between 1 K/min and 20 K/min. If a reduction takes place at a certain temperature, hydrogen is consumed which is recorded by the detector. In practice the production of water is a more accurate way of measuring the reduction. This is due to the potential for varying hydrogen concentrations at the inlet, so the decrease in this number may not be precise, however as the starting concentration of water will be zero, any increase can be measured more accurately [52,53].

Chapter 3

Experimental Work

3.1 Catalyst prepared

Below table shows the number of catalyst prepared by citrate method and co-precipitation method at calcination temperature 800 ºC and 600 ºC. The catalyst prepared was of both non-substituted as well as substituted single side and both the side A and B side substitution for synergistic effect to get more CO conversion and to get the maximal 100 % activity of catalyst.

The catalyst prepared was 10 gm that is for 10 gm net catalyst calculation with the help of molecular weight is done and final product that is out of 10 gm we can get approximately 7-9 gms of catalyst at the final stage of catalyst after calcination.

The loss in weight in citrate method is due to evaporation and formation of gel in oil bath or may be due to slow drying in oven. The loss of catalyst weight in co-precipitation is mainly due to the washing process with the help of filter paper to get the pH of 7 many catalyst was washed out with water during the washing step in this method but to over come this loss of catalyst vacuum pump for washing can be used and secondly less manual error.

Due to manual error and other possibe preparation method or even not following the proper steps of preparation method it may be possible that we can get loss of weight of catalyst.

The table shows the 10 gm catalyst prepared by both citrate and co-precipitation method.

Figure 3.1: Catalyst Prepared by Citrate and Co-Precipitation Method

SR.NO	NAME OF CATALYST	METHOD OF PREPARATION	CALCINATION TEMPERATURE	WEIGHT OF CATALYST
1	$LaFeO_3$	Citrate	600 °C and 800 °C	10 gm
2	$LaMnO_3$	Citrate	600 °C and 800 °C	10 gm
3	$LaCoO_3$	Citrate	600 °C and 800 °C	10 gm
4	$LaCuO_3$	Citrate	600 °C and 800 °C	10 gm
5	$LaNiO_3$	Citrate	600 °C and 800 °C	10 gm
6	$LaFeO_3$	Co-precipitation	750 °C	10 gm
7	$LaMnO_3$	Co-precipitation	750 °C	10 gm
8	$LaCo_{0.8}Cu_{0.2}O_3$	Citrate & Co-precipitation	800 °C	10 gm
9	$La_{0.8}Sr_{0.2}CoO_3$	Citrate & Co-precipitation	800 °C	10 gm
10	$La_{0.8}Sr_{0.2}Co_{0.8}Cu_{0.2}O_3$	Citrate & Co-precipitation	800 °C	10 gm
11	$La_{0.8}Ce_{0.2}Co\ O_3$	Citrate & Co-precipitation	800 °C	10 gm
12	$LaCo_{0.95}Pd_{0.05}O_3$	Citrate & Co-precipitation	800 °C	10 gm

3.2 $LaCoO_3$ Catalyst Prepared by Citrate Method

[A] : Calculation of citrate method

Molecular weight of Lanthanum (La) : 138.91 ~ 139 gm/mol

Molecular weight of Cobalt (Co) : 58.93 ~ 59 gm/mol

$LaCoO_3 = 139 + 59 + (3\times16)$

$= 246$ gm/mol

Molecular weight of Lanthanum Nitrate [$La(NO_3)_3.6H_2O$]

$= 138.91 + 42 + (16\times9) + 12 + (6\times16)$

$= 432.91$ gm/ mol

~ 433 gm/mol

Molecular weight of Cobalt Nitrate [$Co(NO_3)_2.6H_2O$]

$= 58.93 + 28 + (16\times6) + 12 + (16\times6)$

$= 290.93$ gm/mol

~291 gm/mol

Preparation of Catalyst: 10 gm

Calculation of Lanthanum (La) and Lanthanum Nitrate [La(NO_3).6H_2O]

246 gm $LaCoO_3$ = 139 gm Lanthanum (La)

10 gm $LaCoO_3$ = ?

= 10×139 / 246

= 5.650 gm Lanthanum (La)

139 gm Lanthanum (La) = 433 gm Lanthanum Nitrate [$La(NO_3)_3.6H_3O$]

5.650 gm Lanthanum (La) = ?

= 5.650×433 / 139

= 17.60 gm Lanthanum Nitrate [$La(NO_3)_3.6H_3O$]

Calculation of Cobalt (Co) and Cobalt Nitrate [$Co(NO_3)_2.6H_2O$]

246 gm $LaCoO_3$ = 59 gm Cobalt (Co)

10 gm $LaCoO_3$ = ?

= 10×59 / 246

= 2.398 gm Cobalt (Co)

59 gm Cobalt (Co) = 291 gm Cobalt Nitrate [$La(NO_3)_3.6H_3O$]

2.398 gm Cobalt (Co) = ?

= 2.398×291 / 59

= 11.82 gm Cobalt Nitrate [$Co(NO_3)_2.6H_2O$]

Calculation of Citric Acid

Molecule Weight of CA ($C_6H_8O_7$) : 192.13 gm/mol

Molecule Weight of CA ($C_6H_8O_7.H_2O$) : 210.14 gm/mol

(Citric acid / Total metal Cations) =1

Citric Acid = (5.650 / 135 + 2.398 / 59)

= 0.0812 mol

= 0.0812×192.13

= 15.60 gm

10 % excess = 17.16 gm Citric acid

[B] : Flow-Chart of $LaCoO_3$ catalyst by citrate method

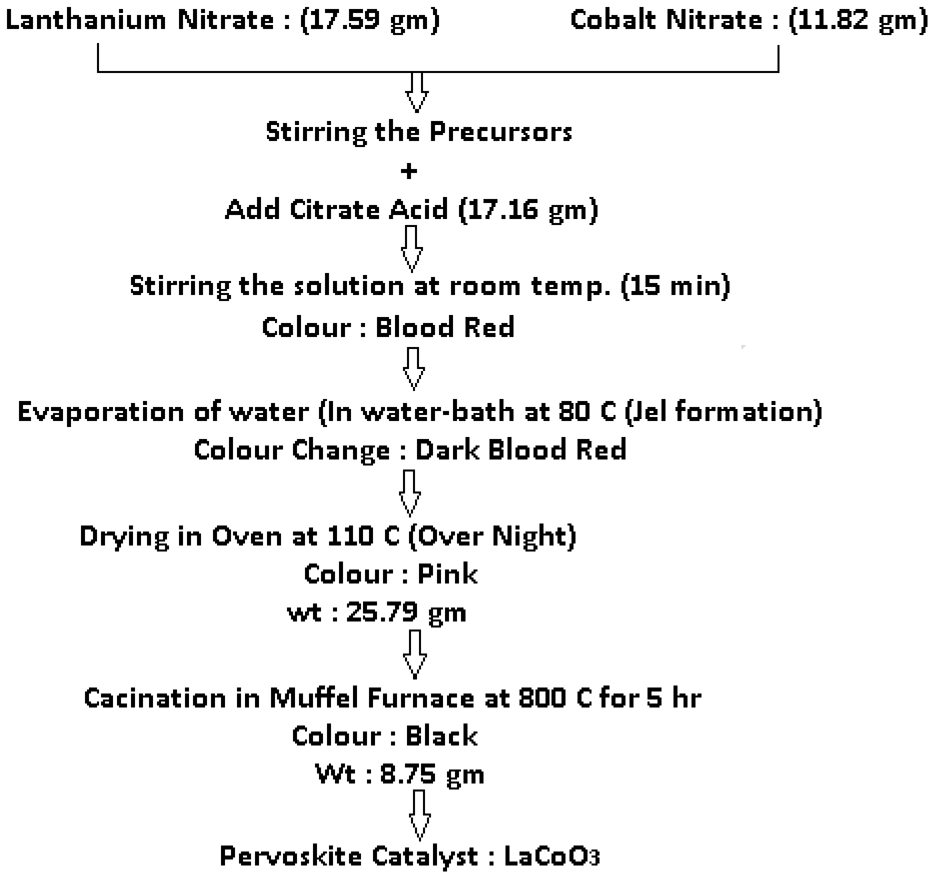


Figure 3.2: Flow chart of $LaCoO_3$ Catalyst by Citrate Method

[C] : Experimental Set-up of $LaCoO_3$ catalyst by citrate method

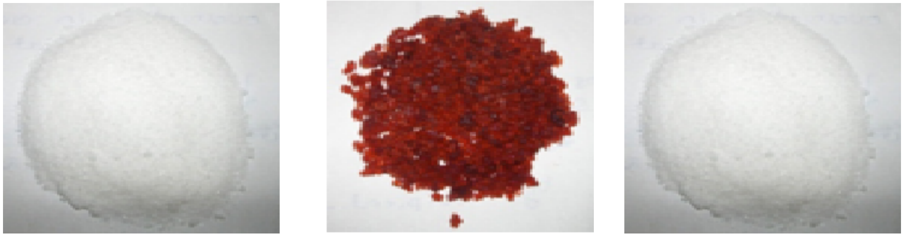


Figure 3.3: Lanthanum Nitrate / Cobalt Nitrate / Citric acid

Figure 3.4: Lanthanum Nitrate / Cobalt Nitrate / Citric Acid Mix with 15 ml distilled water

