

## CHAPTER III

### EXPERIMENTAL

#### 3.1 Materials

##### 3.1.1 Chemicals

Catalyst preparation required the following chemicals:

- $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  (Hydrogen tetrachloroaurate (III)) Au 49.5% from Alfa AESAR.
- $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$  (Dihydrogen hexachloroplatinate (IV)) Pt 37.5% from Aldrich Chemical Company, Inc.
- $\text{Al}(\text{OH})_3$  supplied by Sigma Chemical Co., Ltd.
- $\text{SiO}_2$  (Fume Silica) supplied by Sigma Chemical Co., Ltd.
- $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$  (Triethanolamine, TEA) supplied by Fluka Chemical AG.
- $\text{N}(\text{CH}_2\text{CH}(\text{CH}_3)\text{OH})_3$  (Triisopropanolamine, TIS) supplied by Carlo Erba Reagenti Co., Ltd.
- $\text{HOCH}_2\text{CH}_2\text{OH}$  (Ethylene Glycol, EG) supplied by J.T. Baker Inc.
- NaOH supplied by EKA Chemical Co., Ltd.
- NaCl supplied by AJAX Chemical Co., Ltd.
- $\text{CH}_3\text{CN}$  (Acetonitrile) supplied by Lab Scan CO., Ltd.

##### 3.1.2 Gases

Gases used in this research work were:

- 20%  $\text{CO}_2$  in He from Praxair (Thailand) Company Limited.
- 3.00% CO in He from Thai Industrial Gases Public Co., Ltd.
- Ultra high purity (99.999%) He from Thai Industrial Gases Public Co., Ltd.
- Ultra high purity (99.999%)  $\text{H}_2$  from Thai Industrial Gases Public Co., Ltd.

- 7.87% O<sub>2</sub> in He form Thai Industrial Gases Public Co., Ltd.

## 3.2 Equipment

The experiment setup is shown schematically in Figure 3.1. It can be divided into three main parts.

### 3.2.1 Gas Blending Section

The reactant gas mixture was composed of CO (1%), O<sub>2</sub> (1%) and H<sub>2</sub> (40%) with the balance being He. Each stream was passed through the micro filter to remove particles before it enters the mass flow controllers and check valve to prevent reverse flow. After that, all reactants were sent to the mixing chamber and mixed there before going to the reactor with a total flow rate of 50 ml/min under atmospheric pressure.

### 3.2.2 Catalytic Reactor

The preferential oxidation of CO was conducted under atmospheric pressure in a Pyrex glass U-tube micro-reactor with an inside diameter of 6 mm. The catalyst was packed between glass wool plugs in the middle of the reactor. The temperature of catalyst bed was monitored and controlled by PID temperature controller equipped with a thermocouple (Type K)

### 3.2.3 Analytical Instrument

The effluent gas from the reactor was qualitatively and quantitatively analyzed by auto-sampling into an 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).

