CHAPTER III
EXPERIMENTAL

In this chapter, catalyst preparation techniques, experimental conditions and reactor set-up employed in the determination of activity of catalysts and various catalyst characterization techniques will be explained. The preparation techniques used in this dissertation are impregnation, co-precipitation and sol-gel. After the introduction of preparation techniques, a reactor set-up connected with a Gas Chromatograph (GC), which quantify the concentration of the reactant and product streams, is explained. In the final part of this chapter, X-ray powder diffraction (XRD), Transmission electron microscopy (TEM), Scanning electron microscopy (SEM) and BET surface area measurements, utilized to characterize the surface, bulk and morphological properties of catalysts will be discussed.

3.1 Catalyst Preparation Techniques and Activation Procedures

Catalyst can be prepared in several ways. In this work, impregnation, co-precipitation and sol-gel techniques were used to synthesize catalysts. In the following sections, these techniques will be explained in detail.

3.1.1 Impregnation Method

This method is the simplest classical method to prepare catalysts. In the absence of specific interactions between the preformed support and the components of the impregnating solution, the impregnation process stages can be described quite simply (Twigg, 1989). A solution is made up containing the component to be put on the catalyst. In the next stage, either the support is dipped into this solution or the solution is added to the support. In both methods the take-up of the solution is governed by the porosity of the support, so the level of active component incorporated in the catalyst is a function of the solution absorbed in the pore system of the support. After adsorption of the solution into the pore system of the support, the resulting catalyst is then usually dried and calcined.
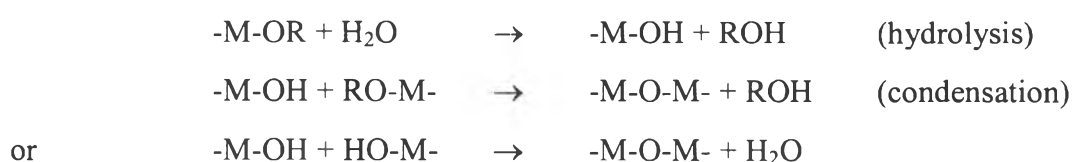
3.1.2 Co-precipitation Method

In a common procedure to form a high surface area oxide, an aqueous metal salt solution is contacted with an alkali such as sodium hydroxide or sodium carbonate, to cause the precipitation of an insoluble metal hydroxide or carbonate (Satterfield, 1991). Usually, if more than one element is precipitated, the word "co-precipitation" is used, instead. The starting compounds are generally chosen because of their availability and high water solubility. After filtration and washing, the precipitate is dried and heated to decompose the hydroxide/carbonates to the corresponding oxides. The final size of crystallites present in precipitated catalyst are typically in the range 3-15 nm, while overall surface areas can be 50-200 m^2/g or more.

3.1.3 Sol-gel Method

This method involves the formation of a sol followed by formation of a gel, typically uses either colloidal dispersions or inorganic precursor as the starting material (Ward and Ko, 1995). This description of sol-gel chemistry identifies two ideas. First, a gel forms because of the condensation of partially hydrolyzed species into three-dimensional polymeric network. Second, any factors that affect either or both of these reactions are likely to impact on the properties of the gel. The catalytic implications are that sol-gel prepared oxide-metal systems can have very different activation and deactivation behavior from conventionally prepared supported-metal systems. However, it is important to realize that sol-gel preparation can be done with a wide variety of precursors.

Hydrolysis and condensation reactions are usually described at the functional group level as follows:

$$-M-OR + H_2O \rightarrow -M-OH + ROH \quad \text{(hydrolysis)}$$
$$-M-OH + RO-M- \rightarrow -M-O-M- + ROH \quad \text{(condensation)}$$
$$\text{or} \quad -M-OH + HO-M- \rightarrow -M-O-M- + H_2O$$

where M stands for a metal in an alkoxide and R indicates the hydrocarbon functional group of the alkoxide.

Hydrolysis reactions produce hydroxide and an alcohol. At the same time, hydroxide and unreacted alkoxide react to produce metal oxide and alcohol. The important parameters in sol-gel techniques are the followings: the rate of hydrolysis related to that of condensation, aging process, drying method, and calcination procedure. Figure 3.1 shows the four key steps in taking a precursor to a particular product form via sol-gel preparation. The versatility of this preparative approach lies in the number of preparation variables that can be manipulated in each of these steps.

