

Chapter 1 Introduction

1. General

Air Pollution is the most prominent and dangerous form of pollution. An air pollutant is a substance in the air that can have adverse effects on humans and the ecosystem. The substance can be solid particles, liquid droplets, or gases. A pollutant can be of natural origin or man-made. Pollutants are classified as primary or secondary. Primary pollutants are usually produced by a process, such as ash from a volcanic eruption. Secondary pollutants are not emitted directly. Rather, they form in the air when primary pollutants react or interact. The increase in population, the numbers of vehicles are increasing causing more air pollution problem in the world. The major air pollutants present in the air are carbon monoxide (CO), nitrogen oxide (NO_x), unburned hydrocarbons (HC) and particulate matter (PM). These air pollutants harmful effects on all the living beings. The emissions of pollutants are a byproduct of the combustion of fossil fuels [Ogur and Kariuki, 2014]. Out of all these pollutants, CO is one of the most poisonous gas and known as the silent killer of the 21st century. It is colorless, odorless, tasteless and nonirritating gas which makes it very difficult for humans to detect. CO is emitted in the environment by the incomplete combustion of carbon-containing fuels. It combined with hemoglobin present in the blood cells and converted into carboxyhemoglobin; which reduces the oxygen carrying capacity of a human body [Amin *et al.*, 2012]. The health effects of CO explored are a headache, fatigue, seizure, coma, fatality, nausea, vomiting and death also. [Behar *et al.*, 2012]. The worldwide background concentrations of CO range between 0.06-0.14mg/m³ (0.05-0.12ppm). The emissions from vehicles are usually the reason for two-thirds of CO produced into the environment [Bhandarkar 2013; Hasunuma *et al.*, 2014].

The ambient temperature oxidation of CO is a very important reaction for life support in enclosed atmospheres such as submarines and spacecraft. A catalytic converter is an emission control device applied for reducing the toxicity emissions from the combustion of products. There are two different types of work done by the catalysts present in a catalytic converter such as reduction and oxidation catalyst. In both conditions, the catalysts consist of a ceramic monolith structure and coated with a metal support [Chauhan 2010]. The catalytic reaction is the reaction between the catalyst surfaces and the remaining gases present in the exhaust. The performance of catalytic converter is highly depending upon the types of the catalyst is used. In the presence of catalyst the rate of chemical reaction is increased, it acts as an agent that reduces the activation energy of the reactions. The efficiency of a catalytic converter is highly depending upon the temperature. The noble metals (Pt, Pd, Rh, Au) base metals (Cu, Mn, Cr, Co, Ni, Fe) and metal oxide (Cu_2O , ZnO , CeO_2 , ZrO_2) is widely used as a catalyst in the catalytic converter [Biemelt 2015; Cai *et al.*, 2012]. The noble metal catalysts have a high activity and thermal stability. The copper-based catalyst is more concerning to oxidize CO and HC into CO_2 and H_2O in the exhaust system [Benjamin and Alphonse 2016].

Compared to noble metal catalysts, the hopcalite (CuMnOx) is one of the oldest known catalysts for CO oxidation at a low temperature. To date, there are various methods have been applied to the preparation of CuMnOx catalysts, including co-precipitation, sol-gel, reduction and pyrolysis method, etc. Among these methods, the co-precipitation can be produced the highly active CuMnOx catalyst for CO oxidation [Cai *et al.*, 2012]. The optimum preparation conditions have been recognized the maximum activity of CuMnOx catalyst. The effect of preparation conditions, ageing time and calcination strategy highly effects on the performance of CuMnOx catalyst [Cholakov 2010]. The other preparation parameters such as pH, temperature, and Cu: Mn molar ratio is highly

influenced by the activity of resulting catalysts. In the CuMnOx catalyst, the addition of other components, such as silver, gold, cobalt, zinc and ceria etc. is enhanced their performance for CO oxidation [Njagi *et al.*, 2010]. The important role of doping in CuMnOx catalyst is providing additional active sites or created surface oxygen vacancy for a potential modification of the reaction mechanisms.

The material's heat treated under an oxygen-containing atmosphere produced the CuMnOx spinel phase, while the oxygen-free environments resulted in the reduction of Cu phases to produce Cu metal and MnOx phases [Clarke *et al.*, 2015]. The CuMnOx catalyst is highly active in the amorphous state, but they are lost their activity at a temperature above 500°C, where the crystallization of CuMnOx has occurred [Mirzaei *et al.*, 2003]. The performance of the catalyst can be associated with the presence of CuMn₂O₄ spinel phase, with excellent content resulting in a higher catalytic activity [Cole *et al.*, 2010]. The Cu-Mn mixed oxide under these conditions distinct phases can be maintained and it could be significant for catalytic reactions [Kondrat *et al.*, 2011]. From the TPR results, we have to find out that the CuOx can be reduced at a lower temperature than MnOx, so that the reducibility of CuOx is higher than MnOx phases [Mirzaei *et al.*, 2013]. The presence of Au into the CuMnOx catalyst has also increased their water poisoning resistance. The effect of surface improvement in Cu and Mn is an addition to being used as a model system for the design of oxidation catalysts [Cole *et al.*, 2010; Haruta *et al.*, 1989]. The co-precipitation method is a very useful method for the preparation of microporous or mesoporous materials with a constant distribution of different elements at a high-surface area [Kramer 2006].

1.1 Sources of CO emission

CO is a neutral oxide which burns in air to give CO₂. It's a good reducing agent. There are several natural and anthropogenic sources of CO emissions. The natural concentration of CO in the air is around 0.2 parts per million (ppm), and that amount is not harmful to humans [Bhandarkar 2013]. The three main primary anthropogenic sources of CO emissions are residential, industrial and transportation. The source of CO emissions into the environment is shown in Figure 1.1. The transportation sector is the largest source of CO emissions in the environment. In an urban area, the motor vehicles contribute more than 90% CO emissions. The CO emission from vehicles increases dramatically in cold weather as compared to hot weather [Badr and Probert 1994].

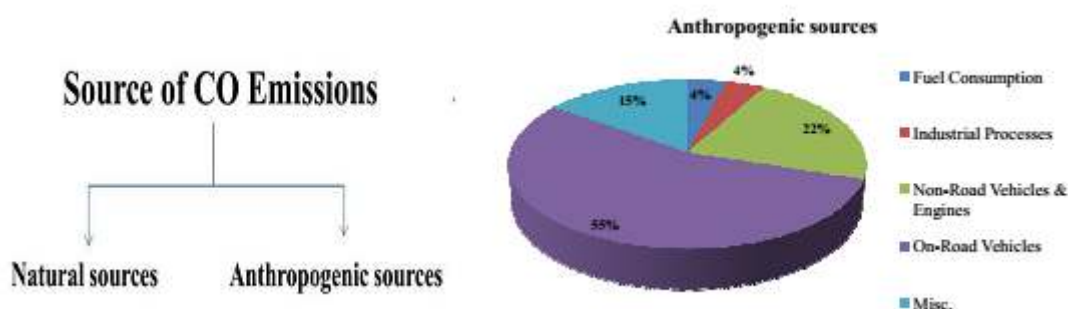


Figure 1.1: Sources of CO emission

The other sources of CO emissions include manufacturing processes (such as processing of metals and chemical industry), residential wood burning and natural sources such as forest fires [Chauhan 2010]. The gas stoves, wood stoves, cigarette smoke and kerosene space heaters are indoor sources of CO emissions [Chen 2011]. The composition of CO in a dry atmosphere by volume is shown in Table 1.1. The highest levels of CO typically occur during the colder months of the year when inversion conditions (when the air pollution becomes trapped near the ground beneath a layer of warm air) are more frequent.

Table 1.1: Composition of CO in dry atmosphere (by volume)

Concentration	Source
0.1 ppmv	Natural atmosphere level (MOPITT)
0.5–5 ppmv	Average level in homes
5–15 ppmv	Near-properly adjusted gas stoves in homes, modern vehicle emissions
5,000 ppmv	Exhaust from a home wood fire
7,000 ppmv	Undiluted warm car exhaust without a catalytic converter

ppmv: parts per million by volume

MOPITT: measurement of pollution in the troposphere

The diesel engines are extensively used in heavy-duty vehicles for its improved fuel efficiency and power yield than petrol engines. In comparison of a diesel engine, the petrol engine produces more CO into the atmosphere and it is represented in Table 1.2 [Chhatwal *et al.*, 1975; Cholakov 2010]. In the current scenario the fuel shifting towards the CNG fuels to overcome this vehicular emissions problem [Badr and Probert 1994]. The CO emission from CNG vehicles is two times less than the gasoline engine vehicles.

Table 1.2: Exhaust component of diesel engines and gasoline powered engines

Exhaust Component	Diesel Engines	Gasoline Engines
CO	300-1200ppm	1500-4000ppm
HCS	50-330ppm	50-5000ppm
NO _x	350-1000ppm	100-4000ppm
Particulate Matter	20-200mg/m ³	12-40mg/m ³

1.2 The adverse effect of CO emission

The emissions of CO from different sources highly impact on human, animal, vegetation and the environment.

1.2.1 Effects of CO on human health

The adverse effect of CO on human health is a long-term recognized. CO profoundly affects the cardiovascular system of human and animals, and its affinity to combines with hemoglobin is 210 times higher than the oxygen [Prockop and Chichkova 2007]. When CoHb percentage is reached more than 50%, therefore, the permanent brain damage of the human beings causes death. The oxygen-carrying capacity of the blood decreases, causing tissue hypoxia [Liu *et al.*, 2012]. The chronic effect of CO poisoning on human health increases the pulse rate, respiration system failure, neurological reflexes, headaches and dizziness. After CO exposure arrhythmias, angina attacks and increased the level of cardiac enzymes [Cole *et al.*, 2010]. The effect of CO emission on the human health is shown in Figure 1.2.

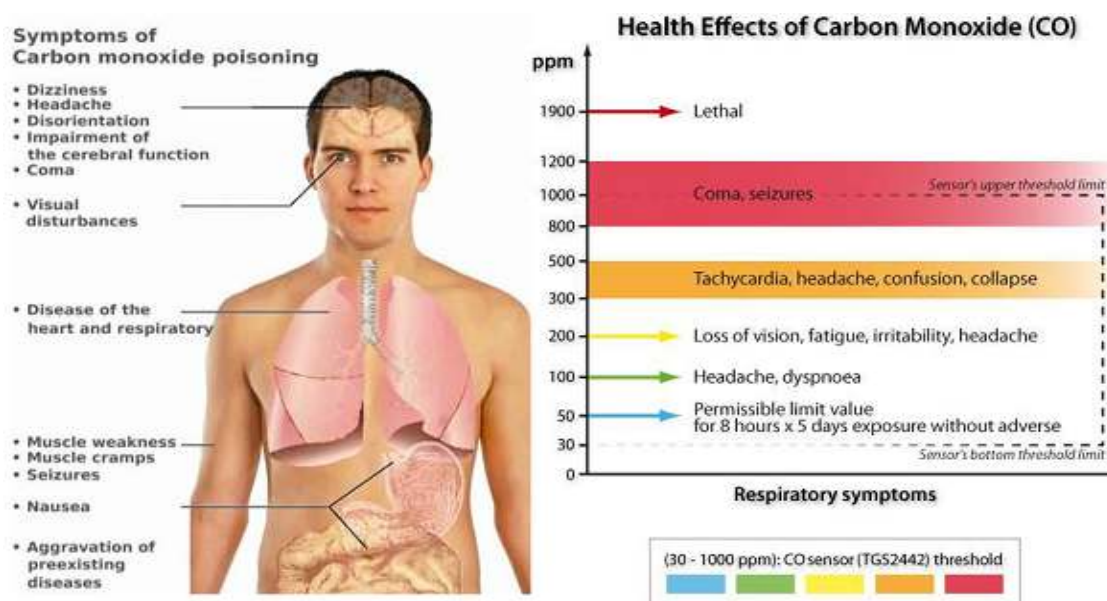


Figure 1.2: Effect of CO on human health

(Source: https://en.wikipedia.org/wiki/Carbon_monoxide_poisoning)

The disturbance of brain function due to acute CO intoxication results in headache. Neurological symptoms of CO include dizziness, weakness, nausea, vomiting, confusion, disorientation and visual disturbances. Due to CO emissions more than one-half of the fatal poisoning occurs in different countries [Cole *et al.*, 2010; Raub *et al.*, 2010].

