CHAPTER – I
INTRODUCTION

Air pollution is one of the major concerns due to its effects on human health, vegetation and other materials. Among the major sources of air pollution are power generation, the burning of solid wastes, industrial processes, and especially transportation.

Transport sector is of vital importance for rapid development of various sectors of national economy such as agriculture, industry, tourism, security, etc. However, it leads to deterioration of the environment by toxic air pollutants in the atmosphere and consequently, causes serious health hazards to biotic community and damage to material properties. Over the years, there has been a substantial increase in air pollution caused by the vehicular exhaust emissions due to addition of more and more vehicles on roads to meet the transportation demand.244,304

Primary pollution from motor vehicles is the pollution that is emitted directly into the atmosphere, whereas secondary pollution results from photo-chemical reactions between pollutants after these have been released into the air.

In developing countries, migration of population from the countryside to the megacities is also one of the reasons for pollutant emissions into the atmosphere. This is mainly produced by the increase of vehicular traffic. In these countries this problem is exacerbated by the tendency to have a stock of old and badly maintained vehicles. These factors have produced far-reaching changes in air quality in urban contexts, especially in the 1990s, when the majority of clean air plans were made stringent.115

In India there has been large growth of vehicular population after independence. Though the number of automobiles per 1000 population in India is much less as compared to that in developed countries yet, the problem of exhaust pollution is very severe because of poor fuel quality, improper operating and maintenance conditions, faulty traffic management, bad conditions of roads, boom in number of two and three wheelers, most of which have very inefficient two-stroke, spark-ignition gasoline powered engines. The growing numbers of various types of vehicles and the secondary problems due to this have made our cities severely polluted and uninhabitable.
1.1 AIR POLLUTION FROM AUTOMOBILES

Most of the big cities in India face the problem of deterioration in air quality, mainly because of mobile sources of air pollution. In general, numerous short low speed trips accompanied by frequent starting, acceleration, deceleration and stopping make very inefficient and highly polluting automobile operation. In India, the operational cost of a vehicle has been estimated to go up by 20-25% on bad roads, in addition to the aggravation of air pollution problem. Due to bad conditions of roads, the fuel of about Rs. 20 millions is wasted everyday, i.e. wastage of about Rs. 7,300 millions every year.

Engine exhausts consist of a complex mixture, the composition depending on a variety of factors such as: type of engine (two- or four-stroke, spark- or compression-ignited), driving conditions, e.g. urban or extra-urban, vehicle speed, acceleration/ deceleration, etc. Compositions of different air pollutants found in automotive exhaust for some common engine types are listed in Table 1.1. The six major types of pollutants are carbon monoxide, hydrocarbons, nitrogen oxides, particulates, sulfur dioxide, and photochemical oxidants. Carbon monoxide, usually emitted from many industrial processes, transportation and domestic activities, is the major air pollutant. CO is one of the most abundant of the gaseous pollutants found in automobile exhaust. It is a colourless, odourless, tasteless but flammable gas, which is a product of incomplete combustion. It accounts for more than 50% of air pollutants pool in USA and also worldwide. More than $4 \times 10^{12}$ kg of CO is emitted globally every year.

Many studies reveal the effect of various operating parameters on the exhaust emission from vehicles.
Table 1.1: Exhaust conditions for two and four stroke, engines

<table>
<thead>
<tr>
<th>Exhaust Components and conditions</th>
<th>Diesel Engine</th>
<th>Four Stroke Spark Ignited Engine</th>
<th>Two stock Spark Ignited engine</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOx</td>
<td>350 – 1000 ppm</td>
<td>100 – 4000 ppm</td>
<td>100– 200 ppm</td>
<td>Non-toxic</td>
</tr>
<tr>
<td>HC</td>
<td>50 – 330 ppm</td>
<td>500 – 5000 ppm</td>
<td>20,000–30,000 ppm</td>
<td>Toxic</td>
</tr>
<tr>
<td>CO</td>
<td>30 – 1200 ppm</td>
<td>0.1 – 6%</td>
<td>1- 3%</td>
<td>Poisonous</td>
</tr>
<tr>
<td>O₂</td>
<td>10 – 15%</td>
<td>0.2-2%</td>
<td>0.2 – 2%</td>
<td>Non-toxic</td>
</tr>
<tr>
<td>H₂O</td>
<td>1.4 – 7%</td>
<td>10 – 12%</td>
<td>10 – 12 %</td>
<td>Non-toxic</td>
</tr>
<tr>
<td>CO₂</td>
<td>7%</td>
<td>10 – 13.5%</td>
<td>10 13%</td>
<td>Non-toxic</td>
</tr>
<tr>
<td>SO₂</td>
<td>10 – 1000 ppm</td>
<td>15 – 60%</td>
<td>10 -13%</td>
<td>Toxic</td>
</tr>
<tr>
<td>PM</td>
<td>65 mg/m³</td>
<td>-</td>
<td>-</td>
<td>Toxic</td>
</tr>
</tbody>
</table>

