



## CHAPTER III EXPERIMENTAL

### 3.1 Materials and Equipment

#### 3.1.1 Chemicals

Mordenite zeolite supplied by Tosoh Co., Ltd.

Hydrogen tetrachloroaurate (III) trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ )

Dihydrogen hexachloroplatinate (IV) hydrate ( $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ )

Nitric acid ( $\text{HNO}_3$ )

Potassium hydroxide (KOH)

Sodium nitrate ( $\text{NaNO}_3$ )

Sodium hydroxide (NaOH)

Silver nitrate ( $\text{AgNO}_3$ )

Urea ( $(\text{NH}_2)_2\text{CO}$ )

#### 3.1.2 Gases

Carbon dioxide ( $\text{CO}_2$ ) 20% purity in Helium from Praxair (Thailand) Company Limited.

Carbon monoxide (CO) 10% purity in Helium from Thai Industrial Gases Public Company Limited.

Helium (He) of 99.99% purity from Thai Industrial Gases Public Company Limited.

Hydrogen ( $\text{H}_2$ ) of 99.99% purity from Thai Industrial Gases Public Company Limited.

Oxygen ( $\text{O}_2$ ) 5% purity in Helium from Thai Industrial Gases Public Company Limited.

#### 3.2.3 Equipment

Mass Flow Controller

Gas Mixer

Glass Tube Reactor

Water Bubbler  
 X-Ray Diffractometer (XRD)  
 Temperature-Programmed Reduction (TPR)  
 Atomic Absorption Spectroscopy (AAS)  
 Gas Chromatograph (GC)

### 3.2 Catalyst Preparation

The catalysts used in this study were prepared by deposition-precipitation (DP) of  $\text{HAuCl}_4$  and  $\text{H}_2\text{PtCl}_6$  on Mordenite zeolite. Mordenite in sodium form of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  (mol/mol) = 17.7 supplied by Tosoh Co., Ltd. was calcined at 550 °C for 4 h and then underwent the process to modify the surface-acidity. The cooled zeolite was suspended in deionized water and the solution pH was adjusted to 6 by adding 1 M  $\text{HNO}_3$  solution. A sample was filtered and dried at 60 °C for 1 h. For loading Au and Pt, the procedures were as follows: a desired amount of Au-precursor ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ) from Alfa AESAR and Pt- precursor ( $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ ) from Aldrich Chemical was prepared, and its pH was adjusted to 6 by adding NaOH solution; after 2 g of zeolite was added, the solution was heated to 80 °C and maintained at this temperature for 16 h. The samples was obtained after filtration and washing until free from  $\text{Cl}^-$  ions, as was detected by a  $\text{AgNO}_3$  solution, and then dried at 60 °C for 12 h under air (Wan *et al.*, 2006). The notations for all catalysts are given in Table 3.1.

**Table 3.1** Notations for the catalysts with varied ratio Au and Pt (1% total metal loading)

Au:Pt	Notation
1:0	1%Au/MOR
1:1	(1:1) Au:Pt/MOR
1:5	(1:5) Au:Pt/MOR
0:1	1%Pt/MOR

### 3.3 Catalyst Characterization

A variety of methods was used to characterize the prepared catalysts, including Brunauer-Emmet-Teller method (BET), X-ray diffraction (XRD), Inductively Coupled Plasma (ICP), Transmission Electron Microscopy (TEM), Temperature programmed reduction (TPR) and H<sub>2</sub> Pulse Chemisorption.

#### 3.3.1 X-ray Diffraction (XRD)

The crystallite size and the relative content of Au and Pt on the surface and the crystalline structure of the mordenite zeolite support were estimated by using a Rigaku X-ray diffractometer system (RINT-2200) with Cu tube for generating CuK<sub>α</sub> radiation (1.5406 Å) and nickel filter. X-ray diffraction (XRD) was based upon the fact that the X-ray diffraction pattern was unique for each crystalline substance. The identity of the crystalline phases can be found by matching the pattern of the unknown and standard. In addition, 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° (2θ)/min with scan step of 0.02 (2θ) was used for the continuous run in 5° to 90° (2θ) range. The goniometer parameters were took place as follows:

divergence slit: 1° (2θ),  
scattering slit : 1° (2θ),  
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 3.1 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 (Å),
- $K$  = Scherrer constant, 0.9,
- $\lambda$  = X-ray wave length (Å),
- $B_d$  = angular width of peak in term of  $\Delta(2\theta)$

### 3.3.2 Surface Area Measurement (BET)

The surface area, total pore volume and average pore diameter of all prepared 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 h 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 3.2.

