

Chapter 3

Experimental

3. General

The most important characteristics of catalyst for CO oxidation are its activity, selectivity and stability. To obtain reliable and meaningful results, catalysts need to be designed with utmost care. Experimental conditions must be adjusted so that the intrinsic activity of the catalyst was measured, rather than the effect of mass and heat transfer. Determination of catalytic activity is closely associated with the development of catalysts for new processes or improved formulation for practical application. New catalysts are usually tested on a relatively small scale before putting them to a large scale. Therefore, the plug flow tubular reactor has been used in this study for the measurement of catalytic activity and carrying out the kinetic studies.

3.1 Synthesis of Catalysts

Materials Required

Chemicals: $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$, $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, AgNO_3 , $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Aqueous NH_3 solution, KMnO_4 , Na_2CO_3 , KOH (all AR grade chemicals).

The following methods were used for the preparation of Hopcalite catalysts:

3.1.1 Co-precipitation method

Co-precipitation is carrying out for simultaneous precipitation of more than one component. This is the easiest method to prepare catalysts based on more than one component. The bulk catalysts as well as support catalysts are prepared by this method. The most common method for the preparation of mixed oxide catalysts is crystallization

or co-precipitation in solution of a precursor form (hydroxide, oxide, insoluble salt) of the catalyst [Njagi *et al.*, 2011]. The process of precipitation involves two main stages, nucleation and growth. During the nucleation process, the initial minute crystals of the solid phase begin to form, these tend to have a high specific surface area and high free energy, so are considered as relatively unstable. A certain critical size of nuclei, the free energy of formation of the solid phase is lower than its surface energy so the new phase is thermodynamically unstable. Above this critical size solid particles can grow. The growth step tends to be controlled by interface or diffusion phenomena [Cai *et al.*, 2012]. The primary case involves the creation of complicated solid structures, while the second is more ordinary in the precipitation processes used in the catalyst preparation [Mele *et al.*, 2012]. Koleva has reported that the most preparations of hopcalite involve the utilize of nitrate precursors because of their high solubility and the ease of elimination of the nitrate anion during the calcination step [Koleva *et al.*, 1997]. In this way, the nitrate leaves no residue on the catalyst, unlike during the use of chlorides or sulphates which have usually lead to the retention of the metal anion on the surface. For alumina supported hopcalites, it has been found that the use of manganese acetate in place of the nitrate leads to a highly discrete oxide phase. Another popular route to the hopcalite catalyst is the decomposition of the copper and manganese oxides at 350-450°C [Stoilova *et al.*, 2000]. Variations of the co-precipitation method appear to be the most accepted routes towards the resulting catalyst where the use of nitrate precursors predominates.

3.1.2 Sol-gel method

In materials science, the sol-gel process is a method for producing the solid materials from small molecules. This method is use for the production of metal oxides. The process involves conversion of monomers into a colloidal solution (*sol*) that acts as the

precursor for an integrated network (or *gel*) of either discrete particles or network polymers [kumar *et al.*, 2008]. Typical precursors are metal alkoxides. In this chemical procedure, the sol (or solution) slowly evolves towards the formation of a gel-like di-phasic system containing both a liquid phase and solid phase whose morphologies range from discrete particles to continuous polymer networks [Hench and West, 1990]. In case of the collide, the volume fraction of particles (or particle density) may be so low therefore a significant amount of fluid may need to be removed initially for the gel-like properties to be recognized [Cauqui and Rodríguez-Izquierdo, 1992]. Sol-gel derived binary copper manganese oxides for CO oxidation in dry air at room temperature have been investigated. These types of catalysts are use in proton exchange membrane fuel cells and have high catalytic activity. The high activity is due to an arrangement of high surface area, an amorphous state and the presence of Cu^{2+} and Mn^{3+} [Kramer *et al.*, 2006]. The CuMnOx catalysts prepare by the sol-gel method has shown that the high activity for CO oxidation at a low temperature [Cai *et al.*, 2012].

3.1.3 Wet-impregnation method

Impregnation consists in contacting a solid support with a liquid containing the components to be deposited on the surface. During impregnation different processes take place with different rates. Selective adsorption of species (charged or not) by coulomb force, Vander Waals forces or H-bonds; ion exchange between the charged surface and the electrolyte; polymerization/de-polymerization of the species (molecules, ions) attached to the surface; partial dissolution of the surface of the solid. The type of product depends on (i) the nature of both reactants (the liquid and the solid surface), and (ii) the reaction conditions [Munnik *et al.*, 2015]. The main parameters affecting the liquid are the pH, the nature of the solvents and the concentrations of dissolved substances. The initial parameter affects ionization and, in many cases, the nature of the