1.2.2 Effects of CO on plants

CO is a lower molecular weight diatomic gas and it's able to influence the plant seed germination, induce the adventitious rooting process [Fortunato *et al.*, 2000]. Due to the CO poisoning, the plant leaf is curling, reduces leaf size, premature ageing of the chlorophyll as shown in the Figure 1.3. It reduces the cellular respiration system of the plants and also reduces the agriculture productivity [Ghaffari *et al.*, 2008; Xuan *et al.*, 2008]. The longtime CO exposure causes reduce the length of primary roots and reduce the distance from seed to the tip of the leaf. Due to the CO exposure plant leaf is decolorized and drops its shape. The current indication suggests that the concentration of atmospheric CO is a major implication for plant physiology and growth [Goldsmith and Aronow 1975].



Figure 1.3: Effect of CO on plant

(Source: <https://www.skepticalscience.com/co2-plant-food.htm>)

Under rising CO most plant species show advanced rates of photosynthesis, decreased water use and lowered tissue concentrations of nitrogen and protein [Richards and MacDougal 1904]. The rising of CO concentration is highly affected both the agricultural production and the food quality.

1.2.3 Effects of CO on environment

CO is only a weak direct greenhouse gas but has a significant indirect effect on global warming. It reacts with hydroxyl (OH) radicals in the atmosphere, reducing their abundance. The increasing CO percentage in the environment to increases the global warming level and ozone layer depletion [Ogur and Kariuki 2014]. It is one of the main reactive trace gasses in the earth atmosphere. In the atmosphere the CO level concentration ranging from 15-30ppmV, it affects the earth's radiation directly as the oxidation of CO would result in supplying more CO₂ from the greenhouse gas into the atmosphere [Guo *et al.*, 2016; Rudolf 1994].

1.3 Emission of CO from automobiles

The exhaust gas emitted as a result of the combustion of fossil fuels such as coal, natural gas, gasoline and diesel, etc. The motor vehicles discharged CO into the atmosphere through an exhaust pipe, flue gas stack or propelling nozzle. Exhaust gas temperature (EGT) is essential to the performance of the catalytic converter in an internal combustion engine [Mishra and Prasad 2014]. The motor vehicle CO emissions are a part of the anthropogenic contribution to the expansion of CO concentrations in the environment which some claim is causing the climate change. The CO emission level depends more on the vehicle technology and the state of maintenance [Prockop and Chichkova 2007].

1.3.1 Formation of CO in internal combustion engines

The internal combustion (I.C.) engine is operating by the burning of fossil fuels like petrol or diesel, both are contains a mixture of HC. When an I.C. engine gets a stoichiometric mixture of air and fuels (A:F= 14.7:1), it emits a minimum amount of pollutants. The CO is formed as an intermediate reaction during the incomplete combustion of HC [Chen *et al.*, 2009]. When the air-fuel (A/F) ratio is too low and there is insufficient oxygen to convert all the carbon present in a fuel into the CO₂. The CO concentration is raises as the A/F ratio decreases and its maximum when the automobile is an idled condition [Chhatwal *et al.*, 1975]. The ratio of A/F plays an important role in the efficiency of the combustion process. There are different conditions in the combustion chamber which prevent perfect combustion and the cause of unwanted chemical reactions has occurred. It causes harmful exhaust gases are emitted in the environment [Venkatesan *et al.*, 2017]. The effect of A/F ratio and the formation of CO in internal combustion engine as shown in Figure 1.4.

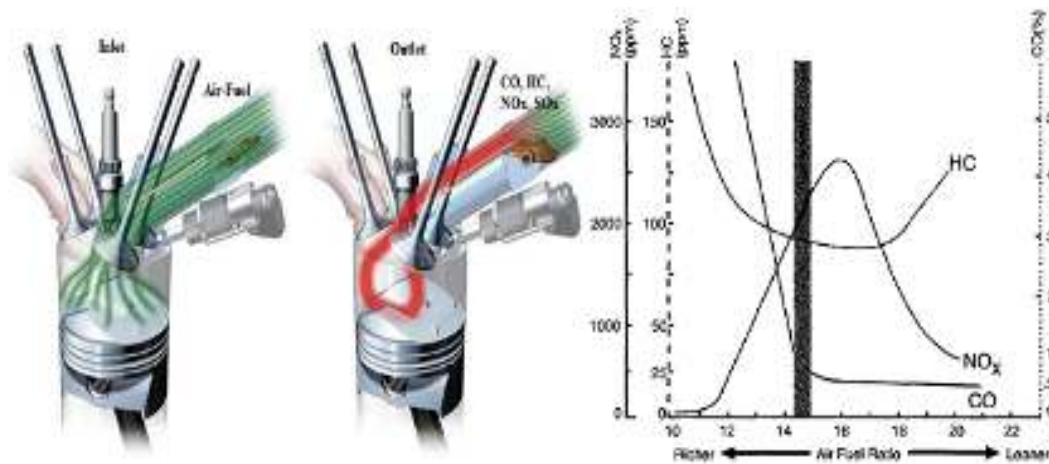
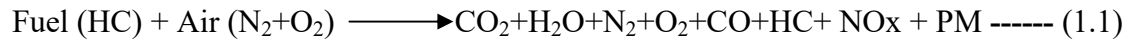


Figure 1.4: Formation of CO in internal combustion engines [Chhatwal *et al.*, 1975]

The excess HC can also be influenced by the amount of A/F mixture as it enters into the combustion chamber. If the A/F mixture does not have sufficient oxygen present during the combustion, it will be not burn completely. When combustion takes place in an

oxygen starved environment, there was insufficient oxygen to convert all CO into CO₂. When carbon atom bonded only with one oxygen atom CO was formed. The main primary pollutants (CO, HC and NO_x) are formed in the IC engine by the complex reactions as presented by the Eq.1.1.



The engine design modification, clean fuels, proper maintenance and post-combustion control device reduce the CO emissions from the vehicles [Cholakov 2010]. The diesel combustion is heterogeneous in nature, but petrol combustion is homogeneous in nature. The hydrocarbon (HC) pollutant also enters into the atmosphere through fuel evaporation [Clarke *et al.*, 2015]. The fuel evaporation is done from the fuel tank, carburetor and tailpipe of the vehicle. When the engine is warm idle, therefore very little CO is produce. The reason behind this the presence of sufficient oxygen during the combustion process to fully oxidize all the carbon atoms.

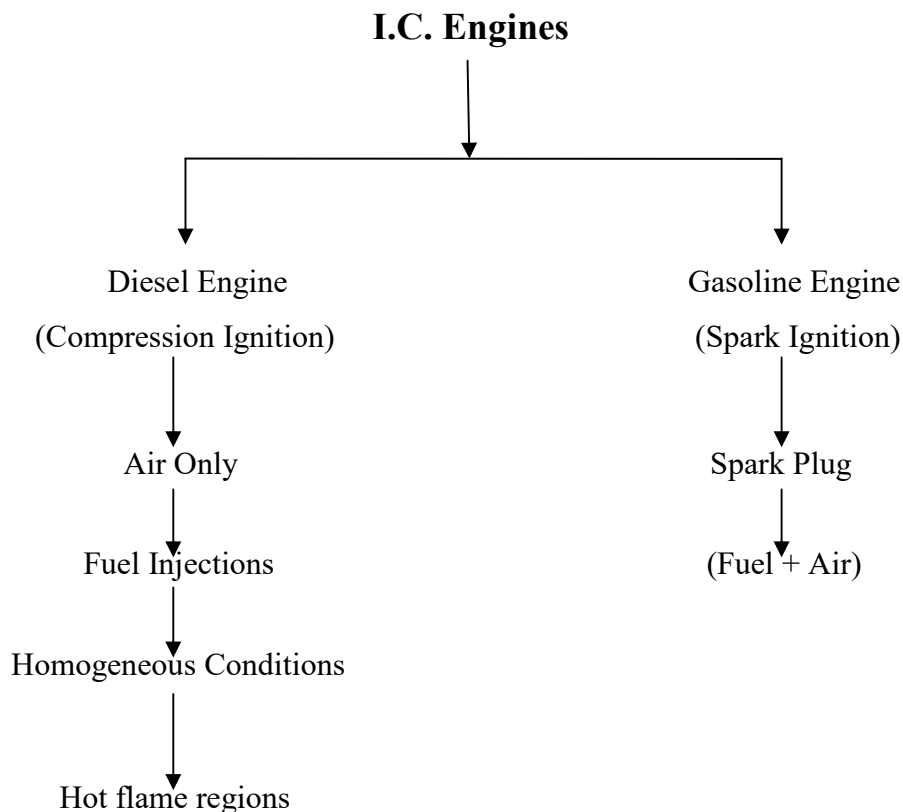


Figure 1.5: Internal combustion engine

1.3.2 Emissions Regulations

The motor vehicle emission controller can be done most effectively by designing the vehicles to have a lower emission in the beginning. Gasoline and diesel engine vehicles are also among the leading sources of the toxic air contaminant in most countries around the world [Pulkrabek 2004]. Due to increasing the number of vehicles on the roads, the production of CO has reached an alarming rate into the environment [Venkatesan *et al.*, 2017]. To control the regulation of CO emissions by the help of Bharat Gas Standard in India and Euro standard follows the world [Faiz *et al.*, 1996]. The norms and regulations of Bharat Gas Standard and Euro standard improved the standard of the vehicle for reducing the emissions of pollutants [Mokhtar *et al.*, 2010]. The emission norms in Bharat Gas and Euro standard as presented in Table 1.3.

Table 1.3: Emission Standards in India and EU emission (Gasoline engines)

Norms	European	Year	CO (g/Km)	HC + NO _x (g/Km)
1991 Norms	-	-	14.3-27.1	2.0(Only HC)
1996 Norms	-	-	8.68-12.40	3.00-4.36
1998 Norms	-	-	4.34-6.20	1.50-2.18
India Stage 2000 norms	Euro 1	2000	2.72	0.97
Bharat Stage-II	Euro 2	2001	2.2	0.5
Bharat Stage-III	Euro 3	2005	2.3	0.35(combined)
Bharat Stage-IV	Euro 4	2010	1.0	0.18(combined)
Bharat Stage-V	Euro 5	2017	0.63	0.10(combined)
Bharat Stage-VI	Euro 6	2020	0.50	0.07(combined)

The changing in fuel composition is necessary for emission control technology and it reduces the emissions from vehicle exhaust [Faiz *et al.*, 1996]. The national effort to control this automobile pollution can be traced to the 1970 Clean Air Act, which required a 90% reduction in CO, HC and NO_x emissions from automobile vehicles [Venkatesan *et al.*, 2017]. The U.S. Environmental protection agency has also adopted ultra low emissions vehicle standards for heavy-duty vehicles covered under the cleaner fuel feet programs [Katara 2015]. India has established limits on CO emissions (at idle) for gasoline-fueled cars, motorcycles and new emissions standards for gasoline-fueled cars took effective in 1991 [Einaga *et al.*, 2016]. The vehicle emissions are affected by driving pattern, traffic speed, congestion, temperature, vehicle's engine conditions and emissions control equipment and its maintenance [Mokhtar *et al.*, 2010]. The refueling and evaporative emissions have become a more considerable fraction of total emissions as a consequence of the steady decline in exhaust hydrocarbon emissions [Faiz *et al.*, 1996]. India has established limits on CO emissions (at idle) for gasoline-fueled cars, motorcycles, three-wheelers and diesel smoke emissions. The growing of environmental concerns over the past three decades has resulted in regulatory action around the globe to begin more rigorous emission standards successively [Martino *et al.*, 1994; Alfuso *et al.*, 1993]. The control activities have also changed the composition of source emissions. For controlling the CO emissions a catalytic converter is the primary emission control device applying in the vehicles nowadays.