Figure 3.5: Mixture of above 3-Solution (Stirring) for 15 minutes

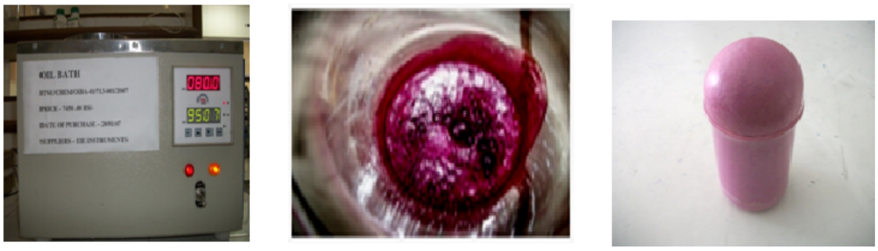


Figure 3.6: After Evaporation of Water / Gel Formation / Oven

Figure 3.7: After Calcination in Muffle Furnace at 800 ºC

3.3 $LaCoO_3$ Catalyst Prepared by Co-Percipitation Method

[A] : Calculation of $LaCoO_3$ catalyst by Co-precipitation method

$LaCoO_3$ = 139 + 59 + (3×16)

= 246 gm/mol

Molecular weight of Lanthanum (La) : 138.91 ~ 139 gm/mol

Molecular weight of Cobalt (Co) : 58.93 ~ 59 gm/mol

Molecular weight of Lanthanum Nitrate [$La(NO_3)_3.6H_2O$]

= 138.91 + 42 + (16×9) + 12 + (6×16)

= 432.91 gm/ mol ~ 433 gm/mol

Molecular weight of Cobalt Nitrate [$Co(NO_3)_2.6H_2O$]

= 58.93 + 28 + (16×6) + 12 + (16×6)

= 290.93 gm/mol ~ 291 gm/mol

Preparation of Catalyst: 10 gm

Calculation of Lanthanum (La) and Lanthanum Nitrate [$La(NO_3)_3.6H_2O$]

246 gm $LaCoO_3$ = 139 gm Lanthanum (La)

10 gm $LaCoO_3$ = ?

= 10×139 / 246

= 5.650 gm Lanthanum (La)

139 gm Lanthanum (La) = 433 gm Lanthanum Nitrate [$La(NO_3)_3.6H_2O$]

5.650 gm Lanthanum (La) = ?

= 5.650×433 /139

= 17.60 gm Lanthanum Nitrate [$La(NO_3)_3.6H_2O$]

Calculation of Cobalt (Co) and Cobalt Nitrate [$Co(NO_3)_2.6H_2O$]

246 gm $LaCoO_3$ = 59 gm Cobalt (Co)

10 gm $LaCoO_3$ = ?

= 10×59 / 246

= 2.398 gm Cobalt (Co)

59 gm Cobalt (Co) = 291 gm Cobalt Nitrate [$Co(NO_3)_2.6H_2O$]

2.398 gm Cobalt (Co) = ?

= 2.398×291/ 59

= 11.82 gm Cobalt Nitrate [$Co(NO_3)_2.6H_2O$]

Calculation of 1 M Na_2CO_3 Solution

M = Nos. of moles of solute Na_2Co_3/ Vol. of solution

1 = moles of solute / 500 ml = 0.5 lit

Moles of solute (Na_2CO_3) = 0.5 mol

Weight of solute = 0.5 x molecular wt of Na_2CO_3

= 0.5×105.98 g/mol

= 52.99

~ **53.00 gm of Na_2CO_3 (1 M in 500 ml)**

[B] : Flow-Chart of $LaCoO_3$ catalyst by Co-precipitation method

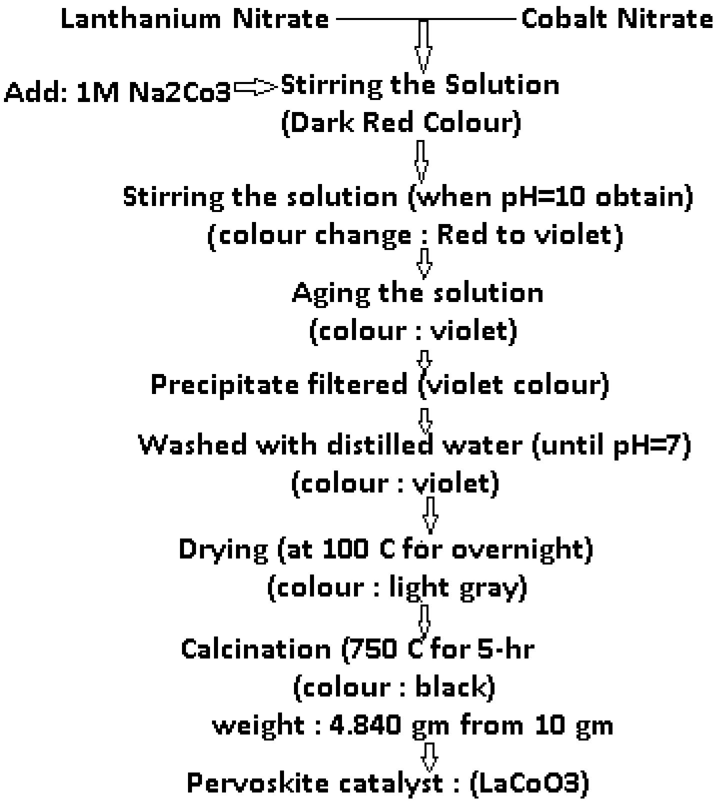


Figure 3.8: Flow chart of $LaCoO_3$ Catalyst by Citrate Method

[C] : Experimental Set-up of $LaCoO_3$ catalyst by Co-precipitation method

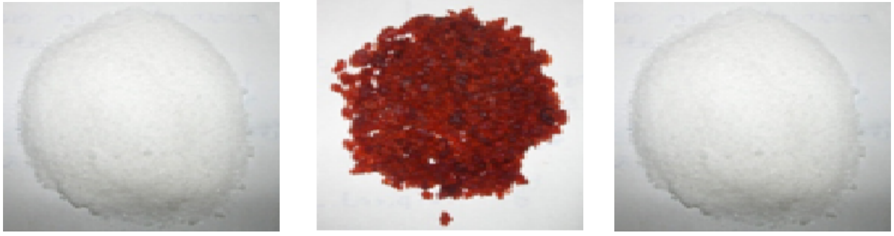


Figure 3.9: Lanthanum Nitrate / Cobalt Nitrate / Na_2Co_3

Figure 3.10: Lanthanum Nitrate / Cobalt Nitrate / Na_2Co_3 Mix with 15 ml distilled water

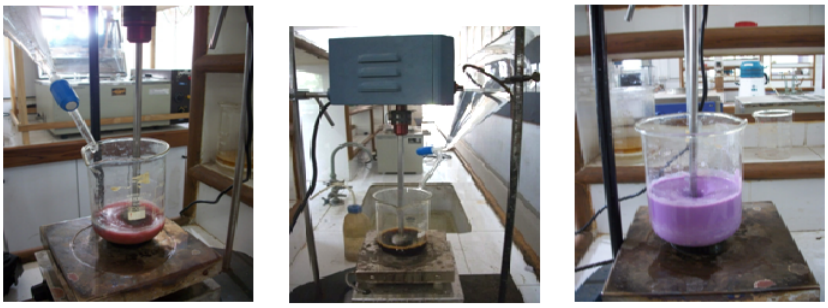


Figure 3.11: Addition of Na_2Co_3 dropwise to maintain pH

Figure 3.12: Filtering and Drying

Figure 3.13: Calcination at 750 ºC in Muffle Furnace

3.4 Total number of experiment done

From the below table catalyst prepared by citrate method and co-precipitation method and calcination temperature 600 ºC and 800 ºC many of the experiment were seems to be fail due to 50,100 and 500 µlit of syringe as my composition of simulated gas is (1 % CO , 98% N_2,1%O_2) is there and in Lab Scale Atmospheric Catalytic Reactor

By passing the simulated composition gas at Flow rate of simulated gas = 400 Nml/min and Space velocity = 32000 Ncm^{-3}/gm hr passed from bed of catalyst for CO conversion sand reaction is done in a reactor then with 2000 µlit of syringe if the sample is injected in gas chromatography then only our 1 % of CO is detected in chromatograph of GC if less volume is injected then the detection of CO is not possible so my experiment was fail.