Livage *et al.* (1988) pointed out that the most important variations are the relative rates of hydrolysis and condensation. Examples are given in Table 3.1.
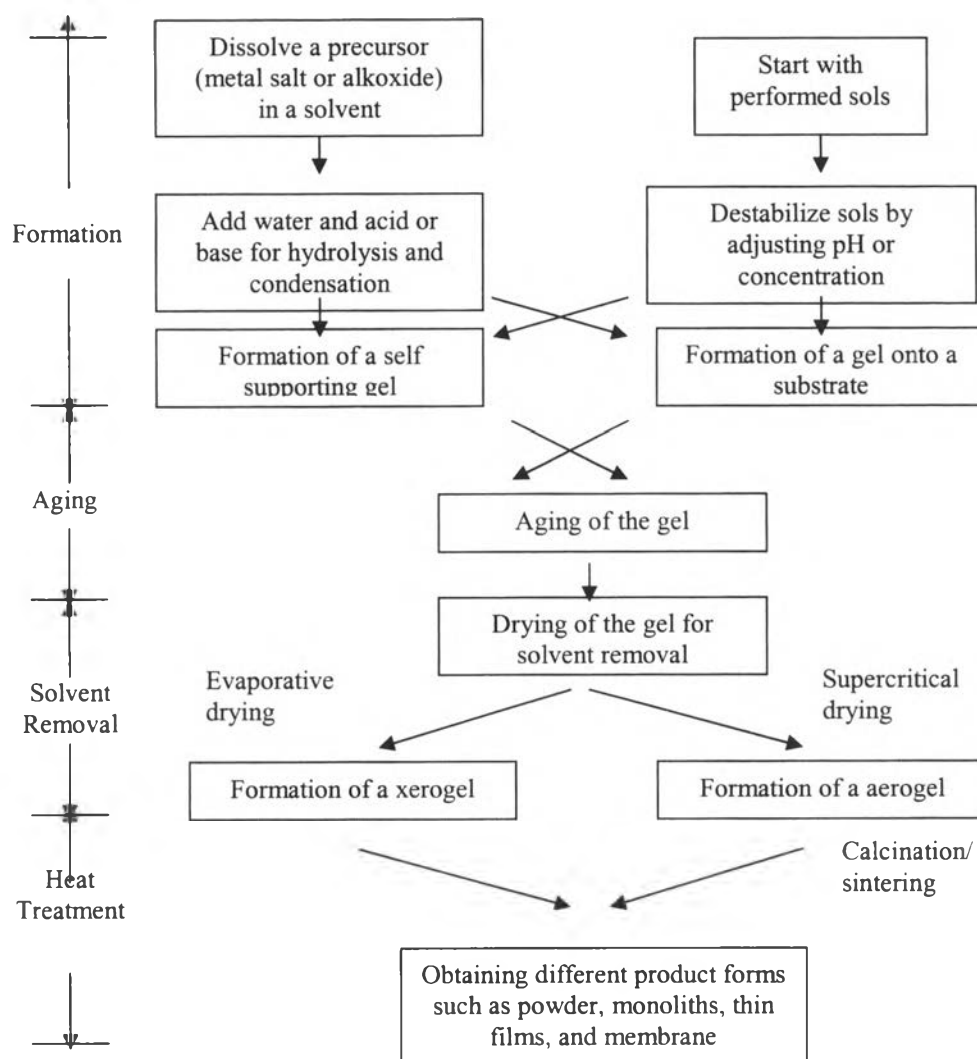
Figure 3.1 Schematic diagram showing the various steps of sol-gel process.
(Livage *et al.*,1988)

Table 3.1 Effect of relative rates of the hydrolysis and condensation on gel quality.

Hydrolysis rate	Condensation rate	Resulting material
Slow	Slow	Colloids/Sols
Fast	Slow	Polymeric gel
Fast	Fast	Colloids gel or Gelatinuous precipitate
Slow	Fast	Controlled precipitate

3.1.4 Single Step Sol-gel Synthesized Catalysts

The active metal ingredient can be introduced onto the support material in two ways: either during the sol state, called single step sol-gel synthesis, or using the impregnation technique after the sol-gel support material is obtained. In this work, transition metals supported on alumina and ceria catalysts were prepared. The platinum, gold, and palladium were the active ingredients of the catalyst.