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

where:

- $W$  = weight of gas adsorbed at relative pressure  $P_o$
- $W_m$  = weight of adsorbate constituting a monolayer of surface coverage
- $P$  = pressure of gas
- $P_o$  = saturated vapor 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

$A_{nitrogen}$  = Cross-section area of one molecule nitrogen (0.162 nm<sup>2</sup> at -196°C)

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

### 3.3.3 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. 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.

### 3.3.4 Temperature-Programmed Reduction (TPR)

Temperature-Programmed Reduction (TPR) by using Temperature Programmed Desorption Reduction Oxidation (TPDRO/MS 1100) was employed for evaluating the reducibility of supported oxide catalysts quantitatively and the quantity of cationic versus auto-reduced Au on the support oxide surface. The mixture of 5.32 % H<sub>2</sub> in N<sub>2</sub> was used to reduce the catalyst in TPR experiment. The temperature was increased from 30 to 900 °C with a heating rate of 10 °C/min. 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.

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

A H<sub>2</sub> pulse chemisorption measurements were also done on a Thermoquest TPD/R/O 1100 instrument which 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.

### 3.3.6 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. In preparation for TEM imaging approximately 10 mg of each sample was dispersed in ethanol by ultrasonification. A drop of this fine dispersion was deposited on a Cu grid and then dried. TEM was carried out in a JEOL 2000 CX 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 Catalytic Activity

#### 3.4.1 Lab-scale Experiment

The lab-scale experiment was studied under a simulated stream from steam reformer, and the apparatus is shown in Figure 3.1. It can be divided into three main parts including gas blending system, catalytic reactor and analytical instrument.

##### 3.4.1.1 *Gas Blending System*

The composition of the gaseous mixture used was 1% CO, 1% of O<sub>2</sub> and 40% of H<sub>2</sub> balanced of He. Each stream was passed through a micro filter to remove particles before entering the mass flow controller and check valve to prevent reverse flow. After that, all reactants were sent to the mixing chamber. The total volumetric flow rate of the reactant mixture was hold at 50 ml/min.

##### 3.4.1.2 *Catalytic Reactor*

The preferential oxidation of CO was conducted in a Pyrex glass U-tube micro-reactor with an inside diameter of 6 mm under atmospheric pressure. The catalyst, used in a powder with 100 mg catalyst of 80-120 mesh particles, was placed between two quartz 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). The effluent gas from the reactor was trapped by passing through a water trapper.

##### 3.4.1.3 *Analytical Instrument*

The effluent gas was analyzed both qualitatively and quantitatively 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). The conditions of GC are listed as follows:

Injector temperature	:	120°C
Oven temperature	:	100°C
Carrier gas	:	He (UHP grade)
Carrier gas flow rate	:	30 ml/min

TCD condition:

Temperature	:	175 °C
Reference gas	:	He (HP grade)