Table 3.1: Experiment Performed

Volume injected with 50,100, 500, µlit syringe

SR NO.	NAME OF CATALYST	METHOD OF CATALYST PREPARED	RESULT OF EXPERIMENT
1	$LaCoO_3$ 800 ˚ C	Citrate	Fail
2	$LaCo_{0.8}Cu_{0.2}O_3$ 800 ˚ C	Citrate	Fail
3	$LaFeO_3$ 800 ˚ C	Citrate	Fail
4	$LaFeO_3$ 600 ˚ C	Citrate	Fail
5	Without catalyst	Citrate	Fail
6	$LaMnO_3$ 800 ˚ C	Citrate	Fail
7	$LaFeO_3$ 800 ˚ C	Citrate	Fail
8	$LaFeO_3$ 750 ˚ C	Co-Precipitation	Fail

Volume injected with 2000 µlit syringe

SR NO.	NAME OF CATALYST	METHOD OF CATALYST PREPARED
1	$LaFeO_3$ 800 ˚ C	Citrate
2	$LaMnO_3$ 800 ˚ C	Citrate
3	$LaCoO_3$ 800 ˚ C	Citrate
4	$LaCoO_3$ 600 ˚ C	Citrate
5	$LaFeO3_3$ 600 ˚ C	Citrate
6	$LaMnO3_3$ 600 ˚ C	Citrate
7	$LaFeO_3$ 750 ˚ C	Co-Precipitation
8	$LaCoO_3$ 750 ˚ C	Co-Precipitation
9	$LaCo_{0.8}Cu_{0.2}O_3$ 800 ˚ C	Citrate & Co-Precipitation
10	$La_{0.8}Sr_{0.2}CoO_3$ 800 ˚ C	Citrate & Co-Precipitation
11	$La_{0.8}Sr_{0.2}Co_{0.8}Cu_{0.2}O_3$ 800 ˚ C	Citrate & Co-Precipitation
12	$La_{0.8}Ce_{0.2}CoO_3$ 800 ˚ C	Citrate & Co-Precipitation
13	$LaCo_{0.95}Pd_{0.05}O_3$ 800 ˚ C	Citrate & Co-Precipitation
14	Without catalyst	-

Chapter 4

Result & Discussion of Characterization

4.1 Characterization X-Ray Diffraction (XRD) Result

XRD result of $LaCoO_3$ catalyst

Phase analysis, lattice parameters and particle sizes were determined by X-ray diffraction (XRD) using PW1774 Spinner Diffractometer system XPERT-MPD operated at 40 kV and 30 mA with Ni-filtered Cu Ka radiation (lembda = 1.5406 Å). Spectra were recorded with step scans from 2 ° to 99 ° in 2∂ angle and 1s for each 0.05 ° step. Lattice parameters were calculated from the reflections appearing in the 2∂ =2-99 range using the software program.

The identification of the crystal phases took place using the JCPDS data bank. Particle sizes (D) were calculated by means of the Scherrer equation D=K lembda/ßcos ∂ after Warren's correction for instrumental broadening.

K is a constant equal to 0.9, lembda wavelength of the X-ray used, B the effective line width of the observed X-ray reflection, calculated by the expression B2=B2-b2 (where B is the full width at half maximum (FWHM), b the instrumental broadening determined through the FWHM of the X-ray reflection at 2∂= 28 ° of crystalline SiO_2 with particles larger than 1000 Å,∂ the diffraction angle. It can be seen that the major diffraction peaks recorded are of 2 ∂ angles.

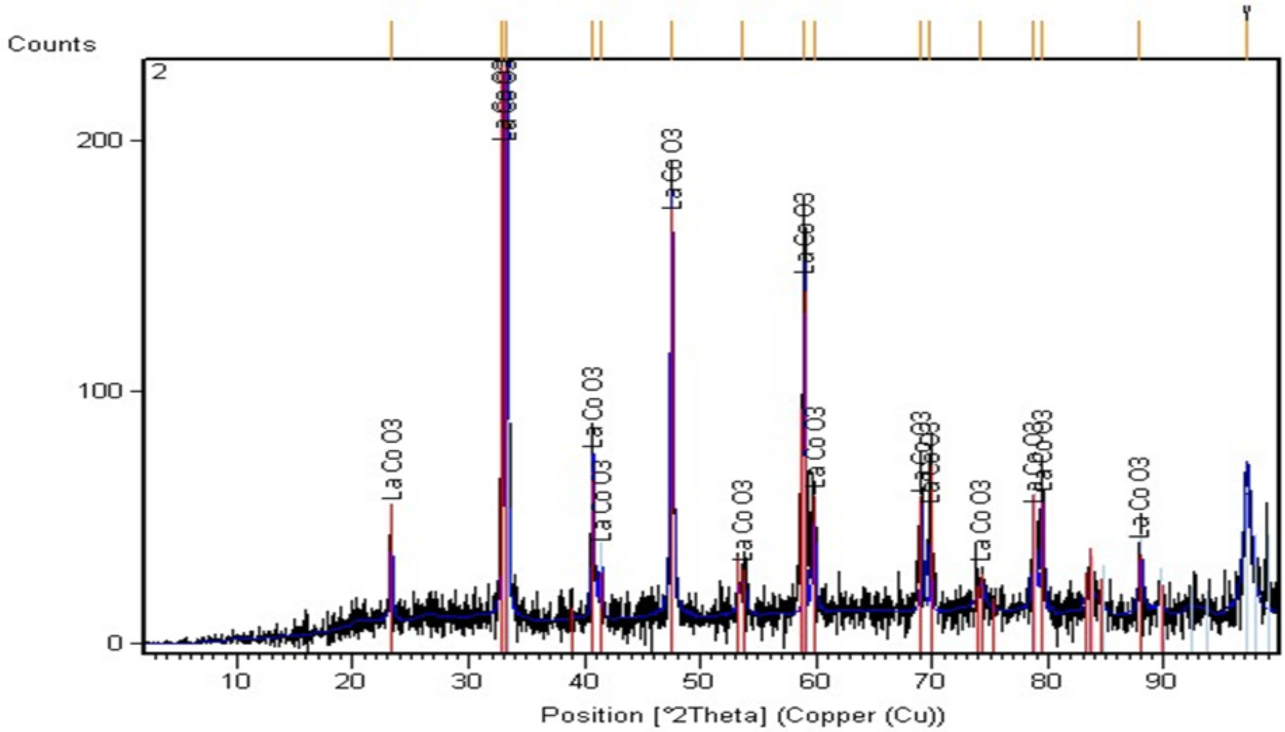


Figure 4.1: XRD graph with Phases of $LaCoO_3$

The above charactarization graph of XRD of catalyst $LaCoO_3$ at calcination temperature 800 ºC shows pure phases of $LaCoO_3$ and partical size were calculated to be 38.79 nm with the help of Scherrer equation. From the result we can conclude that as temperature of calcination increases the phases of catalyst increases as water /air gas mixture accelerates cryatalization of compound. The identification of crystal phase took place using JCPDS data bank graph this shows that all samples are essentially pervoskite type catalyst by composition of spectra.

Table 4.1: XRD data for $LaCoO_3$ Citrate Method

Sr.no	Pos. [º 2Th.]	FWHM [º 2Th.]	d-spacing [Å]	Rel.Int. [%]
1	23.2242	0.1968	3.83007	24.19
2	25.8925	0.1968	3.83007	24.19
3	30.4411	0.1968	3.44111	3.00
4	32.8921	0.1968	2.93650	4.67
5	33.2842	0.1968	2.72308	100.00
6	35.6411	0.4920	2.69189	89.16
7	38.8569	0.2952	2.51910	1.93
8	40.5957	0.2460	2.31771	3.52
9	41.2683	0.1968	2.22236	28.20
10	44.5636	0.252	2.03326	3.79

Scherrer formula

The crystal sizes of the samples based on the half-width of a diffraction peak using Scherrer formula. From this XRD chart (XRD data) we can calculate diameter of $LaCoO_3$ particles as follows:

Scherrer Formula

D = $\frac{K\times\lambda}{\beta\times cos\theta}$, Where

λ = wavelength of X-Ray being used for XRD

β = FWHM (Full Width Half Maximum),

∂= Angle of diffraction

[1] D = $\frac{K\times\lambda}{\beta\times cos\theta}$

K = 0.9,

λ = 1.54060 Angestrum

$2\partial = 23.2204$, $\partial/2$

so $\partial = 11610.2\times\cos\theta$

$\cos\partial = 0.9795$

$0.9 \times 1.54060/ (3.4348 \times 10^{-3}$ radian $\times 0.9795)$

D = 412.12 Å

For other values ,

D = 41.212 nm

D = 42.088 nm

D = 56.17 nm

D = 34.467 nm

So, we can say the size of $LaCoO_3$ particles is between 35-56 nm.