Pure Alumina Synthesis by Sol-gel Method

In the synthesis of pure alumina support, aluminum isopropoxide (AIP) was used as an alkoxide precursor. AIP was dissolved in hot water at $85^{\circ}C$ with a small amount of nitric acid to form a fibrillar sol. Then, sol was dissolved in 1,3-butanediol and stirred at $85^{\circ}C$ for an hour. After one day of stirring at room temperature, the gel was dried for 24 h and calcined at $500^{\circ}C$ for 5 h.

3.1.5 Heat Treatment of Catalysts

After the preparation step, the next step is drying and calcination. The purpose of drying is to remove the solvent used during the preparation step and also to evaporate the water from pores of the support that is introduced during the impregnation. This is usually performed at $110^{\circ}C$ in a conventional oven. After that,

the dried catalysts are put in a furnace for calcination. Calcination is further heat treatment beyond drying. The purpose of the calcination is as follows:

1) to generate an active phase, e.g. forming the oxide.

2) to eliminate chemically bound water and unstable ions and cations introduced during preparation and to burn the solvent and other organic precursors left in pores after drying.

3) to change the pore size distribution.

4) to enhance the mechanical properties of the material.

The calcination temperature is usually made based on the type of support material. In this work, catalysts were calcined at 400-500°C for 2-5 h (with 10°C/min heating rate).

The final step in the heat treatment is catalyst activation. In the activation step, a metal oxide is formed by oxidizing at an elevated temperature in flowing oxygen. In this work the catalysts were activated under an oxygen atmosphere by increasing the catalyst bed temperature to 110°C and keeping it at this temperature for 2 h.

3.2 Reactor Set-up and Product Analysis

Figure 3.2 shows the schematic diagram of the reactor set-up used in this study. Catalytic reaction study is conducted in a pyrex glass U-tube reactor having an internal diameter of 6 mm at atmospheric pressure. One hundred mg of catalyst is packed between glass wool plugs in the middle of the reactor. The reactor is electrically heated in small oven. The temperature of catalyst bed is monitored and controlled by a PID temperature controller equipped with a chromel-alumel thermocouple.

The reactant gas contains 1% CO, 0.5-2% O_2, 2% CO_2, 2.6% H_2O, 40% H_2 and helium at a total flow rate of 50 ml/min. The space velocity is 30,000 ml/g.h. Each gas is supplied from a compressed gas cylinder. The reactant gases are passed through filters to remove particles and check valves to prevent reverse flow. The individual stream flow rate is controlled by an electronic mass flow controller to

achieve the desired composition. The mixed stream is switched to desired direction by three way valves, and delivered to the reactor.
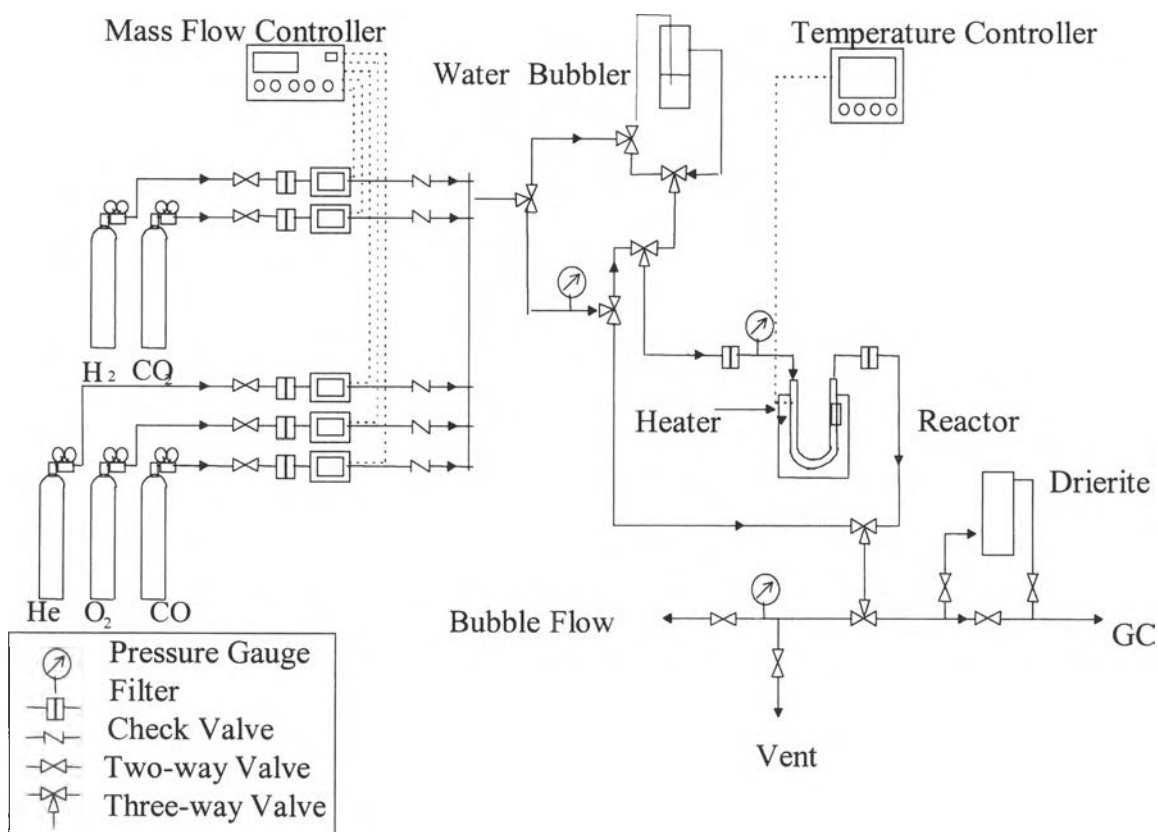