ions containing the active elements. The second and third influence salvation. The main properties of the solids are the texture, the nature of functional groups (e.g., the number and strength of the acidic and basic centers), the presence of exchangeable ions, and the reactivity (surface dissolution in acidic or basic solution, etc.) [Komiyama, 2012]. Haruta and co-workers showed that the incipient wetness impregnation is unsuitable to produce highly dispersed gold supported hopcalite catalysts and that in order to obtain high activity this catalysts, the materials have to be prepared via co-precipitation or deposition-precipitation method [Haruta *et al.*, 1993]. The Au-containing Hopcalite catalysts for low temperature CO oxidation are prepared by a co-precipitation method. The addition of Au into the CuO-MnO_x system resulted in a noticeable improvement in the catalytic activity [Solsona *et al.*, 2004].

3.1.4 Incipient wetness method

Incipient wetness impregnation (IWI), also called capillary impregnation or dry impregnation, is a commonly use technique for the synthesis of heterogeneous supported catalysts. Typically, the active metal precursor is dissolve in an aqueous or organic solution. Then the metal-containing solution is added into a catalyst support containing the same pore volume as the volume of the solution that is added [Valencia *et al.*, 2010]. Capillary action draws the solution into the pores. Solution added in excess of the support pore volume causes the solution transport to change from a capillary action process to a diffusion process, which is much slower. The precursor was dried and calcined to drive off the volatile components within the solution, depositing the metal on the catalyst surface. The maximum loading is limited by the solubility of the precursor in the solution [Isaeva *et al.*, 2010]. The concentration profile of the impregnated compound depends on the mass transfer conditions within the pores during impregnation and drying. Incipient wetness (IW) techniques use minimum

volume solution to dissolve metal salts, which was mixed with the support [Hong *et al.*, 2010]. Standard Co-precipitated CuMn_2O_4 is subjected to an incipient wetness procedure to synthesize Pd impregnated CuMn_2O_4 catalyst. Pd is added in the form of palladium nitrate onto the calcined CuMn_2O_4 support. Incipient wetness impregnation of metal salts onto support normally results in macroscopic agglomerated particles of precious metal and thus limited Pd \leftrightarrow Cu/Mn interactions [Aldridge 2011]. The relatively lower loadings of Pd in this experiment compared to the doped catalysts could also be an explanation. A synergetic effect between PdO/Pd(s) and CuMn_2O_4 the activity was increased can only be attributed to increased CO oxidation by Pd⁰ [Jones 2006].

3.2 Different calcination conditions

The catalyst precursor was calcined under the following three different conditions:

(I) **Stagnant air calcination:** The calcination of the precursor was carried out in a furnace in the presence of stagnant air at 300°C for 2 hours to produce the CuMnOx catalyst. The calcined catalyst was stored in an air tight glass bottle.

(II) **Flowing air calcination:** The calcination of the precursor was performed *in situ* under flowing air at a flow rate of 60mL/min in the reactor at 300°C for 2 hours, just before the activity measurement experiment.

(III) **Reactive calcination:** Reactive calcination of the precursor was carried out by the introduction of a low concentration of chemically reactive CO–Air mixture (4.5% CO) at a total flow rate of 32.5 ml min⁻¹ over the hot precursors. The temperature of the reactor bed was increase from room temperature to 160°C where CO conversion has started. This temperature was maintained for a defined period of time where the CO

concentration has measured in the exit stream of the reactor at a regular interval until 100% CO conversion was achieved. After achieving the total CO conversion the resultant catalyst was annealed for half an hour at the same temperature then the temperature was increase up to 300°C and upheld for an hour followed by cooling to room temperature in the same environment.

3.3 Characterization techniques used for catalysts

The characterization helps to understand the inter-relationship between the activity and selectivity of a catalyst and its different physical and chemical properties. The catalyst characterization, i.e. the investigation of relevant aspects of the catalyst structure may also be required for quality control on the basis of previous empirical observations.

Table 3.1: Techniques used for characterization of catalysts

Techniques Applied	Physico-Chemical Properties
Low temperature N ₂ adsorption	Textural properties: surface area, pore volume, pore size distribution, average pore diameter
Fourier transform infrared spectroscopy (FTIR)	Infrared spectrum of absorption, emission and photoconductivity
X-ray photoelectron spectroscopy (XPS)	Elemental composition, empirical formula, chemical state
Scanning electron microscopy (SEM)	Surface structure (texture), particle size estimation
Energy-dispersive X-ray spectroscopy (EDX)	Elemental analysis
X ray diffraction (XRD)	Phase analysis, mean crystallite size, crystal size, crystal size distribution and lattice parameter

The information based on characterization of the catalyst is helpful for catalytic process optimization and manufacturing of the catalyst. The prepared catalysts were characterized by various techniques like X-ray Diffraction (XRD), Fourier Transform Infrared Spectrum (FTIR), Scanning Electron Microscopy (SEM) and Low Temperature N₂ Adsorption as given in Table 3.1. The catalysts were characterized by different techniques as XRD, FTIR, SEM-EDX, XPS, TPR, BET surface area etc, to investigate their morphology and activity.