1.4 Control of CO emissions

The controlling of CO emissions from automobile vehicles has become a global challenge in achieving improved urban air quality. To concentrate this problem, significant efforts have been made since 1970 [Martino *et al.*, 1994]. The emissions from gasoline-fueled vehicles can be reduced through changes in engine design, combustion

conditions and catalytic after treatment. The emissions of CO can be controlled by A/F ratio, ignition timing, turbulence in the combustion chamber and exhaust gas re-circulation [Aguila *et al.*, 1991].

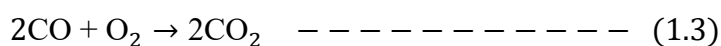
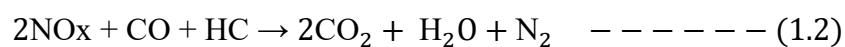
1.4.1 Technological advance and Fuel modifications

For reduction of CO emissions automobile sources used a new technology and modification in fuel mixtures. The general approach to reducing automotive emissions is as follows:

- I. The inspection and maintenance programs of a vehicle at certain intervals of time.
- II. The improvements of new technology, fuel adjustment and modifications in motor engines.
- III. Using catalytic converter.

1.4.2 Catalytic Control

A catalytic converter is an automobile emissions control device that converts more toxic pollutants present in the exhaust gas to the less toxic pollutants by catalyzing a redox reaction [Katara 2015]. The basic reactions of CO and HC in the exhaust are oxidation with the desired products being CO₂ and H₂O, while the NO_x reaction is a reduction with desired products of N₂. All the three major pollutants (CO, HC and NO_x) are simultaneously removed from the exhaust by a single converter [Chhatwal *et al.*, 1975]. Reactions occurring on the automotive exhaust catalysts are very complex as listed below.



During this period, since the temperature of tailpipe-gases is relatively low ($<150^{\circ}\text{C}$) the conventional three-way catalysts illustrate especially low catalytic efficiency to convert all the destructive gases. The catalyst employs in a ceramic honeycomb structure or monolith held in a converter apply for an exhaust stream [Cholakov 2010].

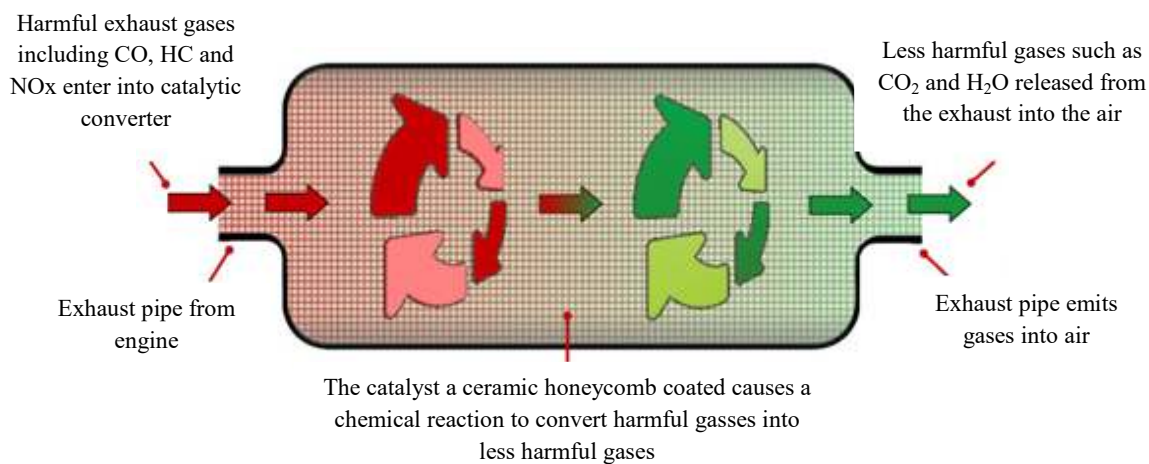


Figure 1.6: Schematic diagram of an automobile catalytic converter

At the time when the automobile vehicle initial starts up both the engine and catalyst are in cold conditions. After startup, the heat combustion reaction is transferred from the engine to the exhaust piping begins to heat up. Finally, a temperature is reached inside the catalyst that initiates the catalytic reactions [Ismaila *et al.*, 2013]. In Figure 1.6, we have seen that the operation of catalytic converter. The reaction temperature and kinetic reaction rate depended upon the chemistry of catalyst. The activity, selectivity and stability of the catalyst are a fundamental step for improving the combustion reaction between the catalyst and the reaction gasses [Sharaf 2013]. Although the catalytic converters are most frequently apply to the mining equipment, electrical generators, trucks, buses, locomotives, motorcycles, forklifts and airplanes etc [Ghaffari *et al.*, 2008].

1.4.3 Automobile Three-Way Catalytic Converter

The most frequently used design of a catalytic converter is a monolithic structure, which is coated with a wash coat that supports the catalyst material. The development of such a catalytic converter is a complex process concerning the optimization of different physical and chemical parameters [Brandt *et al.*, 2000]. The construction of catalytic converter is shown in the Figure 1.7.

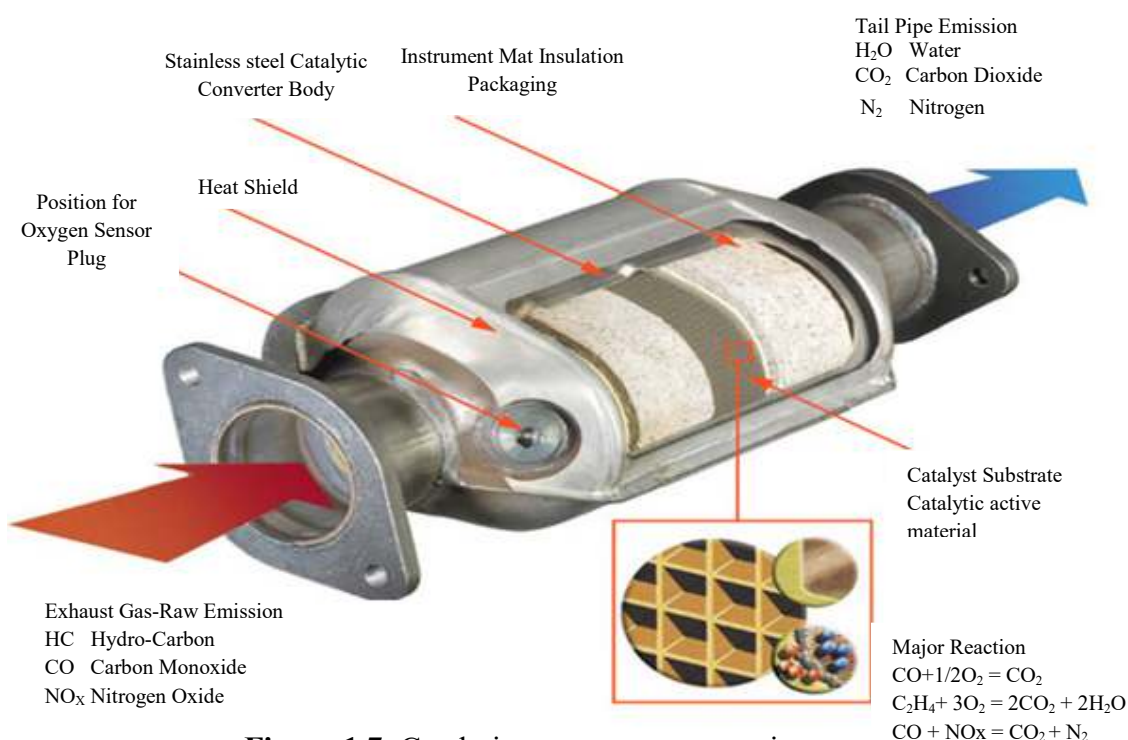


Figure 1.7: Catalytic converter construction

(Source: <https://www.newroads.ca/blog/catalytic-converter-problems/>)

I. The catalyst support or substrate. For automotive catalytic converters, the core is usually a ceramic monolith with a honeycomb structure. Metallic foil monoliths made of Kanthal material (FeCrAl) are used in applications where mainly high heat resistance is required. The material is a large surface area. The cordierite ceramic substrate was used in most catalytic converter [Bera and Hegde 2010].

II. The wash coat. A wash coat is a carrier for the catalytic materials and it used to disperse the materials over a large surface area. Aluminum oxide, silicon dioxide,

titanium dioxide or a mixture of alumina and silica can be used. The catalytic materials are suspended in the wash coat preceding to applying to the core. Wash coat materials are selected from a rough irregular surface, which greatly increases the surface area compared to the smooth surface of the bare substrate [Koltsakis and Stamateios 1997].

III. The catalyst itself. A catalytic converter is an automobile emissions control device that converts more toxic pollutants present in the exhaust gas into non toxic pollutants by catalyzing a redox reaction (oxidation or reduction).

1.5 Catalyst Design Parameters

Catalysts can be homogeneous or heterogeneous, depending upon whether a catalyst exists in the same phase as the substrate. In the experimental work we have to use the heterogeneous type of catalysts only. Most heterogeneous catalysts are solids that act on the substrates in a liquid or gaseous mixture. For catalyst design purposes it is necessary to translate the catalyst performance parameters into the physical picture of the catalyst structure. As we see that, the different performance parameters give rise to different structural features and so a compromise is generally required. Therefore we have discussed some of the relationships between the catalyst performance parameters and physical structure.

A) Activity: In general activity arises from maximizing both the dispersion and availability of the active catalytic material. Ideally, from an activity viewpoint, the catalyst material should be highly dispersed and concentrated on the external surface of the support.

B) Stability: By stability we refer to the loss in activity over time. This is due to one or several of four main causes; fouling of the active surface with in-volatile reaction by-

products, sintering or crystal growth of the active material, poisoning of the active surface by feed impurities and blockage of the support pore structure.

C) Selectivity: Catalyst selectivity can also be change due to physical or chemical reasons. For sequential reactions diffusivity and mass transport through the pore structure can lead to apparent loss in selectivity in the formation of intermediate products. Location of active ingredients and pore-size distributions are again of importance. Changes in selectivity can also arise from changes in intrinsic chemical activity of the active component.

D) Regenerability: Regenerability refers to the reactivation of a catalyst, which typically involve an air calcination followed in some cases by a redispersion of the active components. From the catalyst design viewpoint this will be implied enhanced thermal-hydrothermal stability of the support itself, combined with stability of the active components under the high temperature oxidizing environments required for the oxidation of deactivating carbonaceous deposits.

1.6 Groups of Catalysts for CO oxidation

In the exhaust gases, CO proves the most perilous so that more attention has been focused on catalytic control of CO emissions from motor vehicle exhaust [Votsmeier 2005]. The emission of CO is highly depending upon the engine A/F ratio, and it also seen that the break power of engine increases the CO content due to the supply of a rich mixture of A/F [Yasar *et al.*, 2013]. A wide variety of catalysts used in a catalytic converter, which initiates the oxidation of CO such as noble metal, base metal, perovskite, spinel, hopcalite and monel based catalyst, etc [Perego and Villa1977].