1.2 HEALTH EFFECTS OF AIR POLLUTION

The health effects of the pollution generated by automotive traffic are yet to be fully understood. The increasing incidences of asthma, other respiratory diseases and certain types of cancer have been linked to the pollutants emitted from vehicles such as carbon monoxide, oxide of nitrogen and volatile organic compounds.⁶²,⁶⁷ Polycyclic Aromatic Hydrocarbons are known carcinogens, the effects of which may not be apparent for years. The consequences may be more severe for children. Continued pollution levels above ambient air quality standards are likely to create a number of adverse health consequences.¹¹⁵ Polycyclic Aromatic Hydrocarbons (PAH), found in automobile exhaust are known to cause skin scrotum and lung cancer. Environmental estrogens like benzopyrene, benzoanthracene, lead particulates etc. emitted in the exhaust may cause endometriosis and cancers of uterus, breast, vulva and vagina.¹¹³

High levels of particulate matter for example, have been linked to a number of significant health problems, ranging from decreased lung function to increased respiratory and cardiac hospital admissions to premature death. NO₂, in recent epidemiological studies, has been increasingly associated with a number of
respiratory and cardiovascular conditions, including worsening bronchitis, emphysema, heart disease, and even premature cardiovascular mortality.

There have been about 40,000 deaths in India every year, mainly due to the ailments caused by air pollution generated by automobiles. In Delhi alone, the air pollution related mortality rose to 7,500 deaths per year as the city air received more than 2000 tonnes of air pollutants from automobile exhaust every day.\textsuperscript{29,259}

It is well established that many factors like temperature and its variation, time, meteorological conditions etc. have very strong influence on air pollution level at a place.\textsuperscript{232} In big cities, due to largely obstructed airflow, prolonged periods of stagnation lead to inadequate dispersion and consequently result in enhancement of ambient concentration of CO in air.

CO levels vary with type of traffic, traffic volume, and many meteorological variables. As CO emission increases with decreasing engine speed, traffic congestion, increasing the number of vehicles and also, by enhancing the value of emission rate per unit road length travelled by each of the vehicles. CO concentrations in ambient air encountered in heavy traffic is about three times higher in comparison to that in developed countries. Estimations of the CO concentration in and around roadways and urban arterials are considered essential to design the layout of different transportation routes.\textsuperscript{63,183} The interior of an automobile in slow moving of stationery traffic (traffic jam condition) is a prime site for high exposure to CO as revealed in a study.\textsuperscript{94}

Literature on CO poisoning is extensive and well established. In the period 1979-88 some 11,547 unintentional deaths due to CO poisoning occurred in USA alone.\textsuperscript{18} Severe poisoning by CO often results in lasting damage to the central nervous system (CNS), which may be delayed, progressive, irreversible and even lethal.

CO molecules attaches to hemoglobin in blood to form carboxyhemoglobin (COHb) in precisely the same way as O\textsubscript{2} molecules, but with about 240 times higher affinity. Hemoglobin tied cannot serve its normal function to transport oxygen in the blood as oxyhemoglobin (O\textsubscript{2}Hb). Carboxyhaemoglobin (COHb) in blood with 1-2% concentration can cause headache, fatigue, drowsiness and may have effect on human behavioural performance, 2-5% concentration may cause impairment of time interval discrimination, visual acuity, brightness discrimination and certain other psychomotor
functions which may lead to accident on roads. 5-10% concentration can lead to changes in cardiac and pulmonary functions and 10-80% can cause coma, respiratory failure and death.\textsuperscript{361}

It not only affects human beings but also vegetations by interfering with plant respiration and nitrogen fixation. The vehicle emission is the major source of CO in urban air, accounting for slightly over half of all the anthropogenic air pollutants.

