



CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Catalyst Preparation Materials

All chemicals which are used in both preparation and characterization of catalyst are shown as the following:

- 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.
- Ammonium ZSM-5-zeolite (CBV 28014, $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio = 280, surface area = $400 \text{ m}^2/\text{g}$) was obtained from Zeolyst International Co., Ltd.
- 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.

3.1.2 Gases

The gases used in the catalytic reaction as follows:

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

3.2 Experimental Apparatus and Reaction

The schematic diagram of steam reforming process is shown in Figure 3.1. All of apparatuses appear in this. It can be divided into three sections: (1) gas mixing zone, (2) catalytic reactor, and (3) analytical instrument (Senathipbodee, 2004).

3.2.1 Gas Mixing Zone

The desired flow rate and concentration of the reactant gases which are methane and steam were prepared in this zone before being sent to a catalytic reactor. Each reactant flow rate is controlled by the electronic mass flow controllers. Hydrogen is used as a reduction gas while helium is used as a purge gas in the catalyst reduction and used as a diluent gas in the reaction. At the first step, the impurities in the influent gases were trapped by a 7- μm stainless steel filter before passing through the mass flow controllers in order to avoid a contamination problem in a system. Check valves are also installed in-line of the system to prevent a deterioration of the mass flow controller from back pressure. For steam production at 160°C, water is injected to a steam generator (evaporator) by a syringe pump. The steam was carried by helium gas, and then mixed with methane in a gas mixing chamber before entering the reactor. This gas mixing chamber plays a role in the upgrading of reactant gases blending.

3.2.2 Catalytic Reactor

The catalytic steam reforming occurred in a fixed bed flow reactor of stainless steel tubing with an outside diameter 10 mm. About 0.2 g of the catalyst was placed at the center of reactor between quartz wool layers to prevent flowing down of the catalyst. The reactor was installed and electrically heated in the furnace. And the PID temperature controller equipped with a K-type thermocouple is used to monitor and control the temperature of a catalyst bed. For the temperature measuring of catalyst bed, thermocouple is placed inside the reactor with its one end centered at the catalyst bed. In the reactor, steam reforming reaction was operated at 700°C and atmospheric pressure.

3.2.3 Analysis Instrument

The product gases from the reaction passed through the water trapper before entering to a gas chromatograph. They were quantitatively and qualitatively analyzed by a Hewlett Packard 5890 series II gas chromatograph equipped with a thermal conductivity detector (TCD). Carbosphere, 80/100 mesh, 10 ft x 1/8 inch stainless steel is a packed column that used in the column of the chromatography for

separating the product gases, H₂, CH₄, CO, and CO₂. The GC conditions used in this work are summarized as follows:

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

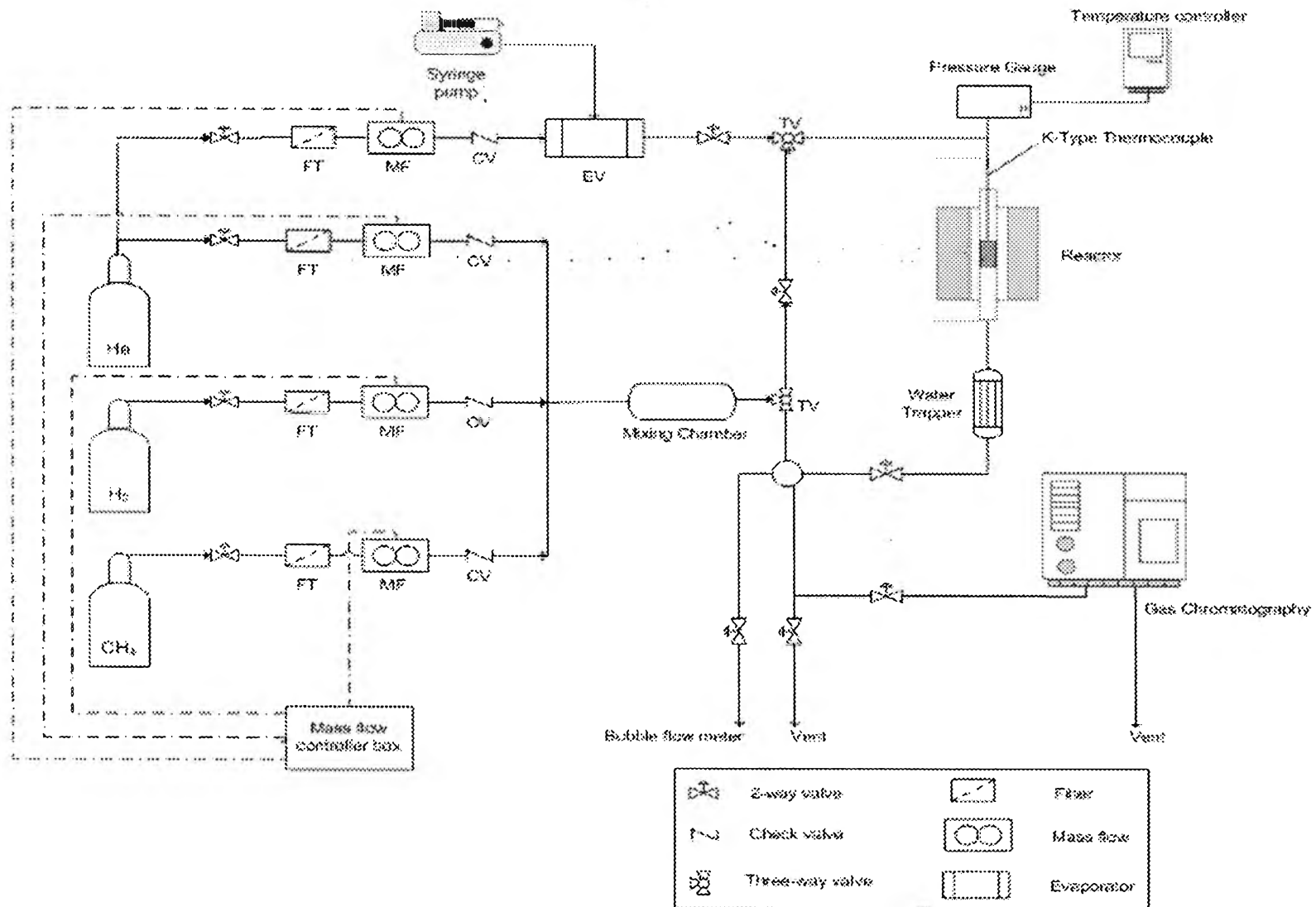


Figure 3.1 Scheme of experimental apparatus in methane steam reforming.

3.3 Experiment

3.3.1 Catalyst Preparation Procedure

According to previous study of the effect of the preparation method on the catalytic performance in steam methane reforming by Chankham (2007), Incipient Wetness Impregnation (IWI) method was used. Therefore, in this study, the Ni supported on ZSM-5 zeolite catalysts were prepared by incipient wetness impregnation. Firstly, the ZSM-5 zeolite was dried in an oven at 110°C for 12 hours. Ni nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Fluka, 98 %) was weighed for a desired amount and then brought to dissolve with the deionized water as a precursor solution. After that, the precursor solution was slowly dropped on ZSM-5 zeolite support. Next, the impregnation catalysts were left at room temperature for 2 hours before drying in an oven at 110°C overnight. Lastly, they were calcined in air flow at 700°C for 4 hours. For ceria promoted Ni/ZSM-5 zeolite catalysts, the ZSM-5 zeolite was impregnated by Cerium (III) nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Aldrich Chemical, 99%), then they were dried and calcined at 500°C for 3 hours before impregnated by Ni nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$). After that, the promoted catalysts were left at room temperature for 2 hours before drying in an oven at 110°C overnight and calcined in air flow at 700°C for 4 hours again. The final catalysts from a preparation were labeled and stored in a desiccator for preventing the humidity in an environment.