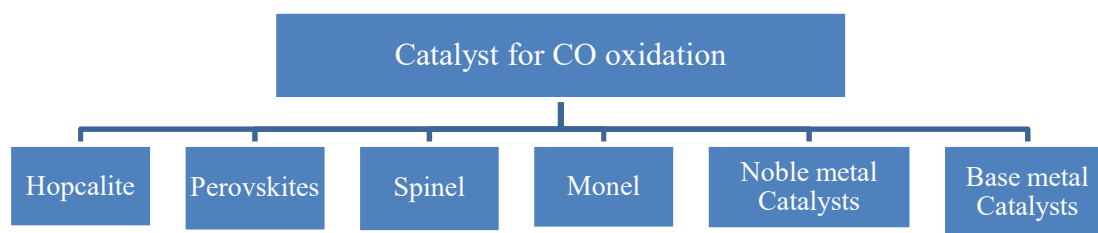


Figure 1.8: Catalysts for CO oxidation

1.6.1 Hopcalite

In 1920 Lamb, Bray and Frazer discovered that various mixture oxides of Cu, Mn, Ag and Co, identified as a group of catalysts known as hopcalite (CuMnOx). Jones and Taylor confirmed the catalytic properties of such a system called hopcalite in the year 1923. It can be efficiently catalyze the oxidation of dry CO even at room temperature [Solsona *et al.*, 2004]. A literature survey reported that the hopcalite is highly active in the amorphous state even at room temperature but has been observed to lose their activity after exposition at temperatures above 773K where crystallization of the spinel CuMn₂O₄ has occurs [Lee *et al.*, 2016]. Recently, the low-temperature oxidation of CO has seen a revival in its importance to the catalytic community. The addition of Au, Ag, Ce and Co enhances the activity of hopcalite catalyst [Taylor *et al.*, 1999; Zhang *et al.*, 2010; Jones *et al.*, 2009]. A modification of hopcalite catalyst to eliminates its faults of moisture deactivation and lower activity [Qian *et al.*, 2013]. The preparation of catalyst by other methods including anti-solvent precipitation [Taylor *et al.*, 1999] and sol-gel method [Kramer *et al.*, 2006] is reported to give better CO conversion than commercial hopcalite. The structural, morphological and catalytic property of hopcalite catalyst is highly depending upon the preparation methods. The recent work shows that the addition of gold into the hopcalite catalyst not only improved its activity but also prevents the deactivation of the catalyst [Cole *et al.*, 2010]. The hopcalite represent the outstanding performance for CO oxidation produced by many different synthesis

method such as sol-gel method, supercritical anti-solvent precipitation method, redox methods and the majority of cases by the co-precipitation method [Hoshyar *et al.*, 2015]. The basic parameter such as ageing time and calcination strategy is highly effect on the activity of CuMnOx catalyst.

1.6.2 Perovskite

Many perovskite catalysts are highly active for CO oxidation at a high temperature. The general formula of perovskites is ABO_3 ; typically the A elements are rare earth alkaline (La, Ce, Pr), alkaline earth metals (Cs, Sr, Ba, Ca) and the B sites are usually occupied by transition metals (Co, Fe, Cu, Ni, Mn and Cr). The main advantage of the perovskites lies in the fact that they posses higher activity and stability compared to the pure oxides [Chand *et al.*, 2000]. There are several problems associated to the perovskite-based catalyst such as thermal stability, catalytic activity and deactivation of the catalyst by the potential poisons of sulfur and lead in the fuel. Very few number of perovskite was until reported, which was active for CO oxidations at the ambient conditions. Example Au/LaMnO₃ has converted 60% CO at 50°C [Einaga *et al.*, 2016]. The major drawback of this mixed oxide catalyst is that it has a lower surface area to improved the performance for CO oxidation by impregnated them on the support materials such as alumina or cordierite [Patel and Patel 2003]. The unique ordered macro porous structures can provide easy mass transfer to the reactants molecules, facile accessibility to the active sites and suitable loading of the active component. The Au/3DOM LaCoO₃ catalysts with a rhombohedral crystal structure could be synthesized by the reduction method have a high surface area. The full conversion of CO is obtained by this catalyst at a 202°C temperature [Li *et al.*, 2013].

1.6.3 Spinel

The spinels are minerals of general formulation $A^{2+}B^{3+}_2O_4$ which crystallize in the cubic (isometric) crystal system, with the oxide anions set in a cubic close-packed lattice. A and B can be divalent, trivalent cations, including Mg, Zn or Fe, Mn, Al, Cr, Ti and Si [Mokhtar *et al.*, 2010]. The ferric and aluminum based spinels are approximately entirely homogeneous due to their large size difference. The $NiFe_2O_4$ spinel catalyst obtained by the combustion reaction method and is preferred for the CO oxidation. The highest conversion of CO is observed with 89.5% at 350°C temperature. The spinel catalysts are active for CO oxidation at the high temperature [Severino *et al.*, 1998].

1.6.4 Monel

Monel is a nickel-copper mixture catalyst and it's used for controlling the emissions of CO, HC and NO_x from automobile exhaust. The composition of monel catalyst which usually contains 66.5% by weight of nickel, 31.5% by weight of copper and 2% by weight of impurities. It has a lower cost, short life and less durability catalyst [Tavares *et al.*, 1986].

1.6.5 Noble metal catalysts

The noble metals are most commonly considered to be (Rh, Ru, Ag, Pd, Ir, Pt and Au) and secondary use of this element in automobiles as a catalytic converter [Votsmeier *et al.*, 2005]. In the noble metal catalysts, Rh is use as a reduction catalyst, Pd is use as an oxidation catalyst, and Pt is use for both the reduction and oxidation catalyst. Au is very active for the low-temperature oxidations of CO, if dispersed on suitable metal oxides and composite oxides [Marino *et al.*, 2004]. Gold supported on reducible oxides is known to catalyze the oxidations of CO efficiently at a low temperature (even below 0°C).

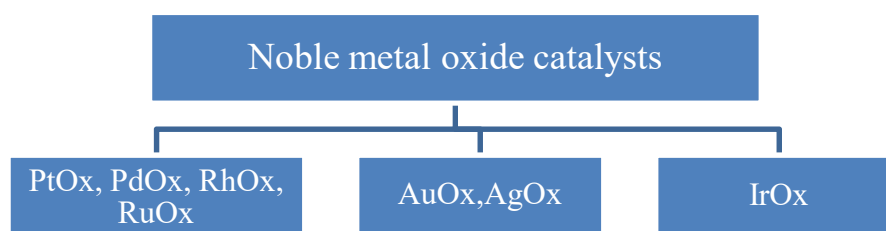


Figure 1.9: Noble metal oxide catalysts

The Pt/SnO₂ and Pd/SnO₂ catalysts are most widely used for the low-temperature oxidation of CO [Arana *et al.*, 1998]. Figure 1.9 shows, the various noble metal oxide catalysts use for CO oxidation. The catalytic performance of PtO_x, PdO_x, RhO_x and RuO_x is strongly influenced by the oxygen coordination around their surfaces. It has been observed that the oxidized noble-metal oxide catalyst has been indeed more active than the completely reduced particles [Gardner and Hoflund 1991]. The disadvantage of noble metal catalyst is a high-cost material and lower availability. Silver is an excellent catalyst for several catalytic oxidation reactions for a long time. The performance of silver oxide catalysts strongly depends on their surface structure and the surface active sites [Argyle and Bartholomew 2015]. The activation of silver oxide catalyst is often attributed to the presence of various Ag-O interactions.

1.6.6 Base metal catalysts

The base metal includes (Co, Ni, Cr, Fe, Mn and Cu) which are mostly active for the catalytic oxidation of CO. The base metal oxides like Co₃O₄, CuO and MnO₂ has a high catalytic activity per unit surface area for CO oxidation. The low-cost and high performance supported base metal oxide catalysts may have high potential to find its application to the catalytic reaction [Marino *et al.*, 2005]. The different supported base metal oxide catalysts used for CO oxidation is as follows Co₃O₄, Cu₂O, Fe₂O₃, MnO, NiO, Cr₂O₃ and V₂O₅, etc which is shown in the Figure 1.10 [Zheng *et al.*, 2006].

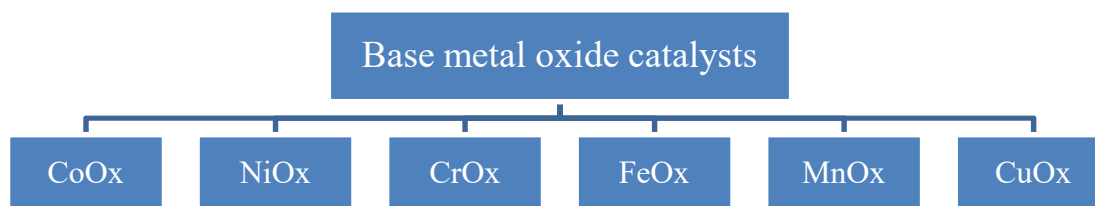


Figure 1.10: Base metal oxide catalysts

The $\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ catalyst is highly active for CO oxidation at a low temperature and it is extremely sensitive to the presence of moisture [Dissanayake 2006]. In comparison to Co_3O_4 , the unsupported copper oxides have been found more rarely used in CO oxidation. The copper oxides are not very stable; the oxidation state of copper may differ in the course of reaction, CO/O₂ ratio and temperature [Cole *et al.*, 2010]. The excellent behavior of Cu_2O in CO oxidation at room temperature has studied the kinetics of O₂ chemisorptions over the same cuprous oxide. The manganese oxide nanoparticles reported are readily prepared by self-assembly in a one-pot reaction under ambient conditions [Larsson and Andersson 2010].

1.6.7 Comparison of noble metal to base metal Catalysts

The role of noble metals (Pt, Pd and Rh etc.) cannot be substituted by the base metal catalysts, due to their higher intrinsic activity for CO oxidation. The role of precious metal catalyst is more resistant for sulfur; potassium poisoning and are chemically sensitive which degrade rapidly in the existence of fuel impurities. Due to the high cost and low availability of noble metal catalyst consider used as an alternative base metal catalyst [Jansson 2000]. The base metals like copper and copper based catalyst have much interest in heterogeneous catalysis because of their higher catalytic activity towards CO oxidation. The Cu-based catalyst (CuFe_2O_4) is more active for CO oxidation at a high temperature. However, the copper oxides are not very stable, and oxidation state of copper may differ in the course of reaction [Huang and Tsai 2003].

The base metal catalysts are less active for CO oxidation as compared to the noble metal catalysts. In base metal catalyst, copper has been explored as a substitute of the noble metal catalyst due to its excellent activity for CO oxidation at the ambient conditions [Makwana *et al.*, 2013]. The base-metal oxides including MnO, Fe₂O₃, Co₃O₄, NiO and CuO are very active for low-temperature CO oxidation [Gardner and Hoflund 1991]. The manganese oxide nano particles reported are readily prepared by self-assembly in a one-spot reaction under ambient conditions. These materials are very active for CO oxidation at a low temperature [Cole *et al.*, 2010].

1.6.8 Comparison of hopcalite to other metal oxide catalysts

Compared to noble metal catalysts, the hopcalite have a many practical advantages due to their cost efficiency, high availability and high catalytic activity that results from their ability to provide an active oxygen species by changing oxidation states [Royer and Duprez 2011]. In the hopcalite catalysts, the manganese-based mixed oxide catalysts have recently been proposed as good candidates for the CO oxidation without the use of precious metals [Choi *et al.*, 2016]. The hopcalite catalysts mainly composed of CuOx and MnOx. It has been reported that these catalysts' high catalytic activity in CO oxidation could be ascribed to the resonance system $\text{Cu}^{2+} + \text{Mn}^{3+} \rightleftharpoons \text{Cu}^{+} + \text{Mn}^{4+}$ and the high adsorption of CO onto $\text{Cu}^{2+}/\text{Mn}^{4+}$ and of O₂ onto $\text{Cu}^{+}/\text{Mn}^{3+}$. The additional Cu into MnOx enhanced its catalytic activity for CO oxidation [Peng *et al.*, 2011]. The reason behind the improves catalytic activity due to their better lattice oxygen mobility, specific surface area, and pore volume of the catalysts. These all may be contribute together to the overall performance of CuMnOx catalysts in CO oxidation at a low temperature.