3.3.1 X-ray Diffraction (XRD)

X-ray measurement of the catalyst was carried out by using Rigaku Ultima IV X-ray diffractometer (Figure 3.1) for phase identification. The patterns were run with Cu-K α radiation at 40kV and 40mA. The mean crystallite size (d) of the phase was calculated from the line broadening of the most intense reflection using the Scherrer Equation.

$$d = 0.89\lambda / \beta \cos\theta \text{ ----- (3.1)}$$

Where d is the mean crystallite diameter, 0.89 is the Scherrer constant, λ is the X-ray wave length (1.54056Å), and b is the effective line width of the observed X-ray reflection, calculated by the expression $\beta^2 = B^2 - b^2$ (where B is the full width at half maximum (FWHM), b is the instrumental broadening) determined through the FWHM of the X-ray reflection at 2 θ of crystalline SiO₂.



Figure 3.1: XRD instrument

Principle of XRD

X-rays are electromagnetic radiations of accurately the same nature as light but very much shorter wavelength lying approximately in the range $0.5\text{--}2.5\text{\AA}$. X-rays are emitted from a source to the sample and interact with electrons in matter. Matter absorbs X-rays in two different ways, by scattering and by true absorption. When a beam of X-rays impinges on the material it was scattered in various directions by the electron cloud of the atoms. X-ray diffraction peaks are created by constructive interference of monochromatic light scattered by each set of lattice planes at specific angles. From the scattering, a pattern of the intensity as a function of the scattering angle is obtained, and can be compared to known patterns to identify the crystal structures of elements. X-ray diffraction is most commonly use and the least ambiguous method for the precise determination of the positions of atoms in all kinds of matter ranging from fluids and powders to perfect crystals. It was a non-destructive technique applied for the characterization of crystalline materials. It provides information about the structure,

phases, preferred crystal orientation and other structural parameters such as lattice parameters, crystallite size, crystallite strain and crystal defects.

3.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) of the prepared catalyst sample was recorded in the range of $400\text{--}4000\text{cm}^{-1}$ on Shimadzu 8400 FTIR spectrometer (Figure 3.2) with KBr pellets at room temperature.



Figure 3.2: FTIR spectrometer

Principle of FTIR

In FTIR, a single optical device called interferometer is used. Most interferometers use as a beam splitter which takes the incoming infrared beam and divides into two optical beams. One beam reflects off of a flat mirror which was fixed in place. The other beam reflects off of a flat mirror which was on a mechanism which allows this mirror to move a very short distance (typically a few millimeters) away from the beam splitter. The two beams reflect off of their respective mirrors and recombined when they meet back at the beam splitter. Because the path that one beam travels in a fixed length and the other was

constantly changing as its mirror moves, the signal which exits the interferometer is the result of these two beams—interfering with each other. The resulting signal is called an interferogram which has the unique property that every data point (a function of the moving mirror position) which makes up the signal has information about every infrared frequency which comes from the source. Infrared spectroscopy has been a workhorse technique for materials analysis. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. With modern software algorithms, infrared is a brilliant tool for quantitative analysis. It can identify unknown materials and determine the quality or consistency of a sample.

3.3.3 Scanning Electron Microscopy (SEM)

Scanning electron micrographs (SEM) and SEM-EDX were recorded on Zeiss EVO 18 scanning electron microscope (SEM) instrument as shown in Figure 3.3. An accelerating voltage of 15 kV and magnification of 5000X was applied.

Principle of SEM

SEM consists of an electron gun and electromagnetic lens system. A well-defined electron beam focused to a small spot, 50-100Å in diameter, on the surface of the sample. Electron beams which have been accelerated through a voltage lying between 1 and 50 kV, was used for the most applications. Accelerated electrons from electron gun carry significant amounts of kinetic energy, and this energy is degenerate as a variety of

signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals lead to the generation of secondary electrons (that produce SEM image), backscattered electrons (BSE), diffracted backscattered electrons (EBSD that are used to determine crystal structures), photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light and heat. The secondary electrons can be detected by suitable detectors. These are the most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e. for rapid phase discrimination).