4.2 BET surface area

BET result of $LaCoO_3$ catalyst

Surface area (SSAs) were determined by nitrogen adsorption at the liquid nitrogen temperature (77.55 K) on a Micromeritics ASAP 2020 instrument. Before each adsorption, the catalyst powder was degassed for 3-4 hr at 300 $^\circ$C under vacuum of typically 10^{-3} Pa in order to remove adsorbed species.

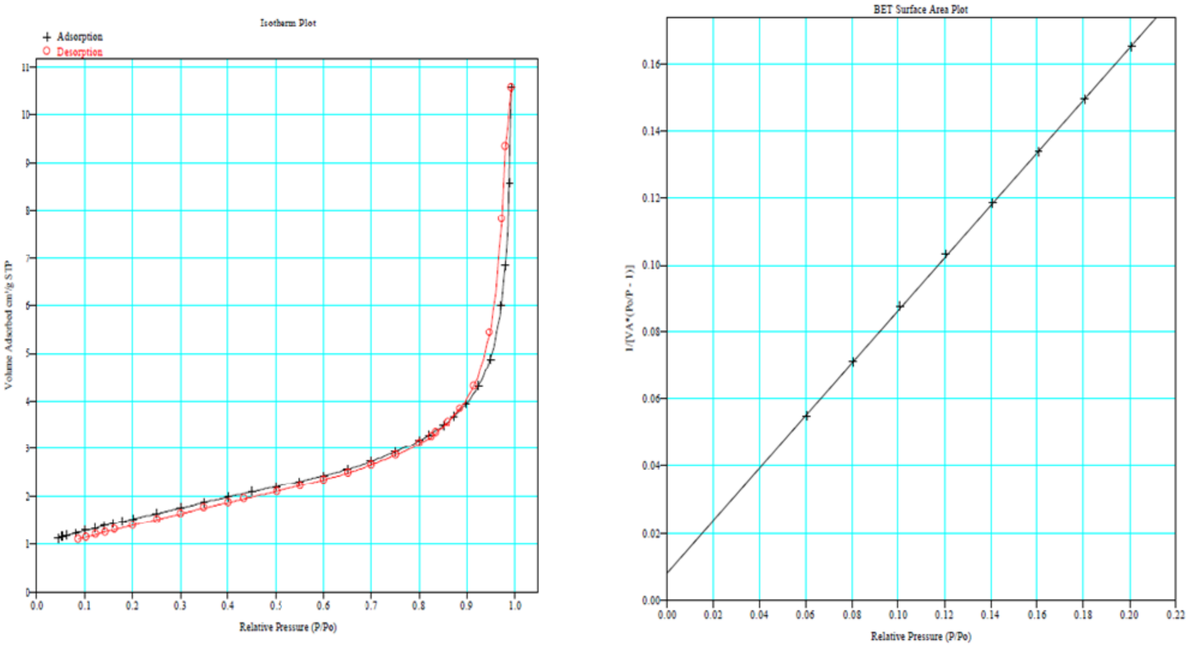


Figure 4.2: BET Graph of $LaCoO_3$ catalyst by citrate method 800 ºC

4.3 Result of XRD and BET of different catalyst

From the below table of charactartization result we can say that in XRD all the pure phases are formed except in $La_{0.8}Sr_{0.2}Co_{0.8}Cu_{0.2}O_3$ prepared by CM 800 ºC calcination temperature the impure phase was obtain was of $P^+SrCoO_{2.80}$ Partical size range was from 22-38 of all the catalyst and for BET the surface area ,pore diameter .pore volume of non substituted catalyst was more then substituted catalyst.

The prepared catalyst $LaCoO_3$ calcination temperature 800 ºC XRD pure phase BET size of particle 38.79 nm surface area 8.78 m^2/g and pore diameter 9.77 and pore volume 0.0215 cm^3/vol. substituted catalyst has good activity and poor surface area then non substitutde, thus catalyst prepared by 600 ºC BET result of catalyst was very good but in XRD the pure phases was not developed so at 800 ºC partical size and phases were achieved.

Table 4.2: Result of XRD and BET of all the catalyst prepared by citrate and co-precipitation method 600 ºC and 800 ºC

Sr.No	CATALYST PREPARED (at calcination temp.ºC)	XRD PHASES	SIZE OF PARTICLE D = nm	BET SBET (m^2/g catalyst)	PORE DIAMETERnm	PORE VOLUME cm^3/g
1	$LaCoO_3$ CM 600 ºC	Pure	20-22.17	13.7199	11.9657	0.041042
2	$LaCoO_3$ CM 800 ºC	Pure	24-38.79	8.78	9.770	0.0215
3	$LaMnO_3$ CM 600 ºC	Pure	23-38.84	15.4573	10.7845	0.041675
4	$LaMnO_3$ CM 800 ºC	Pure	23-38.80	6.1575	10.0062	0.015403
5	$LaFeO_3$ CM 600 ºC	Pure	20-22.22	15.4784	17.8092	0.068914
6	$LaFeO_3$ CM 800 ºC	Pure	24-38.89	12.0326	7.5590	0.022739
7	$LaMnO_3$ CP 750 ºC	Pure	22-38.85	3.3255	8.2769	0.006881
8	$LaCo_{0.8}Cu_{0.2}O_3$ CM 800 ºC	Pure	23-42	3.04	11.29	0.0086
9	$La_{0.8}Sr_{0.2}CoO_3$ CM 800 ºC	Pure	25-56	3.91	8.32	0.0081
10	$La_{0.8}Sr_{0.2}Co_{0.8}Cu_{0.2}O_3$ CM 800 ºC	Pure + $SrCoO_{2.80}$	25-34	3.76	9.97	0.0094

Chapter 5

Result & Discussion of Catalytic Activity

5.1 Experiment Activity :Lab-scale Atmospheric gas/solid catalytic reactor

CO oxidation test Tubular fix-bed catalytic reactor operating pressure 1bar maximum operating temperature 800 ° C made of SS tube of 18.05 mm inner diameter of 19.05 mm outer diameter and tube length 500 mm. Pore testing catalytic activity first we have to prepare bed of 1 gm catalyst and 3 gm Silicon dioxide (SiO_2) pallets between Ceramic Blanket wool for sipport balanced with a space velocity 32000 $Ncm^3g^{-1}h^{-1}$. Pretreatment is given to the bed for 2 hr with N_2 at 250 ºC and Cooling with N_2 at 100 ºC reactor temperature was raised from 50 to 800 ºC.

Product stream was analyzed by gas chromatography using a Resteks New Shin carbon ST Micro packed GC column and micro TCD detector.

Injection port: direct 150 ºC

Column temperature: 60 ºC

Column flow : 20 ml/min

Detector temperature: 100 ºC

Detector current : 90 mA

Injecting the 2000 µlit of gas sample after making the composition of simulated gases in the reactor activity in GC and CO_2 being the only reaction product detected.