1.7 Hopcalite catalysts - Early research

Hopcalite (CuMnOx) as catalysts for the CO oxidation have been extensively researched since the beginning of 20th century. The hopcalite name was derived from the Johns Hopkins University (“Hop”) and the University of California (“Cal”), in which the procedure from fundamental investigations of CO oxidation during the First World War was discovered [Papavasiliou *et al.*, 2005]. The development of the Hopcalite catalyst was supported by funding from the US Navy department for the manufacture of a CO mask for naval use. It is decided that it is essential to discover a catalyst that would rapidly oxidize CO at a low temperatures, have considerable capacity, be hard and firm enough to retain a porous structure with rough handling and be chemically stable. Investigation into CO oxidation by Xia gave positive results at room temperature for the oxidation of CO in air [Xia *et al.*, 1999].

1.8 Application of hopcalite catalysts for CO oxidation

The hopcalite catalysts have long been used in the removal of environmental damaging gasses over a wide range of temperatures, from low to high temperature [Njagi *et al.*, 2011]. At higher activity, selectivity and stability of hopcalite catalyst are the basis of their increasing use in various reactions of commercial, environmental and other importance [Qian *et al.*, 2013]. An increase of CO oxidation with the increasing of temperature has been observed. The hopcalite catalyst also used for the applications in air purification devices for respiratory protection in aircraft, mining, space labs, closed room burning activities, the military and in industrial emission control [Shi *et al.*, 2015]. The hopcalite catalysts are also used for the direct oxidation of CO from various fuels in the fuel cell application. Such catalysts can effectively catalyze the oxidation of dry CO even at room temperature and it also active for CO oxidation at low temperature -20°C

but it fails in catalytic converter operating at higher temperatures due to sintering [Kireev *et al.*, 2009]. Towards the end of World War I, Lamb *et al.* discovered a Hopcalite catalyst for application in gas mask canisters. Later work focused on developing the catalyst in gas masks at the coal mining, military and fire fighting situations [Qian *et al.*, 2013]. This catalyst is typically used in emergency breathing masks for terrestrial applications. It is environmental friendly and economically efficient as there are no solvents used any waste from washing, fewer synthesis steps and no requirement for product recovery or separation. The commercial variety of hopcalite catalyst has been synthesized by a solid-state reaction between an active component of MnO_2 and CuO [Cong and Yu 2009]. The hopcalite catalyst is highly use as a catalyst in the designing of a catalytic converter to overcome the air pollution problem from the transportation sector, especially CO exhaust from gasoline motors [Irawan *et al.*, 2015].

1.8.1 Copper oxide based catalysts

At the high temperature, conversion of CO proceeded fastest over Cu^0 , metallic copper at 300°C , followed by Cu^+ and Cu^{2+} , in order of rising oxidation state. The higher surface area in mixed metal oxide catalyst beds also makes the catalyst more resistant to non-selective poisoning, which is a common problem in emission control [Huang and Tsai 2003]. Martinez-Arias *et al.* have shown that the level of CO oxidation over ceria supported copper oxide to be similar in magnitude to oxidation over precious metal catalysts [Martinez-Arias *et al.*, 2000]. On studying several mixed oxide systems, it was found that $\text{CuO}/\text{Al}_2\text{O}_3$ more active for total oxidation of CO. Copper oxide has been a major component of the hopcalite catalyst, which has been used in connection with air pollution control and for the oxidation of waste industrial gases for more than 80 years [Shi *et al.*, 2015]. Singularly, CuO is found to be weakly active for CO oxidation, but in conjunction with other metal oxides in proper proportions, some very active catalyst

systems are generated [Qian *et al.*, 2013]. Many systems containing CuO mixed with other transition metal oxides have been studied over the years. Oxides of iron, nickel, cobalt and manganese have all been shown to improve the activity of copper oxide under the suitable conditions [Luo *et al.*, 2005, Bond 1974]. Copper based catalysts have been considered as possible substitutes for noble metal catalysts in a catalytic converter [Gawande *et al.*, 2016]. Transition metal catalysts are found to be different to the noble metal catalysts in terms of the adsorption behavior of the reactants and products. The reaction of CO on CuO has often leads to the creation of carbonate intermediates upon the reaction of O₂ from the catalyst surface [Qian *et al.*, 2013]. Even at 298K, CO is reported to adsorb on the surface of CuO as a carbonyl complex that can be quickly oxidised to a carbonate species by reaction with O₂ both from the surface and the environment. It is thought that the interface of CuO with CO might eventually lead to the reduction of the oxide to Cu₂O, but it is noted that the other ions present on the catalyst surface could moderate the decrease of CuO. One of the main drawbacks of CuO based systems investigated is the ease of poisoning by water vapors [Shi *et al.*, 2015].

1.8.2 Manganese oxide based catalysts

The manganese oxide has long been used as a main component in catalysts for CO oxidation. During the early years of research the oxidizing ability of metal oxide systems, the preferred formulation for the Hopcalite I catalyst contained 50% MnO₂. Manganese oxide alone has not been reported as active catalyst for CO oxidation at ambient temperature; however, when combined with other metal oxides and mainly at the elevated temperature, a potent oxidizing system can be formed [Njagi *et al.*, 2011]. Ramesh *et al.* are amongst the first to be noted that the activity of manganese oxide, which represented the first example of an industrially important catalyst. A material

catalytically active at sub ambient temperatures is synthesized by treatment of potassium permanganate with sulphuric acid and subsequent treatment of the product with nitric acid [Ramesh *et al.*, 2008]. The oxidation of CO over manganese-based catalysts does not appear to be well understood over the years; varieties of mechanisms have been postulated. The oxidation control has shown that two types of oxygen are present on the Mn(>2) surface; a species of high oxidizing power consisting of only a fraction of the surface and a species of much lower oxidizing power populating the huge majority of the surface. The high oxidizing power species were thought to be either O₂' or O' ions [Craciun *et al.*, 2003].

1.9 Recent works involving hopcalite catalysts

Effect of synthetic conditions on the activity of hopcalite catalysts for CO oxidation has been shown to a great importance. Variables such as precipitate ageing time, pH, temperature, Cu:Mn molar ratio, as well as catalyst drying and calcination temperature, time interval have also been shown to be important in controlling the composition and activity of the CuMnO_x catalyst [Elmhamdi *et al.*, 2017, Ahna *et al.*, 2017]. The relationships between the bulk phases and catalytic activity are found to be complex. Generally, the catalysts showed X-ray diffraction features related to amorphous mixed copper manganese oxide phases [Dasireddy *et al.*, 2018]. Catalysts that are calcined above 500°C are highly crystalline and show high specific activity, however this is found to be a significance of the low surface areas of the material due to a high CO oxidation activity [Yap *et al.*, 2018]. The un-aged calcined catalyst is create to be comprised of copper manganese oxide Cu_{1.4}Mn_{1.6}O₄ with Mn₂O₃ and CuO. Samples aged between 60 and 240 minutes comprise of Cu_{1.4}Mn_{1.6}O₄, Mn₂O₃ and CuO [Ye *et al.*, 2018]. The 300 minute aged catalysts are mainly Cu_{1.2}Mn_{1.4}O₄ with Mn₂O₃ and CuO present as small phases. The 12h aged catalyst is less crystalline with CuMn₂O₄ and

CuO the major phase present [Li *et al.*, 2017]. These results indicate that the increasing of sample ageing time and the proportion of manganese which was incorporated within the mixed oxide phase has increased [Adánez-Rubio *et al.*, 2018]. The porous Cu–Mn oxides with high surface area are successfully obtained through low-temperature coprecipitation method in alcohol/water solvent and then post-annealing. The addition of alcohol showed huge influences on the shape and catalytic activity for CO oxidation. Li *et al.* studied the dumbbell-like Cu–Mn oxide particles with splitting ends displayed high catalytic activity and total conversion of CO was achieved at 45°C, suggesting a shape-dependent catalytic activity [Li *et al.*, 2017]. Runxia *et al.* studied the doping with 0.5% (molar percentage) La extensively enhanced the catalyst reduction property, and made the Cu and Mn components uniformly distributed in the catalyst, it oxidized CO completely at 300°C [Runxia *et al.*, 2016]. Gao *et al.* studied the CO conversion over Cu_{0.1}MnOx increases rapidly from 10% to nearly 100% from 50 to 100°C, suggesting that Cu_{0.1}MnOx can function as a very active catalyst for CO oxidation [Gao *et al.*, 2016].

1.10 Preparation of hopcalite catalysts

The preparation methods affect textural characteristics and their performance for CO oxidation. The key of preparation parameter is identifying as the ratio between the amounts of (Cu:Mn) impregnation solution and the volume of support. The fundamental understanding of the base metal species use as a catalyst precursor and the active metallic species involved in catalysis [Feaviour and Schofield 2007]. The various methods have been applied for the preparation of hopcalite catalyst is shown in the figure. The methods of hopcalite catalyst preparation are very diverse and each catalyst may be formed via various routes. There are three fundamental stages of catalyst preparation which may be distinguished as follows:

- I. Selection of the primary materials such as nitrate, chloride, oxalate, etc. of desired elements.
- II. Processing of that primary solid to obtain the catalyst precursor, for example precipitation, gel formation, physical mixing of solids, etc.
- III. Heat treatment of the precursor such as drying, calcination and activation to give the active catalysts. The activation may be carried out in different oxidizing, reducing or redox environments.

Each stage of catalyst preparation affects textural characteristics and their performance in CO oxidation. The methods of hopcalite catalyst preparation are very diverse and each catalyst may be produced via different methods as shown in the Figure 1.11. Each method affects the activity of resultant catalysts for CO oxidation.

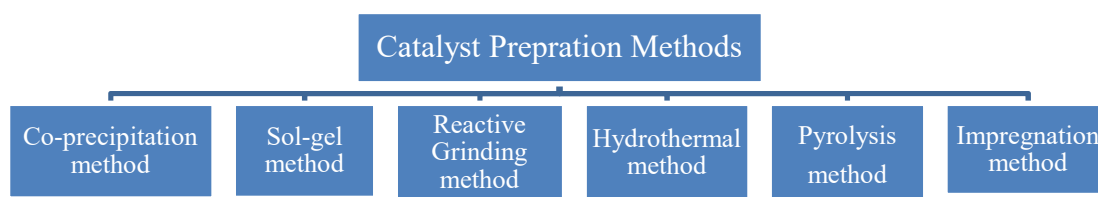


Figure 1.11: Catalyst preparation methods

There is several methods use for the preparation of hopcalite catalyst and each method affects the activity of resulting catalysts for CO oxidation.

