CHAPTER III
EXPERIMENTAL

In this chapter, materials, catalyst preparation, reaction conditions, reactor set-up; both of lab-scale and prototype of bench-scale fuel processor employed in catalytic activity testing, and including catalyst characterization will be explained at the beginning. The catalyst preparation comprises of impregnation and ion-exchangetechniques. Besides these, reactor set-up connected to gas chromatograph (GC), which quantifies concentration of gas reactant and products are also described. The catalysts will be characterized by various techniques; Atomic Adsorption Spectroscopy (AAS), BET surface area measurement, X-Ray Diffractometry (XRD), Temperature Programmed Reduction/Oxidation (TPR/O), Thermogravimetric Analysis (TGA), Transmission Electron Microscopy (TEM), and Nuclear Magnetic Spectroscopy (NMR). All of them will be further discussed.

3.1 Materials

3.1.1 Chemicals for Catalyst Preparation

All chemicals used in this work were described as follows:

1.) Nickel (II) nitrate hexahydrate (Ni $(NO_3)_2 \cdot 6H_2O$) of 98 % purity obtained from Fluka Co., Ltd. was used as a precursor.

2.) NaY-zeolite (HSZ-320NAA, $SiO_2/Al_2O_3 = 5.5$, surface area = 700 m^2/g) obtained from Tosoh Singapore PTE. Ltd. was used as a support.

3.1.2 Gases

All gases used in this work are listed as follows:

1.) Methane of 99.99% purity supplied from Thai Industrial Gas Public Co., Ltd. was used as an reactant gas.

2.) Helium of 99.99% purity supplied from Thai Industrial Gas Public Co., Ltd. was used as a diluted gas in feed stream, purged gas and carrier gas of a gas chromatograph.

3.) Hydrogen of 99.99% purity supplied from Thai Industrial Gas Public Co., Ltd. was used as reduction gas.

4.) Nitrogen of 99.99% purity supplied from Thai Industrial Gas Public Co., Ltd. was used as the gas for driving the auto-sampling valve.

5.) Natural gas (NG) supplied from PTT Public Co., Ltd. was used as reactant gas. The composition of natural gas is shown in Table 3.1.

Table 3.1 Natural gas composition*

Gas Composition	Mole percent (% mole)
N_2	2.05
C_1	78.74
C_2	10.12
C_3	5.8
$i\text{-}C_4$	1.28
$n\text{-}C_4$	1.21
$i\text{-}C_5$	0.36
$n\text{-}C_5$	0.23
C_6	0.16
C_7	0.05
Total	**100**

*Source: Unit 5 of Gas Separation Plant, PTT Co., Ltd (public).

3.2 Catalyst Preparation Procedure

The catalyst preparation is one parameter strongly affecting to catalytic performance since preparation and pretreatment are also affect to the distribution of active metal on the support. In this following section, the two different techniques were used in preparation; incipient wetness impregnation and ion-exchange.

3.2.1 Incipient Wetness Impregnation (IWI) method

Impregnation is the simplest technique and practically used for catalyst preparation in prevalent industries. In this case, the aqueous solution of nickel nitrate hexahydrate (Ni $(NO_3)_2$ $6H_2O$, Fluka, 98 %) as a Ni precursor was brought into contact with Sodium-exchanged Y zeolite (NaY, SiO_2/Al_2O_3 = 5.5, surface area = 700 m^2/ g). Prior to be used, the support was calcined. The pore volume of the support was determined by dropping deionized water. To achieve various loading of Ni metal; 5, 7, 11, and 15 %wt Ni, the precursor was weighed with the desired amount then dissolved in deionized water. The solution was then slowly dropped and mixed with NaY zeolite supports, followed by waiting for 2 hours at room temperature. The impregnation catalysts were dried overnight at 110°C, and subsequently calcined in air at 700°C for 4 hours. Finally, the catalysts were sieved in the 80-120 mesh. The prepared catalyst is designated IM and kept in desiccator.