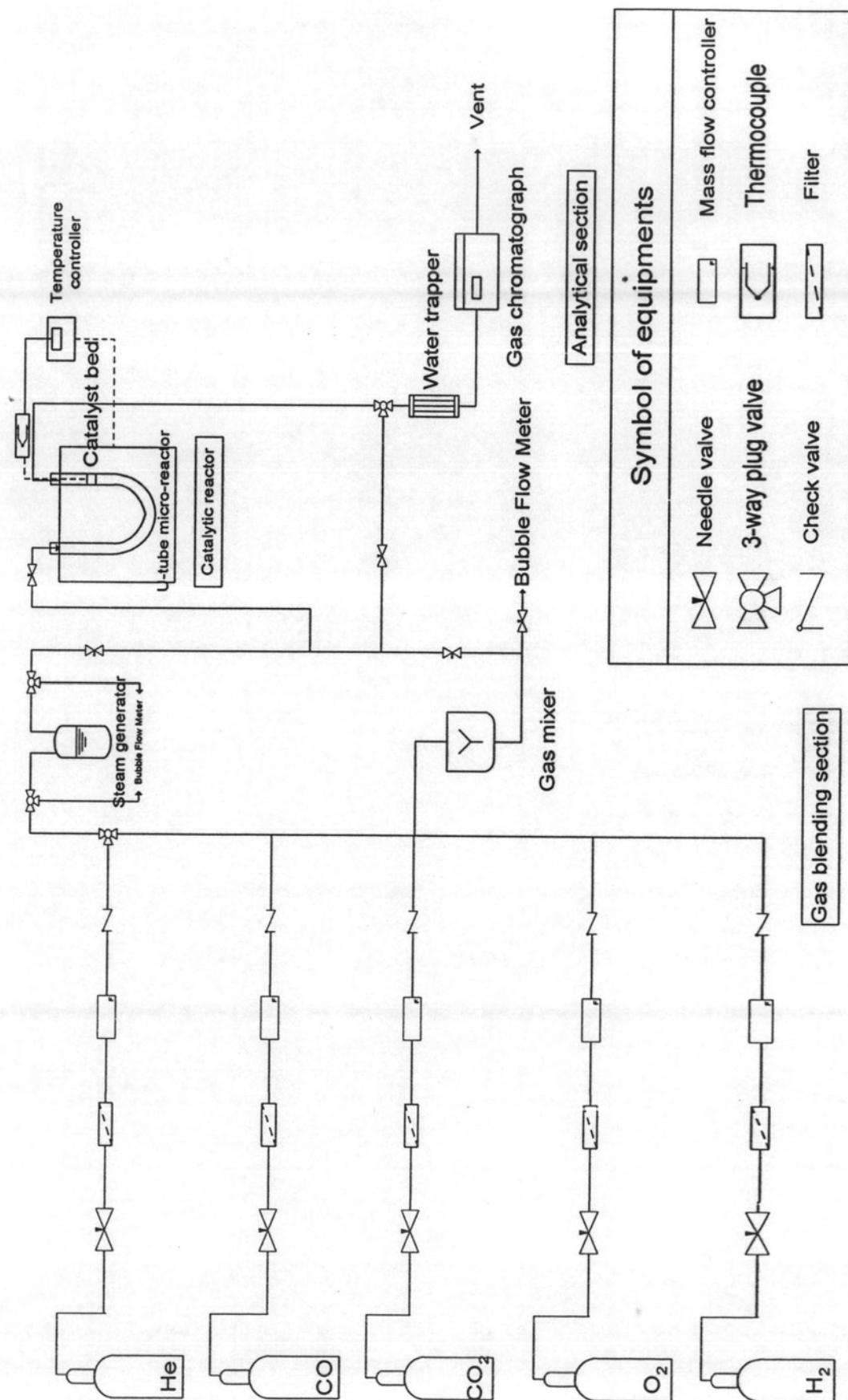


Figure 3.1. The schematic flow diagram of the experimental setup.

### 3.3 Catalyst Preparation Procedure

#### 3.3.1 A-Type Zeolite Synthesis

A zeolite can be synthesized by sol-gel microwave techniques of silatrane and alumatrane as precursors that derived from the reaction of silica and alumina with trialkanolamine. The gel mixture was mixed with NaOH and then obtains the A zeolite. Precursors can be prepared via Oxide One Pot Synthesis (OOPS)

##### 3.3.1.1 *Precursor Synthesis (Sathupunya et al., 2003)*

For silatrane synthesis, the mixture of 0.10 mol silicon dioxide and 0.125 mol triethanolamine was mixed together with 100 ml ethylene glycol as solvent that contain in a simple distillation set. The reaction was carried out at the boiling point of ethylene glycol under nitrogen atmosphere for 10 hours to remove water as a by-product and ethylene glycol from the system. Then, the rest of ethylene glycol was removed under vacuum condition at 110°C for 8 hours. The brownish white solid was washed with acetonitrile and centrifuged at 10000 rounds per minutes for three times to remove undesired organic residues.

For alumatrane synthesis, the mixture is 0.1 mol aluminium hydroxide and 0.125 mol triisopropanolamine and then following the similar process as silatrane synthesis.

##### 3.3.1.2 *Sol-gel Process and Microwave Techniques (Sathupunya et al., 2003).*

To synthesize Na-A zeolite, silatrane and alumatrane were mixed with NaOH at the ratio of  $\text{SiO}_2:\text{Al}_2\text{O}_3:x\text{Na}_2\text{O}:y\text{H}_2\text{O}$ , where  $x = 10$ ,  $y = 410$ . The mixture was aged for at least 12 hrs at room temperature to form gel. Then, the gel was brought to hydrothermal treatment using the microwave technique for 5 min. The product was washed by distilled water for three times.

### 3.3.2 Incipient Wetness Impregnation

Both synthesized A zeolite from sol-gel microwave technique (Sathupunya *et al.*, 2003) and commercial A zeolites was used as catalyst supports. The appropriate concentration of  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  and  $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$  precursor aqueous solutions was impregnated onto each catalyst support. After that, it was dried in an oven at  $110^\circ\text{C}$  overnight and subsequently calcined for 5 hours with  $10^\circ\text{C}/\text{min}$  ramping rate. Prior to the reaction, the catalysts were in-situ pre-treated in the U-tube micro-reactor in a He flow at  $110^\circ\text{C}$  for 1 h.