1.10.1 Co-precipitation method

The co-precipitation is one of the simplest and mostly used methods for the preparation of hopcalite catalyst. The synthesis of hopcalite catalyst by co-precipitation of soluble salts of the constituent metals in an appropriate solvent then co-precipitated by adding an acid/base or another reagent to cause the precipitation [Jones *et al.*, 2008]. The precipitation of the catalyst has three stages: Super saturation, nucleation and growth. After ageing, filtration, washing thoroughly with de-ionized water then the precipitate

solution is obtained in an amorphous phase or crystalline phase [Mirzaei *et al.*, 2013]. These precursors can be readily converted into the catalyst by heat treatment. The various characterization techniques confirmed that the co-precipitation method produces lower crystalline and higher surface area than the other methods [Puckhaber *et al.*, 1989]. In the co-precipitation method, the chemical phases dispersed the high surface area, porous structure, particle size and shapes are formed in a single step. It can be reached very high metal loading up to 80% and low solubility in hydroxides, alkaline media [Tanaka *et al.*, 2003]. The pH, temperature, stirring, precursor's recovery and thermal treatment are key features in the resulting material morphology, structure and performance [Cong and Yu 2009]. In the co-precipitation method the phase association contains two elements, if one of them contained in an anion and the second one contained cation, the precipitate would have a fixed or at least very inflexible composition [Paldey *et al.*, 2005]. There are many procedures use for the precipitation and co-precipitation method, one of the simple processes is that adding drop-wise to the solution containing the active component to the precipitate solutions [Mirzaei *et al.*, 2003]. Njagi *et al.*, studied the CuMnOx catalysts are prepared by the co-precipitation method. A solution of Mn-Acetate is added to copper (II) nitrate and stirred for 1h. The mixed solution is taken in the burette and added drop-wise to a solution of KMnO₄ under vigorous stirring conditions for co-precipitation purpose. The precipitate is filtered and washed several times with hot distilled water to remove all the anions. The cake thus obtained is dry into the oven and calcined into the furnace [Njagi *et al.*, 2010].

1.10.2 Sol-gel method

The hopcalite catalyst is also prepared by a sol-gel method is as follows: the reagents (nitrate, acetate salts of desired oxides) first dissolved in distilled water in stoichiometric amounts. The solution is adjusted to pH (7.5-8.0) with propionic acid or

ammonia or acetic acid, stirring and heating to 100°C for 24h in air, followed by calcination at (450°C-600°C) for 2h. After calcination, the catalyst is obtained; it has a high surface area [Kramer *et al.*, 2006]. A typical example of CuMnOx catalyst synthesized by the sol-gel method is given by the Hasegawa. The analytical grade of KMnO₄ and Cu-sulphate are weighted according to the stoichio-metric ratio and dissolved in distilled water. An addition of maleic acid in distilled water for reducing agent and stirred for 1h. The sample slowly becomes solution, and then gel. After ageing for 24h at room temperature, it produced black and brown gel washes with distilled water. The CuMnOx catalyst prepared by the sol-gel method has shows the high activity for CO oxidation. It adsorbed CO on the highly active site of the catalysts [Hasegawa *et al.*, 2009; Jones *et al.*, 2008].

1.10.3 Reactive grinding method

The reactive grinding is an important preliminary operation and its sometime use for the production of particular catalysts. In powder, this is a collection of particles relatively very small size (typically 0.5µm–1mm), the particles may have diverse shapes, and this influences the catalytic activity strongly. The crushing and grinding operation is aimed at producing particles of smaller size than after forming the operation pores of desired sizes [Liu *et al.*, 2012]. It is use with the materials of natural origin or with the products of action category. The grinding may take place in the absence (dry) or presence (wet) of a liquid, usually water. This is a unique and valuable process to make CuMnOx catalyst. The fused mass is crushed into irregular lumps and sieved into the proper size [Stacchiola 2015]. The sample we obtained after reactive grinding, it has a broad particle size distribution. The preparation of catalyst is more art than a science. A typical example of CuMnOx catalysts prepared by the reactive grinding method is given by Clarke et al. [Clarke *et al.*, 2015]. In this preparation method they use 10cm zirconia

grinding vessel with six 15mm zirconia grinding balls and grinding is performed at 25°C temperature in the presence of $\text{Cu}_2(\text{OH})_2\text{CO}_3$ and MnCO_3 are mixed in a Cu to Mn molar ratio at (1:2). A mixture of precursor is ground for varying periods of time (0.5-72h) at 400 rpm and calcined in static air 415°C for 2h with a ramp rate of 2°C/min from ambient temperatures [Clarke *et al.*, 2015; Kondrat *et al.*, 2011].

1.10.4 Hydrothermal method

The hydrothermal method considers the modification of precipitates and gel induced by temperature under ageing in the presence of water. These transformations are usually carried out at a certain temperatures (100-300°C). This method involves textural or structural modifications of solid summarized as follows:

- I. The small crystals converted into large crystals.
- II. The small amorphous particles turned into large amorphous particles.
- III. The amorphous solids into crystalline solids.
- IV. The high porous gel into a lower porous gel.

The hydrothermal transformations usually occur within the liquid phases. The variables of these types of operations for a given solid are pH, temperature, pressure, time and concentration [Guo *et al.*, 2016]. In other instance, the hydrothermal transformations are usually carried out during the unit operations such as precipitation, washing, drying and extrusion. Fuzhen *et al.*, studied the manganese doped CuOx catalyst with Mn/Cu molar ratio of (1:5) at variable calcination temperature are prepared by the hydrothermal method. The appropriate calcination temperature can promote the creation of CuMnOx ternary oxide solid solution, adjust the degree of crystallinity and improve the formation of oxygen vacancies [Fuzhen *et al.*, 2015].

1.10.5 Pyrolysis method

Pyrolysis is a thermo chemical decomposition of organic materials at elevated temperature in the absence of oxygen. It concerned with the simultaneous modify of chemical composition and physical phase are irreversible. Pyrolysis is a type of thermolysis and its most commonly observed in organic materials exposed to high temperatures [Fortunato *et al.*, 2000]. The flame spray pyrolysis is used to produce a broad range of high purity nano powders ranging from single metal oxides to more complex mixed oxides. The flame spray pyrolysis is a one-step process in which a liquid feed – a metal precursor dissolved in a solvent – is sprayed with an oxidizing gas into a flame zone [Biemelt *et al.*, 2015]. The spray is combusted and the precursors are converted into nanosized metal or metal oxide particles. The flame spray pyrolysis techniques allow for the preparation of a vast range of materials, including metastable phases due to the rapid quenching process [Fuzhen *et al.*, 2015].

The mixture of different precursors like Mn-nitrate and Cu-nitrate added into the de-ionized water and fed through a commercial nozzle with fluid feed rates ranging from 2.5 to 5mL/min ignited by a surrounding supporting flame to prevent the main flame from self-extinguishing. The supporting flame gas flow consisted of 1.5mL/min CH₄ and 3mL/min O₂ [Nisar *et al.*, 2011]. Thermal mass flow controller controlled all the gas flows and the synthesis black voluminous powders are collected by a binder less glass fiber filter with the help of a rotary vane pump. Biemelt *et al.* studied the CuCl₂·2H₂O and MnCl₂·2H₂O are dissolved in a 1:1 volume mixture of ethanol and water to give an overall metal concentration of 0.6M. The hopcalite catalyst synthesized mixtures gave Cu_{1.5}Mn_{1.5}O₄ with different mass fractions depending on the initial (Cu:Mn) ratio. The different precursor solutions are fed through a commercial nozzle with liquid feed rates ranging from 2.5 to 5.0mL/min ignited by a surrounding

supporting-flame to avoid the main flame from self-extinguishing. All gas flows are controlled by thermal mass flow controllers. A manganese rich X-ray amorphous phase is assumed to be nearby in the powders due to higher initial Mn:Cu-ratios up to 2.8 mol mol⁻¹, contributing to the overall specific surface area of the powders [Biemelt *et al.*, 2015].

1.10.6 Impregnation method

The impregnation is associated to an ion exchange or adsorption processes and it consists in contacting a solid with liquid components to be deposited on the surfaces. During impregnation, many different processes take places with different rates. The particular adsorption species by coulomb force; ion exchange between the charged surface and the electrolyte; partial dissolution on the surface of solid. The type of product is depending upon the nature of reactants (liquid and solid surfaces) and the reaction conditions [Severino *et al.*, 1998]. The major parameters affecting the liquid are pH, nature of solvent and concentrations of dissolved substances. The impregnation is one of the simplest method of synthesis the supported catalysts. The water solution containing the metal precursor is contacted with a porous support. The dry impregnation (pore volume impregnation) the exact amount of liquid to fill the pore volume of support and wet impregnation the amount of liquid is only prohibited by the solubility of the metal precursor [Zaki *et al.*, 2009]. The electrostatic forces monitor the adsorption mechanism and process conditions of different profile of active phases. Qian *et al.*, studied the calculated amount of Cu-nitrate added into the distilled water and then added MnO₂ support under stirring conditions. The solution is dried overnight at 80°C then calcined at 400°C for 2h. A series of CuO/MnO₂ catalyst with different CuO loading are prepared by the incipient wetness impregnation method [Qian *et al.*, 2013].

1.11 Effect of preparation parameters on the hopcalite catalyst activity

The effect of preparation conditions including metal concentration, ageing time, pH, drying temperature and calcination temperature is highly effective on the catalytic property of the catalyst. The various parameters which are highly influenced on the activity of resulting catalyst, it includes reduction temperature, calcination temperature and reduction time, etc [Solsona *et al.*, 2004].

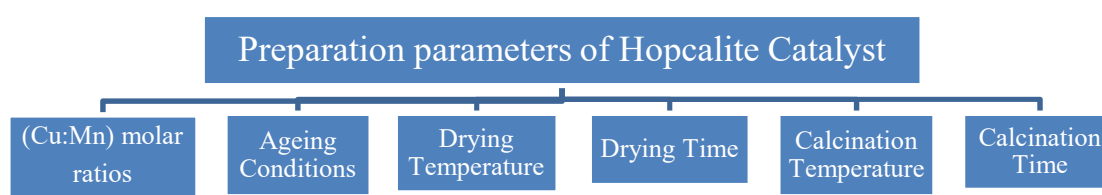


Figure 1.12: Preparation parameters of hopcalite catalysts

The preparation parameter of hopcalite catalyst is shown in the Figure 1.12. The metallic area of CuMnOx catalyst is often determined by a series of competing processes, such as conversion from nitrate to an oxide phase and onset of crystalline versus reaction with the support at the higher calcination temperatures [Zhengqian *et al.*, 2007]. The steady-state reaction provides further information about the metallic Cu and Mn center may be the active sites for CuMnOx catalyst. The addition of copper apparently decreases the reduction temperature of manganese oxides by the TPR profiles, revealing a strong interaction between manganese oxides and copper oxides therefore it is an easier reduction. With a further increasing in the Cu content, there are more CuMn₂O₄ spinel oxides to form bigger nanoparticles on their surfaces [Fang *et al.*, 2014].

1.12 Effect of thermal treatment

After synthesis of the precursors the thermal treatment like drying, calcination and activation are carried out in this sequence to obtain a highly active catalyst. These thermal steps have strong influence on the chemical composition and physico chemical properties and so on the activity of the resulting catalyst.

1.12.1 Effect of drying

Earlier research indicated that the drying step is often thought to be trivial in the preparation of precipitated catalysts. The recent studies have been conducted on the effects of drying on the distribution of active sites in supported catalysts. Among many, these studies have shown that the desired distribution of active sites can be obtained by changing the drying temperature [Gao *et al.*, 2016], and drying rate has been shown to affect the particle morphology and particle size, as well [Hasegawa *et al.*, 2009]. However, higher drying temperatures are associated with faster drying rates, which might have affected the development of the optimal pore structure, through either surface tension and the capillary effects as the residual solvent water left the structure or the formation of a more defective structure because the faster drying rate did not allow time for a more ordered crystalline structure to be set in place [Baltacioglu *et al.*, 2007]. The thermal decomposition of the CuMnOx results in a high surface area of the material with a very well defined mesopores and narrow pore size distribution [Ivanov *et al.*, 2015]. It is recognized that the phase composition and reduction properties of mixed Cu-Mn catalysts depends on the drying conditions [Wei *et al.*, 2010].