Figure 3.3: SEM instrument

Morphological characterization is performed by using scanning electron microscopy (SEM). Topographical images in a SEM are produced from back-scattered primary or low-energy secondary electrons. The best resolution is about 2-5 nm but many routine studies are satisfied with a lower value and exploit the ease of image interpretation and the extraordinary depth of field to obtain a comprehensive view of the specimen. With

non-crystalline catalysts, SEM is especially useful for examining the distribution and size of mesopores.

3.3.4 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is used to monitor the surface compositions and the chemical states of the constituent elements performed on an Amicus spectrometer (Figure 3.4) equipped with Al K α X-ray radiation. For typical analysis, the source was operated at a voltage of 15kV and current of 12mA. The binding energy scale was calibrated by setting the main C(1s) line of the adventitious impurities at 284.7eV, giving an uncertainty in peak positions of 0.2eV.



Figure 3.4: XPS instrument

Principle of XPS

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive quantitative spectroscopic technique that measures the elemental composition at the parts per thousand ranges. A typical XPS spectrum is a plot of the number of electrons detected (sometimes per unit time) (*Y*-axis, ordinate) versus the binding energy of the electrons

detected (*X*-axis, abscissa). Each element produces a characteristic set of XPS peaks at characteristic binding energy values that directly identify each element that exists in or on the surface of the material being analyzed. These characteristic spectral peaks correspond to the electron configuration of the electrons within the atoms, e.g., 1s, 2s, 2p, 3s, etc. The number of detected electrons in each of the characteristic peaks is directly related to the amount of element within the XPS sampling volume. To generate the atomic percentage values, each raw XPS signal must be corrected by dividing its signal intensity (number of electrons detected) by a "relative sensitivity factor" (RSF), and normalized over all of the elements detected. Since hydrogen is not detected, these atomic percentages exclude hydrogen.

To count the number of electrons during the attainment of a spectrum with a minimum of error, XPS detectors must be operated under ultra-high vacuum (UHV) conditions because electron counting detectors in XPS instruments are typically one meter away from the material irradiated with X-rays. This long path length for detection requires such a low pressure. XPS detects only those electrons that have actually escaped from the sample into the vacuum of the instrument and reach the detector. In order to escape from the sample into vacuum, a photoelectron must travel through the sample. XPS is a quantitative spectroscopic technique that measures the elemental composition of the surface, empirical formula of pure materials, chemical state and electronic state of the elements that exist within the material, elements that contaminate a surface, uniformity of elemental composition across top surface.

3.3.5 Brunauer, Emmett and Teller isotherm Analysis (BET)

The standard method for measuring the specific surface area by gas adsorption and the application of Brunauer, Emmett and Teller (BET) equation which is described in details in a number of reference books. BJH analysis can also be employed to determine the pore area and specific pore volume using adsorption and desorption techniques. This technique characterizes pore size distribution independent of external area due to particle size of the sample. The parameters like surface area, pores sizes distribution, particles and pore shapes play a major role in governing the vital reaction parameters like catalytic activity, selectivity and stability as well as the physical factors such as permeability, diffusivity, effectiveness factor and mechanical strength.



Figure 3.5: BET instrument

Principle of BET analysis: The principle of BET analysis is that at low relative pressure, gas adsorbs to a solid in a monolayer (multilayer form at higher pressures). By knowing the number of gas molecules in a monolayer and the dimensions of an individual molecule, the surface area covered by the monolayer can be calculated. The BET equation (Smith 1970) models measured a number of moles of adsorbate (n)

adsorbed on 1g of sample with the applied gas pressure (P) following the relationship given in equation below.

$$\frac{P/P_o}{n(1-\frac{P}{P_o})} = \frac{1}{n_m c} + \frac{c-1}{n_m c} \left(\frac{P}{P_o}\right) \text{----- (3.2)}$$

Where;

n_m = calculated number of moles adsorbed as a monolayer on 1g of adsorbent,

P = gas pressure,

P_o = saturation vapour pressure of the gas, and

c = a constant that is dependent upon the shape of the isotherm.

n_m is obtained by plotting $P/V_a(P_o - P)$ against P/P_o , where V_a is the volume of gas adsorbed per gram of sample normalized to standard temperature and pressure (STP) (mL/g). Generally the plot is linear at low relative pressures ($P/P_o < 0.3$). The slope of the linear part of the graph has a slope (s) of $c - 1/V_m c$ and an intercept (i) of $1/V_m c$, where V_m is the volume of gas required to form a monolayer on a unit gram of the sample (mL/g). Both s and i have units of cm^3/g at STP.

