



CHAPTER III METHODOLOGY

3.1 Materials

3.1.1 Gases

The following are the gases, which were used in this research work.

- High purity of Helium gas (99.99% of He).
- High purity of Hydrogen gas (99.99% of H₂).
- Carbon dioxide in Helium gas (20% of CO₂ in He)
- Carbon monoxide in Helium gas (10.3% CO in He)
- Oxygen in Helium gas (5.46% of O₂ in He)
- Pure nitrogen

All the gases used in this research work are from Thai Industrial Gases Public Company limited.

3.1.2 Chemicals

The chemicals which are needed in preparation of the catalysts, are listed below.

- Anhydrous Sodium carbonate (Na₂CO₃) from MERCK.
- Hydrogen tetrachloroaurate (III) trihydrate (99.9% H₂AuCl₄·3H₂O), from ACROS.
- Ferric (III) nitrate nonahydrate (99.9% Fe(NO₃)₃·9H₂O) from CARLD ERBA.
- Cerium (III) Nitrate (Ce(NO₃)₃·6H₂O).
- Lanthanum (III) Nitrate (La(NO₃)₃·6H₂O).

3.2 Equipment

The experiment system used in the catalytic activity can be divided into 3 main parts. The schematic of this experimental set up is in Figure 3.1.

3.2.1 Mass Flow Controller and Gas Mixer

The dust particles in every gas streams were removed before entering the mass flow controller, using a micro filter. The mass flow controller is the equipment used in adjusting the flow of gases into desired percentage composition. The composition of the reactant gases used in this experiment is 1% CO, 1% O₂, 40% H₂, and He. Subsequently, after the gases leave the mass controller, they entered the gas mixer section where all the gases are mixed together. Then mixed gases were passed to the catalytic reactor. The desired flow rate in this experiment is 50 ml/min under atmospheric pressure.

3.2.2 Catalytic Reactor

The gases mixture entered the micro catalytic reactor where the preferential oxidation (PROX) of CO is taken place under atmospheric pressure. The reactor is a U-shape Pyrex glass tube with an inside diameter of 6 mm. The catalyst was packed in the middle of the reactor, between two glass wools. The temperature of the catalyst bed was monitored and controlled by PID temperature controller equipped with a chromel-alumel thermocouple (Type K).

3.2.3 Analytical Instrument

After the effluent gas left the reactor, the effluent gas was passed to the analytical instrument, gas chromatograph. However, the water content in effluent gas must be removed. Thus, the effluent gas was passed through water trapper before being qualitatively and quantitatively analyzed by auto-sampling into on-line gas chromatograph equipped with a packed carbosphere column, 80/100 mesh and 10 ft x 1/8 inch, and a thermal conductivity detector (TCD).

The result peaks were recorded by Agilent Chemstation software and compared with the retention time of the standard, in order to identify the peaks. The

concentration of each gas was calculated from the area under the peaks. And the gas chromatograph conditions used in this study are summarized as follows:

- Injection Temperature: 95°C
- Oven Temperature: 95°C
- Detector Temperature: 145°C
- Carrier gas: He (99.99% purity), at the flow rate of 30 mL/min.