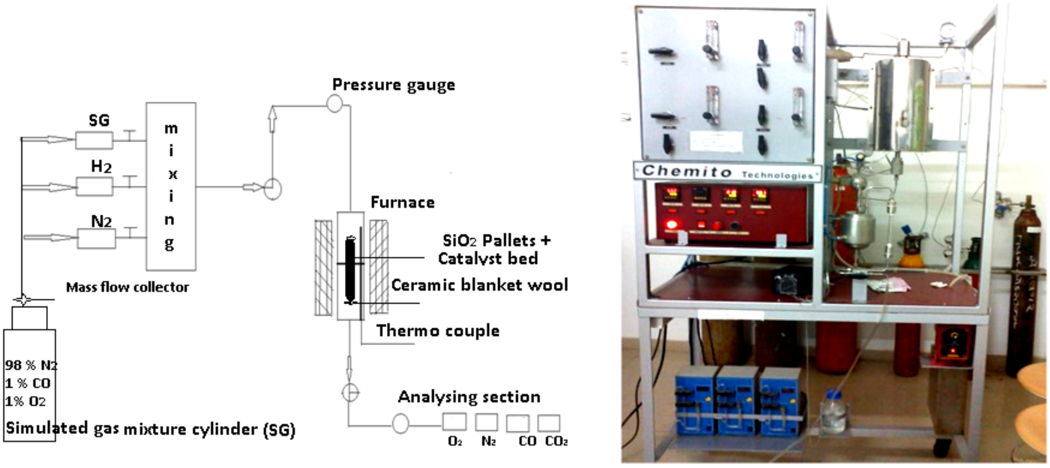


Figure 5.1: Activity : Lab-scale Atmospheric-gas solid catalytic reactor

Experimental Result of Gas Chromatography

$LaCoO_3$ by Citrate Method 800 ° C Calcination Temperature

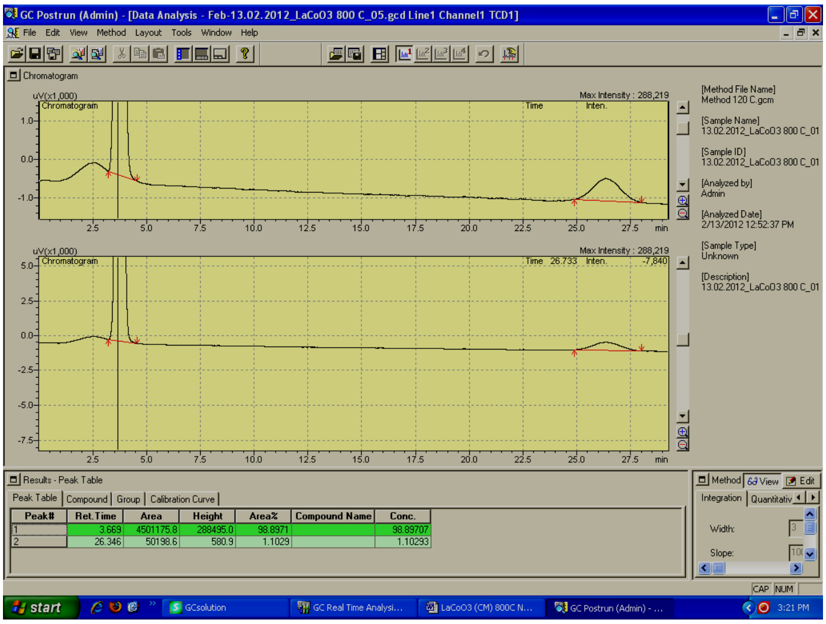
13.02.2012_ $LaCoO_3$,800 ° C _CM_05 : (1 % CO : Area = 42483.3)

FT : 3000C BT : 352 ° C Flow : 310.52 Nml/min

Inlet CO = 0×310.52/100 = 0 ml/min %

CO Conversion = COin-COout/COin

= (3.9 - 0)/3.9, = 100 % Simillarly, other samples are calculated.



GC Postrun (Admin) - [Data Analysis - Feb-13.02.2012_LaCoO3 800 C_05.gcd Line1 Channel1 TCD1]

[Method File Name]
Method 120 C.gcm

[Sample Name]
13.02.2012_LaCoO3 800 C_01

[Sample ID]
13.02.2012_LaCoO3 800 C_01

[Analyzed by]
Admin

[Analyzed Date]
2/13/2012 12:52:37 PM

[Sample Type]
Unknown

[Description]
13.02.2012_LaCoO3 800 C_01

Peak#	Ret.Time	Area	Height	Area%	Compound Name	Conc.
1	3.669	4501175.8	288495.0	98.8971		98.89707
2	26.346	50198.6	580.9	1.1029		1.10293

Figure 5.2: Post-run of Gas Chromatograph of $LaCoO_3$ 800 ºC experiment

Table 5.1: Table of $LaCoO_3$800 ºC experiment

TEMP. ºC	% CO - CONVERSION
196	9.74
284	88.20
352	100
398	100
446	100
498	100
549	100
653	100

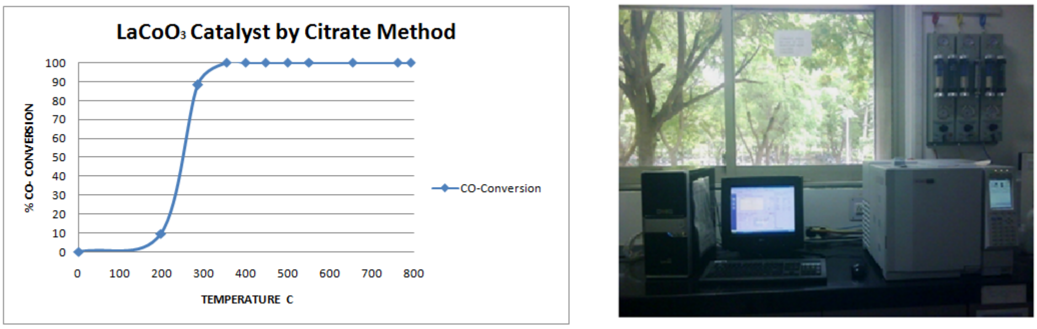


Figure 5.3: $LaCoO_3$ Catalyst by Citrate Method CO-Conversion

Product stream was analyzed by gas chromatography using a Resteks New Shin carbon ST Micro packed GC column and micro TCD detector. Injection port= direct 150 °C, Column temperature= 60 °C, Column flow= 20 ml/min, Detector temperature= 100 °C, Detector current=90 m A, Injecting the 2000 µlit of gas sample after making the composition of simulated gases in the reactor the activity in GC and CO_2 being the only reaction product detected. Thus from the above experiment we can conclude that $LaCoO_3$ Catalyst prepared by CM on seeing the graph of CO conversion at 352 ºC the 100 % conversion was obtain it seems to be good catalyst as we got the conversion at low temperature and sintering of catalyst was also not seen at even 800 ºC of temperature in catalytic reactor.

The catalytic performances of the samples for carbon monoxide were evaluated. Catalytic activity tests with space velocity 32000 Ncm^{-3}/gm hr showed that all samples gave CO oxidation for $LaCoO_3$ prepared by citrate and 100 % conversion in substitution catalyst for (1% CO, 1% O_2, 98% N_2) selectivity to CO_2 below 352 °C. Catalytic activity of substituted catalyst were investigated and seems to be more effective than non-substituted catalyst as leading to maximal conversion of carbon monoxide at low temperature.

5.2 CO oxidation test (1% CO, 1% O_2, 98% N_2)

The below table shows the comparision of non-substituted and substituted catalyst prepared by Citrate method for CO oxidation test and the best result obtain was in substituted catalyst $La_{0.8}Sr_{0.2}Co_{0.8}Cu_{0.2}O_3$ done with all temperature condition mention below.

Also CO conversion graph of Conversion Vs Temperature gives the clear result of 100 % CO Conversion at lowest temperature of 262 ºC

Table 5.2: Comparision of non-substituted & substituted Catalyst

$LaCoO_3$ CM-800 ºC	$La_{0.8}Sr_{0.2}Co_{0.8}Cu_{0.2}O_3$ CM-800 ºC
Weight of catalyst: 0.75 gm + 3 gm SiO_2 Flow rate of simulated gas = 391.66 Nml/min Space velocity: 31332.8 Ncm^{-3}/gm hr	Weight of catalyst:0.75 gm +SiO_2 Flow rate of simulated gas =400 Nml/min Space velocity: 32000 Ncm^{-3}/gmhr
Pretreatment: N_2 flow: 277.05 ml/min Furnace T = 250 ºC, Bed T = 292 ºC Cooling with N_2 till 115 ºC	Pretreatment: N_2 flow: 264.81 ml/min Furnace T = 250 ºC, Bed T = 138 ºC Cooling with N_2 till 183 ºC

TEMP. ºC	% CO-CONVERSION	TEMP. ºC	% CO-CONVERSION
0	0	0	0
196	9.74	133	21.25
284	88.2	196	64
352	100	262	100
398	100	307	100
446	100	359	100
498	100	462	100
549	100	563	100
653	100	674	100

The above table shows that catalyst $La_{0.8}Sr_{0.2}Co_{0.8}Cu_{0.2}O_3$ CM-800 ºC which is substituted catelyst gives better CO conversion that is at low temperature of 262 ºC where as catalyst $LaCoO_3$ CM-800 ºC needs more temperature for complete 100% conversion.

