

## **CHAPTER III**

### **EXPERIMENTAL**

#### **3.1 Materials**

##### 3.1.1 Chemicals

- Nickel (II) nitrate hexahydrate,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  of 98% purity was obtained from Fluka Co., Ltd.
- Clinoptilolite was obtained from Marineland, Moorpark, CA.
- Cerium (III) nitrate hexahydrate,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  of 99% purity was obtained from Aldrich Chemical Co., Ltd.
- Zirconyl chloride hydrate,  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  of 99.99% purity was obtained from Aldrich Chemical Co., Ltd.

##### 3.1.2 Gases

- Methane of 99.99% purity used as a reactant gas was supplied from Thai Industrial Gas Public Co., Ltd.
- Helium of 99.99% purity used as the balanced gas in the feed stream and used as the carrier gas of gas chromatograph was supplied from Thai Industrial Gas Public Co., Ltd.
- Hydrogen of 99.99% purity used for catalyst reduction was supplied from Thai Industrial Gas Public Co., Ltd.
- Nitrogen of 99.99% purity used for driving the auto-sampling valve was supplied from Thai Industrial Gas Public Co., Ltd.
- Carbon dioxide 20% purity in Helium was used as a reactant gas and supplied from Praxair (Thailand) Co., Ltd.

#### **3.2 Catalyst Preparation**

A series of Ni/Clinoptilolite catalysts were prepared by using incipient wetness impregnation technique. Supported Ni catalysts with various Ni loadings were prepared by impregnating appropriate amount of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  on to supports

followed by drying at 110°C and calcining at 500°C for 5 hours in air. For the catalysts modified with Ce and Zr, the aqueous solution of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  or  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  was added to clinoptilolite first. After that the modified support was impregnated by aqueous solution of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . The impregnated catalysts were dried at 110°C overnight and then calcined in air at 500°C for 5 hours. The notations for all catalysts were given in Tables 3.1-3.3.

**Table 3.1** Notation for the catalysts with varied %Ni loading

wt% Ni	wt% Ce	wt% Zr	Notation
1	-	-	1%Ni/Clino
3	-	-	3%Ni/Clino
5	-	-	5%Ni/Clino
8	-	-	8%Ni/Clino
10	-	-	10%Ni/Clino
15	-	-	15%Ni/Clino

**Table 3.2** Notation for the catalysts with varied %Ce loading

wt% Ni	wt% Ce	wt% Zr	Notation
8	1	-	8%Ni-1%Ce/Clino
8	2	-	8%Ni-2%Ce/Clino
8	3	-	8%Ni-3%Ce/Clino
8	4	-	8%Ni-4%Ce/Clino
8	5	-	8%Ni-5%Ce/Clino
8	6	-	8%Ni-6%Ce/Clino

**Table 3.3** Notation for the catalysts with varied %Zr loading

wt% Ni	wt% Ce	wt% Zr	Notation
8	-	1	8%Ni-1%Zr/Clino
8	-	2	8%Ni-2%Zr/Clino
8	-	3	8%Ni-3%Zr/Clino
8	-	4	8%Ni-4%Zr/Clino
8	-	5	8%Ni-5%Zr/Clino
8	-	6	8%Ni-6%Zr/Clino

### 3.3 Catalyst Characterization

#### 3.3.1 Surface Area Analysis

The surface areas of the catalysts were determined by Brunauer-Emmet-Teller equation (BET), using Sorptomatic 1990 measuring the physical multi-layer adsorption of liquid nitrogen at 77 K, which has cross sectional area of  $16.2 \times 10^{-20} \text{ m}^2$  per molecule. Before performing the adsorption the sample must be degassed by flowing of He at 200°C for 4 hours in order to eliminate the adsorbed species at the surface. The surface area of the catalysts calculated from twenty-one

point adsorption isotherms. The average radius and pore volume were calculated at  $P/P_0$  ratio close to unity.

### 3.3.2 X-ray Diffraction

Structural characterization of catalysts was investigated by X-ray Diffraction technique to analyze the fresh and used catalysts qualitatively and quantitatively. The qualitative analysis was based on the fact that the X-ray diffraction pattern is unique for each crystallite phase. The mean metal crystallite diameter was estimated by the Scherrer equation. The X-ray diffraction patterns of the catalysts were obtained by using a Rigaku X-Ray diffractometer system equipped with a Cu tube for generating  $\text{CuK}_\alpha$  radiation with the wavelength of 1.5406 Å. The goniometer parameters were divergence slit =  $1^\circ$  ( $2\theta$ ), scattering slit =  $1^\circ$  ( $2\theta$ ), and receiving slit = 0.3 mm. A scan speed of  $5^\circ$  ( $2\theta$ )/min and a scan step of  $0.02^\circ$  ( $2\theta$ ) were applied for the continuous run in the 5 to  $90^\circ$  ( $2\theta$ ) range. The sample powder was packed on the glass slide specimen holder. The signal was sent to an online computer to record and analyze.

