

CHAPTER III

EXPERIMENTAL SECTION

3.1 Experimental Setup

The experimental setup in this research is schematically shown in Figure 3.1. It consists of 3 parts, (i) gas blending, (ii) reaction, and (iii) analytical.

The gas blending section was utilized to prepare reactant gases to a desired concentration and flowrate before being introduced into the catalytic reactor. Methane (99.97%, Praxair Distribution Inc.) and carbon dioxide (99.999%, Thai Industrial Gas Public Co., Ltd.) were used as reactant gases. Helium (99.99%, Thai Industrial Gas Public Co., Ltd.) was used as the diluent gas for the reaction and used as the purge gas for the catalyst reduction, which used hydrogen (99.99%, Thai Industrial Gas Public Co., Ltd.) as the reduction gas. At first, each gas was passed through a 7-micron stainless steel filter to remove small contaminants from the gases. In order to control a volumetric flow rate, Sierra mass flow controllers equipped with a control box model 904C-PE-11-BM were used for each gas. Check valves were installed to prevent deterioration of the mass flow controller from backpressure. A gas-mixing chamber was used to promote the complete blending of the reactant gases before proceeding through the reactor.

After the reactant gases were prepared, they were fed to the bottom of a vertical 4-mm-inside-diameter quartz reactor. The 0.02 g of catalyst was kept in place by 0.04 g quartz wool plugged at the center of the reactor. The reactor was installed and electrically heated in the furnace. The