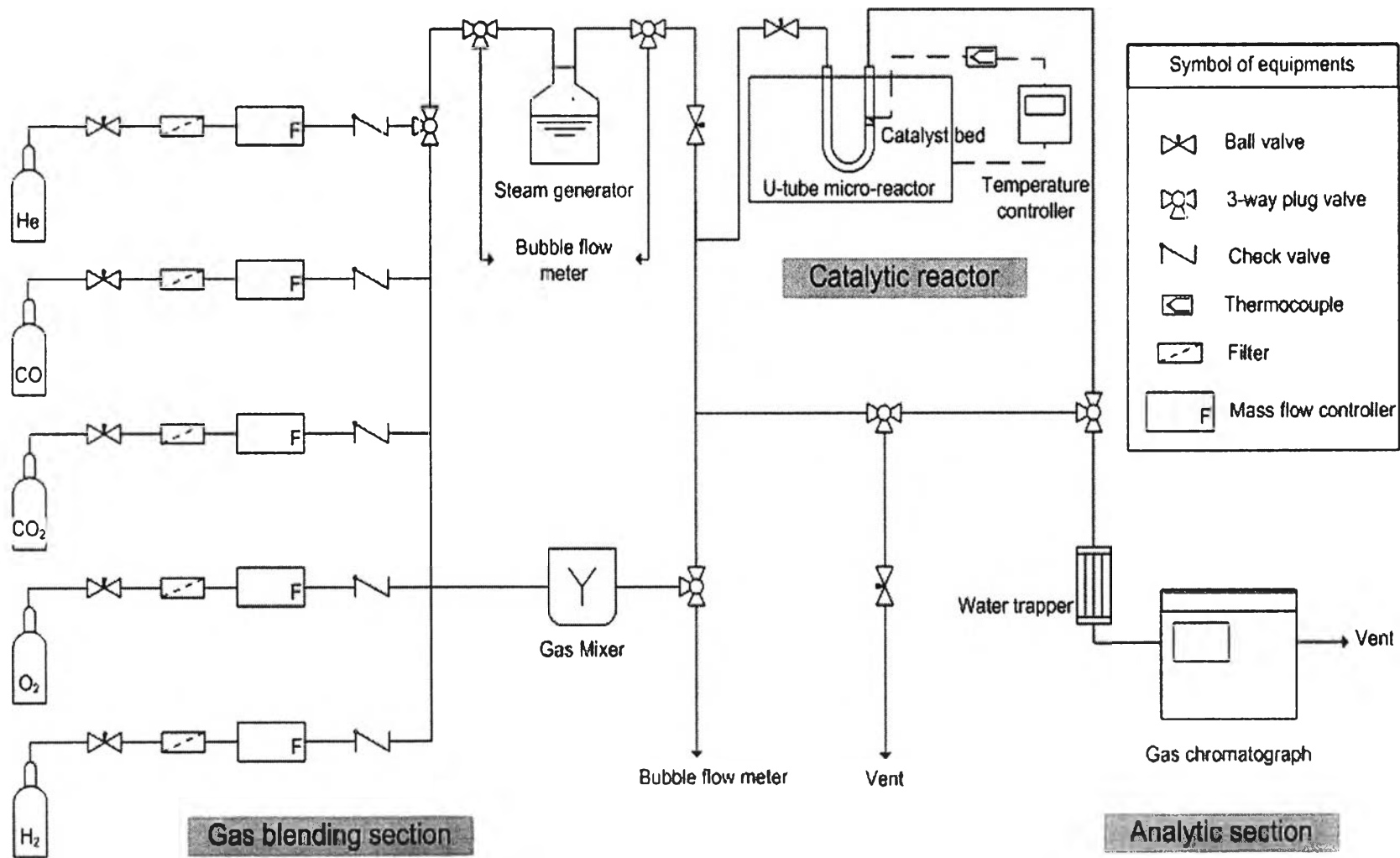


Figure 3.1 The schematic flow diagram of the lab-scale experimental apparatus.



### 3.4.2 Bench-scale Experiment

As shown in Figure 3.2, the bench-scale experimental apparatus was intended to produce H<sub>2</sub> at a rate of 50 l/day. It was constructed to describe a series of reactions including the steam reforming of natural gas (CNG), the high- and low-temperature water-gas shift (WGS) reactions and the preferential oxidation (PROX) of CO reactions. Moreover, the absorber unit was used to purify the hydrogen.

The reaction conditions and the appropriate catalysts that can assure high activity and good thermal have been derived from previous lab-scale tests.

Steam reforming (SR) catalyst was 1 g of 11% Nickel supported on Na-Y zeolite catalyst (11%Ni/NaY) prepared by incipient wetness impregnation. It was pressed into 1mm×1mm approximately and was tested at 700 °C under atmospheric pressure with GHSV of 4,200 ml h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup> with dry basis, at a natural gas/water ratio of 1:1. During the reaction, 50 ml/min of natural gas, 50 ml/min of steam and 20 ml/min of helium gas was mixed before entering the reactor.

High-temperature water gas shift (HT-WGS) catalyst was 4.5 g of Shift Max 120 from Sud-Chemie (Thai) Co., LTD. It was pressed into 1mm×1mm approximately and was tested at 450 °C under atmospheric pressure with GHSV of 1,067 ml h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup> with dry basis. During the reaction, 25 ml/min of steam and 10 ml/min of helium gas was mixed before entering the HT-WGS reactor.

Low-temperature water gas shift (LT-WGS) catalyst was 4.5 g of Shift Max 230 from Sud-Chemie (Thai) Co., LTD. It was pressed into 1mm×1mm approximately and was tested at 250 °C under atmospheric pressure with GHSV of 1,200 ml h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup> with dry basis. During the reaction, 25 ml/min of steam and 10 ml/min of helium gas was mixed before entering the LT-WGS reactor.

Preferential CO oxidation (PROX) catalyst was 0.7 g of 1% Pt supported on mordenite zeolite catalyst (1%Pt/MOR) prepared by deposition-precipitation. It was pressed into 1mm×1mm approximately and was tested at 200 °C under atmospheric pressure with GHSV of 9,428 ml h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup> with dry basis. During the reaction, 20 ml/min of 5% O<sub>2</sub> in He was mixed before entering the PROX reactor.

