CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals

- $Al(OH)_3$ supplied by Sigma Chemical Co., Ltd.
- SiO_2 (Fume Silica) supplied by Sigma Chemical Co., Ltd.
- $N(CH_2CH_2OH)_3$ (Triethanolamine, TEA) supplied by Fluka Chemical AG.
- $N(CH_2CHCH_3OH)_3$ (Triisopropanolamine, TIS) supplied by Carlo Erba Reagenti Co., Ltd.
- $HOCH_2CH_2OH$ (Ethylene Glycol, EG) supplied by J.T. Baker Inc.
- NaOH supplied by EKA Chemical Co., Ltd.
- NaCl supplied by AJAX Chemical Co., Ltd.
- CH_3CN (Acetronitrile) supplied by Lab Scan CO., Ltd.

3.1.2 Gases

- 99.99% Carbon dioxide
- 3.00% Carbon monoxide in Helium form Thai Industrial Gases Public Co., Ltd.
- Ultra high purity (99.999%) Helium form Thai Industrial Gases Public Co., Ltd.
- Ultra high purity (99.999%) Hydrogen form Thai Industrial Gases Public Co., Ltd.
- 7.87% Oxygen in Helium form Thai Industrial Gases Public Co., Ltd.

3.2 Equipment

The apparatus used in this experiment and their alignment are schematically shown in Figure 3.1. It can be roughly divided into three main sections: gas blending section, catalytic reactor section and analytical instrument section.

3.2.1 Gas Blending Section

The reactant gas consisted of 40% H_2, 1% CO, 10% CO_2, 1%O_2 balanced in He. These reactants must flow through 7 micron filters to trap the particles before entering mass flow controllers (AALBORG model GFC1715). The mass flow controllers were used to control the flow rate of the reactant gases in order to achieve the desired composition. Check valves with psig cracking pressure were installed after the mass flow controller to prevent reverse flow. Then, all streams were mixed in the mixing chamber before entering through the reactor (Figure 3.1).

3.2.2 Catalytic Reactor

A pyrex glass U-tube reactor with 6 mm inside diameter was used as a catalytic reactor. The reactor placed in a furnace where the temperature of the catalyst bed was monitored and controlled by PID temperature controller (Shinko FCR-13A-S/M model) equipped with a type K thermocouple. Catalysts were packed inside the U-tube reactor between two layers of glass wool.

3.2.3 Analytical Instrument

Gas chromatograph (GC, Agilent Technologies 6890N model) equipped with a thermal conductivity detector (TCD) was used to analyze effluent gas. The effluent gas steam from the reactor was first dehumidified by cold water-trap before auto-sampling into the GC. The carbosphere, 80/100 mesh, and 10 ft X 1/8 inch stainless steel packed column was used for separating all components. The conditions of GC are listed as follows:

Injector Temperature	:	120 °C,
Oven Temperature	:	100 °C,

TCD condition :

- Temperature 175 °C,
- Reference gas He (99.999% purity)

Carrier gas : He (99.999 purity).

The results were recorded by Agilent chemstation software. The observed peak were identified by comparison with the retention time of the standard gas. For quantitative analysis, the peak area was used to determine the concentration of each component based on the calibration curves obtained from known composition gases.