Table 1.2: Effects at various COHb levels in human blood\textsuperscript{253}

<table>
<thead>
<tr>
<th>% of blood hemoglobin converted to COHb</th>
<th>Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3 – 0.7</td>
<td>Physiologic norm for nonsmokers</td>
</tr>
<tr>
<td>2.5 – 3.0</td>
<td>Cardiac function decrements in impaired individuals; blood flow alternations; and, after extended exposure, changes in red blood cell concentration.</td>
</tr>
<tr>
<td>4.0 – 6.0</td>
<td>Visual impairments, vigilance decrements, reduced maximal work capacity</td>
</tr>
<tr>
<td>3.0 – 8.0</td>
<td>Routine values in smokers. Smokers develop more red blood cells than nonsmokers to compensate for this, as do people who live at high elevations, to compensate for the lower atmospheric pressure.</td>
</tr>
<tr>
<td>10.0 – 20.0</td>
<td>Slight headache, lassitude, breathlessness from exertion, dilation of blood cells in the skin, abnormal vision.</td>
</tr>
<tr>
<td>20.0 – 30.0</td>
<td>Severe headaches, nausea, abnormal manual dexterity.</td>
</tr>
<tr>
<td>30.0 – 40.0</td>
<td>Weak muscles, nausea, vomiting, dimness of vision, severe headaches, irritability, and impaired judgment.</td>
</tr>
<tr>
<td>50.0 – 60.0</td>
<td>Fainting, convulsions, coma</td>
</tr>
<tr>
<td>60.0 – 70.0</td>
<td>Coma, depressed cardiac activity and respiration, sometimes fatal</td>
</tr>
<tr>
<td>&gt; 70.0</td>
<td>Fatal</td>
</tr>
</tbody>
</table>
Carbon Monoxide is a poisonous pollutant emitted in large quantity from automotive exhaust which needs to be transformed into harmless CO\textsubscript{2} needed for photosynthesis by vegetations. Therefore, in vehicular emission control, the catalytic oxidation of CO is of prime importance.

1.3 ENVIRONMENTAL REGULATION SCENARIO IN INDIA

Emission standards are requirements that set specific limits to the amount of pollutants that can be released into the environment. Many emission standards focus on regulating pollutants released by automobiles (motor cars) and other powered vehicles but they can also regulate emissions from industries, power plants etc.

The first Indian emission regulations were became effective in 1989. Since the year 2000, India started adopting European emission and fuel regulations for vehicles.

Article 48 of the Constitution of India states that all the States of India must endeavour to protect and improve the environment. A National Committee on Environmental Planning and Coordination (NCEPC) was constituted in 1972, to identify, investigate and propose solutions for the problems affecting the quality of the life of Indian people. Government of India has promulgated and enacted several legislations to prevent, control, reduce and restrict the environmental pollution due to release of different types of pollutants into all three components of the biosphere, i.e., atmosphere, hydrosphere and lithosphere. The relevant legislation on control of atmospheric pollution are available in detail elsewhere.

The Air (Prevention and Control of Pollution) Act, 1981 lays down in section 16(I) that the main function of the Central Pollution Control Board shall be to improve the quality of air and to prevent, control or abate air pollution in India and that without prejudice to the generality of the foregoing functions, the Central Pollution Control Board may lay down standards for the quality of air.

During 1990-91, mass emission norms for vehicles at manufacturing stage as well as for those in-uses were notified for the first time. From April 1995, only the passenger cars fitted with catalytic converters were allowed to be registered. Automobile manufacturers were required to make modifications in the engine design, particularly concerning crankcase and evaporative emission control as per the emission norms along with fuel quality specifications laid down in 1996.
1.3.1 Euro Norms

In October 2003, the Indian Auto Fuel Policy has been announced, which envisages a phased program for introducing Euro 2 – 4 emission and fuel regulations by 2010.\textsuperscript{66}

The Vehicular Exhaust Emission Norms are given in Table 1.3.