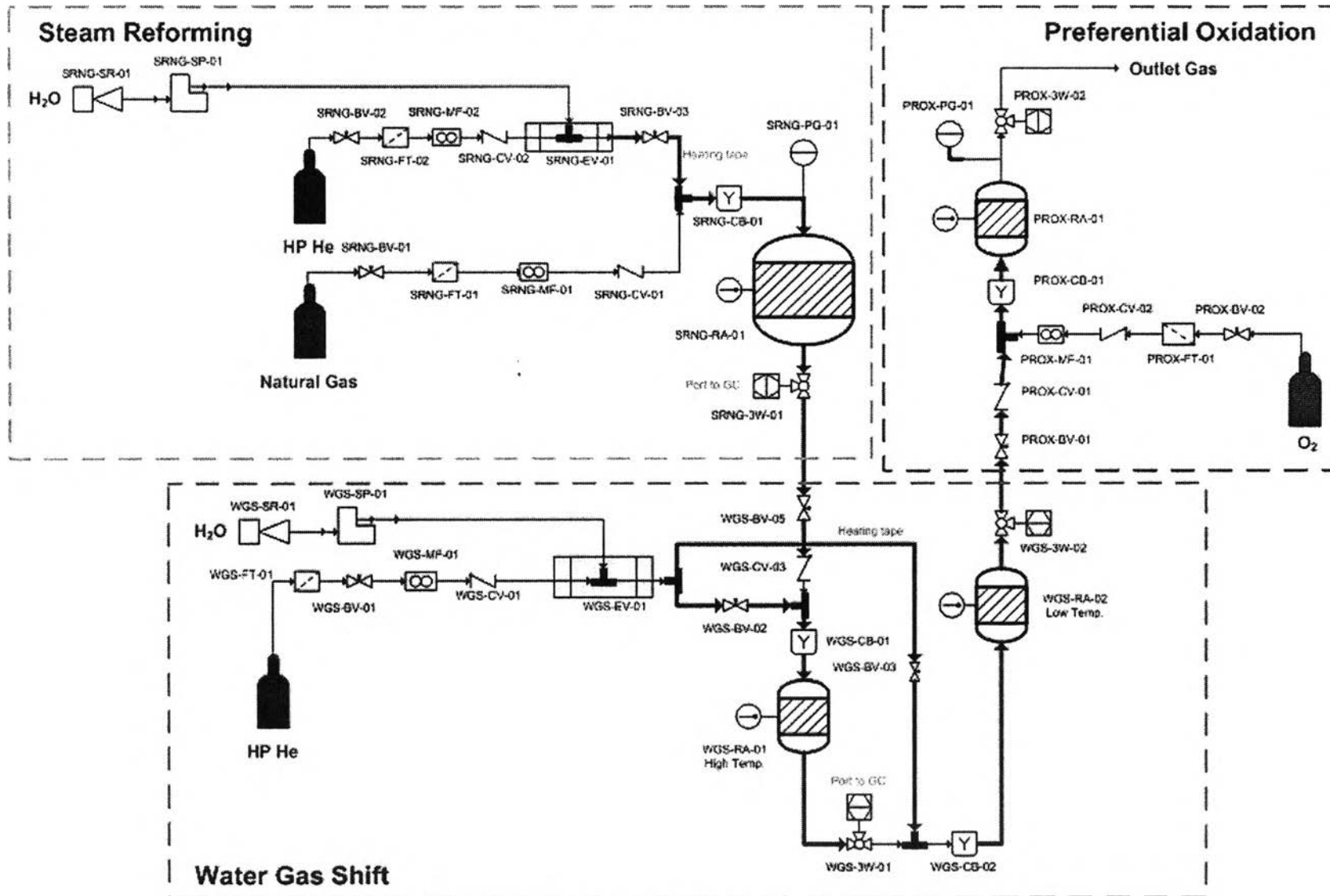
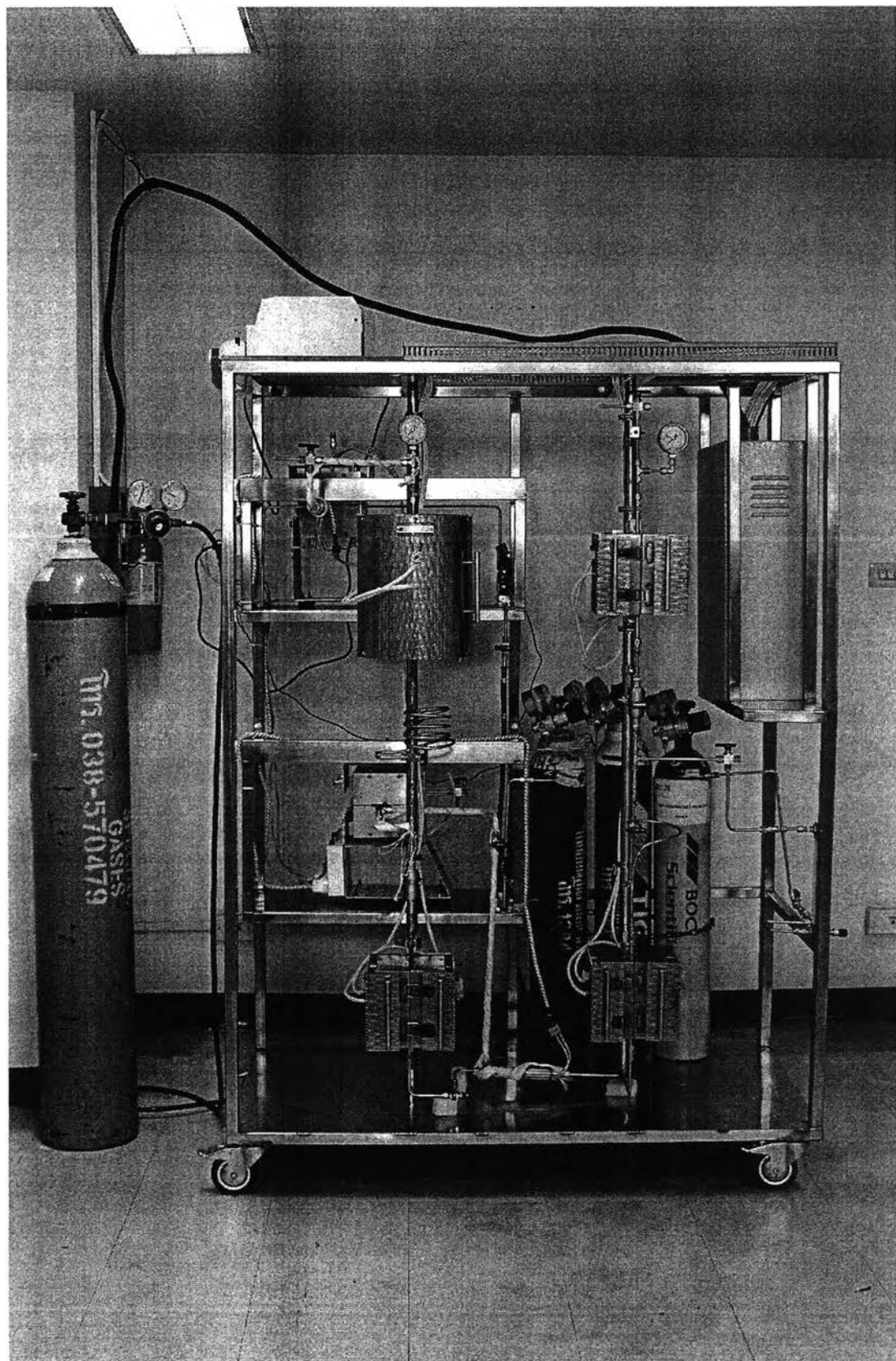