Figure 3.2 Schematic diagram of the reactor set-up.

3.2.1 Product Analysis

The reactant and product composition is analyzed both qualitatively and quantitatively by an on-line gas chromatograph (Hewlett Packard 5890 Series II) equipped with a thermal conductivity detector (TCD). The column utilized in the chromatography is a Carbosphere, 80/100 mesh, 10 ft x 1/8 inch stainless steel packed column. The helium carrier flow rate is 40 ml/min. The temperature of oven, injector and detector are maintained at 110, 55 and 175°C, respectively. The observed peaks are identified by comparison with retention time of standard gases. The composition of the effluent gas is quantitatively determined by comparison of peak areas with calibration curves obtained from known composition gases.

3.3 Analytical Techniques for Product Analysis

This section briefly explains the principles of analytical techniques used in this study to analyze the gas reactants and products and also to characterize bulk and surface properties of all catalysts.

3.3.1 Gas Chromatography

In this technique, a gas mixture is first separated into its components and then detected by a suitable detector. The separation of the gas mixture into its components is achieved by contacting a small amount of sample gas mixture with a stationary phase. The stationary phase can be liquid or solid. Usually, a solid adsorbent is used as a stationary phase. However, for certain applications, the solid phase is coated with a non-volatile liquid to increase the separation efficiency. There are many types of solid materials that can be used as adsorbents. The most commonly used ones are silica gel, porous polymer beads and molecular sieves. Each separation application requires a specific adsorbent and an operating condition to get the desired separation of the given gas mixture. After the chromatographic separation, each component is carried to the detector by the stream of carrier gas, such as helium, nitrogen, or hydrogen. The function of the detector is to indicate the presence and to measure the concentration of the effluent component by producing an electrical signal. The sensivity of the detector to the component under an analysis

condition is very important but the separation of that component from the rest of the mixture is the controlling factor for reliable determination of its concentration. The most common detectors are the thermal conductivity detector (TCD) and flame ionization detector (FID).

The thermal conductivity detector is a simple universal detector. It is detection principle is based upon changes in the thermal conductivity of the gas stream going around a heated filament. The resistance of the filament changes as the thermal conductivity of the gas cooling it changes. The change in the resistance provides the detection signal.

3.4 Catalyst Characterization

3.4.1 X-ray Diffraction

This is one of the most widely used catalyst characterization techniques. It allows the identification of the bulk phase and the estimation of particle sizes. Since the wavelength of the X-ray is almost the same as the distance between atoms in a periodic lattice, the diffraction of the incident X-ray occurs. The strongly diffracted beam can be observed when the scattered X-rays give constructive interference.

A stationary X-ray source and a movable detector are usually used to measure the XRD pattern of samples. A Rigaku X-ray diffractometer system (RINT-2200) equipped with graphite monochromator and a Cu tube for generating CuK_α radiation (1.5406 Å) was used to obtain the XRD patterns at a generator of 40 mA current and 40 kV voltage. The CuK_α is diffracted by the sample and the detector scans the intensity of this diffracted radiation as a function of 2θ. 2θ is the angle between the incident radiation and the diffracted radiation.