### 3.3.3 Thermogravimetric Analysis

The amount and the oxidized temperature of carbon deposition on catalysts were estimated by Thermogravimetric Analyzer (TGA). After the catalytic reaction, the catalyst was removed from the catalyst bed. The weight loss from the combustion of the deposited carbon was observed under air flowing by using the Du Pont TGA 2950 Thermogravimetric Analyzer. The temperature was increased from 30 to  $800^\circ\text{C}$  with heating rate of  $10^\circ\text{C}/\text{min}$ . The mass change of the catalysts was monitored and recorded by the TGA instrument thermal analyst system. The purge gas was used to prevent back diffusion of the evolved gases from the operation. Heating rate and sample temperature were measured by the thermocouple located above the sample.

### 3.3.4 Temperature Programmed Oxidation

Temperature programmed oxidation (TPO) was performed for studying the reactivity of carbon deposits by oxidizing sample under the flow of air while the temperature increases linearly with time. In other words, carbons with different morphology or different locations are burnt at different temperatures. The reaction was conducted in quartz tube fixed bed reactor. About 40 mg of spent catalyst was packed between quartz wool. Carbon deposited was oxidized in the reactor to carbon dioxide, which was converted again to methane in the methanator using Ni/activated alumina as the catalyst. The effluent gas from the methanator was detected by FID SRI model 110. The temperature of the reactor and methanator were heated by a furnace and controlled by a temperature controller.

### 3.3.5 Temperature-Programmed Reduction

Temperature programmed reduction (TPR) was performed for monitoring the reduction of the metal oxide while the temperature increased linearly with time. The temperature was increased from 30 to 900°C with heating rate of 10°C/min. Mixture of 5% H<sub>2</sub> in N<sub>2</sub> was used to reduce the catalyst in TPR experiment because it provides the thermal conductivity difference between the reactant and the carrier gas. A thermal conductivity detector measured the H<sub>2</sub> content of gas mixture before and after reaction. The temperature at the maximum consumption rate of H<sub>2</sub> was the temperature that the catalyst was reduced.

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

H<sub>2</sub> pulse chemisorption was carried out by using Temperature Programmed Desorption Reduction Oxidation (TPDRO/MS 1100). About 500 mg of catalyst was placed in a quartz reactor. Prior H<sub>2</sub> pulse chemisorption, the catalyst was reduced in 5% H<sub>2</sub>/N<sub>2</sub> at 600°C for one hour. Then, the system was purged and cooled to 50°C in flowing N<sub>2</sub>. H<sub>2</sub> pulse chemisorption was performed at 50°C using H<sub>2</sub> 99.99% purity and repeated at 5 min intervals for 10 times. The Ni dispersion was calculated by assuming the adsorption stoichiometry of one hydrogen atom per nickel surface atom (H/Ni = 1).

### 3.4 Experimental Apparatus

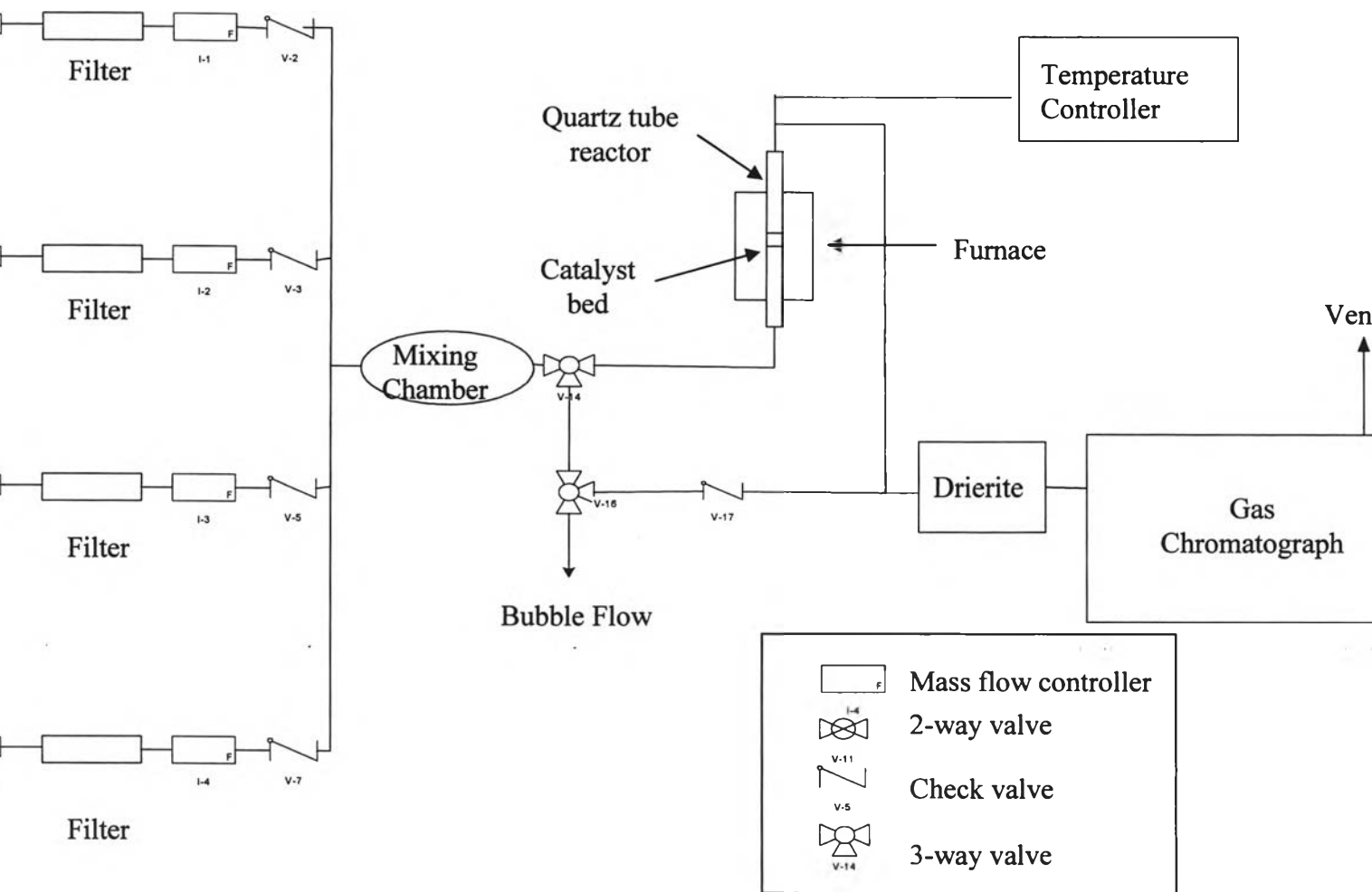
The experimental setup used in this thesis is schematically shown in Figure 3.1. It can be divided into 3 main parts. (i) gas mixing section, (ii) catalytic reactor, and (iii) gas analytical instrument.