Table 1.3: Emission Norms for Gasoline Powered Vehicles\textsuperscript{66}

<table>
<thead>
<tr>
<th>Vehicle</th>
<th>Year</th>
<th>CO</th>
<th>HC</th>
<th>NOx</th>
<th>HC+NOx</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two wheelers</td>
<td>1991</td>
<td>12 - 30</td>
<td>8 - 12</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1996</td>
<td>4.50</td>
<td>-</td>
<td>-</td>
<td>3.60</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>2.00</td>
<td>-</td>
<td>-</td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td>2005 BSII</td>
<td>1.50</td>
<td>-</td>
<td>-</td>
<td>1.50</td>
</tr>
<tr>
<td></td>
<td>2010 BS III</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
</tr>
<tr>
<td>Three Wheelers</td>
<td>1991</td>
<td>12 - 30</td>
<td>8 - 12</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1996</td>
<td>6.75</td>
<td>-</td>
<td>-</td>
<td>5.40</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>4.00</td>
<td>-</td>
<td>-</td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td>2005 BSII</td>
<td>2.25</td>
<td>-</td>
<td>-</td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td>2010 BS III</td>
<td>1.25</td>
<td>-</td>
<td>-</td>
<td>1.25</td>
</tr>
<tr>
<td>Car</td>
<td>1991</td>
<td>14.3 - 27.1</td>
<td>2.0 - 2.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1996</td>
<td>8.68 - 12.4</td>
<td>-</td>
<td>-</td>
<td>3 - 4.36</td>
</tr>
<tr>
<td></td>
<td>1998</td>
<td>4.34 - 6.20</td>
<td>-</td>
<td>-</td>
<td>1.5 - 2.18</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>2.72</td>
<td>-</td>
<td>-</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>BS II*</td>
<td>2.2</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>BS II**</td>
<td>2.2 - 5.0</td>
<td>-</td>
<td>-</td>
<td>0.5 - 0.7</td>
</tr>
<tr>
<td></td>
<td>BS III*</td>
<td>2.30</td>
<td>0.20</td>
<td>0.15</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>BS III**</td>
<td>2.3 - 5.22</td>
<td>0.20 - 0.29</td>
<td>0.15 - 0.21</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2010 BS IV*</td>
<td>1.00</td>
<td>0.10</td>
<td>0.08</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2010 BS IV**</td>
<td>1.00 - 2.27</td>
<td>0.10 - 0.16</td>
<td>0.08 - 0.11</td>
<td>-</td>
</tr>
</tbody>
</table>

Note: For Catalytic Converter Fitter Vehicles
* Upto 6 seaters and Gross Vehicle Weight (GVW) upto 2500 kg
** More than 6 seaters and GVW upto 3500 kg.
1.4 ENGINE COMBUSTION

In the present scenario the motor vehicles are one of the largest contributors to the air pollution in cities. There are over 700 millions motor vehicles running on the road today, contributing 30% of total CO₂ and NOₓ emitted. In the motor vehicles generally used fuels are petrol, diesel, CNG, etc. A typical engine combustion results as given below:

Fuel + Air $\rightarrow$ Hydrocarbons + Nitrogen Oxides + Carbon Dioxide + Carbon Monoxide + Water

Because of the incomplete combustion of fuel in the engine hydrocarbons, oxides of carbon and nitrogen are the major emitted pollutants which are described below.

Carbon Monoxide: Carbon monoxide (CO) a colorless, odorless, poisonous gas, is a product of incomplete combustion of hydrocarbon-based fuels. Carbon-Monoxide is a poisonous pollutant emitted in large quantity from automotive exhaust. Most CO is produced when air-to-fuel ratios are too low in the engine during vehicle starting, when cars are not tuned properly, and at higher altitudes, where thin air reduces the amount of oxygen available for combustion. Two-thirds of the carbon monoxide emissions come from transportation sources.

Hydrocarbon pollutants: Hydrocarbon pollutants are mainly released from auto exhaust and industries. Hydrocarbon emissions result when fuel molecules in the engine do not burn or burn only partially. A number of exhaust hydrocarbons are also toxic.

Nitrogen Oxides (NOₓ): Under high pressure and temperature conditions in an engine, nitrogen and oxygen atoms react to form nitrogen oxides, NOₓ. Nitrogen oxides, like hydrocarbons, are precursors to the formation of ozone and contribute to acid rain.

Carbon Dioxide: U.S. Environmental Protection Agency (EPA) originally viewed carbon dioxide as a product of perfect combustion, but now views CO₂ as a pollution concern. Carbon dioxide does not directly impair human health, but it is a greenhouse gas that traps the earth's heat and contributes to global warming.

In cities across the globe, the personal automobile is the single greatest polluter, as emissions from a billion vehicles on the road add up to problems. Driving a private car is a typical citizen's most air polluting activity. The negative effects of automotive
emissions are more when you sit in traffic surrounded by cars, their engines idling. Everyone in a traffic jam is getting poisoned.

Out of these CO being poisonous is most dangerous for living world.

1.5 CONTROL OF THE EXHAUST POLLUTION

Various primary measures: (engine modifications, fuel modifications, fuel/air ratio, etc.) failed to match the complete emission requirements.