3.2.2 Ion-exchange (IE) Method (Pawelec et al., 2004)

The starting material was a zeolite NaY (NaY, SiO_2/Al_2O_3 = 5.5, surface area = 700 m^2/ g). The ion-exchanged Ni/NaY catalysts, containing 5.38, 6.37, and 7.28 %wt Ni, were prepared by using nickel nitrate hexahydrate (Ni $(NO_3)_2$ $6H_2O$) as a Ni precursor. The amount of 2.5 g of the parent NaY were brought into 50 cm^3 of 0.3 mol/dm^3 of nickel nitrate $Ni(NO_3)_2$ solutions (a solution-to-zeolite volume ratio of 20:1). The ion-exchange was achieved under constant agitation (600 rpm) at 60 °C for 16 hours. Then, the suspension was filtered and thoroughly washed with deionized water (3 x 50 cm^3) in order to remove occluded salt. Following this, the ion-exchanged catalyst was dried in oven at 110 °C for 24 hours and then

calcined in air flow at 700 °C for 4 hours. To obtain higher loading, the repetitions of the experimental were required. The catalyst was sieved in the 80-120 mesh. The prepared catalyst is designated IE-x (x being the weight percentage of Ni determined by Atomic Adsorption Spectroscopy (AAS) and calculated on the basis of dry zeolite) and was kept in a desiccator.

3.3 Reactor set-up and catalytic testing

3.3.1 Lab-scale steam reforming unit

The steam reforming unit is schematically displayed in Figure 3.2. The system consists of three main parts:

(a) Gas mixing section

The gas mixing section dominantly consists of gas stream line connected with mixing chamber. The function of this section was used to make the desired concentration and flow rate of reactant gas prior to enter the catalytic reactor.

(b) Catalytic fixed bed reactor

(c) Analytical instrument – Gas Chromatograph (GC)

The experimental study was conducted in a fixed bed flow reactor of stainless steel tube having an outside diameter of 10 mm. For preliminary study in lab-scale, 0.2 g of catalyst was placed at the center of reactor between two quartz wool plugs as shown in Figure 3.1. The catalyst was supported with ceramic ball and then thin layer of quartz wool to prevent flowing down of the catalyst. The reactor was installed and electrically heated in the furnace. The temperature of catalyst bed was monitored and controlled by PID temperature controller equipped with a K-type thermocouple. The thermocouple was placed inside the reactor with its one end centered at the catalyst bed for measuring the bed temperature. The reaction was conducted at 700°C and atmospheric pressure; with a total flow of 100 ml/min.

Before the reaction, the catalyst was pretreated by reduction with pure H_2 at 700°C for 1 h. After pretreatment, the flow of the reactant gases, methane and steam carried by helium, were controlled by electronic mass flow controllers. Methane and carrier gas, helium, were trapped with 7-µm filter before passing through the mass flow controllers to prevent impurities in the gases entering to the system. To prevent

the deterioration of the mass flow controller from back pressure, check valve was installed in-line. Water was injected using a syringe pump at 3.1 ml/h to an evaporator for operating at 150°C. The steam was carried by helium gas, and then mixed with methane in a gas mixing chamber before entering the reactor.

In analytical section, the product gases were trapped by a water trapper before entering to a gas chromatograph. The gas composition of product gases were quantitatively analyzed by a gas chromatograph (Hewlett Packard 5890 series II) equipped with a thermal conductivity detector (TCD). The packed column (Carbosphere, 80/100 mesh, 10 ft x 1/8 inch stainless steel) was used for separating the product gases, H_2, CH_4, CO, and CO_2. The GC conditions used are summarized as follows:

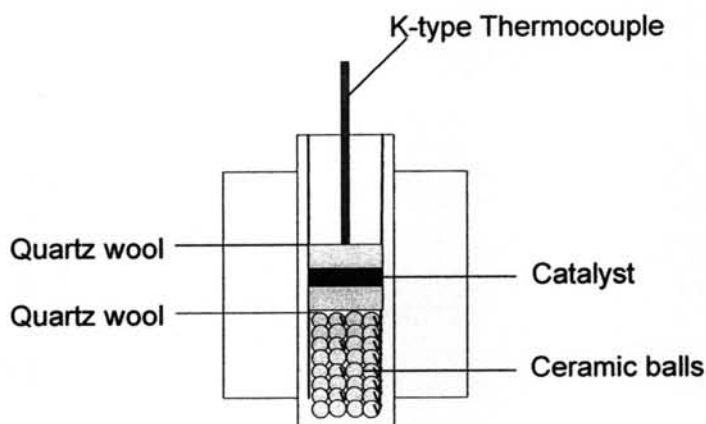|	
Injection Temperature:	110 °C
Oven Temperature:	110 °C
Detection Temperature:	175 °C
Carrier Gas:	HP He (99.99% purity)

Figure 3.1 Schematic of catalyst bed in the reactor.