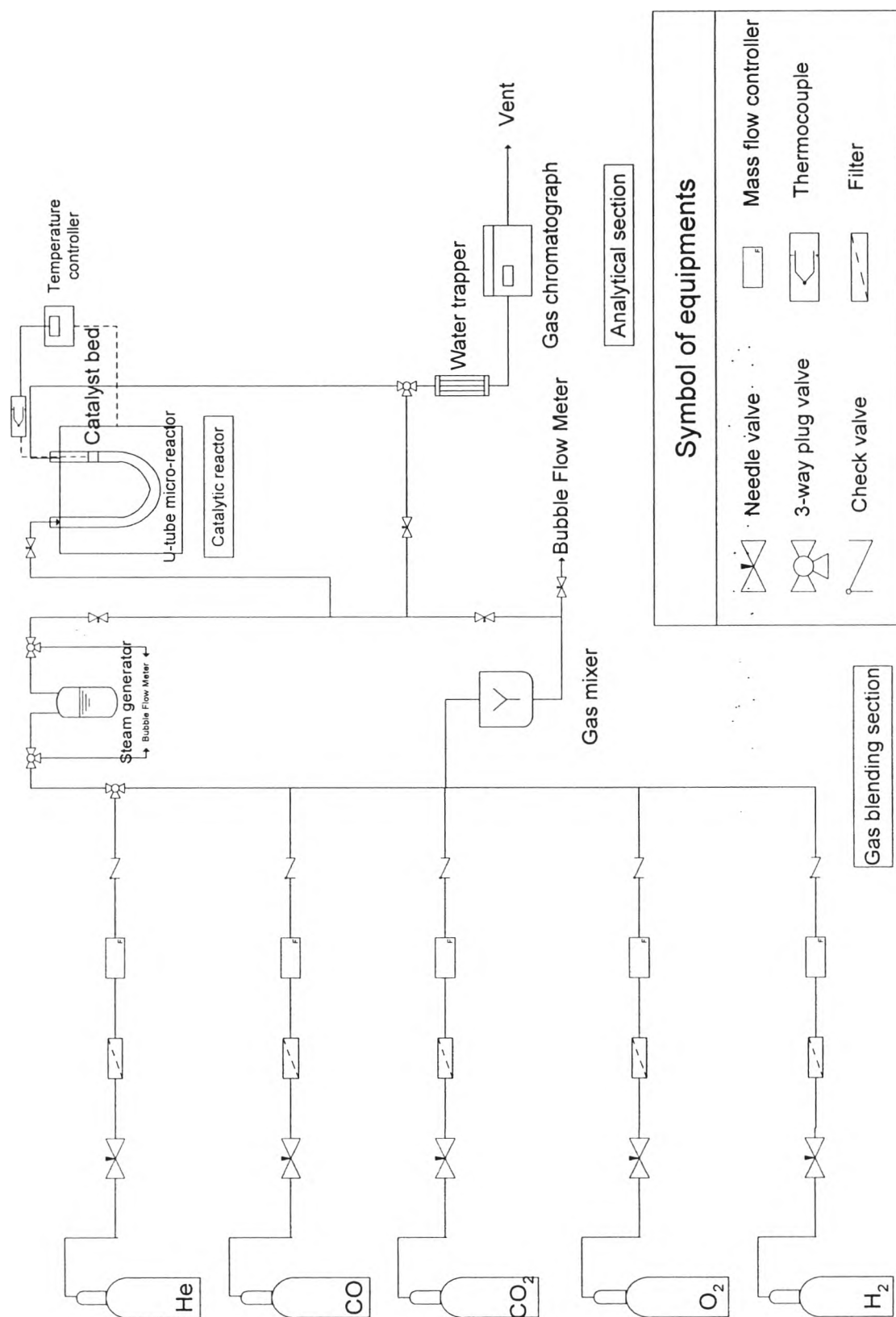


Figure 3.1 Schematic flow of PROX process.

3.3 Experimental

This research work can be divided into 3 main parts, which are the preparation of catalyst, catalyst characterizations, and catalyst activity measurement.

3.3.1 Catalyst Preparation

In this research, the La-CeO_x supports were prepared by urea-gelation co-precipitation, co-precipitation (by NH₄OH), and step precipitation. In addition, deposition-precipitation technique was also used for loading gold on to the supports.

3.3.1.1 La-CeO_x Support Preparation

The La-CeO_x supports used in this work were prepared by the same methods, which are as follow.

3.3.1.1.1 *Urea gelation Co-precipitation Technique*

The desired weight amount of cerium (III) nitrate, lanthanum (III) nitrate, and urea (or only cerium (III) nitrate and urea) were dissolved in deionized water, and simultaneously the solution is kept on a hot plate stirrer for continuous stirring and heating (at 60°C). Then NH₄OH was added in order to adjust the pH of solution (~8). The mixture was allowed to stand for 3 hours. Next the suspension was washed by warm deionized water, in order to get rid of the residue ions, and the deionized precipitate was obtained. The deionized precipitate is dried in the oven for 12 hours (at 100°C) and after that, the dried precipitate was calcined in air for 4 hours at 500°C. Finally, the support was obtained and kept in a desiccator.