3.4 Catalytic Activity Test

The Schematic diagram of the experimental set up for catalytic activity measurement is shown in the Figure 3.4. It can be divided into the following three sections:

- i) Air feeding section,
- ii) Reaction section, and
- iii) Reactants and product analysis section

3.4.1 Air feeding section

Air from the compressed cylinder is fed into the reactor, after purifying free from moisture and CO₂ by passing through a tower packed with CaO and KOH pellets. The air is monitor with the help of digital gas flow meter. A safety device in the form of mercury sealing was provided in the feeding line to check any pressure build up.

3.4.2 Reaction section

The catalytic performance of the synthesized catalyst for CO oxidation was evaluated in a compact fixed bed tubular quartz reactor has shown in the Figure 3.6. The reactor was consisting of two co-axial tubes of 20mm and 50mm diameter. A helical coil of quartz tube in between the co-axial tubes served as a pre-heater of the air. There was a hole in the lower part of the outer tube, to take care of breakage due to the expansion or contraction of air in between co-axial tubes as the unit was subjected to the variation of the temperature from ambient to the reaction temperature. The pre-heated air enters into the catalyst bed, kept in the inner tube as shown in the Figure 3.6.

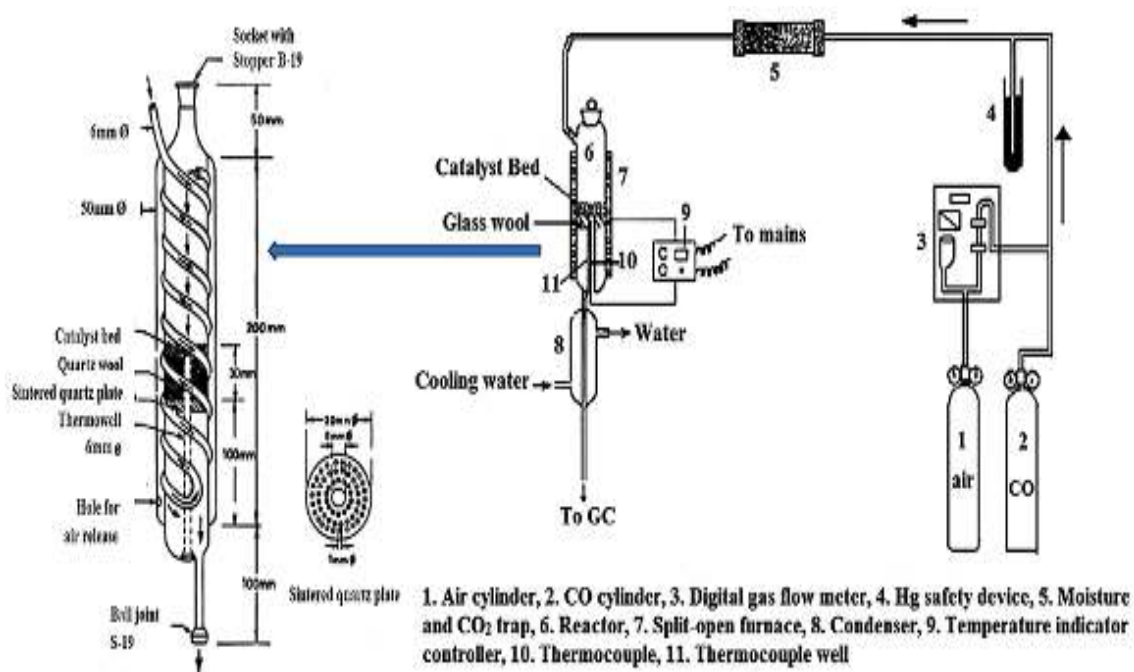


Figure 3.6: Schematic diagram of Experimental Set up

The reactor was placed vertically in a split-open furnace with the following reaction conditions were maintained: Catalyst particle size 40–100 mesh, using a lean mixture of 2.5% CO(v/v) in air, maintaining the total flow rate at $60 \text{ ml}\cdot\text{min}^{-1}$. The catalytic oxidation of CO over all the catalysts was carried out at atmospheric pressure in a fixed bed down flow tubular reactor containing 100mg catalyst was diluted to 1 ml of α -alumina at different temperatures. The down stream of air was used to avoid any deformation of the bed. The catalyst (catalyst bed diameter 20mm and height 1.27mm) was placed on a thin layer of quartz wool which was supported on perforated quartz disc inside the inner tube.



Figure 3.7: Experimental Set up

The thermocouple-well made of 4mm diameter tube was inserted axially from the bottom all the way to the centre of the disc for temperature measurement and control. The meaningful kinetic data can be obtained from a packed bed reactor, only if the flow

pattern within the reactor resembles plug flow. It provides a simple relationship between the feed rate and the rate of reaction.