#### 3.4.1 Gas Mixing Section

The reactant gas mixture consisted of methane, carbon dioxide, and helium as a balanced gas. The composition and flow rate of the reactant gas mixture were controlled before entering the catalytic reactor, by using 840 Sierra Instruments model mass flow controllers. The contaminants, which might be contained in the gas stream, were collected by 7-micron stainless steel filters. Then the reactant gases were mixed together in the mixing chamber before going through the catalytic reactor.

#### 3.4.2 Catalytic Reactor

In this work, 8 mm. inside diameter quartz tube was used as a reactor. The reactant gas mixture was fed through 0.2 g catalyst, which was packed between quartz wool at the center of the reactor. The temperature of the reactor was electrically heated by temperature controller using K-type thermocouple placed inside the tube with one end centered at the catalyst bed in order to measure the bed temperature. A variac was used to control electrical current to the temperature controller and heating coil in the furnace. The variation of the temperature was  $\pm 2^{\circ}\text{C}$ .



Schematic diagram of the experimental apparatus.

### 3.4.3 Analytical Instrument

The effluent gas stream from the catalytic reactor was analyzed by using Hewlett Packard 5890 seriesII gas chromatograph. The packed column that was used for the separation was carbosphere, 80/100 mesh, and 10ft×1/8-inch stainless steel. Each cycle of GC analysis took 15 minutes to complete before starting the next injection. The conditions of GC are shown as follows:

Injector Temperature:	110°C
Oven Temperature:	110°C
Detector Temperature:	175°C
Carrier Gas:	He (99.99% purity)

## 3.5 **Experimental Procedure**

The catalytic reaction was carried out under atmospheric pressure. Typically, 0.2 g of catalyst was used in each run. Reactant gas was composed of CH<sub>4</sub>:CO<sub>2</sub> = 1:1. Prior to each catalytic measurement, the catalyst was reduced in a pure H<sub>2</sub> flow of 30 ml/min at 500°C for one hour, followed by an increase to reaction temperature in He with the flow rate of 40 ml/min. The reactant mixture was balanced by using He with a total flow rate of 100 ml/min for all of the experiments. Using a by-pass line to a GC, the concentrations of the reactant gases were analyzed.

### 3.5.1 Effect of Ni Loading

A series of Ni/Clinoptilolite catalysts with various amounts of Ni loading, 1, 3, 5, 8, 10, and 15wt% were tested for their activity at 700°C. The activity of each catalyst, in terms of conversion, selectivity and stability of each catalyst were compared to select the appropriate loading amount of Ni for studying the effect of promoter.



### 3.5.2 Effect of Promoter Loading

The Ni/Clinoptilolite catalysts with various amounts of promoters were prepared by incipient wetness impregnation method. The selected promoters were Ce and Zr. The amount of 1, 2, 3, 4, 5, and 6wt% of each promoter were used. The catalyst, which gave the best activity and stability, was selected for studying the effect of reaction temperature in the next part.

### 3.5.3 Effect of Reaction Temperature

The catalyst that gave the best activity and stability from the previous part was tested at 600, 700, and 800°C to examine the appropriate temperature for carbon dioxide reforming of methane reaction. All of the catalysts were tested under atmospheric pressure. The activity and stability of the catalyst at different temperatures were compared.