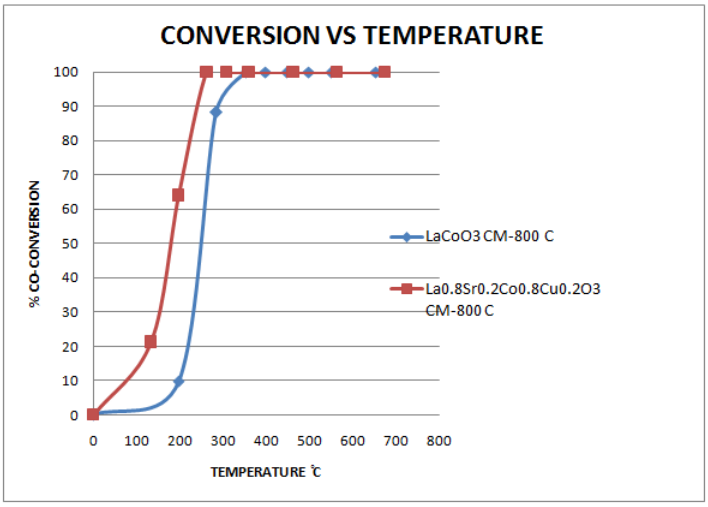


Figure 5.4: Graph of CO-Conversion for comparision of substitutsd & non substituted catalyst

From the above graph the comparision of substituted & non substitutds catalyst is due to synergistic effect on both the sides of catalyst due to divalent and trivalent bond and cation substituted catalyst activity increases which increases the oxidation activity of pervoskite that is at low temperature more conversion is obtain.

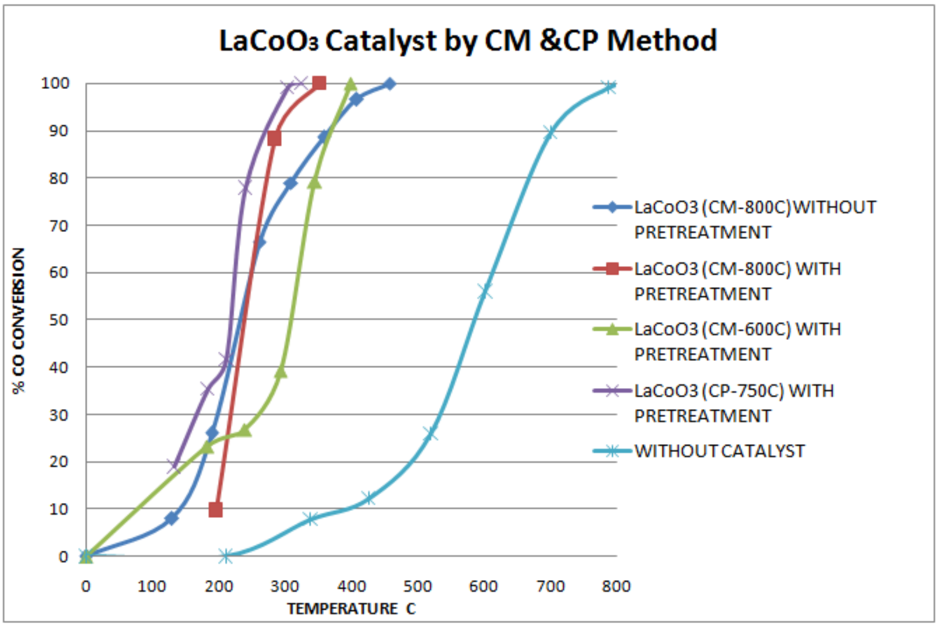


Figure 5.5: Result CO-Conversion of $LaCoO_3$Catalyst by Citrate & Co-precipitation Method

Citrate Method catalyst discussion

In this graph of CO Conversion the catalyst prepared by CM and CP method and activity done by without and with catalyst bed is discussed. Due to pre treatment the catalyst moisture , impurities is removed and catalyst side gets activated so we get CO conversion at less temperature then without pretreatment .We can also see that if calcination temperature is less then we can gain conversion at low temperature.Thus the best result obtain was of $LaCoO_3$ catalyst by CM with pretreatment due to less sintering and good active sides of catalyst that is below 300 ºC temperature while the activity without catalyst was seems to be at 800 ºC temperature.

The present study showed that the preparation method of $LaCoO_3$ perovskites influences the catalytic activity of CO decomposition. Results showed that morphology and surface changes may induce strong differences in the catalytic activity of $LaCoO_3$ in CO decomposition. $LaCoO_3$ prepared by the citrate method exhibits the highest activity for the catalytic decomposition of CO. This was related to higher specific area and higher density of oxygen vacancies results obtained also indicate that the overall activity is closely related to the mobility of oxygen species with different extent of interactions between carbonates and nitrates. It has been concluded that the partial incorporation impurities during the preparation of $LaCoO_3$(CM) governs the catalytic performances towards the decomposition of CO.

Co-precipitation Method catalyst discussion

In coprecipitation method due to less calcination temperature we get the conversion below 300 ºC. Single perovskite structure was formed in synthesizing catalyst through coprecipitation method adding Na_2Co_3 as precipitating agent the sintering temperature for obtaining a single perovskite phase were generally higher than 850 ºC . These results indicate that the Na_2CO_3precipitating agent allow the components of these metal ions to be uniformly dispersed in the precursors, which decreased the activation energy of the solid state reaction in the perovskite structure forming process.

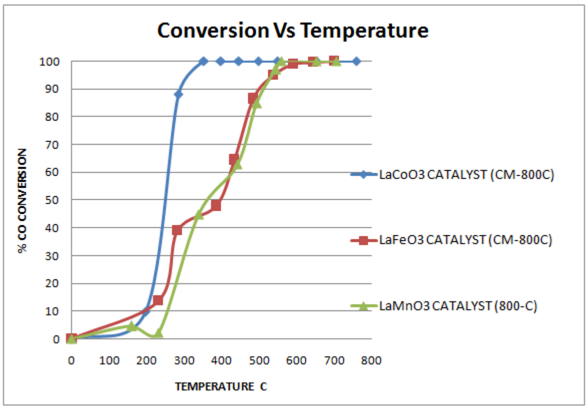


Figure 5.6: Comparision of non-substituted catalyst

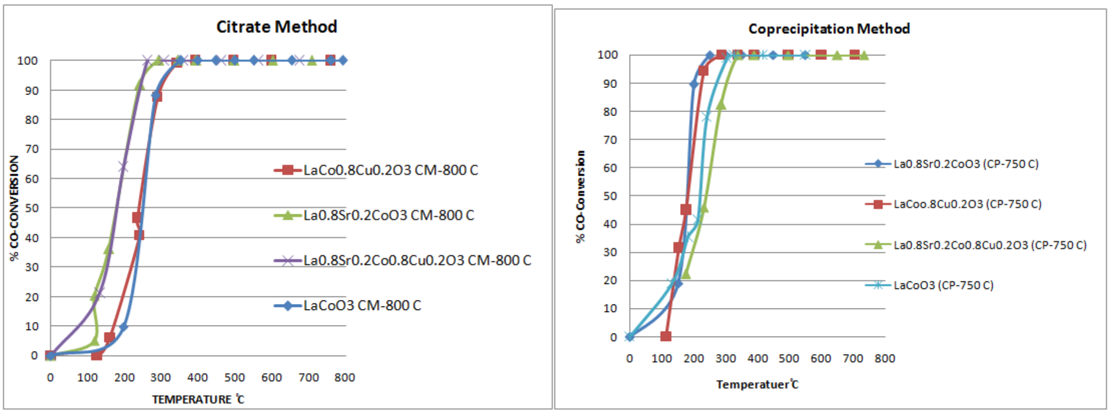


Figure 5.7: Comparision of substituted catalyst

Result

From the above graph of CO conversion of different catalyst we can compare the substituted and non substituted catalyst by CM and its activity and charactarization result. Prepared catalyst $La_{0.8}Sr_{0.2}Co_{0.8}Cu_{0.2}O_3$ perovskites prepared by citrate method and calcined at 800 ºC have been investigated as catalysts for CO combustion. The formation of the perovskite structure and pure phase formation with partical size has been shown by X-ray diffraction (XRD).

The surface area (SA) values . Catalytic activity tests showed that this samples gave CO complete conversion with 100% selectivity to CO_2 at 262 ºC the conversion was achieved at very less temperature then the other catalyst ,as this catalyst due to synergistic effect of the substitution of A and B both the side divalent bond develop and conversion obtain was at low temperature in Lab scale Catalytic Reactor. In 600 ºC calcination temperature fast reaction is achieved then in 800 ºC.

Substituted catalyst discussion

The symmetry and the valence state of B-site cations, substitution-induced non-stoichiometry leading to improved transport of bulk oxygen ions and the crystallite size of the samples that depends upon the adopted synthesis procedure.