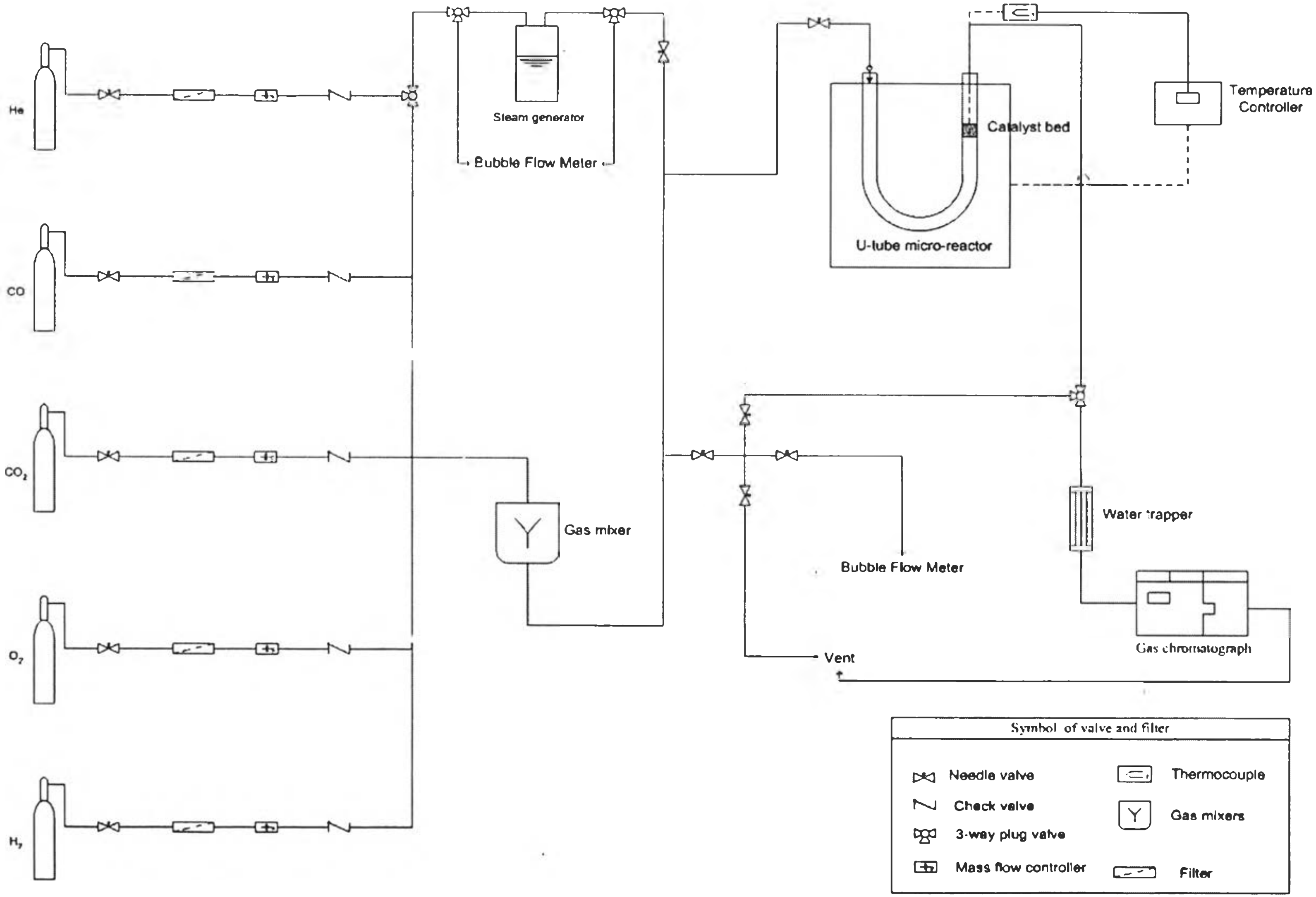

Figure 3.1 Schematic flow diagram of the experimental setup.

3.3 Catalyst Preparation Procedure

3.3.1 A-type Zeolite Synthesis

A-type zeolite was first synthesized by using silatrane and alumatrane as precursors, via the sol-gel and microwave heating techniques.

3.3.1.1 Precursor Synthesis (Sathupanya *et al.*, 2002)

Silatrane was synthesized by mixing silicon dioxide, 0.10 mol, triethanolamine, 0.125 mol, in 100 ml ethylene glycol (EG) solvent, in the simple distillation set. The reaction was conducted under flowing nitrogen, in order to remove by product water and ethylene glycol from the system, at the boiling point of the EG for 10 hrs. Then, the left EG was removed under vacuum at 110 °C for 8 hrs. After EG removal, the brownish powder was obtained. It was washed by dried acetonitrile three times to remove an undesired organic residue.

Alumatrane was synthesized by similar process, but aluminum hydroxide, 0.1 mol, and triisopropanolamine, 0.125 mol, were used as reactants (Sathupanya *et al.*, 2002).

3.3.1.2 Sol-gel Process and Microwave Techniques

In order to synthesize Na-A zeolite, silatrane and alumatrane were mixed with NaOH at the ratio of $SiO_2:Al_2O_3:xNa_2O:yH_2O$, where $x = 7$, $y = 410$ (Sathupanya *et al.*, 2002). 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 18 min. The product was washed by distilled water for three times.

3.3.2 Incepient Wetness Impregnation

In this study, both commercial and synthesized Na-A zeolite were used as a support. To obtain the desired amount of Pt-loading, the appropriate amount of Pt-precursor (H_2PtCl_6) was prepared by impregnating onto the zeolite support. Then, it was dried in an oven at 110 °C overnight and calcined the catalysts at 500 °C for 5 hrs with 5 °C/min ramping rate. Prior to each catalytic measurement, the catalyst was ground and sieved to a 80-120 mesh size in order to control the mass transfer effect.

3.4 Catalyst Characterization

A variety of methods was used for characterizing the catalyst, including Brunauer-Emmet-Teller method (BET), X-ray diffraction (XRD), Atomic Absorption Spectroscopy (AAS), Scanning Electron Microscopy (SEM) and H_2 pulse chemisorption.

3.4.1 BET Surface Area Measurement

In order to determine the total surface area and pore size, the Brunauer-Emmett-Teller mrthod (BET) method, which is the most common method and routinely used in most catalyst studies, was used. The measurements were conducted by using an autosorb-1 Gas Sorption System (Quantachrome Corporation), which is a BET based instrument. Before measuring, the volatile species that adsorbed on the catalyst surface has to be eliminated by heating the sample under vacuum atmosphere to 200 °C for 2 hrs. Nitrogen gas was used as adsorbate. It would adsorb on to the catalyst surface at liquid nitrogen temperature (-196 °C). The adsorption data were analyzed by using Autosorb ANAGAS Software Version 2.10. The software fits the adsorption data to BET equation (Equation 3.1) and determines amount of adsorbate that corresponding to a monolayer of surface coverage.