3.4.3 Reactants and Product analysis section

The product stream coming from reactor was analyzed with the help of a Gas chromatography (GC) as shown in the Figure 3.8. It has following components:

1. Carrier gas
2. Sample injection port
3. Columns
4. Column oven
5. Methaniser
6. Detector
7. Retention time (R.T.)

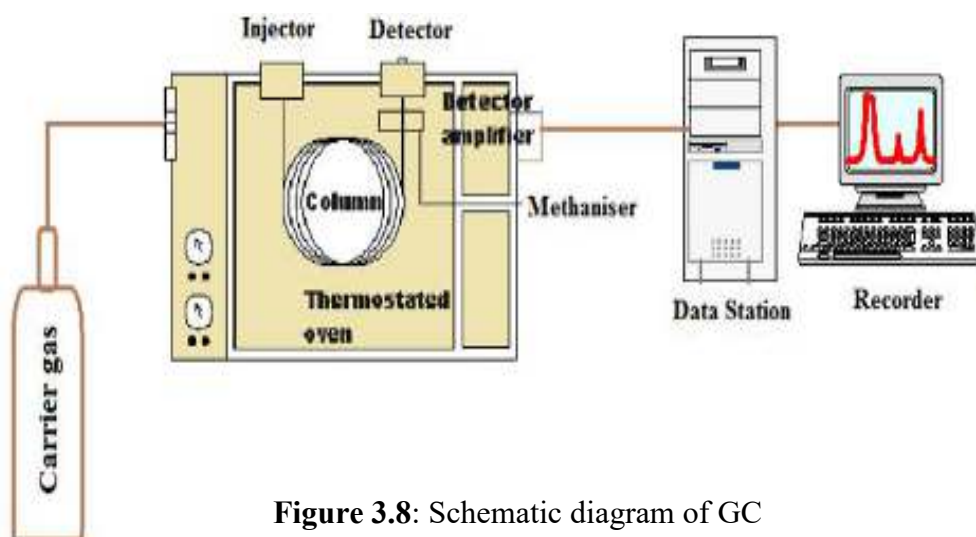


Figure 3.8: Schematic diagram of GC

3.4.3 (A) Carrier Gas

A carrier gas (mobile phase) was the gas which was passed continuously through the column and whose passage promotes the elution of components of the sample. The carrier must be chemically inert. The most common gas used was helium. Helium has a larger range of flow rates that were comparable to hydrogen in efficiency, with the added advantage that helium was non-flammable, and works with a greater number of detectors.

3.4.3 (B) Retention time (RT)

Retention time (RT) was the time it takes a solute to travel through the column. The retention time was assigned to the corresponding solute peak. The retention time was measured the amount of time a solute spends in a column.

3.4.3 (C) Columns

There were two types of column used in a gas chromatography, packed and capillary. A packed column typically used a stainless steel or glass tube with an 1/8th inch inner diameter packed with a solid stationary phase. A capillary column was an open tube made of fused silica with an outer coating of durable plastic and an inner coating of stationary-phase material. However, in spite of its problems with sample injection, the packed column was seen as the 'state of the art' column and by distant the most popular column system in general use. The columns used in the GC analysis for this analysis were all packed columns. The packed columns were detailed with the GC experimental procedure. The effectiveness of a chromatographic column in separating analyses was dependent on a number of variables. Variables that affect division include distribution equilibrium constants, retention time, retention (capacity) factors and selectivity factors.

3.4.3 (D) Sample Injection point

For optimum column efficiency, the sample should not be too large, and should be introduced onto the column as a "plug" of vapors - slow injection of large samples causes band broadening and loss of resolution. The most common injection method was a micro syringe used to inject sample through a rubber septum into a flash vaporizer port at the head of the column. The temperature of the sample port was usually about 50°C higher than the boiling point of the least volatile component of the sample. For packed columns, the sample size ranges from tenths of a micro liter up to 20 micro

liters. Capillary columns, on the other hand, need much less sample, usually around 10-30ml. For capillary GC, split/split less injection was used. The mixture of components in the sample was introduced into the chromatograph through the injection port. Sample injection point, the analytes were vaporized (if not already in the gas phase) by the high temperature maintained in the injection port. The gas phase analytes were the immediately swept onto the chromatographic column by the mobile phase. There were two methods for delivering samples into the column, through a gas tight syringe and through a rotary gas sampling valve. The later was the form used during analysis of gas samples.