Obtained diffraction patterns are first used to identify whether the sample, or a component of it, is non-crystalline or quasi-crystalline. Second, they yield an estimate of the size of the microcrystallites that may be present. Third, XRD patterns yield d-spacings and unit cell dimensions. Long-range order in the lattice is required to get clear diffraction peaks. For perfect crystals, the width of diffraction

peaks is infinitely narrow. However, line broadening occurs when the lattice thickness is below 100 nm. The minimum lattice thickness that gives the clear diffraction peaks is about 3-5 nm. Above 50 nm, the width of a diffraction peak changes only slightly. Hence, the measurement of changes in the crystallite size above 20 nm is difficult. In the range of 5 nm to 50 nm, the Debye Scherrer equation can be used to calculate the crystallite thickness, as shown below.

$$\overline{d}_{B(hkl)} = \frac{K\lambda}{B_d Cos\,\Theta_o}$$

$\overline{d}_{B(hkl)}$ = the mean crystallite thickness at hkl crystalline plane

K   = the Scherrer constant (0.9 when the width is measured at half the maximum peak height

λ = the X-ray wavelength (0.154 nm for Cu Kα radiation)

B_d = the line width at half the maximum peak height

θ_o = the Bragg angle

3.4.2 Scanning Electron Microscopy

The Scanning Electron Microscope (SEM) is a microscope that uses electrons rather than light to form an image. The SEM has a large depth of field, which allows a large amount of the sample to be in focus at one time. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. Preparation of the samples is relatively easy since most SEMs only require the sample to be conductive. The combination of higher magnification, larger depth of focus, greater resolution, and ease of sample observation makes the SEM one of the most heavily used instruments in research areas today.

3.4.2 Transmission Electron Microscopy

In transmission electron microscopy technique (TEM), electrons are emitted from an electron gun, which is a heated pointed cathode (filament), and accelerated through two electrodes, the second of which is an anode. The electrons then pass through a condenser system, the specimen, and a magnetic lens system. Size and microstructure can be determined for materials in the range of about 1 nm to 30 µm (Satterfield, 1991). The limit of resolution for a microscope is proportional to the wavelength of the illumination.

In this work, characterization of TEM samples was performed using a JEOL 2010, operating at an accelerating voltage up to 200 kV and can reveal useful information on specimens less than about 100 nm thick. Transmission electron microscopy is useful for indicating the size of supported metal crystallites and changes in their size, shape, and position with catalyst use.

3.4.4 BET Surface Area Measurement

The principle of measuring total surface area of porous structure is by adsorption of a particular molecular species from a gas or liquid onto the surface. This method was developed by Brunauer, Emmett, and Teller (1938). The surface area, total pore volume and average pore diameter of all samples was determined using Autosorb-1 Gas Sorption System (Quantachrome Corporation). N_2 gas was used as the adsorbate at liquid N_2 temperature (77K). All samples were outgassed by heating under vacuum at 180°C for 3 h before measurement. This method extended to multilayer adsorption and summation over a finite number of adsorbed layers gives the final expression as follows:

$$\frac{P}{V(P_o - P)} = \frac{1}{V_m C} + \frac{(C-1)P}{V_m C P_o}$$

where   V   = volume of gas adsorbed at pressure P

V_m = volume of gas adsorbed in monolayer

P_o = saturation pressure of adsorbate gas at the
          experimental temperature

C   = a constant related exponentially to the heats of adsorption and liquefaction of the gas

$$C = e^{(q_1 - q_L)/RT}$$

where q_1 = heat of adsorption on the first layer

             q_L = heat of liquefaction of adsorbed gas on all other layers

             R   = the gas constant

             T   = absolute temperature

$P/(V(P_o-P))$ is plotted as a function of P/P_o. The linearity of the plot is usually observed in the range of 0.05 and 0.3 of P/P_o.

3.5 Calculation of Conversion and Selectivity

The CO conversion was calculated based on the CO_2 formation. The selectivity is defined as the ratio of oxygen consumption for the CO oxidation reaction over the total oxygen consumption, which includes the oxygen loss due to H_2 oxidation.

$$\text{CO conversion} = \frac{[CO_2]}{[CO]_o} x100\%$$

and

$$S = \frac{[O_2]_{(CO)}}{[O_2]_{(CO)} + [O_2]_{(H_2)}}$$

where S is selectivity

$[CO_2]$ is the concentration of CO_2 formation

$[CO]_o$ is the inlet CO concentration

$[O_2]_{(CO)}$ is the O_2 consumption for the CO oxidation reaction

$[O_2]_{(H_2)}$ is the O_2 consumption for the H_2 oxidation reaction.