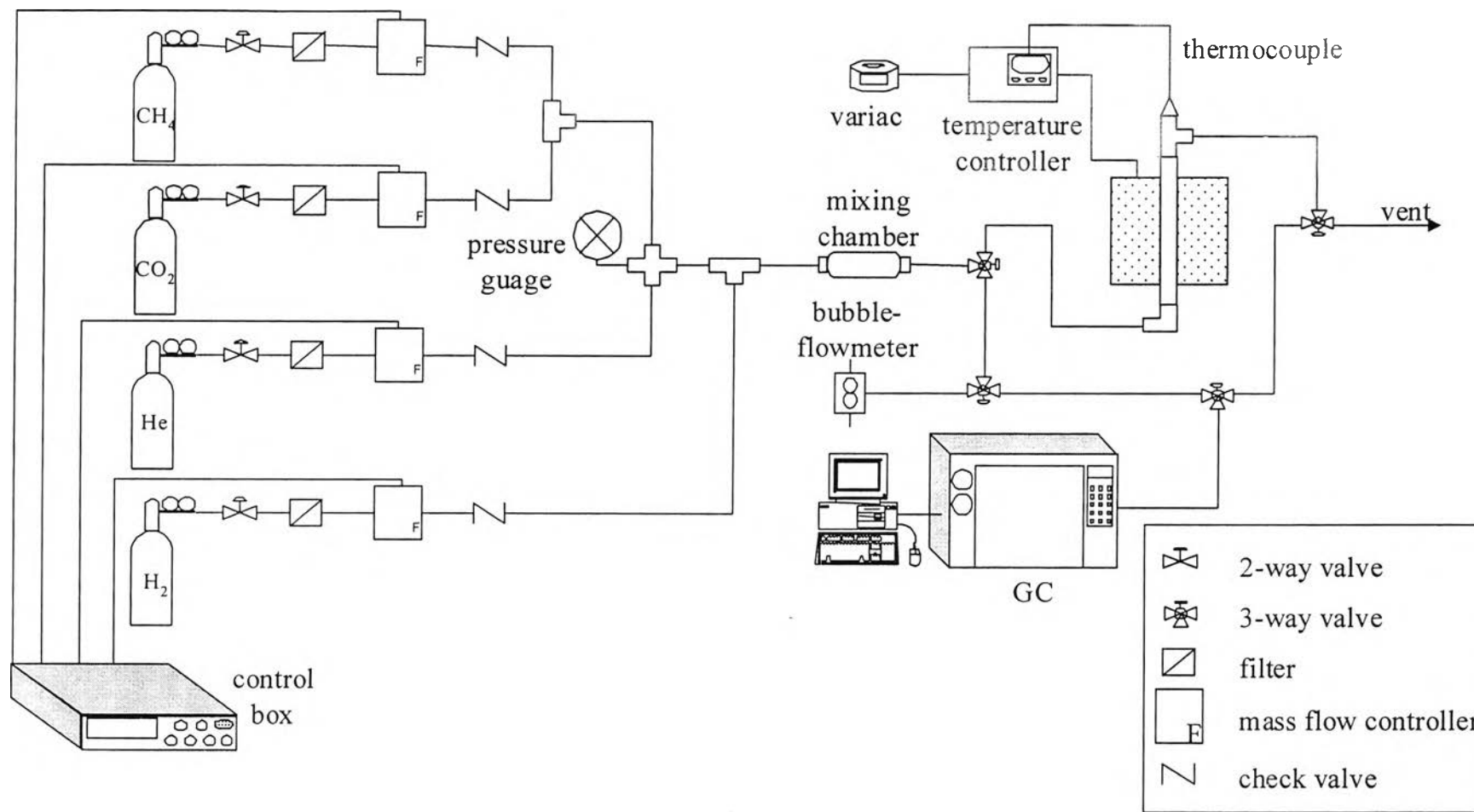


Figure 3.1 Schematic of the experimental apparatus

furnace temperature was controlled by a digital temperature controller equipped with a type-K thermocouple, which was inserted into the center of the catalyst bed. A variac was used to control electrical current to the temperature controller and heating coil in the furnace. By the appropriate adjustment of the variac and the temperature controller, isothermal conditions can be achieved with a maximum variation of $\pm 2^{\circ}\text{C}$ at steady state.

Products from the reaction were analyzed by a Hewlett Packard (HP 5890 seriesII) gas chromatograph (GC). The Hayesep DB packed column, 4m x 1/8in, stainless steel, which was connected to a thermal conductivity detector (TCD), was selected for the analysis. A 6-port valve was used for the sample injection, which used nitrogen gas (99.99%, Thai Industrial Gas Public Co., Ltd.) to drive the auto-sampling valve. Helium was used as the GC carrier gas at the flow rate of 15 ml/min. The injector temperature, oven temperature, and detector temperature were set at 110, 120, and 130 $^{\circ}\text{C}$, respectively. Each cycle of this analysis took 15 minutes to complete. The detector output was transmitted to an on-line computer running the HP Chemstation to automatically evaluate data and report the results.

3.2 Experimental Procedures

3.2.1 Catalyst Preparation

Two techniques were employed to prepare the catalysts used in this research. The first technique, which was used for every catalyst prepared, was impregnation. The second technique, co-precipitation, was applied when the catalysts with mixed-promoter were prepared. The notations for all catalysts were given in Tables 3.1-3.3.

Table 3.1 Notation for the unpromoted catalysts

Support	Notation
ZrO ₂	Pt/Z

Table 3.2 Notation for the promoted catalysts

wt% Promoter loading	Type of promoter	
	Ce	Y
3%	Pt/3CeZ	Pt/3YZ
5%	Pt/5CeZ	Pt/5YZ
7%	Pt/7CeZ	Pt/7YZ
9%	Pt/9CeZ	Pt/9YZ

Table 3.3 Notation for the mix-promoter catalysts

Catalyst Preparation	wt% Ce	wt% Y	Notation
Impregnation	2.5	2.5	Pt/2.5-2.5im
	5	5	Pt/5-5im
	15	15	Pt/15-15im
Co-precipitation (calcined 600°C)	5	5	Pt/5-5co(600)
	15	15	Pt/15-15co(600)
Co-precipitation (calcined 800°C)	5	5	Pt/5-5co(800)
	15	15	Pt/15-15co(800)