$$\frac{1}{W(\frac{P}{P_o}-1)}=\frac{1}{W_m C}+\frac{(C-1)}{W_m C}\frac{P}{P_o} \qquad (3.1)$$

where:

W = weight of gas adsorbed at relative pressure P_o

W_m = weight of adsorbate constituting a monolayer of surface coverage

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

From knowledge of amount of monolayer nitrogen, the surface area can be obtained from Equation 3.2

$$A = \frac{W_m A_{nitrogen} \times 6.02 \times 10^{23}}{M_{w,nitrogen}} \qquad (3.2)$$

where:

A = Surface area of sample

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

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

3.4.2 X-ray Diffraction

The crystalline structure of the zeolite support and the approximated particle size of the Pt were analyzed by powder X-ray diffraction technique (Rigaku RINT-2200 model). RINT-2200 equipped with Cu tube and Ni filter was used for generating and separating the CuK_α radiation (1.5406 Å) with generator voltage and current of 40 kV and 30 mA, respectively. The goniometer parameters were set as follows:

divergence slit: 1° (2θ),

scattering slit : 1° (2θ),

receiving slit : 0.33 mm.

The powder form of sample was packed in a thin wall glass container which is placed in the sample holder. The signal from detector was sent to analyze and record by an on-line computer. From the XRD pattern, the mean crystallite size larger than 5 nm can approximate by using Scherrer's equation (Equation 3.1). The Scherrer's equation is an equation that shows the relation between the mean crystallite diameter (D_b) and broadening of the diffraction line corresponding to the Bragg's angle (θ) using wavelength (λ).

$$D_b = \frac{K \times \lambda}{B_b \times \cos(\theta)} \qquad (3.1)$$

where:

D_b = mean crystallite diameter (Å),

K = Scherrer constant, 0.9,

λ = X-ray wave length (Å),

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

θ = Bragg's angle of reflection (degree).

It must be noted that the number obtained from the Scherrer's equation is the thickness of particle measuring perpendicular to diffraction plane where is corresponded to the Bragg's angle of reflection θ. To determine the actual particle size, the correction factor which is related to the shape of particle and the Milller indices have to be applied. The correction factors for some common geometry are given in Table 3.1.

Table 3.1 Geometric correction factor (g), such as $d = gD_b$

Geometry of the crystallite	g	Definition of d
Sphere	4/3	Diameter
Hemisphere	8/3	Diameter

3.4.3 H_2 Pulse Chemisorption

To determine the exposed metal surface in distinct from the total surface area, the H_2 pulse chemisorption was carried out by using a TPDRO instrument (Thermoquest TPDRO 1100 model). Prior to H_2 pulse chemisorption, the sample was pretreated by reducing under H_2 flow at 500 °C for 2 hrs. Then, the pulse chemisorption was performed in isothermal condition at 50 °C. An inert gas licked the sample. A certain amount of reactive gas, H_2, was injected into the flow tank. It came to contact and chemisorbed onto the sample active site which was accessible to the reactive gas molecules. Amount of the gas adsorbed was calculated from a difference between area peaks during sample analysis and the area peak during blank analysis, namely, an analysis carried out under the same conditions of sample analysis without any sample to adsorb. From amount of H_2 uptake by sample and amount of metal in the sample, the metal surface area and degree of metal dispersion are derived.

3.4.4 Scanning Electron Microscopy

JEOL 5200-2AE scanning electron microscope (SEM) was utilized to capture the micrograph of the support morphology. The powder sample was placed on stub and coated with gold in sputtering device before taking the micrograph. Moreover, the crystalline size of the zeolite support was roughly estimated.

3.5 Activity Measurement

A 100 mg of catalyst was packed inside the U-tube microreactor as mentioned previously. After installation of the microreactor, 50 Nml/min of H_2 was flowed through the catalyst bed and the temperature was raised 10 °C per min to 400 °C and held at 400 °C for 1 hr. Then, He gas was switched to flush out the remaining H_2 and the catalyst bed was cooled down to room temperature before being heated to the reaction temperature. The activity was investigated in the range of 80° to 320 °C with 40°C increment.

Using gas chromatograph, the concentrations of the reactant and effluent gases, were determined. CO conversion, selectivity and O_2 conversion are calculated (Equations 14-16) as follows:

$$X_{CO} = \frac{[CO]_o - [CO]}{[CO]_o} \times 100 \qquad (14)$$

$$S = \frac{[O_2]_{CO}}{[O_2]_{CO} + [O_2]_{H_2}} \times 100 \qquad (15)$$

$$X_{O_2} = \frac{[O_2]_o - [O_2]}{[O_2]_o} \times 100 \qquad (16)$$

where:

X = CO conversion (%),

S = selectivity (%),

$[O_2]_{CO}$ = amount of O_2 for CO oxidation,

$[O_2]_{H2}$ = amount of O_2 for H_2 oxidation,

$[CO]_O$ = concentration of CO in the reactant gas,

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

$[O_2]_O$ = concentration of O_2 in the reactant gas and

$[O_2]$ = concentration of O_2 in the product gas.