The primary measures for vehicular exhaust emission control aim at reducing the generation of the pollutants at the source itself by making modifications in the engine substituting the fuel (fully or partially) or by other appropriate strategies. Various strategies designed to achieve this purpose are mentioned in below:

1.5.1 Engine Modifications

1. Modification of the engine components.
2. Design and addition of new components to reduce evaporative emissions from the fuel handling system.
3. Research and design to develop a new type of prime mover to replace conventional IC engines.

1.5.2 Fuel Modification/Replacement

Additives like tetra ethyl lead (TEL) and tetra methyl lead (TML) have been used as additive for improving the knocking characteristics of gasoline for long, but because of their property to deactivate the automotive catalytic converter and increase the lead loading of the biosphere, these have been abandoned. Other additives like highly branched ethers such as MTBE and ETBE are being used as alternatives to these lead based anti-knocking compounds.

Several other fuels have been used for many years in slightly modified automobile engines for reasons of cost, availability and their lower potential to cause environmental pollution. The gases used are like CNG and LNG. H$_2$ may also be used. There are very good prospects for biomass derived liquid fuels to become competitive with fossil fuels in the foreseeable future.

Natural gas (CNG or LNG), LPG (mostly propane), methanol and ethanol are being promoted as clean fuels. By partial substitution or gasoline with ethanol as shown in
Table 1.4, substantial decrease in CO concentration in exhaust of a car has been observed.

**Table 1.4: Decrease in CO emission with ethanol blend**

<table>
<thead>
<tr>
<th>Ethanol (% v/v)</th>
<th>CO(%) with 27 °btdc</th>
<th>CO(%) with 32 °btdc</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>3.5</td>
<td>0.8</td>
</tr>
<tr>
<td>14</td>
<td>2.0</td>
<td>1.3</td>
</tr>
</tbody>
</table>

1.5.3 Other Options

Battery Operated Automobiles: These produce negligible local air pollutant emissions and are quieter than IC powered automobiles. The main difficulties are the extra load of traditional lead acid batteries, lower distance travelled between successive recharging and the difficulties encountered in change or recharging of batteries. Because of these problems, these engines fail to stand as a very strong competitor.

Hybrid Electric Vehicle: It is run on electric power obtained by suitable combination of two sources, which may be traction batteries located inside the vehicle and overhead trolley wires.

Hydrogen Fuel and Fuel Cell Technology: Fuel cells make the fuel react electrochemically with $O_2$ without burning it and generate DC power which is used to move the motor of fuel cell vehicle. Fuel cell-based automobiles have gained attention in the last few years due to growing public concern about urban air pollution and consequent environmental problems. At present, direct hydrogen FCVs fuelled with liquid hydrogen appear to be the best option.

1.6 CATALYTIC COMBUSTION

Catalysts are considered as chemical elements or compounds, which are capable of directing and accelerating feasible reactions, but these substances remain unaltered at the end of the reaction. The most sought after properties of a catalyst are its activity, selectivity, stability and life. These qualities of the catalyst are dependent on its physiochemical properties like surface area, pore size distribution, pore volume, mechanical strength, thermal characteristics, regeneration properties and
reproducibility etc. Catalysts have tremendous scope in air pollution control, e.g. in abatement of industrial odors, organic vapors and flue gases, reduction of oxides of nitrogen to nitrogen gas, purification of air in domestic and working environment and treatment of automobiles exhaust.

Emission Control (IEC) Program of USA demonstrated first the feasibility of catalytic purification of the tail pipe exhausts. Initially, emissions of CO and unburned hydrocarbon were controlled. The more stringent NOx emissions standard after 1980 brought out the introduction of three way catalytic converter, which could simultaneously convert CO, HC and NOx to normal atmospheric gases such as N\textsubscript{2}, O\textsubscript{2}, CO\textsubscript{2} and H\textsubscript{2}O vapor. Today exhaust catalytic converters are found on nearly all vehicles. The reactions taking place are:

The oxidation of HC and CO

\[
C_xH_y + (x + y/4)O_2 \text{(air)} \rightarrow xCO_2 + y/2H_2O
\]

1.1

\[
CO + \frac{1}{2} O_2 \rightarrow CO_2
\]

1.2

The reduction of NOx which occurs mostly through the reaction with CO

\[
NO_x + xCO \rightarrow \frac{1}{2} N_2 + xCO_2
\]

1.3

NO Reduction by HC:

\[
26NO + 2C_4H_{10} \rightarrow 13N_2 + 10H_2O + 8CO_2
\]

1.4

Because of this threefold functions, the catalyst is also known as three way catalyst. The three way catalyst usually consists of noble metals (Pt, Pd, Rh) with promoter, stabilizer, support etc. The three-way catalytic converter has effectively reduced emissions of these pollutants from automobiles.