3.2.1.1 Impregnation Technique

The Ce- or Y- doped ZrO₂ support was made by the aqueous impregnation of CeN₃O₉.6H₂O or Y(NO₃)₃.6H₂O (Fluka Co., Ltd.), respectively to the Zr(OH)₄ (MEI Chemical). The weight of Ce, Y, or mixed-promoter was varied to achieve the desirable %loading in final material. The incipient wetness of the zirconium hydroxide was 0.1 cm³/g. To obtain the

oxide form of support and promoter, the material was dried at 110°C overnight, prior to calcination at 800°C for 4 hours in air. Finally, the incipient wetness impregnation of the aqueous solution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Merck Chemical Co., Ltd.) was prepared to obtain 1.5 wt% Pt loading. The catalyst was dried overnight at 110°C, and then calcined at 400°C for 2 hours in air.

3.2.1.2 Co-precipitation Technique

$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, $\text{CeN}_3\text{O}_9 \cdot 6\text{H}_2\text{O}$, and $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Fluka Co., Ltd.) were used as the precursors for this technique. At first, solution containing 0.1 M of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, $\text{CeN}_3\text{O}_9 \cdot 6\text{H}_2\text{O}$, and $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was prepared to obtain a desirable final concentration. The solution was then stirred with a high rate while 1 M of NH_4OH (Carlo Erba) was added at a slow rate. When pH reached around 8, the basic solution addition was stopped while the solution was further stirred for another hour. After that, the solution was precipitated by centrifuge method at 2000 rpm for 5 minutes with the ALC centrifuge instrument model 4236. The precipitate was washed thoroughly by warm deionized water (60°C), and then centrifuged again. The washing procedure was repeated for 8 times to ensure the total elimination of the excess ions. The precipitate material was separated from supernatant and dried overnight at 110°C. To observe the effect of calcination temperature, the dried material was then calcined either 600°C or 800°C for 4 hours in air. After the support was prepared, the incipient wetness impregnation of an aqueous solution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Merck Chemical Co., Ltd.) was prepared to yield a catalyst with 1.5 wt% Pt. The catalyst was dried overnight at 110°C, and then calcined at 400°C for 2 hours in air.

3.2.2 Catalyst Characterization

3.2.2.1 *BET Surface Area Measurement*

The catalyst physical surface area was approximated by a Quantachrome Corporation Autosorb-I instrument. This characterization is based on the physical adsorption of the adsorbate, which was nitrogen (N₂) at the liquid nitrogen temperature (77 K) in this study, onto the surface of the samples. Before the analysis, 0.3±0.02 g of a sample was outgassed to eliminate volatile adsorbates on the surface by heating the sample under vacuum in a flow of He (99.99%, the Thai Industrial Gas Public Co., Ltd.) at 200°C for at least 1 hour. The sample specific surface area was calculated from the five-point nitrogen adsorption isotherm using the Brunauer-Emmett-Teller (BET) equation. The average pore radius and average pore volume were calculated at P/P₀ ratio close to unity.

3.2.2.2 *X-ray Diffraction (XRD) Analysis*

X-ray diffraction technique was used to identify crystallographic phase of the material for both qualitative and quantitative analyses. The qualitative analysis is based upon the fact that an x-ray diffraction pattern is unique for each crystalline substance. Chemical identity can be assumed if an exact match can be found between the patterns of an unknown and reference substance. The relatively quantitative analysis for the same crystalline pattern substance can be determined by the comparison of the diffraction lines intensity. The higher intensity indicates the higher content of that crystalline form.

A Philips X-ray diffractometer system (PW 3020) equipped with a graphite monochromator and Cu anode x-ray tube, which gives CuK radiation, was used to obtain the XRD patterns. The grinding well-mixed homogeneous powder was scattered on a thin glass slide that was put against the x-ray beam. Constructive interference can be achieved with monochromatic irradiation by varying the angle of incidence from 5 to 90

degrees. Each sample was scanned twice, once to perform qualitative peak location and the other time for quantitative data gathering. The digital outputs of the proportional x-ray detector and the goniometer angle measurements were acquired by an on-line microcomputer for the storage and subsequent data analysis by PC-APD version 3.5B.