3.4.3 (E) Column oven

The thermostatic oven serves to control the temperature of the column within a few tenths of a degree to conduct the precise work. The oven can be operated in two manners: isothermal programming or temperature programming. In isothermal programming, the temperature of the column was held constant throughout the entire separation. The optimum column temperature for isothermal operation was about the middle point of the boiling range of the sample. However, isothermal programming works best only if the boiling point range of the sample was low. If a low isothermal column temperature was used with a wide boiling point range, the low boiling fractions were well resolved but the high boiling fractions were slow to elute with extensive band broadening. If the temperature was increased closer to the boiling points of the higher boiling components, the higher boiling components elute as sharp peaks but the lower boiling components elute so quickly there was no separation. In the temperature programming method, the column temperature was increased continuously or in steps as the separation progresses. This method was well suited to separating a mixture with a broad boiling point range. The analysis begins at a low temperature to

determine the low boiling components and increases during the separation to resolve the less volatile, high boiling components of the sample. Rates of 5-7°C/minute were typical for temperature programming separations.

3.4.3 (F) Methanizer

Methanizer is an appliance used in the gas chromatography, which allows detecting very low concentrations of carbon monoxide and carbon dioxide. It converts CO and CO₂ proportionally into CH₄ by a hydrogenating reactor, which can be easily detected by a flame ionization detector.

3.5 Principle of gas chromatography

One or more high purity gases were supplied into the Gas chromatography. One of the gases (called the carrier gas) flows into the injector, through the column and then into the detector. A sample was introduced into the injector usually with a micro syringe or an exterior sampling device. The injector was usually heated to 80°C which causes the sample solutes to vaporize. The vaporized solutes were transported into the column by the carrier gas. The column was maintained in a temperature controlled oven. The solutes travel through the column at a rate of primarily determined by their physical properties, temperature and composition of the column. The various solutes travel through the column at different rates. The fastest moving solute exists (elutes) the column first then it followed by the remaining solutes in corresponding order. As each solute elutes from the column, it enters the heated detector. An electronic signal was generated upon interaction of the solute with the detector. The size of the signal was recorded by a data system and was plotted against elapsed time to produce a chromatogram.



Figure 3.9: Gas Chromatograph

The ideal chromatogram has closely spaced peaks with no overlap of the peaks. Any peaks that overlap were called co eluting. The time and size of peaks were important in that were used to identify and measure the amount of the compound in the sample. A larger peak was obtained as the concentration of the corresponding compound increases. If the column and all of the operating conditions were kept the same, a given compounds always movements through the column at the same rate. Thus a compound can be identified by the time required for it to travel through the column (called the retention time). The identity of a compound cannot be determined solely by its retention time. A known amount of an authentic, pure sample of the compound has to analyzed and its retention time and peak size determined. This value can be compared to the results from an unknown sample to determine whether the target compound was present (by comparing retention times) and its amount (by comparing peak sizes).

3.6 Operating parameters for gas Chromatography

Oven temperature = 60°C N₂ gas cylinder valve open at a pressure = 1.5 bar

Detector (F.I.D.) temperature = 80°C Air pressure = 1 bar

Injector temperature = 80°C Inlet observation = CO

Outlet observation = CO+CO₂ H₂ gas cylinder valve open at a pressure = 1bar

3.7 Detectors

There were many detectors which can be used in a gas chromatography. Different detectors will give different types of selectivity. A non-selective detector responds to all the compounds except the carrier gas, a selective detector responds to a range of compounds with an ordinary physical or chemical property and a specific detector responds to a single chemical compound. Detectors can also be grouped into concentration dependent detectors and mass flow dependent detectors. The signal from a concentration dependent detector was associated to the concentration of solute in the detector, and does not usually destroy the sample dilution of make-up gas will lower the detectors response. Mass flow dependent detectors usually destroy the sample, and the signal was associated to the rate at which the solute molecules enter the detector. The response of a mass flow dependent detector was unaffected by make-up gas.

3.7.1 Thermal Conductivity Detector

The TCD consists of four tungsten-rhenium filaments in a Wheatstone bridge configuration. Electric current flows through the four filaments causing them to heat up. The carrier gas (typically helium which has very high thermal conductivity) flows across the filaments removing heat at a constant rate. When a sample molecule with lower thermal conductivity exits the column and flows across the two sample filaments,

the temperature of the filaments increase unbalancing the Wheatstone bridge and generating a peak as the sample molecules transit through the detector. The TCD detector detects all molecules, not just hydrocarbons, so it was commonly used for fixed gas analysis (O_2 , N_2 , CO , CO_2 , H_2S , NO , NO_2) where the target analyses do not respond well on other more sensitive detectors.