3.3.1.1.2 *Co-precipitation Technique*

The desired weight amount of cerium (III) nitrate and lanthanum (III) nitrate (or only cerium (III) nitrate) were dissolved in deionized water, and simultaneously the solution was kept on a hot plate stirrer for continuous stirring and heating (at 60°C). Then NH₄OH was added in order to adjust the pH of solution (~8). The mixture was allowed to stand for 3 hours. Next the suspension was

washed by warm deionized water, in order to get rid of the residue ions, and the deionized precipitate was obtained. The deionized precipitate was dried in the oven for 12 hours (at 100°C) and after that, the dried precipitate was calcined in air for 4 hours at 500°C. Finally, the support was obtained and kept in a desiccator.

3.3.1.1.3 Step-precipitation Technique

The desired weight amount of cerium (III) nitrate was dissolved in deionized water, and simultaneously the solution was kept on a hot plate stirrer for continuous stirring and heating (at 60°C). Then NH₄OH was added in order to adjust the pH of solution (~8). After that, desired amount lanthanum (III) nitrate was dropped, with NH₄OH, into the mixture. This step can be skipped, if the mixture was allowed to stand for 3 hours. Next the suspension was washed by warm deionized water, in order to get rid of the residue ions, and the deionized precipitate was obtained. The deionized precipitate was dried in the oven for 12 hours (at 100°C) and after that, the dried precipitate was calcined in air for 4 hours at 500°C. Finally, the support was obtained and kept in a desiccator.

3.3.1.2 Gold Loading

Deposition-precipitation was the method chosen for loading gold in this work. This method was used to load gold on the La-CeO_x support, as well as on to the CeO₂ support.

3.3.1.2.1 Deposition-precipitation (DP) Method

The desired weight amount of hydrogen tetrachloroaurate (III) was dissolved in deionized water, and simultaneously the solution was kept on a hot plate stirrer for continuous stirring and heating (at 80°C). Then the dried support was added to the solution, followed with 0.1 M Na₂CO₃. The purpose of adding 0.1 M Na₂CO₃ was to adjust the pH of solution (~8). The mixture was allowed to stand for 1 hour. Next the suspension was washed by warm deionized water, in order to get rid of the residue ions, and the deionized precipitate was obtained. The deionized precipitate was dried in the oven (for 12 hours at 110°C).

After that, the dried precipitate was calcined in air for 4 hours at various temperatures. Finally, the sample was ground and sieved to 80–120 mesh size and kept in a desiccator.

3.3.2 Catalyst Characterization

As a result of varying gold content, supported molar ratio, and calcination temperature in this research, the properties and characteristics of the prepared catalysts are dissimilar. Moreover, the different in properties could also have an effect on the activities and selectivity of the catalyst. And for that reason, the characterization of catalyst is crucial. In this work, several characterizations are utilized.

3.3.2.1 *X-Ray Diffractometry (XRD)*

The prepared catalysts were characterized by an X-ray diffractometer (XRD; RINT 2200V, Rigaku) using $\text{CuK}\alpha$ radiation operated at 40 kV and 30 mA, to confirm the crystalline phases of oxide support and to determine the mean particle size of gold. XRD is capable of analyzing the intensity of the peak; the higher of the peak indicates the higher content of that phase.

The goniometer parameters of RINT 2200 are divergence slit equals to 1° (2θ); scattering slit is 1° (2θ); with receiving slit equals 0.3 mm. The scan speed of 5° (2θ) per minute with scan step of 0.02 (2θ) is used for the continuous run in 5 to 90°C (2θ) range. Normally, the sample is ground down to the fine powder particle and the ideal sample is homogeneous and the crystallites are randomly distributed. The sample is then pressed into a sample holder and held in a beam. The signal is sent to the on-line computer to record and analyze. The average dimension of crystallites can be determined by the Scherrer method from the broadening of the diffraction peaks taking into account the instrumental broadening. The Sherrer equation is as in the form of Equation (3.1).

$$D_b = \frac{K \cdot \lambda}{B_d \cdot \cos \theta} \quad (3.1)$$

where:

- D_b = mean crystalline diameter (Å),
 K = Scherrer constant, 0.9,
 λ = X-Ray wavelength (Å),
 B_d = angle width of peak in term of $\Delta(2\theta)$ (radian), and
 θ = Bragg angle of the reflection (degree).

It is essential to understand that the Scherrer equation gives a crystalline thickness that is perpendicular to the diffraction planes rather than an actual particle size. It is also compulsory to apply a correction factor that depends on the actual shape of the crystallinities and on the Millers indices of the diffraction planes in order to obtain the actual crystallite size from the thickness.