Catalytic converters can operate efficiently at all temperatures above the light-off temperature of the catalyst.

It has been widely accepted that new vehicles equipped with three way catalytic converters generally emit more N\textsubscript{2}O than older vehicles without catalytic converter and therefore, concern is being raised that N\textsubscript{2}O emission may substantially increase as the global fleet of old vehicles is replaced with the modern one, fitted with three way catalytic converter to reduce urban air pollution.
Automotive catalytic converter (ACC) has been proposed as an end-of-the pipe treatment technology. ACC carry out both reduction and oxidation reactions in the presence of catalysts, to convert pollutants to normal atmospheric gases i.e. \(N_2\), \(O_2\), \(CO_2\) and \(H_2O\).

1.7 CATALYSTS FOR CO OXIDATION

The catalytic control of these pollutants has been proposed as an end of the pipe treatment technology. The benefits of catalytic purification of primary pollutants to atmospheric gases (\(CO_2\), \(N_2\), \(O_2\) and \(H_2O\)) using three way catalyst (TWC) for spark ignited engine exhaust have been discussed by Gandhi.\textsuperscript{102}

The catalysts used for the exhaust emission control need be effective over a wide range of exhaust temperature, gas flow rates, exhaust compositions etc.

The development of efficient catalysts, for oxidation of CO and increasingly stringent emission standards, has attracted worldwide research interest due to their potential application in catalytic converter.

There has been large number of catalytic materials reported in literature for their application for auto-exhaust and oxidation reaction of CO but most of these fail to meet the requirements for automotive exhaust purification. This application requires specifically designed catalyst system for satisfactory performance under widely varying conditions.\textsuperscript{90, 97, 102, 201}

The active oxides in the catalytic system applicable for CO oxidation reaction can be broadly classified in two large groups, i.e.,

- weakly basic oxides of heavy metals like Cu, Co, Ni, Ti and Zn
- weakly acidic oxides of Cr, Mn, Mo and Fe.

In addition, a large number of oxides of rarer earth elements like Ce, and Th have also been found suitable.

Mixed oxides having perovskite-structures are also identified as promising catalyst.\textsuperscript{382}

1.7.1 Noble Metal Catalysts

Precious noble metals Pt, Pd and Rh, are predominantly used as catalysts for their high performance despite being very expensive. These have found single largest application
in automotive pollution control. Noble metals unsupported and with supports like alumina, ceria, zirconia, etc., have been studied for catalytic oxidation of CO.

Various catalysts involving noble metals, oxides of base metals, material with complex semiconductor properties (CuO, V2O5 etc.), copper chromite, manganese cobaltites, cobalt maganites etc. and modification of supported noble metal catalysts with alkaline additives (promoters) like K2O, CeO2, Na2O etc. have also been studied.

For the oxidation of CO, use of noble metals based catalysts has also disadvantage for the reasons of their lower intrinsic selectivity (Pt) or high sensitivity to the presence of CO2 (Au) and higher costs.

Ceria has been used as a support with a number of catalysts because of its suitable redox properties. Noble metal based catalytic systems using gold, Pt, Pd and Rh on ceria support has been studied by many workers.

Copper oxide support with noble metal catalyst has been studied. Pt/SnO2 and Pd/SnO2 catalysts are widely used as low temperature CO oxidation catalysts.

A new Pt-Rh three-way catalyst is developed, which gives equivalent or better performance when compared to conventional Pd-Rh three-way catalyst. Additional of CeO2-ZrO2 in 3-way catalyst improves the O2 storage capacity and also increases its thermal stability.

Gold has long been disregarded for catalytic purposes due to the inert nature of massive gold. Recently, it has been demonstrated that gold is very active for the low temperature oxidation of CO, if dispersed on suitable metal oxides and composite oxides.

Noble metal catalysts (Pt, Pd, Rh) are predominantly used in automotive pollution control. In search of an alternative to these highly scarce and costly noble metals, many catalysts have been reported for CO oxidation. Various alternative catalysts involving base metals like Cu, Co, Ni, Fe, etc. are reported to exhibit their capabilities to initiate CO oxidation below 100°C. In addition, a large number of oxides of rare earth elements like Ce, Th, U, etc., and other catalysts like Hopcalite (CuMnO3), copper chromite and manganese cobaltite have also been found suitable.
Mixed oxides having perovskite – structures are also identified as promising catalysts.17, 51, 381

A comprehensive literature review has been done for the Noble Metals and is given in Chapter 2.