The catalyst activity was investigated and presented in term of the conversion of CH_4, selectivity of gas products (H_2, CO, and CO_2). The calculation are defined as exhibited in Appendix A.
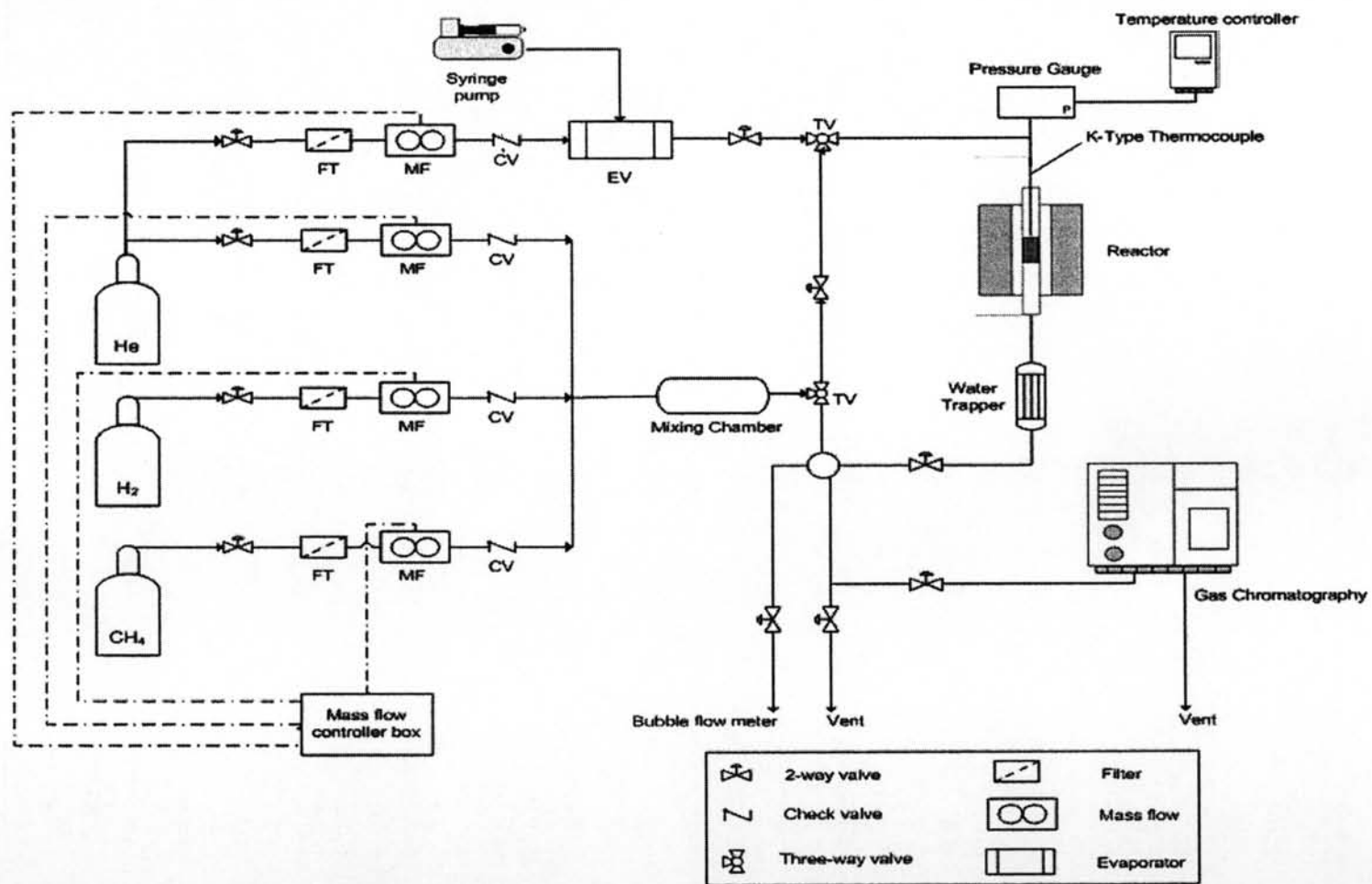
Figure 3.2 Scheme of lab-scale experimental apparatus.