Thus, the decrease in CO conversion and increase in reduction temperature the particle size is an important parameter influencing the catalytic properties. The smaller size crystallites of nanometer scale not only exhibit higher dispersity and greater specific surface area their surface properties may also be different from their bulk analogues.

Our study clearly provides evidence that the powder morphology of a mixed oxide samples, i.e. crystallite size, surface area and surface micro-structure, may depend considerably on the nature of the constituent cation and the procedure adopted for the synthesis of a particular sample.

Discussion

The citrate method, under carefully selected synthesis conditions (highly soluble initial reagents, slow drying and calcination steps), Catalytic CO combustion and CO oxidation were investigated over $LaCoO_3$ and $La_{1-y}Sr_yCo_{1-x}Cu_xO_3$,(x=0.2) for CO oxidations were investigated over $LaCoO_3$ and its substitution of perovskites catalyst prepared by citrate method calcined at 600 ºC and 800 ºC is appropriate for the formation of pure perovskite phases and the avoidance of the segregation of phases.

It is a suitable method for obtaining a calcium substitution for lanthanum without solubility limit in the $LaCoO_3$ perovskite. The specific surface areas obtained are acceptable for applications in catalytic oxidation reactions. The substitution generates oxygen vacancies, preserving charge neutrality and resulting in a ”reductive stoichiometry”

Catalyst demonstrate excellent structural stability under catalytic test conditions neither specific surface area collapse nor structural change was observed ,non-substituted $LaCoO_3$ catalyst was active in the CO to CO_2 conversion, but it became slowly deactivated by carbon residues formed along the course of the reaction. But by substitution of Cu, Ce , Pd,Co caused an increase in the catalytic activity and inhibition of coke formation on the catalyst surface.

Catalysts with substantially improved thermal stability and immune to carbon foul and sulfur poison is one of the keys to making fuel-processing technology commercially viable. Perovskites in the form of pellet and monolithic configurations were developed and their mechanical strength, stabilities and above all hydrogen productivity as well as sulfur tolerance were investigated.

By partially substituting $La_{0.8}Sr_{0.2}Co_{0.8}Cu_{0.2}O_3$, higher activities, mechanical and thermal stabilities, were found.

Moreover, compared with noblemetal-based catalyst, and also more activity then $LaCoO_3$ without substitution catalyst in both citrate and co-precipitation method at low temperature, and was needed to improve the sulfur tolerance of perovskite catalyst

Chapter 6

Conclusion Findings & Application

Air pollution is contributed by every individual vehicle therefore it is necessary for us to have proper knowledge about automotive emission and its control technology with its limitations to control mobile emissions. Engine modifications, fuel modification alone were not sufficient to control them, and catalytic systems were introduced to do this. Efforts for the replacement of supported noble metals are however deemed necessary because of the drawbacks of noble metals in practical application including high cost, volatilization and sintering at high temperature. Hence develop new catalyst that considered as promising alternatives to precious metals acting as effective TWC. Progressively more stringent emissions control legislation has forced IC engine and vehicle manufacturers to research increasingly efficient methods to control certain toxic materials in exhaust gas-particularly CO, hydrocarbons and nitrogen oxides. Due to their high activity, versatile and stable structure and low pgm content, Perovskites based catalyst can offer advantages over conventional catalysts. Their sturdy mineral structure and stability offer advantages wherever high temperatures are involved and in some cases, such as self-regenerating auto catalysts, give distinct benefits where other metal supports are deactivated over time. The Perovskite catalyst presents high performance while dramatically reducing the large amount of precious metals, thus conserving a valuable natural resource and lowering the cost of the catalyst.

Catalytic activity of substituted catalyst were investigated and seems to be more effective than non-substituted catalyst as leading to maximal conversion of carbon monoxide at low temperature

Findings

Due to their high activity, versatile and stable structure and low pgm content, Perovskites based catalyst can offer advantages over conventional catalysts.Their study mineral structure and stability offer advantages wherever high temperatures are involved. Self-regenerating auto catalysts, give distinct benefits where other metal supports are deactivated over time.

Application

Environmental application of Automotive Emission Control, it can completely eliminate the poisonous Carbon Monoxide Gas .

Chapter 7

References

1. M. N. Rao, H. V. N. Rao, Sources and classification of air pollutants, in: M. N. Rao, H. V. N. Rao, Air pollution, Tata McGraw-Hill publishing company limited-New Delhi, Chapter 2, pp. 4, 12.

2. Vinish Kathuria, Vehicular Pollution Control-Concept note, Madras School of economics, pp. 1-6

3. G.C. Kisku, Nature and type of pollution from automobiles and strategies for its control, Industrial Toxicology Research Centre, Environmental Monitoring Division, Lucknow, pp. 1-16

4. J. Wei, Catalysis for motor vehicle emissions, Advances in Catalysis 24 (1975) 57-129.

5. H. Shinjoh, Rare earth metals for automotive exhaust catalysts, Journal of Alloys and Compounds 408-412 (2006) 1061-1064.

6. C. Bartholomew, R. Farrauto, Environmental catalysis: Mobile sources, in: C. Bartholomew, R. Farrauto, Fundamentals of industrial catalytic processes, 2nd edition, John Wiley & Sons, Inc., New York, 2006, Chapter 10, pp. 706, 733-735.

7. R. Heck, R. Farrauto, Automobile exhaust catalysts, Applied Catalysis A: General 221 (2001) 443-457.

8. B. P. Pundir, Engine emissions and air pollution, in: B. P. Pundir, Engine emissions pollutant Formation and Advances in Control Technology, Narosa Publishing house, New Delhi, Chapter No 1, pp. 1-10

9. K. Wark, G. Warner, W. Davis, Mobile sources, in: K. Wark, G. Warner, W. Davis, Air Pollution and its control, 3rd edition, Wesley Longmann., Chapter 10, pp. 489

10. G. J. K. Acres, Catalyst systems for emission control from motor vehicles, in: Roy M Harrison, Pollution causes, effects & control, 2nd edition, The royal society of chemistry, pp. 221.

11. R. Zhang, A. Villanueva, H. Alamdari , S. Kaliaguine, Reduction of NO by CO over nanoscale $LaCo_{1-x}Cu_xO_3$ and $LaMn_{1-x}Cu_xO_3$ perovskites, Journal of Molecular Catalysis A: Chemical 258 (2006) 22-34.

12. M. Bukhtiyarova, A. Ivanova, L. Plyasova, G. Litvak, V. Rogov, V. Kaichev, E. Slavinskaya, P. Kuznetsov, I. Polukhina, Selective catalytic reduction of nitrogen oxide by ammonia on Mn (Fe)-substituted Sr(La) aluminates, Applied Catalysis A: General 357 (2009) 193-205

13. Iwakuni, Y. Shinmyou, H. Yano, H. Matsumoto, T. Ishihara, Direct decompostion of NO into N_2 and O_2 on $BaMnO_3$based perovskites oxides, Applied Catalysis B: Environemntal 74 (2007) 299-306.

14. M. Giorgos, S. Zissis, M. Giorgio, M. Urbano , M. Steve, R. Ken, A vehicle testing programme for calibration and validation of an evaporative emissions model, Fuel 88 (2009) 1504-1512

15. K. Wark, G. F. Warmer, W. T. Davis, Mobile Sources, in: K. Wark, G. F. Warmer, W. T. Davis, Air pollution its origin and control, 3rd edition, Addison Wesley Longmann, pp. 505-508.

16. B.P.Pundir, Engine Emissions: Pollutant Formation and Advances in Control Technology, Ch : 4, page no: 115-155.

17. Yasuo Nishihata et al, The intelligent catalyst having the self regenerative function of Pd, Rh and Pt for automotive emission control, Catalysis Today, 117 (2006) 312-328

18. Kaspar, J., Fornasiero, P., and Hickey, N. Automotive catalytic converters: current status and some perspectives. Catalysis Today 77 (2003), 419-449.

19. Labhsetwar, N., Biniwale, R., Kumar, R., Rayalu, S., and Devotta, S. Application of supported perovskite-type catalysts for vehicular emission control,. Catalysis Survey from Asia 10, 1 (2006), 55-64.

20. H. He, H. X. Dai, C. T. Au., An investigation on the utilization of perovskite type oxides $La_{1-x}Sr_xMO_3$ ($M=Co_{0.77}Bi_{0.20}Pd_{0.03}$)As three way catalyst, Applied Catalysis B: Environmental 33 (2001) 65-80.