1.12.2 Effect of calcination

The calcination temperature has a strong influence on the chemical composition and physicochemical properties of the resultant catalyst. It highly affects on the activity of

resulting catalysts [Paldey *et al.*, 2005]. The catalyst calcined at 200°C showed an initial deactivation followed by a gradual increase in CO oxidation. The catalysts calcined at 200°C do not adequately react to form the active phase mixed oxide. As a result, there are necessities to attain a sufficiently high calcination temperature to form the active phase by solid-state reactions, while calcination at a higher temperature results in a detrimental loss of catalyst surface area [Njagi *et al.*, 2011].

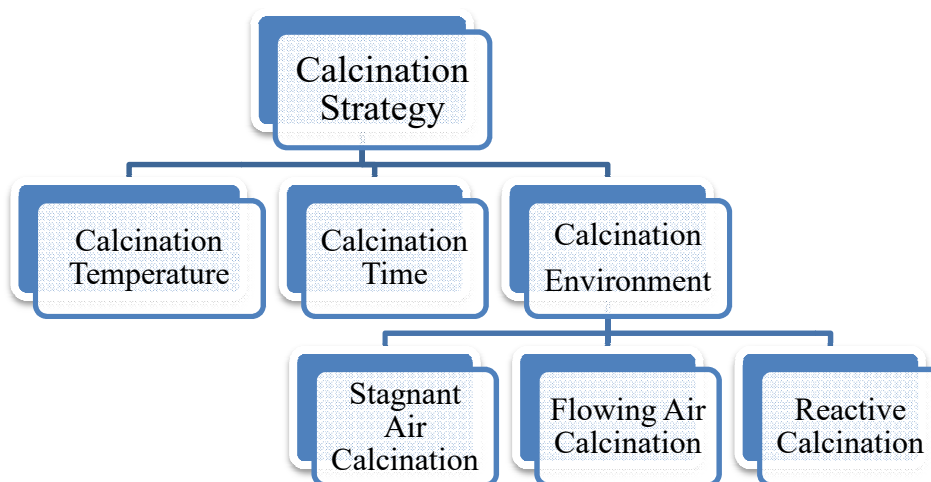


Figure 1.13: Calcination strategy of hopcalite catalysts

Additionally, the hopcalite catalysts calcined at 500°C have a high crystalline structure, and it has been recognized that more amorphous hopcalite catalysts are more active for CO oxidation. Therefore, it is consistent that increasing the calcination temperature reduced the concentration of adsorbed moisture [Solsona *et al.*, 2004]. The calcination strategy of hopcalite catalyst is shown in the Figure 1.13. A literature survey reveals that the hopcalite catalyst is highly active in the amorphous state even at room temperature, but it has observed that the hopcalite lose their activity after exposition at temperatures above 500°C, where crystallization of the spinel CuMn_2O_4 has occurred. The most active CuMnOx catalyst is prepared by using a calcination temperature of 300°C [Hasegawa *et al.*, 2009]. The calcination of catalyst was carried out in three ways; in the first we have to used the stagnant air calcination (SAC) in the absence of air, second

was flowing air calcination (FAC) in the presence of air and third was reactive calcination (RC) in the presence of (CO in air) in a compact bench scale of fixed bed tubular reactor.

1.12.3 Effect of activation

The thermal activation effect, which consist in a sharp increase in the atomic (specific) catalytic activity upon calcination at elevated temperatures, has been found and studied for the Cu-Mn oxide systems [Solsona *et al.*, 2004]. Catalyst testing is a necessary first step in devising an effective catalyst management strategy. In the activity test the catalyst surface is an active participant in the sequence of elementary reaction steps, thus, both physisorption and chemisorptions have to be considered [Puskas *et al.*, 2001]. The amount of CO adsorption sites could be increased by controlling the morphology or particle size of a catalyst and the use of pretreatments on catalysts can produced more oxygen vacancies [Lou *et al.*, 2014]. The CO oxidation process over the catalyst depends on the electronic migration between Cu and Mn cations within the spinel CuMn_2O_4 lattice [Guo *et al.*, 2016].

1.13 Effect of promoters on the hopcalite catalyst activity

The promoters are the substance that increases the activity of the catalyst; they create the ideal conditions for the catalyst and even enhance the life of catalyst by saving them from poison. The catalytic properties of pure substances are generally well identified but the possibilities for improvement through the use of appropriate promoters are widespread. Most of the promoters can be classified as textural or structural promoters. The textural stabilizer (promoter) works on the basis of physical effect, while the structural one, on chemical effect [Cai *et al.*, 2012]. The textural promoter inhibits the sintering of micro crystallites of active component, being present in the form of very

fine particles. These separate the particles of active component from coming in contact with each other, so that they do not coalesce. In contrast, the structural promoter causes alterations in the chemical composition of the catalyst. A promoter can be defined as a substance added to the catalyst during its preparation in small amounts, usually less than 10%, which by itself has little activity but imparts either, better activity, stability or selectivity for the desired reaction than is realized without it [Mirzaei *et al.*, 2003]. The promoters are divided into four parts and it is discussed in below.

- ❖ **Structural Promoters-** One of the most important types of promoter is the one where the surface area of the active component is increased. This usually involves stabilizing the catalyst by inhibiting the loss of surface area during usage.
- ❖ **Electronic Promoters-** Dispersed in the active phase and influences the electronic chemical bonding to the adsorbate. The reaction depends on the ability of the metallic system to accept electrons from and give up electrons to the surface. Many metals have 29 vacant orbitals or “holes”, thus possessing a high affinity for additional electrons. If a foreign substance is added, this affects the number of empty orbital's and consequently the catalytic activity. If the performance is improved more than expected from averaging because of the effect of vacant orbital, the substance may be considered as an electronic promoter.
- ❖ **Lattice Defect Promoters-** The active centers of various oxide catalysts can be strongly associated to the existence of lattice defects that occur near the surface. A small amount of impurity can largely increase the number of lattice defects since each interstitial foreign atom may be at the centre of a lattice defect that extends for 10Å or more. If the promoter increases the catalytic properties by

affecting the number of lattice defects, it can be considered as a lattice defect promoter.

- ❖ **Textural promoters-** These inhibit the growth of catalyst particles to form large, less active sites during the reaction. Thus, they avoid loss of active surface by sintering and raise the thermal stability of the catalyst.

The application of different elements like Co, Ce, Au, Ag, which behave as a promoters in the CuMnOx catalyst has been reported [Tanaka *et al.*, 2003]. The catalytic performance is also improved by the addition of Au into the CuMnOx catalyst. The addition of Au also improved the stability of CuMnOx catalyst, and no further deactivation is observed [Solsona *et al.*, 2004]. Moreover, the distribution of promoters may also be depending on the detailed morphology and the composition of CuMnOx support. The various promoters effects on the activity of CuMnOx catalyst as compared to the un-promoted ones. The application of different promoters in hopcalite catalyst for CO oxidation is shown in the Figure1.14.

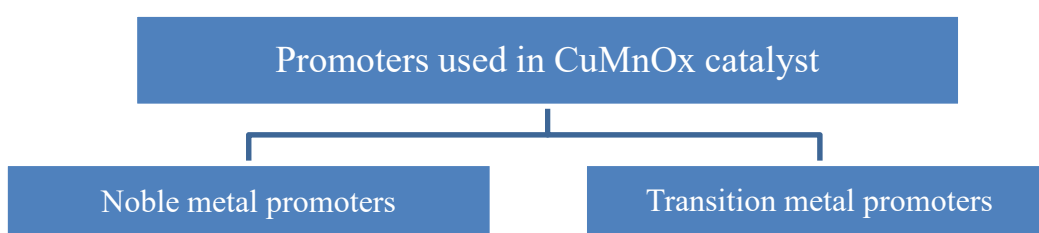


Figure 1.14: Promoters used in CuMnOx catalysts

The addition of Ce or Co into the CuMnOx catalyst leads to an increase in the surface area and shows the better performance for CO oxidation under the ambient conditions [Jones *et al.*, 2008]. The Ce doping influences the structural properties of CuMnOx catalyst and increases their activity for CO oxidation at ambient temperature. After doping little amount of Ce into the CuMnOx catalyst could prevent sintering, aggregating of the catalyst, the size of particles in the catalytic material has decreased

and their reducibility has increased. The specific surface area and the formation of active sites are increase significantly for the CO oxidation [Zhao *et al.*, 2014].

1.14 Effect of Supports on the hopcalite catalyst activity

There are several studies have been conducted to the effect of support on the performance of CuMnOx catalyst for CO oxidation. In the CuMnOx catalysts supported on silica and alumina with different molar ratio to the performance of CO oxidation has been studied. The catalytic activity is highly depending upon the supremacy of alumina supported catalyst, in particular on increasing the calcination temperatures of the catalyst [Kondrat *et al.*, 2011]. The use of different supports in the CuMnOx catalyst for CO oxidation is represented in the Figure 1.15. At the large metal concentration, the supported CuMnOx is more active. A study associated with the optimization of thermal treatment to obtain catalysts with a constant phase composition and the greatest possible specific surface area [Larsson and Andersson 2000].

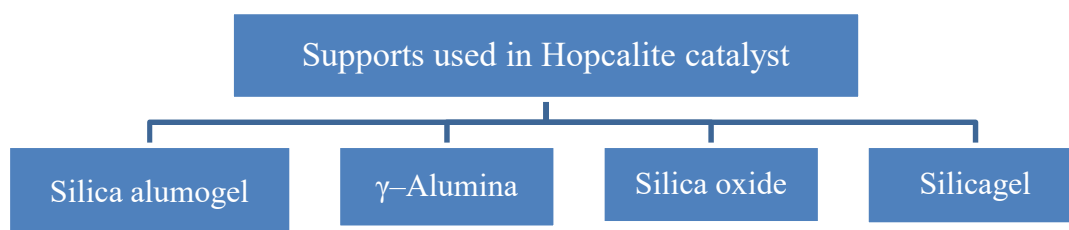


Figure 1.15: Supports used in hopcalite catalysts

The preparation of CuMnOx/ γ -alumina support by wet impregnation method is an appropriate way for the development of catalysts with improved catalytic activity towards CO oxidation. The reduction property and phase composition of mixed CuMnOx/ γ -alumina catalysts depends on the (Cu/Mn) molar ratio in a γ -alumina support [Ivanov *et al.*, 2015]. The use of γ -Al₂O₃ support into the CuMnOx catalyst could be made cheaper the CuMnOx/ γ -Al₂O₃ catalyst without sacrificing their performance.

1.15 Mechanism of CO oxidation over hopcalite catalyst

The ambient-temperature catalytic oxidation of CO is an important reaction and its application in various fields. The effectiveness of solid catalysts for reactions with stable molecules is depending upon chemisorptions. The chemisorptions of the reacting gasses is an important step, which increases the concentration of reactant on the catalyst surfaces which inducing the adsorbed molecules processing on high energy to be accessible the chemical reactions [Santra and Goodman 2002]. The mechanism of CO oxidation over the hopcalite catalyst is shown in the Figure 1.16. The distinct reaction mechanisms are consistent with the observed kinetics. The initial mechanism represents the broadly accepted CO oxidation over a CuMnOx surface that involves O₂ adsorption to form O₂* precursors, which separate on a vicinal vacancy. In the second mechanism, O₂ activation occurs via the kinetically applicable CO*-assisted O₂ dissociation step without the specific involvement of stable O₂* precursors [Solsona *et al.*, 2002].