3.3.2.2 UV-Vis Spectroscopy

The diffuse reflectance spectra were recorded in the wavelength range of 800–200 nm, by UV-vis spectrophotometer-2550, using light in the visible and adjacent near infrared (NIR) and ultraviolet (UV) ranges, which is used in the quantitative determination the transition metal ions. Kubelka-Munk formula is applied to convert the data.

3.3.2.3 Temperature–Programmed Reduction (TPR)

Temperature–programmed reduction (TPR) was used to determine the quantity of the reducible species in the prepared catalysts and the temperature at which the reduction of the reducible species is taking place. TPR was be carried out using an in-house TPR system. First, the sample was placed in a quartz reactor and subjected to TPR analysis using 10% H₂ in Ar for 30 ml/min. The initial temperature was 30°C. But then the reduction temperature was increased 850°C with a ramp rate of 10°C/min. A thermal conductivity detector was used to observe hydrogen consumption which allowed the TPR to calculate the number of reacting sites. The TPR analysis also verified the different states of oxidation of the contained metals.

3.3.2.4 BET Surface Area Measurement

As well known, the reaction usually takes place at the surface area of the catalyst; therefore, it is essential to know the specific surface area of a catalyst. In this work, Autosorb-1 Gas Sorption system (Quantachrome Corporation) was used to measure the total surface area and the pore size analysis of the prepared catalysts (the values are expressed in m^2/g). The equipment measurement uses the principle of Brunauer-Emmet-Teller (BET) theory, which provides a mathematical model for the process of gas sorption (BET equation). This technique is done by calculating the physisorption of a gas on the material, in other words the physical multi-layer adsorption of a gas over the entire exposed surface of a material and the filling of pores. The gas which is used for physisorption is N_2 gas (with the cross-sectional area of $16.2 \times 10^{-20} \text{ m}^2/\text{molecule}$). This process is done at the liquid nitrogen temperature, which is (-196°C) .

Before the surface area analyzing step, the sample will be degassed and then outgassed in order to remove any adsorbed gases at the surface. The surface area will be calculated from the 22 points nitrogen adsorption. The average pore diameter and pore volume will be obtained at P/P_0 ratios close to unity. The result will be analyzed by Autosorb Anygas Software version 2.1, which are calculated using the BET equation, as shown in Equation 3.2.

$$\frac{1}{W \cdot \left(\frac{P_0}{P} - 1 \right)} = \frac{1}{W_m \cdot C} + \frac{(C-1)}{(W_m \cdot C)} \left(\frac{P_0}{P} \right) \quad (3.2)$$

where:

- P = pressure of gas,
- P_0 = saturated vapor pressure of the liquid at the operating temperature,
- W = weight of gas adsorbed at a relative pressure, P_0 ,
- W_m = weight of adsorbate constituting a monolayer of surface coverage, and
- C = constant that is related to the energy of adsorption in the first

adsorbed layer and magnitude of the adsorbent/adsorbate interaction.

The surface area is calculated by Equation 3.3.

$$S = \frac{W_m \cdot A_{N_2} \cdot (6.02 \times 10^{23})}{M_{W,N_2}} \quad (3.3)$$

Where:

S = specific surface area (m^2/g),

A_{N_2} = cross-sectional area of one molecule N_2 ,

= 0.162 nm^2 (-196°C), and

M_{W,N_2} = molecule weight of nitrogen (28 g/g-mol).

3.3.2.5 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) is well known technique for characterizing the microstructure of materials with very high spatial resolution. Information about the morphology, crystal structure and defects, crystal phases and composition, and magnetic microstructure can be obtained by a combination of electron-optical imaging (2.5\AA point resolution), electron diffraction, and small probe capabilities. In this work, this technique is used to determine the average crystalline size of gold particle.

The transmission electron microscope uses a high energy electron beam transmitted through a very thin sample to image. The electrons are focused with electromagnetic lenses and the image is observed. The electrons are accelerated at several hundred kV, giving wavelengths much smaller than that of light: 200kV electrons have a wavelength of 0.025\AA .

Sample preparation for TEM will be started with the grinding and crushing of the sample (catalyst) in a mortar in order to get the fine powder. Then the sample in the form of fine powder will be dispersed in ethanol by use of an ultrasonic bath, and drop of the suspension will be placed on a thin carbon film

supported on a standard electron microscope grid. Image processing for contrast enhancement and image evaluation will be done by means of the programs Digital Micrograph. However, many materials require extensive sample preparation to produce a sample thin enough to be electron transparent, which makes TEM analysis a relatively time consuming process with a low throughput of samples.