3.3.2 Experimental Procedure

The reaction of methane steam reforming was carried out in a fixed-bed reactor under atmospheric pressure. The catalyst prepared by impregnation, was packed in the reactor before it was reduced under flowing H_2 of 30 ml/min at 700°C for an hour. Then, it was flushed with He before start-up. The concentration of reactant gases was measured and ensured by using a by-pass line to a gas chromatograph to get the desired concentration before feeding the reactant gases to the reactor. Due to the influence of the effects of many parameters such as contents of Ni, feed composition, and promoter addition on the catalyst activity and stability, the investigation in these occurred as the following:

3.3.2.1 Effect of Ni Loading

A series of Ni/ZSM-5 catalysts were prepared by using impregnation. The effect of Ni loadings on the ZSM-5 zeolite support was investigated by varying amounts of Ni loadings as 3, 5, 7, 9, 11 and 15 wt% Ni. Finding the optimum Ni loading for impregnated catalysts in reforming process is a main purpose of this study. The reaction conditions are carried out at a steam-to-carbon ratio of 0.8 and a reaction temperature of 700°C. And, the activity of the catalyst in this study was evaluated in terms of methane conversion, hydrogen yield, H₂ and CO selectivity.

3.3.2.2 Effect of the Steam-to-Methane Ratio

The effect of steam-to-methane ratio with different ratios was investigated over the best catalyst. At a reaction temperature of 700°C, the steam to carbon ratios were varied as 0.8, 1, and 2 ratios in order to study and compare the catalytic activity of each condition.

3.3.2.3 Effect of Ceria Content

The 11% Ni/ZSM-5 zeolite promoted with various ceria contents as 3, 5, and 7 wt% were tested on methane steam reforming reaction. In the test, the catalysts were conducted under atmospheric pressure at 700°C and constant steam to carbon ratio of 0.8.

3.4 Catalyst Characterization

It is known that the catalyst characterization is a very important step in order to understand the relationship between the structure of the catalyst and its performance. In this work, many different methods were applied to investigate the structure of both fresh and spent catalysts as follows:

3.4.1 Thermogravimetric Analysis (TGA)

The Perkin-Elmer, Pyris Diamond Model Thermogravimetric Analyzer was used to examine the amount of coke formation on the spent catalysts. This

analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. A derivative weight loss curve can be used to tell the point at which weight loss is most apparent. The equipment is designed to allow precise weight measurements to be performed in a controlled environment. Typically, studies are performed using nitrogen as an inert atmosphere, or oxygen as a reactive atmosphere.

In this study, the samples were placed in the Pt pan and analyzed with a heating rate of 10°C/min from 30°C to 950°C under O₂ flow to discover the weight loss from the combustion of the deposited carbon. The thermocouple located above the sample was used to measure the heating rate and temperature of the sample. And, back diffusion of evolved gases was prevented by the purge gas.

3.4.2 X-Ray Diffraction (XRD)

Rigaku X-Ray Diffractometer system (RINT-2200) was used to characterize the samples as XRD patterns. Due to the specific chemical composition and crystallographic structure of each material which presented on XRD patterns, XRD is an efficient analytical technique used to identify and characterize unknown crystalline materials. Matching of the reference substance's diffraction pattern and sample's diffraction pattern is main principle of this technique. If they have the same pattern, the same crystallite phase will be shown.

3.4.3 Inductively Coupled Plasma/Optical Emission Spectrometry (ICP/OES)

Perkin-Elmer Optima 4300 DV inductively coupled plasma-optical emission spectrometer (ICP/OES) was used for qualitative and quantitative determination of metals and certain non-metals in solution. The concentrations of standard solutions were 1, 5, and 10 ppm. With this technique, liquid samples are injected into a radiofrequency (RF)-induced argon plasma using one of a variety of nebulizers or sample introduction techniques. The sample mist reaching the plasma is quickly dried, vaporized, and energized through collisional excitation at high temperature. The atomic emission emanating from the plasma is viewed in either a radial or axial configuration, collected with a lens or mirror, and imaged onto the entrance slit of a

wavelength selection device. The frequency of this radiation is characteristic of the element that emitted it and as such can be used for identification purposes. The intensity of the radiation is proportional to the concentration of that element within the solution and so can be used for quantitative purposes. The applications of this technique are environmental screening of water samples for contaminants such as lead, cadmium, mercury, and zinc; analysis of biological samples for ion such as sodium and potassium; analysis of geological samples and minerals.