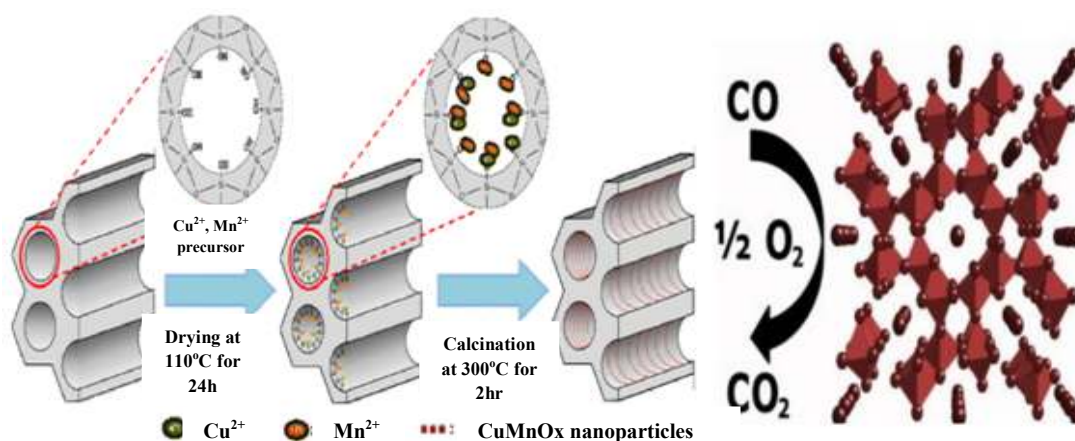


Figure 1.16: Mechanism of CO oxidation over hopcalite catalysts [Lee *et al.*, 2016]

In the CO oxidation process, the oxygen is first adsorbed on the CuMnOx surface with the energy of activation. When the temperature is high at sufficient amount so that the adsorption of oxygen reaches enough proportions, any CO passing over the catalyst surfaces either reacts directly with the adsorbed oxygen or else is first adsorbed and then

reacts, after which the CO produced being desorbed [Lee *et al.*, 2016]. The similar nature of CuMnOx catalyst is synthesized by the redox method and could be one of the main factors contributing to their high catalytic activity. The co-precipitation method is allowed for the preparation of amorphous catalysts with high surface areas and high activity [Njagi *et al.*, 2010]. A better tool for measuring the performance of CuMnOx catalyst for CO oxidation is reported the activation energy of the process. The activation energy data are available for the modeling and design of the catalytic converter [Cole *et al.*, 2010]. It is important to develop kinetic expressions for catalytic oxidation of CO also because they can be implemented into CFD models useful for reactor design and optimization.

1.16 Application of hopcalite catalysts for cold start emissions control

Elevated level characterized the seasonal CO cycle higher in winter and lower in summer, with seasonal means CO concentrations descending as, Winter > Spring > Summer. Many hopcalite catalysts have been examined for their activity in CO oxidation [Badr and Probert 1994]. CuMnOx catalysts operating effectively at the room temperature are a challenging class of materials, that application as varied as the cold start of engines to indoor air quality. The 60% - 80% of CO emissions was done from the automobile engines during this "cold-start" period. In the cold start period, the catalytic converter is totally inactive, because the catalytic converter has not warmed up. The cold start phase is also depending upon the characteristics of vehicles [Singh and Prasad 2014]. The amount of fuel is required for a cold start of the engine is a function of the engine design at ambient air and coolant temperatures. As the temperature in the combustion chamber gets lower, gasoline vapor pressure decreases, and additional fuel is required to ensure ignition. The catalytic converter is used in automobile vehicles are also able to realize the reductions of HCs, CO and NOx up to 95% when they are fully

warmed up. The cold start emissions can be subdivided into two parts: the first was excess emissions due to the starting of engine and the second was excess emissions during the warm-up process of the engine and the catalyst [Favez *et al.*, 2009]. The amount of catalyst was required to trap the toxic pollutants during the cold-start period is also typically much less than that needed in catalytic devices so that added volume of catalyst in adsorbed devices is comparatively low [Gao *et al.*, 2012]. The schematic diagram of catalytic converter for solution of cold start problems is shown in the Figure 1.17.

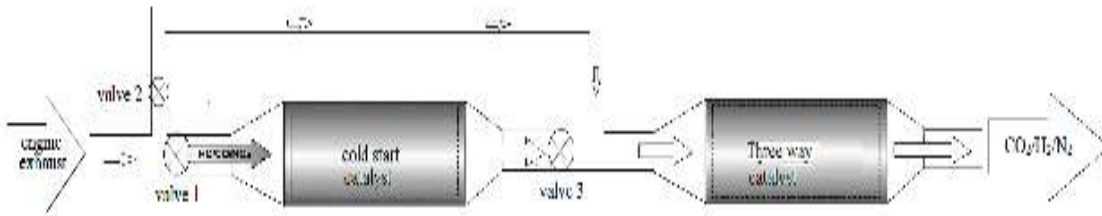


Figure 1.17: Schematic diagram of catalytic converter for solution of cold start problems

Some authors [Mirzaei *et al.*, 2003; Njagi *et al.*, 2010] reported that CuMnOx catalyst could work very well at the low temperature; thus, it can be overcome the problem of cold-start emissions if used in a catalytic converter. The gold based CuMnOx catalyst is also be use for cold start emissions control because they are more sensitive towards the CO oxidation at a low temperature. The presence of gold in the CuMnOx catalyst increases their activity, stability and further reduced deactivation of the catalyst [Solsona *et al.*, 2004].

1.17 Deactivation of hopcalite catalysts

The activity and selectivity of CuMnOx catalyst in a catalytic converter are very crucial for CO oxidation. The long time active catalyst is an essential requirement of the gas masks; it can be defined as the time over which the catalyst performance can be

maintained [Figuerido 1982]. The catalyst deactivation, loss over time in a catalytic activity, and it is a problem of great and continuing concern in the practice of catalytic processes. The catalyst deactivation can be divided into the six distinct types: (i) Poisoning, (ii) Thermal degradation, (iii) Fouling, (iv) Vapor compound formation accompanied by transport, (v) Solid-solid and/or vapor-solid reactions, and (vi) crushing/attrition. The cause of deactivation is mainly divided into three parts: Chemically, mechanically and thermally [Bartholomew 2001]. The lead, sulphur poisoning, carbon formation and sintering is the main cause of catalyst deactivation. The CuMnOx catalyst is easily deactivated by a trace amount of moisture presence in the catalyst [Jackson 1997]. To reduce the deactivation of CuMnOx catalyst for CO oxidation we are added a small amount of Ag, Au and Rh in the catalyst, it is also increases the lifetime of a catalyst. In addition to increase the rate of CO oxidation, a further advantages of incorporating Au into the CuMnOx catalyst is that lower levels of deactivation are observed [Solsona *et al.*, 2004]. The oxidative regeneration procedure is also able to reverse the major deactivation of the catalyst. The regeneration of deactivated heterogeneous catalysts is highly depending on the chemical, economical and environmental factors.

1.17.1 Chemical poisoning of catalysts

The chemical poisoning of CuMnOx catalyst is refreshing to the partial or complete deactivation of a catalyst causes by the exposure to a wide range of chemical compounds. The chemical poisoning involves compounds which bond chemically to the active sites of a catalyst [Rostrup-Nielsen 1991]. This shows two effects; first, the whole number of catalytic sites can promote reaction always decreases and second is the average distance that a reactant molecule must diffuse through the pore structure before undergoing reaction may enhance [Barbier 1985]. The common catalyst poisoning

includes the following: halide, cyanide, sulfide, lead, phosphate and nitrites etc. In the CuMnOx catalyst, the most common susceptible poisoning is moisture. The activity of CuMnOx catalyst is decreases rapidly with the increasing of moisture [Njagi *et al.*, 2010]. The addition of smaller amount of noble metal into the CuMnOx catalyst increases their resistance power towards the chemical poisoning and the reason behind the interaction (synergetic effects) of different metal oxides dispersed on the surface [Hu *et al.* 2000].

1.17.2 Catalyst fouling

The deposit of unwanted materials on the surface of CuMnOx catalyst is known as fouling, and it is a real issue that takes place during the chemical processes of catalyst. The coke formation is one of the most important types of catalytic fouling and is primarily concerned in the deactivation of a catalyst because it reduced the surface area of catalyst if available to the surroundings [Kam and Hughes 2001]. In CuMnOx catalyst the protective coating against fouling, we are added the smaller amount of different compounds like Fe and Co. Another way to protect the CuMnOx catalyst against fouling by reducing the amount of particulate matter present in the exhaust gasses. Coke-forming is also involving the chemisorptions process of different kinds of condensed hydrocarbons that act as a catalyst poisons, it causes chemical deactivation of the catalyst [Dvorak *et al.*, 2010].

1.17.3 Thermal degradation

The thermal degradation is a physical process which leads to a catalytic deactivation at the high temperatures. The thermal degradation of catalyst is initiated at the temperatures range between 800°-900°C, or in various cases, depending upon the catalytic material [Houshmand *et al.*, 2013]. The deactivation is causing by a loss of

catalytic surface area due to the crystalline growth of catalytic phase. Due to the thermal degradation collapse of the catalyst pore structure and chemical transformations of catalytic phases [Nisar *et al.*, 2011]. The activity of CuMn_2O_4 catalyst towards CO oxidation is thermally deactivated at the high temperatures. The thermal activation of CuMnOx catalyst is generated at 400°C temperature a crystalline spinel powder and assuming a very homogenous distribution of the cations. The CuMnOx catalyst reduces their activity after reaches above 650°C temperature so that it is necessary to add a certain amount of other compounds in CuMnOx catalyst to maintain their performance at a high temperature [Lee *et al.*, 2016].

1.18 Kinetic studies conducted on hopcalite catalysts

Chemical kinetics establish the factors, which influences the rate of reaction under consideration and it provides clarification for the measured value of rate and leads to the rate equations, which are valuable in reactor design [Mirzaei *et al.*, 2013]. The kinetics study of CuMnOx catalyst has shown that the highest activity and slowest deactivation rate in comparison to other catalysts. Early study indicated that the catalyst initially oxidized CO before it is oxidized by air, and this is indicative of a Mars van Krevelen-type mechanism [Clarke *et al.*, 2015], which has subsequently found support. A Langmuir–Hinshelwood-type mechanism between the adsorbed oxygen and CO has also been proposed, and it is not clear if either operates exclusively or there is a combination of both [Cole *et al.*, 2010]. The oxidation of CO by the Mars van Krevelen mechanism would explain the relation between the easiness of catalyst activity and reducibility. The oxidation of CO over the CuMnOx catalyst could be described very well by Langmuir-Hinshelwood model, in which molecularly adsorbed CO reacts with dissociative adsorbed oxygen in the first order reaction [Baltacioglu *et al.*, 2007]. Kinetic studies on the CO oxidation process over the catalyst under different

atmospheres are performed, by varying the composition of CO in the feed and keeping the other parameters make constant. For catalyst, the fractional CO oxidations in different atmospheres increase linearly with W/F_{CO} ratio, which implies that more CO could be converted into CO_2 .

1.19 Concluding Remarks

The hopcalite (CuMnOx) catalyst is one of the most prominent transition metal oxide catalysts for CO oxidation at a low temperature. The addition of suitable promoter, support, pretreatment and advanced synthesis methods would lead to improve the activity of CuMnOx catalyst for CO oxidation. The hopcalite phase being produced under the oxygen-rich atmosphere conditions and its confirmation of the retardation of copper oxide and reduction of manganese phases under the oxygen-deficient conditions, to give a residual Cu_2O and $Mn^{2+/3+}$ oxide phases. It is proposed that the addition of noble metal into the CuMnOx catalyst may work at low temperature and increase their stability for a long duration. The preparation parameters and calcination strategy is also highly influences on the activity of resulting catalysts. The precipitant of the precursor shows highly influences on the amount of catalytic active sites present which are directly associated to the CO oxidation. The compositional variations varied the optimization of CuMnOx catalysts and doping was also being explored. In comparison to other catalysts the CuMnOx is a low cost, easily available and highly active catalyst for CO oxidation.