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

22. Sharma, S., Hegde, M., Das, R., and Pandey, M. Hydrocarbon oxidation and three-way catalytic activity on a single step directly coated cordierite monolith: High catalytic activity of $Ce_{0.98}Pd_{0.02}O_2$. Applied Catalysis A: General 337 (2008), 130-137.

23. Ramadas, N. ABO_3 - type oxides - their structure and properties – a bird’s eyes view. Materials Science and Engineering 36 (1978), 231-239.

24. Zhang, R., Villanueva, A., Alamdari, H., and Kaliaguine, S. Reduction of NO by CO over nanoscale $LaCo_{1-x}Cu_xO_3$ and $LaMn_{1-x}Cu_xO_3$ perovskites. Journal of Molecular Catalysis A: Chemical 258 (2006), 22-34.

25. Nishita, Y., Mizuki, J., Tanka, H., Uenishi, M., and Kimura, M. Self regeneration of palladium-perovskite catalysts in modern automobile. Journal of Physics and Chemistry of Solids 66 (2005), 274-282.

26. Ronald M. Heck, Robert J. Farrauto. Automobile exhaust catalysts Applied Catalysis A: General 221 (2001) 443-457

27. B.P.Pundir, Engine Emissions: Pollutant Formation and Advances in Control technology, Ch : 5

28. Applied Catalysis B: Environmental 24 (2000) 243-253, $AMnO_3$ (A = La, Nd, Sm) and $Sm_{1-x}Sr_xMnO_3$ perovskites as combustion catalysts: structural, redox and catalytic properties,Paolo Ciambelli , Stefano Cimino , Sergio De Rossi , Marco Faticanti , Luciana Lisi d, Giuliano Minelli , Ida Pettiti , Piero Porta , Gennaro Russo , Maria Turco

29. Catalysis Today 107-108 (2005) 106-113 Combined methane reforming in presence of CO_2 and O_2 over $LaFe_{1-x}Co_xO_3$ mixed-oxide perovskites as catalysts precursorsM.R. Goldwasser , M.E. Rivas a, M.L. Lugo , E. Pietri , J. Pe´rez-Zurita , M.L. Cubeiro , A. Griboval-Constant , G. Leclercq

30. Cimino, S., Lisi, L., Rossi, S., Faticanti, M., and Porta, P. Methane conversion and CO oxidation on $LaAl_{1-x}Mn_xO_3$ perovskite-type oxidesolid solution. Applied catalysis B: Environmental 43 (2003), 397-406.

31. Microporous and Mesoporous Materials 54 (2002) 51-61 Mesoporous silica supported $LaCoO_3$ perovskites as catalysts for methane oxidation S.V. Nguyen 1,V. Szabo,D. Trong On,S. Kaliaguine

32. Seyfi, B., Baghalha, M., and Kazemian, H. Modied $LaCoO_3$ nano-perovskite catalysts for the environmental application of automotive CO oxidation. Chemical Engineering Journal 148 (2009), 306-311.

33. Nora A. Merino, Bibiana P. Barbero, Paul Grange, Luis E. Cadús, $La_{1-x}Ca_xCoO_3$ perovskite-type oxides: preparation, characterisation, stability, and catalytic potentiality for the total oxidation of propane, Journal of Catalysis 231 (2005) 232-244.

34. S.V. Nguyen 1,V. Szabo,D. Trong On,S ,Mesoporous silica supported $LaCoO_3$ perovskites as catalysts for methane oxidation Kaliaguine Microporous and Mesoporous Materials 54 (2002) 51–61

35. P. Ciambelli a, S. Cimino b, S. De Rossi c, L. Lisi d, G. Minelli c, P. Porta c, G. Russo b, $AFeO_3$ (A D La, Nd, Sm) and $LaFe_{1-x}Mg_xO_3$ perovskites as methane combustion and

CO oxidation catalysts: structural, redox and catalytic properties Applied Catalysis B: Environmental 29 (2001) 239–250

36. Paolo Ciambelli b, Stefano Cimino a, Sergio De Rossi c, Marco Faticanti c, Luciana Lisi d, Giuliano Minelli c, Ida Pettiti c, Piero Porta c; Gennaro Russo a, Maria Turco a, $AMnO_3$ (ADLa, Nd, Sm) and $Sm_{1-x}Sr_xMnO_3$ perovskites as combustion catalysts: structural, redox and catalytic properties, Applied Catalysis B: Environmental 24 (2000) 243–253
37. R.K.C. de Lima a, M.S. Batista b, M. Wallau c, E.A. Sanches d, Y.P. Mascarenhas d, E.A. Urquieta-Gonza´ lez a, catalytic behavior in the reduction of NO with CO , Applied Catalysis B: Environmental High specific surface area LaFeCo perovskites-Synthesis by nanocasting and catalytic behavior in the reduction of NO with CO
38. Giannakas, A., Leontiou, A., Ladavos, A., and Pomonis, P. Characterization and catalytic investigation of O^+CO reaction on perovskites of the general formula $La_xM_{1-x}FeO_3$ (M= Sr and/or Ce prepared via a reverse micelles micro emulsion route. Applied Catalysis A: General 309 (2006), 254-262.
39. Labhsetwar, N., Watanabe, A., Biniwale, R., Kumar, R., and Mitsuhashi, T. Alumina supported perovskite oxide based catalytic materials and their auto-exhaust application. Applied Catalysis B: Environmental 33 (2001), 165-173.
40. Rao, M. N., and Rao, H. V. N. Sources and classifecation of air pollutants CO_2, in: M. N. Rao, H. V. N. Rao, Air pollution. Tata McGraw-Hill publishing company limited - New Delhi. Chapter 2, pp. 4, 12.
41. Tanaka, H., Uenishi, M., Taniguchi, M., Tano, I., Narita, K., Kimura, M., Kaneko, K., Nishihata, Y., and Mizuki, J. The intelligent catalyst having the self regenerative function of Pd, Rh and Pt for automotive emission control. Catalysis Today 117 (2006), 321-328.
42. Zhang, R., Villanueva, A., Alamdari, H., and Kaliaguine, S. Reduction of NO by CO over nanoscale $LaCo_{1-x}Cu_xO_3$ and $LaMn_{1-x}Cu_xO_3$ perovskites. Journal of Molecular Catalysis A: Chemical 258 (2006), 22-34.
43. Zhang, R., Alamdari, H., and Kaliaguine, S. Fe-based perovskites substituted by copper and palladium for NO^+CO reaction. Journal of Catalysis 242 (2006), 241-253.
44. Paolo Ciambelli, Stefano Cimino, Sergio De Rossi, Marco Faticanti, Luciana Lisi, Giuliano Minelli, Ida Pettiti, Piero Porta , Gennaro Russo , Maria Turco , $AMnO_3$ (A=La, Nd, Sm) and $Sm_{1-x}SrMnO_3$ perovskites as combustion catalysts: structural, redox and catalytic properties, Applied Catalysis B: Environmental 24 (2000) 243-253.
45. M.R. Goldwasser , M.E. Rivas, E. Pietri , M.J. Pérez-Zurita , M.L. Cubeiro, L. Gingembre , L. Leclercq , G. Leclercq , Perovskites as catalysts precursors: CO_2 reforming of CH_4 on $Ln_{1-x}Ca_xRu_{0.8}Ni_{0.2}O_3$ (Ln = La, Sm, Nd), Applied Catalysis A: General 255 (2003) 45-57.

46. Hideki Taguchi , Satoshi Yamasaki , Atsushi Itadani , Masashi Yosinaga , Ken Hirota , CO oxidation on perovskite-type $LaCoO_3$ synthesized using ethylene glycol and citric acid, Catalysis Communications 9 (2008) 1913-1915.

47. Mohammad Ghasdi, Houshang Alamdari, CO sensitive nanocrystalline $LaCoO_3$ perovskite sensor prepared by high energy ball milling, Sensors and Actuators B 148 (2010) 478-485

48. C. H. Bartholomew; Robert J. Farrauto, Fundamentals of Industrial Catalytic Processes,2nd ; Wiley-VCH: Weinheim, 2005; pp 118-196.

49. Catalyst Characterization. Encyclopedia of Physical Science and Technology, 3rd , Academic Press: Liverpool, UK, 2004; Chemical Engineering, pp 501-526.

50. Scanning Electron Microscopy ,serc.carleton.edu/.../techniques/UWSEM.jpg.

51. Scanning Electron Microscopy, www.purdue.edu/REM/rs/graphics/sem2.gif.

52. Energy dispersive X-ray spectroscopy, en.wikipedia.org/wiki/EDAX

53. Transmission electron microscopy ,en.wikipedia.org/wiki/Transmission electron microscopy