## 3.4 Catalyst Characterization

Varieties method was used to characterize the prepared catalysts to understand the effect of many parameters over the catalytic activities of catalysts, as the followings:

### 3.4.1 X-ray Diffraction (XRD)

The crystallite size of Au and Pt on the surface and the crystalline structure of the A zeolite support were analyzed by means of a Rigaku X-ray diffractometer system (RINT-2200) with Cu tube for generating  $\text{CuK}_\alpha$  radiation ( $1.5406 \text{ \AA}$ ) and nickel filter. X-ray diffraction (XRD) is based upon the fact that the X-ray diffraction pattern is unique for each crystalline substance. The identity of the crystalline phases can be found by matching the pattern of the unknown and standard. Additionally, the relative quantitative analysis was determined from the intensity of peak. For the same crystalline phase the higher of the peak indicates the higher content of that phase. RINT-2200 system was used to obtain XRD pattern at a generator voltage of 40 kV and a generator current of 30 mA. The scan speed of  $5^\circ (2\theta)/\text{min}$  with scan step of  $0.02 (2\theta)$  was used for the continuous run in  $5^\circ$  to  $90^\circ (2\theta)$  range. The goniometer parameters were took place as follows:

divergence slit:  $1^\circ (2\theta)$ ,  
scattering slit :  $1^\circ (2\theta)$ ,  
receiving slit : 0.3 mm.

Prepared catalysts was grounded to a fine and a homogeneous catalyst then packed in a thin-walled glass container. After that, it was placed in a sample holder. The signal was sent to an on-line computer to record and analyze. The average metal crystallite size can be calculated by Scherrer's equation as shown in Equation 3.3 that shows the relationship between the crystalline thickness ( $D_b$ ) and the broadening ( $\beta$ ) of the diffraction line corresponding to the Bragg angle ( $\theta$ ) using wavelength ( $\lambda$ )

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

where:

$D_b$  = mean crystallite diameter ( $\text{\AA}$ ),

$K$  = Scherrer constant, 0.9,

$\lambda$  = X-ray wave length ( $\text{\AA}$ ),

$B_d$  = angular width of peak in term of  $\Delta(2\theta)$ ,

$\theta$  = Bragg's angle of reflection (degree).

#### 3.4.2 Scanning Electron Microscopy (SEM)

The scanning electron micrographs (JEOL 5200-2AE) were used to identify the microstructure of the sample. The SEM used the electrons that are back-scattered or emitted from the specimen surface. The powder sample (commercial and synthesized zeolite) was placed on stub and sputtered with Au metal to render the surface conductive. Additionally, prepared catalysts were coated with carbon to observation. The specimen is scanned with a narrow beam of electrons. The quantity of electrons scattered or emitted as the primary beam bombards each successive point of the metallic specimen surface is measured by an electron detector and used to modulate the intensity of a second electron beam and forms an image on a television screen.

#### 3.4.3 Transmission Electron Microscopy (TEM)

TEM was employed for investigate the average particle size of metals and identify the microstructure of prepared catalysts such as metals dispersion, the crystalline size of the Au and Pt on the support. Catalysts were prepared in thin form

appropriate for TEM that it was dispersed in pure water and a drop of the suspension was deposited on a copper grid. TEM was carried out in a JEM 2010 operating at an accelerating voltage of 200 kV in bright and dark field modes. A beam was passed through a series of lenses to form a magnified image of a sample that has been inserted in the area of the objective lens. The image from selected area was viewed through projection onto a viewing screen. However, electron beams are easily scattered by air molecules and TEM columns must be kept under high vacuum. Additionally, the electromagnetic lenses were used for focus the electron beam.

#### 3.4.4 Inductively Coupled Plasma (ICP)

Elemental analyses were carried out in a Perkin-Elmer Optima 4300 DV inductively coupled plasma – optical emission spectrometer (ICP-OES) that detects the traces metal in prepared catalysts it can detect a wide range of elements with a sensitivity in the ppb range. An ICP requires that the elements which are to be analyzed be in solution. A liquid is nebulized and then vaporized with in the Argon plasma. The atoms and ions contained in the plasma vapour are excited into a state of radiated light (photon) emission. The radiation emitted can be passed to the spectrometer optic, where it is dispersed into its spectral components. From the specific wavelengths emit by each element. The radiation intensity, which is proportional to the concentration of the element in the sample, is recalculated internally from a stored set of calibration curves and can be shown directly as percent or measured concentration.