1.7.2 Base Metal Catalysts

The catalytic oxidation of CO on transition metal surface has gained increasing importance in recent years in industrial chemistry and automobile emission control.

However, higher cost of noble metals catalyst used in current catalytic converters and recent regulations on emission control of vehicles, present a large challenge and opportunity for development of low cost alternatives such as transition metal oxide catalysts.175, 205, 206, 263

Several materials as substitute for Noble Metals have been reported:

- Base metals (Fe, Cu, Ni, etc.)
- Manganese cobaltite
- Copper chromite
- Base metal containing zeolites
- Hopcalite, mixture of Cu, Mn, Ag, and Co
- Mixed rare earth oxides having perovskite structure, etc.

Base metal oxides like CoO4, CuO and MnO2 have been found to be having high catalytic activity per unit surface area for CO oxidation reaction. But, both CoO4 and MnO2 are observed to get more easily poisoned by sulfur compounds in the exhaust. A large number of oxides of chromium, cobalt and rare earth elements like Ce, Th and U have also been found suitable. Cobalt oxides have also been found to make low cost oxidation catalysts for automobile exhaust pollution control.169, 265

Mixed oxides having perovskite-structures are also identified as promising catalyst.134, 363 Compared to the noble metals, base metal catalysts show a lower, but still sufficient activity as oxidation catalysts, their advantage being the lower costs.

Hopcalite (Cu Mn2O3) have high durability for oxidation of CO in dry conditions, but these are readily poisoned by water vapor. These catalysts also lose their activity due to sintering, if subjected to prolonged heating at temperatures above 250°C.
Perovskites form an interesting category of mixed oxides that have been studied widely in view of their activity in oxidation reactions and relatively lower cost. Rare earth oxides crystallizing in perovskite-structure have been found suitable to make low cost oxidation catalysts for automobile exhaust pollution control\(^{201,265}\). Copper chromite catalyst is found to be the most promising among non-noble metal oxides and exhibits comparable activity for CO oxidation to that of precious metal based auto exhaust purification catalyst.\(^{1,381}\)

### 1.7.3 Promoters for Catalytic Oxidation

Promoters are the substances:

- those favor the catalyst activity
- they create the ideal condition for the catalyst and even increase the life of the catalyst by saving them from the poisons.

Some of the important promoters used generally in the oxidation process for CO are:

- Titanium dioxide (TiO\(_2\)): Titanium dioxide is itself a catalyst, and it showed good performance as a promoter also. It is generally utilized with the noble metal catalysts. Its performance is good for oxidizing the carbon monoxide to carbon dioxide.

- Cerium oxide (CeO\(_2\)): The effectiveness of cerium oxide is well established in three-way catalysts. The main function of CeO\(_2\) is to store oxygen under lean fuel/air mixture condition and to release oxygen under rich condition.

- Potassium Oxide (K\(_2\)O): Potassium is an important promoter for the oxidation catalyst. This is also very useful in removing soot from the diesel engine exhaust.

### 1.7.4 Supports for the Catalytic Oxidation

- Alumina: High purity Alumina can be used up to 1700\(^\circ\)C for oxidation. Alumina also shows good wear resistance and high hardness. These properties of the alumina make it very useful as a support for catalytic oxidation. It also provides high surface area for good dispersion of the active component.

- Zeolite: Zeolites are naturally occurring hydrated Alumino Silicates characterized by high surface area and High permeability.

- Zirconia: Zirconia able to sustain temperature even up to 2400\(^\circ\)C. Other properties like high density, chemical inertness, resistance to molten metal, wear resistance, high
fracture toughness, high hardness makes it an extremely good catalyst support and stabilizer.

Silica: Silica occurs commonly in nature as sandstone, silica sand or quartzite. Silica having zero thermal expansion is a good characteristic for the oxidation process where high temperature condition prevails.

1.7.5 CuO/CeO₂ catalysts

Among the base metals, Copper oxides have been studied as a catalyst for a variety of important reactions including CO oxidation, one kind of modification on the copper oxide catalyst is focused on the improvement of the support. Ceria is well known to increase the low temperature oxidation ability of catalyst due to its oxygen storage capacity.