3.3.2 Bench-scale fuel processor

An integrated fuel processor, combination of hydrogen production unit and purification unit were employed as illustrated in Figure 3.3. The bench-scale fuel processor constitutes 4 units which are;

(a) Steam Methane Reforming Unit (SMR)

(b) High Temperature Water-Gas Shift Unit (HT-WGS)

(c) Low Temperature Water-Gas Shift Unit (HT-WGS)

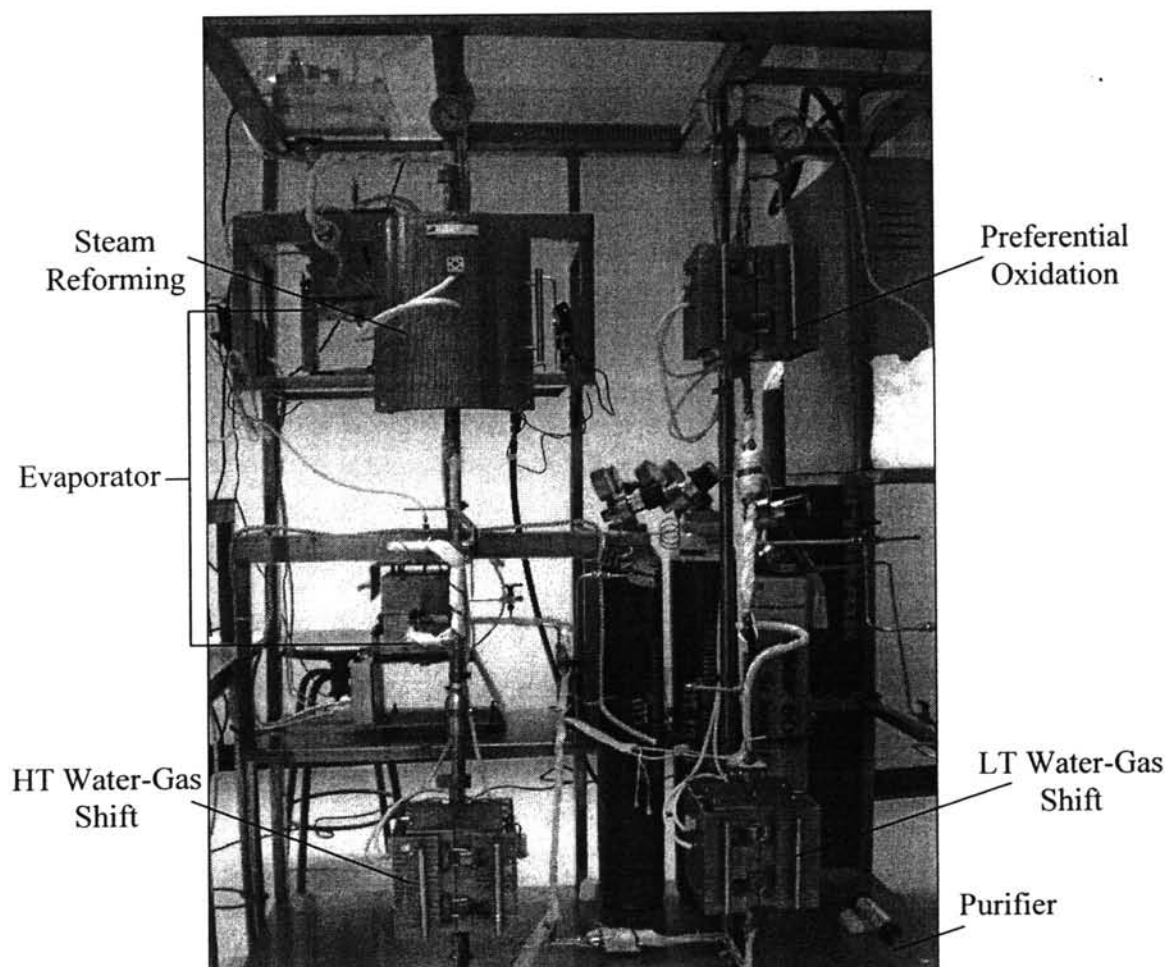(d) Preferential Oxidation Unit (PROX)