#### 3.4.5 Temperature Programmed Reduction Technique (TPR)

Temperature-Programmed Reduction (TPR) was employed for evaluating the number and quantity of the reducible species present in the prepared catalyst and the temperature at which the reduction itself takes place as a function of the temperature. The gas used for analysis is a mixture of reactive gas with an inert gas, as hydrogen in nitrogen at 5.32%. The prepared catalyst sample was submitted to a linear increase of temperature and to a constant flow of the gas mixture. The reaction generally starts at room temperature. At a certain temperature, the reaction speed becomes considerable and the hydrogen consumption can be monitored

through the TCD detector. The signal integration allows calculating the quantity of hydrogen consumed and the number of reacting sites. The TPR analysis also allows checking the presence of different states of oxidation of the contained metals.

#### 3.4.6 Surface Area Measurement (BET)

One of the most essential properties of a heterogeneous catalyst is its surface area because the reaction takes place over the catalyst surface. The surface area, total pore volume and average pore size diameter of all prepared catalyst samples was determined by Brunauer-Emmet-Teller (BET) method using Sorptomatic 1990. N<sub>2</sub> gas was used as the adsorbate at liquid N<sub>2</sub> temperature (-196°C). A sample was outgassed by heating under vacuum at 300°C for 6 hours in order to eliminate adsorbed species on the surface before measurement. The results were analyzed by Autosorb Anygas Software Version 2.1, which were calculated using the BET equation as shown in Equation 3.1.

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

where:

W = weight of gas adsorbed at relative pressure P<sub>0</sub>

W<sub>m</sub> = weight of adsorbate constituting a monolayer of surface coverage

P = pressure of gas

P<sub>0</sub> = saturated vapour pressure of the liquid at the operating temperature

C = constant that is related to the energy of adsorption in the first adsorbed layer and magnitude of adsorbate/adsorbent interaction.

The surface area can be calculated by Equation 3.3.

$$A = \frac{W_m A_{nitrogen} \times 6.02 \times 10^{23}}{M_{w,nitrogen}} \quad (3.3)$$



where:

$A$  = Surface area of sample

$A_{\text{nitrogen}}$  = Cross-section area of one molecule nitrogen ( $0.162 \text{ nm}^2$   
at  $-196^\circ\text{C}$ )

$M_{w,\text{nitrogen}}$  = molecular weight of nitrogen ( $28 \text{ g/g-mol}$ ).

### 3.4.7 H<sub>2</sub> Pulse Chemisorption

A H<sub>2</sub> pulse chemisorption analysis determines mean particle size and percent metal dispersion by applying measured pulses of H<sub>2</sub> gas to the prepared catalysts. The H<sub>2</sub> gas chemically reacts with each active site until they have all reacted. Once the active sites have totally reacted, the discretely injected N<sub>2</sub> gas volumes emerge from the sample tube uncharged. The amount of H<sub>2</sub> gas chemisorbed is difference between the total amount of reactant gas injected and the amount that did not react with the active sites of the prepared catalysts. The size of each pulse of H<sub>2</sub> gas is determined by the loop on an electrically operated valve. Ten loops of different sizes are provided with the analyzer.

## 3.5 Catalytic Activity Measurement

The reaction was carried out in the fixed bed U-tube micro-reactor by packing with 100 mg catalyst of 80-120 mesh inside. Then, He gas was switched to flush out the remaining H<sub>2</sub>O at  $110^\circ\text{C}$  for 1 hour and the catalyst bed was cooled down to room temperature before being heated to the desired reaction temperature. The activity was investigated at varied temperature in the range of 50 to  $310^\circ\text{C}$ . The CO conversion, O<sub>2</sub> conversion and CO selectivity can be calculated by using Equations 3.4, 3.5 and 3.6, respectively.

$$X_{\text{CO}} = \frac{[\text{CO}]_o - [\text{CO}]}{[\text{CO}]_o} \times 100 \quad (3.4)$$

$$X_{\text{O}_2} = \frac{[\text{O}_2]_o - [\text{O}_2]}{[\text{O}_2]_o} \times 100 \quad (3.5)$$

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

where:

X = CO conversion (%),

S = selectivity (%),

[CO]<sub>0</sub> = concentration of CO in the reactant gas,

[CO] = concentration of CO in the product gas,

[O<sub>2</sub>]<sub>0</sub> = concentration of O<sub>2</sub> in the product gas,

[O<sub>2</sub>] = concentration of O<sub>2</sub> in the product gas,

[O<sub>2</sub>]<sub>CO</sub> = amount of O<sub>2</sub> for CO oxidation and

[O<sub>2</sub>]<sub>H<sub>2</sub></sub> = amount of O<sub>2</sub> for H<sub>2</sub> oxidation.