Cu-CeO₂ systems are identified as one of the promising catalysts to substitute for noble metal catalysts for vehicular emission control because of their high activities toward NO, CO and hydrocarbon oxidation.²⁸,⁴⁵,³⁴¹

Copper cerium catalyst is found to be the most promising among non-noble metal and exhibits comparable activity for CO oxidation.²⁰⁶,³⁹⁹ A comprehensive review of catalysts have been given by Libby.²⁰¹ Redox properties of CuO-CeO₂ catalysts have been discussed in Chapter 2.

CuO-CeO₂ catalytic systems have been examined for several processes. All these processes involve oxidation reduction steps, which are promoted by the presence of ceria in comparison to traditional copper-based systems. Cu-CeO₂ systems are identified as one of the promising catalysts to substitute for noble metal catalysts for vehicular emission control because of their high activities toward NO and CO and hydrocarbon oxidation.²⁷

Among the possible doping elements, zirconium is preferred. The introduction of zirconium ions also increases the formation of structural defects, which play an important role in the determination of the oxidation-reduction conditions.³⁴,¹³²,³⁴²

The CuO-CeO₂ catalytic systems are getting popular for catalyzing very actively the various reactions of environmental, commercial and other importance. In recent years, many methods have been in use for the preparation of versatile CuO-CeO₂ catalysts. Reviewing the useful preparation methods of such catalysts is thus the need of the
time in view of the increasing interest towards all the low temperature redox reactions. A short review on seventeen different preparation methods of the copper based catalysts, have been discussed in Chapter II.

1.8 OBJECTIVES

Various primary measures for exhaust pollution control have failed to match the requirements being put forward by regulatory stipulations in different developed and developing countries of the world. Therefore, the catalytic control of these pollutants has been proposed and being adopted as an end-of-the-pipe treatment technology, making use of automotive catalytic converter. It is clear from the facts mentioned earlier that this exhaust purification device in current use contains noble metal (Pt, Pd and Rh) catalysts. However, excessively high cost due to scarcity of these metals and an urgent need for maintaining the clean air in urban areas necessitate the development of an effective low cost base metal catalyst.

To meet the severe conditions of temperature prevailing in the automotive exhaust, the catalyst material need to be heat resistant in nature so that it can maintain its higher catalytic activity for longer periods. The catalytic system, known as copper oxide, has been reported to be one of the most active materials for carrying out the CO oxidation and it has also got the capability to the harsh conditions of high temperature found in automobile exhaust. It is much cheaper as compared to noble metals and thus, this catalyst can prove to be an economically-feasible substitute to the catalytic system being used at present. This catalytic system can also be thought of being used for control of the pollution caused by two wheeler vehicles, which have been found to be the largest contributors to the pollution of urban air environment in the developing countries. Therefore, copper oxide catalyst has been chosen for the present study.

Keeping in view the facts mentioned above, the objectives of the present study are:

1. To fabricate and install the experimental setup for the oxidation of CO.
2. To prepare unsupported and alumina supported copper based catalysts having promoter and stabilizer.
3. To screen various catalysts for identification of most suitable one for CO oxidation.
4. To characterize the catalysts by various techniques: BET surface area, pore volume, pore-size distribution, thermal analysis, X-ray diffraction and Scanning Electron Microscopy.

5. To study the kinetics and modeling of the reaction system based on the best selected catalysts.

With lead and sulfur contents in gasoline going down and because of the regulations becoming more and more stringent, base metal catalysts may become right alternative to Noble Metal catalysts used in three-way catalytic converter.

This work is mostly based on the study of the properties of catalyst and the reaction mechanism and kinetics.

In the present study the following work has been undertaken:

- Unsupported and alumina supported copper based catalysts having ceria as promoter and Zr stabilizer have been prepared by four different methods.

- A compact and versatile laboratory tubular reactor as described and fabricated keeping in view of reducing capital cost and minimising energy consumption for gas-phase heterogeneous catalytic reactions have been used for conducting the studies. The attractive feature of the reactor is that the vaporiser, pre-heater and fixed bed reactor are merged in a single compact unit. Details have been described earlier and are discussed in Chapter 3.

- Experiments have been carried to study activity of catalysts and to conduct the kinetic studies.

- The materials have been characterized by means of XRD, BET, TGA and SEM analysis.

- The results are presented in Chapter 4 and the activity of catalysts and the reaction kinetics has been discussed.

The study of supported and unsupported CuO/\(\text{CeO}_2/\text{ZrO}_2\) systems for the CO oxidation with a special attention to the reaction mechanism, and the influence of catalyst composition on the properties of the system have been evaluated and discussed.