3.2.2.3 *Hydrogen Chemisorption Measurement*

An Autosorb-I-C instrument is used for hydrogen chemisorption measurements, which used to approximate %metal dispersion. The experiments were conducted on several samples of the prepared catalysts in a static volumetric adsorption Pyrex system, equipped with a high capacity, high vacuum pumping station. First, the catalyst was loaded into the quartz tube and the reduction under hydrogen flow for 1 h at 500°C was followed. Second, the hydrogen at the platinum surface was removed by helium flow at the reduction temperature for 30 min and then evacuated for 1.5 h. After that, the catalyst was cooled to 40°C and evacuated at the same time. At this step, all the hydrogen was sucked away from the surface of the platinum, which was studied by reabsorbing hydrogen incrementally. The hydrogen was incrementally dosed at 40°C at elevated pressure. Then, the first isotherm was obtained. The extrapolation back to zero pressure method was used to calculate the adsorbed volume. To quantify the amount of reversibly adsorbed hydrogen, the sample was evacuated for 5 min at 40°C to remove the weakly adsorbed (physisorbed) and the second isotherm was determined.

3.2.3 Methane Reforming with Carbon Dioxide

All catalysts were crushed and sieved to smaller than 0.125 mm to prevent the particle size effect. Before the reaction, the catalysts were pretreated in He with the flow rate of 15 ml/min from room temperature to 500°C at the rate of 10°C/min and then reduced in H₂ with the flow rate of 30 ml/min for 1 hour. Then, the system was flushed with 15 ml/min of He for 30

minutes at 500°C. After that, the same sample was then heated in He (15 ml/min) to 800°C at the rate of 10°C/min, which was the reaction temperature. When all the above steps had been completed, the feed gas mixture was fed into the reactor.

3.2.3.1 Effects of CH₄/CO₂ Ratio

The Pt/5CeZ was used at a GHSV of 4777500 h⁻¹ by varying the CH₄/CO₂ ratios according to Table 3.4.

Table 3.4 Reactant compositions

CH ₄ /CO ₂	vol% CH ₄	vol% CO ₂	vol% He
1/1	20	20	60
2/1	40	20	40
3/1	60	20	20
1/2	20	40	40

The deactivation rate of the catalysts was then analyzed for the effects of CH₄ to CO₂ ratio by comparing the methane and carbon dioxide conversions, and H₂/CO product ratio.

3.2.3.2 Effects of Gas Hour Space Velocity (GHSV)

In this study, the Pt/5CeZ was tested at a CH₄/CO₂ ratio of 2/1. A GHSV was varied by changing the total flow rate of the inlet gases and bed height of the catalysts as shown in Table 3.5.

The deactivation rate of the catalysts was then analyzed for the effects of CH₄ to CO₂ ratio by comparing methane and carbon dioxide conversions, and H₂/CO product ratio.

Table 3.5 GHSV applied in this work

GHSV x 10 ⁻⁵ (h ⁻¹)	Total flow rate (cm ³ /min)	Bed height (cm)
2.390	100	0.20
3.183	100	0.15
4.775	150	0.15
6.366	200	0.15

3.2.3.3 *Effects of Promoters*

The Pt/3CeZ, Pt/5CeZ, Pt/7CeZ, Pt/9CeZ and Pt/3YZ, Pt/5YZ, Pt/7YZ, Pt/9YZ catalysts were studied. The experiment was carried on the most suitable CH₄/CO₂ ratio and GHSV received from 3.2.3.1 and 3.2.3.2. This effect was compared with Pt/Z catalysts. The activity and stability of the catalysts were considered by comparing the methane and carbon dioxide conversions, and H₂/CO product ratio.

3.2.3.4 *Effects of Mixed-promoter*

This study concentrated on the effects of catalysts loaded with Ce and Y together on ZrO₂ support. Two preparation techniques, impregnation and co-precipitation, were used. The amount of promoters loading was varied. The effect of calcination temperature was also studied when using the co-precipitation technique. Characteristics, activity and stability of the catalysts were observed by comparing the methane and carbon dioxide conversions, and H₂/CO product ratio.