3.4.4 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) is a microscopy technique which operates on the same basic principles as the light microscope but uses electrons instead of light. A beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through it. An image is formed from the electrons transmitted through the specimen, magnified and focused by an objective lens and appears on an imaging screen, a fluorescent screen in most TEMs, plus a monitor, or on a layer of photographic film, or to be detected by a sensor such as a CCD camera.

TEMs use electrons as a light source and their much lower wavelength makes it possible to get a resolution a thousand times better than with a light microscope that is limited by the wavelength of light. In addition, due to the possibility for high magnifications (10^{10} m), the TEM becomes a valuable tool in both medical, biological and materials research.

3.4.5 Temperature Programmed Oxidation (TPO)

Temperature Programmed Oxidation technique permits to find the most efficient oxidation conditions. Moreover, the supported precursor phase and the interaction with the support can be identified. It is useful for the evaluation of the role of the added compounds in the multi-metallic system case. In the TPO technique, the catalyst is in the reduced form and is submitted to a programmed temperature linearly increase, a mixture gas of 2% O₂ in He is flowed over the sample. The oxidation rates are continuously measured by monitoring the change in composition of the reactive mixture after the reactor. The reaction progress is controlled by the

initial percentage which relates to the decrease of O₂ concentration in the exit gas. In addition, the TPO analysis can be applied to prove the interaction between the atoms of two metallic components, in the case of bimetallic system or alloy as already cited.

The TPO method is used for both qualitative and quantitative analysis. The amount of carbon formation on spent catalysts can be evaluated. Carbon formation was oxidized into CO₂ and then converted to methane in the methanator. The exit gas from methanator was detected by FID SRI model 110, resulting in the determination of amount of deposited carbon.

3.5 Calculations

The CH₄ conversion, H₂ selectivity, CO selectivity and H₂ yield were determined from the calculations using Equations 3.1 -3.4 as follows:

3.5.1 CH₄ conversion

$$\begin{aligned} \text{CH}_4 \text{ conversion (\%)} &= \frac{\text{moles of CH}_4 \text{ that are used in the reaction}}{\text{moles of CH}_4 \text{ in feed gas}} \times 100 \\ &= \frac{n \text{ CH}_{4,\text{in}} - n \text{ CH}_{4,\text{out}}}{n \text{ CH}_{4,\text{in}}} \times 100 \end{aligned} \quad (3.1)$$

Where CH_{4,in} = mole of methane which fed to reactor

CH_{4,out} = mole of methane which came out from reactor

3.5.2 H₂ selectivity

$$\text{H}_2 \text{ selectivity (\%)} = \frac{\text{H}_2}{(\text{CO} + \text{CO}_2 + \text{H}_2)} \times 100 \quad (3.2)$$

Where H₂ = moles of H₂ in product gas

CO = moles of CO in product gas

CO₂ = moles of CO₂ in product gas

3.5.3 CO selectivity

$$\text{CO selectivity (\%)} = \frac{\text{CO}}{(\text{CO} + \text{CO}_2 + \text{H}_2)} \times 100 \quad (3.3)$$

Where CO = moles of CO in product gas

H₂ = moles of H₂ in product gas

CO₂ = moles of CO₂ in product gas

3.5.4 H₂ yield

$$\text{Yield of H}_2 (\%) = \frac{\text{H}_2 \text{ selectivity} \times \text{CH}_4 \text{ conversion}}{100} \quad (3.4)$$