3.7.2 Flame Ionization Detector (FID)

A flame ionization detector (FID) consists of a stainless steel jet constructed so that the carrier gas existing the column flows through the jet, mixes with hydrogen and burns at the tip of the jet. Hydrocarbons and other molecules which ionize in the flame were concerned to a metal collector electrode located just to the side of the flame. The resulting electron current was amplified by a special electrometer amplifier which converts very small currents to milli volts. The FID is sensitive to almost all molecules that contain hydrocarbons. It is a destructive detector that can be used in series only after non-destructive detectors. The effluent from the column mixed with hydrogen and air, and ignited. Organic compounds burning in the flame produce ions and electrons which can conduct electricity through the flame. A large electrical potential was applied at the burner tip, and a collector electrode was located above the flame. The current resulting from the pyrolysis of any organic compounds was measured. FIDs were mass sensitive rather than concentration sensitive; this gives the benefit that changes in mobile phase flow rate do not affect the detector's response. The FID was a useful general detector for the analysis of organic compounds; it has high sensitivity, a large linear response range and low noise. It was also robust and easy to use, but unfortunately, it destroys the sample.

3.8 Data Acquisition

The acquisition and extensive possibilities of the storage of digitalized raw data can be performed flexibly. The raw data can be re-plotted to form analogue chromatograms in variable scales of retention and the response axis. The computer based systems offer extensive tools to analyze the data produced from systems.

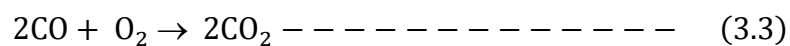
3.8.1 Measurement of catalyst activity by Gas Chromatography

The catalytic activity for CO oxidation was evaluated in a tubular packed bed flow reactor. The 100 mg catalyst was diluted with 1 mL alumina was placed in the tubular reactor, and the oxidation was carried out at ambient temperature. The inlet air was fed into the reactor at a flow rate of 58.50mL/min while CO was fed at a flow rate of 1.50mL/min. The outlet gases were analyzed for CO and CO₂ by an on-line gas chromatography equipped with a porapak Q-Column, a methaniser and a FID detector. Nitrogen was used as a carrier gas and hydrogen as a fuel. The temperatures of the oven, injector and detector were maintained at 60°C, 80°C and 80°C respectively.

3.9 Gas chromatography applications

Gas chromatography was a physical separation method in which the volatile mixtures were separated. It can be used in many different fields such as pharmaceuticals, cosmetics and even for environmental toxins. Since the samples have to be volatile and other secretions containing large amounts of organic volatiles can be easily analyzed using GC. Knowing the amount of which compound in a given sample gives a huge advantage in studying the effects of human health and environment as well. Air samples can be analyzed using GC. Most of the time, air quality control units use GC coupled with FID in order to determine the components of a given air sample. Although the other detectors were useful as well, FID was the most appropriate because of its

sensitivity, resolution and also because it can detect very minute molecules as well. GC/MS was also another useful method which can determine the components of a given mixture using the retention times and the abundance of the samples. This method applied to many pharmaceutical applications such as identifying the amount of chemicals in drugs. Moreover, cosmetic manufacturers also use this method to successfully measure how much of each chemical was used for their products. The following procedures briefly explain the conditions used for catalyst testing and full conversions for the GC systems. Typically, the reactor was heated to the desired temperature with the help of a microprocessor based temperature controller. A temperature control of $\pm 0.5^\circ\text{C}$ was achieved. Eq.3.3 can be representing the air oxidation of CO over the catalyst.



The gaseous products were analyzed by an on-line gas chromatograph (Nucon Series 5765) equipped with a methaniser, porapack q-column and FID detector for the concentration of CO and CO₂. The catalytic activity was measured for the conversion of CO into CO₂.

$$(X_{CO}) = [(C_{CO})_{in} - (C_{CO})_{out}] / [(C_{CO})_{in}] = \frac{[(A_{CO})_{in} - (A_{CO})_{out}]}{[(A_{CO})_{in}]} \text{ --- --- --- --- --- (3.4)}$$

The conversion of CO at any instant was calculate on the basis of values of the concentration of CO ($(C_{CO})_{in}$) in the feed and the concentration of CO₂ ($(C_{CO})_{out}$) in the product stream by the following Eq.3.4. The concentration of CO was proportional to the area of chromatogram A_{CO} ($(A_{CO})_{in}$) at any instant was proportional to the area of chromatogram of CO₂ ($(A_{CO})_{out}$) formed. Where the change in the concentration of CO due to oxidation at any instant [$(C_{CO})_{in} - (C_{CO})_{out}$] was proportional to the area of chromatogram of CO₂ formed at that instant [$(A_{CO})_{in} - (A_{CO})_{out}$] and the concentration

of CO in the inlet stream $(C_{CO})_{in}$ was proportional to the area of the chromatogram of CO₂ formed $(A_{CO})_{out}$ by the oxidation of CO. A thermal conductivity detector was used for the detection and quantification of the products and unreacted gases.