Figure 3.3 Bench-scale fuel processor.

Each unit of the fuel processor comprises of two main parts: (1) gas mixing section and (2) catalytic reactor.

In operation, steam reforming unit produces synthesis gas (hydrogen and carbon monoxide) as main gas products. Each furnace was controlled temperature by main circuit PID controller equipped with thermocouple K-type. The flow of the reactant gases, natural gas and steam carried by helium, were controlled by electronic mass flow controllers. Prior to pass through the mass flow controllers, the reactant gases were trapped with 7-μm filter in order to prevent impurities in the gases entering to the system. To prevent the deterioration of the mass flow controller from back pressure, check valve was installed in-line. Water was injected by syringe pump to an evaporator for producing steam at 150°C. The gas mixtures were obtained in gas mixing chamber before entering a fixed bed reformer, stainless steel tubing with 10 mm. (O.D.), which contains the activated catalyst.

The reformed gas pass through water-gas shift unit combined with steam generated from evaporator at 150°C and then fed into both of HT and LT water-gas shift. The CO, inhere in reformed gas, react with steam for additional producing H_2. The H_2 stream needs to be purified by passing through preferential oxidation process to remove the CO content below 1000 ppm. In fact, real operation requires extra unit; purifier, to get rid of trace contaminants, for instance, CO_2, CO, and remaining hydrocarbon before utilizing in any application.
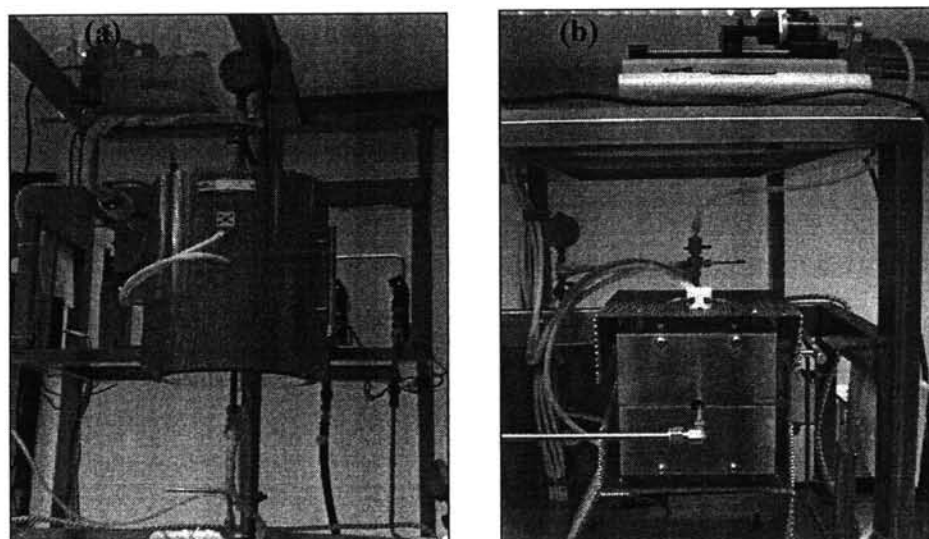