Figure 3.2 The schematic flow diagram of the bench-scale experimental apparatus.



**Figure 3.3** Photograph of the bench-scale experimental apparatus (Fuel Processor).

### 3.5 Catalytic Activity Measurement

The catalytic activity was investigated at varied temperature in the range of 50-330°C. The CO conversion ( $X_{CO}$ ),  $O_2$  conversion ( $X_{O_2}$ ) and CO selectivity ( $S_{CO}$ ) was determined according to Equations 3.4, 3.5 and 3.6, respectively.

$$X_{CO} = \frac{[CO]_{IN} - [CO]_{OUT}}{[CO]_{IN}} \times 100 \quad (3.4)$$

$$X_{O_2} = \frac{[O_2]_{IN} - [O_2]_{OUT}}{[O_2]_{IN}} \times 100 \quad (3.5)$$

$$S_{CO} = \frac{0.5([CO]_{IN} - [CO]_{OUT})}{[O_2]_{IN} - [O_2]_{OUT}} \times 100 \quad (3.6)$$

where:

- $[CO]_{IN}$  = inlet concentration of CO,
- $[CO]_{OUT}$  = outlet concentration of CO,
- $[O_2]_{IN}$  = inlet concentration of  $O_2$  and
- $[O_2]_{OUT}$  = outlet concentration of  $O_2$