3.3.3 Catalyst Activity Measurement

As already mentioned, the reaction will be conducted in a fixed-bed catalytic micro reactor under atmospheric pressure. The activity will be observed at various temperatures over the range of 60–180°C under gas mixture conditions of 1% CO, 1% O₂, and 40% H₂ balanced in He, which is allowed to pass through the 80–120 mesh in size of 100 mg catalyst bed at the total flow rate of 50 ml min⁻¹. The effluent gas from the reactor will be analyzed both qualitatively and quantitatively by auto-sampling in an on-line gas chromatograph equipped with a packed carbon sphere column, 80/100 mesh, 10 ft × 1/8 in. and a thermal conductivity detector (TCD).

3.3.3.1 *Effect of Au Loading*

Additional of gold to the catalysis is one way to improve the catalytic activity of the catalysts in PROX reaction. In this work, the deposition-precipitation method was used to load gold on the support; therefore, the effect of different gold loadings on the support was investigated. The gold loading percentages was varied from 1 %wt to 5%wt.

3.3.3.2 *Effect of Preparation Technique*

There are many ways that can be used for preparation of ceria support. Da Silva *et al.* (2007) studied the activity of the Cu/CeO₂ and Cu/CeO₂-ZrO₂ for low temperature water-gas shift reaction when three different preparation methods for CeO₂ were used, e.g. the urea gelation co-precipitation (CeO₂-UGC), hydrothermal (CeO₂-HT), and Pechini (CeO₂-Pe). Similarly, in order to study the effect of preparation methods on the activity of the catalysts for PROX reaction, the activity of the catalysts prepared by three methods (co-precipitation by NH₄OH, urea gelation co-precipitation, and step precipitation) were examined in this work.

3.3.3.3 Effect of Drying Method

Kwak *et al.* (2006) had mentioned that the drying method has some effect on the activity of the prepared catalysts, as the average pore diameter and total pore volume of a catalyst could be change when different drying methods were used. Thus, in this work, the effect of various drying methods (such as oven, freeze-dry, and vacuum cry) on the activity of prepared catalyst was investigated.

3.3.3.4 Effect of Calcination Temperature

Boccuzzi *et al.* (2001) studied the effect of calcinations temperature on the CO oxidation of Au/TiO₂ nanosized samples. The result showed that the catalyst calcined at lower temperature showed achieved 100% CO conversion at lower reaction temperature. While, the catalyst calcined at higher temperature achieved 100% CO conversion at higher reaction temperature. In addition, the mean diameters increased with the increased in calcination temperature. Therefore, in order to confirm the result, this work also investigated the effect of the calcination temperature (non-calcined, 300, 400, and 500°C) on the activity of the catalyst.

3.4 Calculation

The CO and O₂ conversion calculations are based on the CO and O₂ consumption. The CO selectivity are calculated by the ratio of O₂ consumption for the desired CO oxidation reaction to the total O₂ consumption. CO conversion and the selectivity of O₂ to CO oxidation will be calculated by following equations.

$$\text{CO conversion (\%)} = \frac{[CO]_{in} - [CO]_{out}}{[CO]_{in}} \times 100 \quad (3.4)$$

$$\text{O}_2 \text{ conversion (\%)} = \frac{[O_2]_{in} - [O_2]_{out}}{[O_2]_{in}} \times 100 \quad (3.5)$$

$$\text{Selectivity (\%)} = \frac{[O_2]_{CO}}{[O_2]_{CO} + [O_2]_{H_2}} \times 100 \quad (3.6)$$

where:

$[\text{CO}]_{\text{in}}$ = concentration of CO in the introduced reactant gas,

$[\text{CO}]_{\text{out}}$ = concentration of CO in the effluent gas,

$[\text{O}_2]_{\text{in}}$ = concentration of O₂ in the introduced reactant gas,

$[\text{O}_2]_{\text{out}}$ = concentration of O₂ in the effluent gas,

$[\text{O}_2]_{\text{CO}}$ = amount of O₂ for CO oxidation and

$[\text{O}_2]_{\text{H}_2}$ = amount of O₂ for H₂ oxidation.