Figure 3.4 (a) Steam reforming unit, (b) Steam generator combined of syringe pump and evaporator, and (c) Steam generate through HT and LT water-gas shift unit.
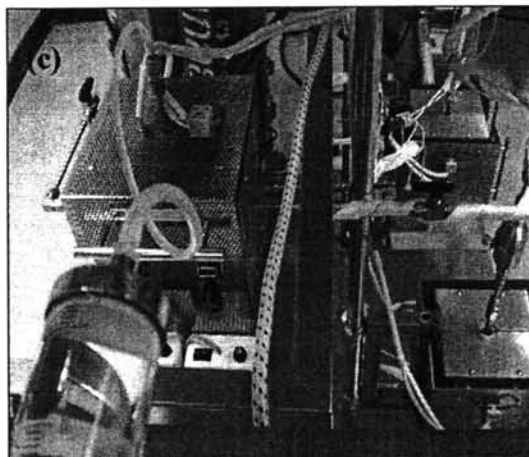
Figure 3.4 (a) Steam reforming unit, (b) Steam generator combined of syringe pump and evaporator, and (c) Steam generate through High Temperature and Low Temperature water-gas shift unit (Continued).

Regarding to identify the gas composition of inlet and outlet gases, gas chromatograph (Hewlett Packed) equipped with a flame ionized detector (FID) is required. The packed column (Port Q, 80/100 mesh, 10 ft x 1/8 inch stainless steel) was used for separating the natural gas composition, for example; methane, ethylene, ethane, propylene, propane, C_4, C_5, C_6, C_7, and C_8 hydrocarbon by using the GC conditions as following:

Injection Temperature:	105 °C
Oven Temperature:	220 °C
Detection Temperature:	110 °C

Additional, the other product gases gas such as H_2, CO_2, CO, and CH_4 were also analyzed with the same condition with lab-scale experimental. Analytical part requires a gas chromatograph (Hewlett Packard 5890 series II) equipped with a thermal conductivity detector (TCD) and the packed column (Carbosphere, 80/100 mesh, 10 ft x 1/8 inch stainless steel).

Figure 3.5 Scheme of bench-scale fuel processor.

3.4 Experimental condition

The steam reforming of methane reaction was carried out under atmospheric pressure. The prepared catalysts, both the impregnated and the ion-exchanged catalysts, were activated by reduction in pure H_2 flow of 30 ml/min at 700°C for an hour and then were flushed with He for 60 min before start-up.

Prior to feed the reactant gases to the reactor, the concentration of reactant gases were determined by using by-pass line to a gas chromatograph to achieve the desired concentration. Several parameters were investigated as follows:

3.4.1 Effect of Ni loading and preparation technique

The various amounts of Ni loading of 5, 7, 11, and 15 wt % Ni on the NaY zeolite support were determined in term of activity in order to investigate optimum loading for the impregnated catalysts. In addition, the effect of Ni loading on NaY prepared by ion-exchanged catalysts on the catalytic activity also were studied in term of activity. The suitable loading of Ni over NaY prepared by impregnation was used to compare with those of the ion-exchanged catalyst. The activity was investigated for 4 hours at 700°C under atmospheric pressure with a steam to carbon ratio of 1.

3.4.2 Effect of feed ratio

The effect of steam to carbon ratio on the catalytic activity was investigated and the catalytic activity of each condition was compared by varying the feed ratios of 1, 1.5, and 2 at reaction temperature of 700°C under atmospheric pressure.

3.4.3 Effect of feed component

It is known that natural gas is a mixture of CH_4, other hydrocarbons, N_2, CO_2, and some gas compounds. The effect of natural gas on the steam reforming performance was studied at 700°C, 1 atm, and steam to carbon ratio of 1.

3.4.4 Bench-scale testing

The impregnated catalyst containing 11wt% was used to investigate the activity in bench-scale fuel processor at 700°C, 1 atm and feed ratio of 1 for 9 h.

3.5 Catalyst Characterization

The several techniques and equipment were applied for the characterization of catalysts as follows:

3.5.1 Atomic Absorption Spectroscopy (AAS)

Elemental analyses were performed by Atomic Absorption Spectroscopy using Varian, SpectrAA 300 instrument. The technique was used to measure the actual amount of metal in the prepared catalyst. Prior to analysis, the samples were solubilized in a mixture of HF and HNO_3:HCl (3:1) with ratio of 4:1 at 50°C and then the mixture were diluted to 50 ml with deionized water. The concentrations of standard solutions were prepared in range of 2, 5, and 10 ppm. The actual concentrations of the sample were determined base on the absorption intensity. Each element can emit the specific wavelengths. The wavelengths generated from cathode lamp were absorbed by the considered element in sample. The absorbed 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.

3.5.2 BET Surface Area Measurement (SAA)

Sorptomatic 1990 was used to determine the textural properties; the BET surface area, total pore volume and average pore diameter of the prepared catalysts. The measurement was based on Brunauer-Emmet-Teller (BET) equation. The technique evaluated the properties by caculating the physical multilayer of the N_2 adsorption-desorption isotherms over the whole range of relative pressures. A sample was evacuated by heating at 300°C for at least 10 hours to eliminate volatile absorbents on the surface prior to the analysis. A value of 0.162 nm^2 was taken for

the cross-section of the physically adsorbed N_2 molecule under cooling condition at liquid N_2 temperature (-196°C). BET specific areas were calculated from these isotherms by applying the BET method over the 0.05-0.3 P/P^0 range. The average pore diameter and pore volume were obtained with correlation coefficients above 0.999 or approach to unity.

3.5.3 X-Ray Diffraction (XRD)

The XRD diffraction patterns were used to identify the crystalline phases of supported Ni catalysts before and after reaction. The X-Ray Diffraction patterns were obtained according to the step-scanning procedure (step size 0.02°, scan speed 5°/ min) by using a Rigaku X-Ray Diffractometer system (RINT-2200) and CuK$_\alpha$ radiation at 40 kV and 30 mA with the wavelength of 1.5406 angstrom. Scanning 2θ angles were employed ranging from 3° and 70°. The samples were finely ground and then placed on the glass slide. Phase identifications were carried out by comparing the collected spectra with spectra in the database. The mean metal crystallite diameter was estimated by XRD line-broadening using the Scherrer equation.

$$D = \frac{K\lambda}{\beta \cos\theta}$$

Where D is the average crystallite size, K the Scherrer constant, λ the wavelength of incident X-rays (1.5406 A°), β the peak width at half height and θ corresponds to peak position.

3.5.4 Temperature Programmed Reduction (TPR)

The Temperature Programmed Reduction (TPR) experiments were performed in a quartz reactor heated by an electrical furnace. The experiments involved heating about 30 mg of catalyst at a rate of 10°C/min to 900°C with a gas mixture consisting of 5% H_2 in N_2. The H_2 consumption was measured by analyzing the effluent gas with a thermal conductivity detector (TCD) and monitored the

different H_2 consumption as a function of temperature. The steam formed during reduction was removed by a cooling trap. This technique can be used to evaluate the reducibility of zeolite-supported Ni catalyst.

3.5.5 Temperature Programmed Oxidation (TPO)

The Temperature Programmed Oxidation of carbon deposit was carried out in a quartz reactor. The TPO experiments were used to determine the amounts and locations of carbon that were deposited under reaction condition. Carbons with different morphology or different locations are burnt at different temperatures. About 30 mg of catalysts were loaded in the reactor and thermocouple was placed near the catalyst layer. The samples were heated up to 800°C at a rate of 12°C/min in a flow of 2%O_2/He mixture (a total flow of 26.3 ml/min). Carbon formation was oxidized into CO_2 then convert to CH_4 in the methanator. FID SRI model 110 was used to detect the effluent gas from methanator.

3.5.6 Thermogravimetric analysis (TGA)

The amount of coke formation on the catalysts after deactivation tests at 700°C for 5 hours were examined by oxidation in air using a Du Pont TGA 2950 Thermogravimetric Analyzer. The samples were placed in a Pt pan. The weight loss from the combustion of the deposited carbon was examined with a heating rate of 10°C/min from room temperature to 800°C under air flow (50 ml/min). The purge gas was used to prevent back diffusion of the evolved gases from the operation. Heating rate and sample temperature are measured by the thermocouple located above the sample.

3.5.7 Transmission Electron Microscope (TEM)

The size and the shape of Ni particles were observed by TEM. TEM images of the catalysts before and after reaction were taken with a JEM 210 electron microscope using primary electron energy of 120 keV. The catalysts were dispersed in ethanol then put in an ultrasonic bath and deposited on a Cu TEM grid. Electron microscope can be used for an evaluation of particle size and the result can also be calculated in term of the average particle size by count from images.