

CHAPTER III

EXPERIMENTAL SECTION

3.1 Experimental Setup

A schematic of the experimental setup used in this study is shown in Figure 3.1. It can be divided in three sections; (i) gas mixing, (ii) reaction, and (iii) analytical.

3.1.1 Gas Mixing

The reactant gases mixture was prepared to a desired concentration and flow rate before being flowed to the catalytic reactor. Methane (99.97%, Praxair Distribution Inc.), oxygen (99.7%, Praxair Distribution Inc.) and carbon dioxide (99.999%, Thai Industrial Gas Public Co., Ltd.) were used as reactant gases for the reaction. Helium (99.99%, Thai Industrial Gas Public Co., Ltd.) was used as the diluent gas for the reaction and the purge gas for the catalyst reduction. Hydrogen (99.99%, Thai Industrial Gas Public Co., Ltd.) was used as the reduction gas. All gases were passed through a 7-micron stainless steel filter to remove any small particles in the gases. Sierra mass flow controllers (Model 904-PE-I1-PM) equipped with a control box (Model 904C-PE-I1-BM) and AALBORG mass flow controller (Model GFC 17) were used to control the volumetric flow rate of each gas. Check valves were installed to prevent deterioration of the mass flow controller from backpressure.

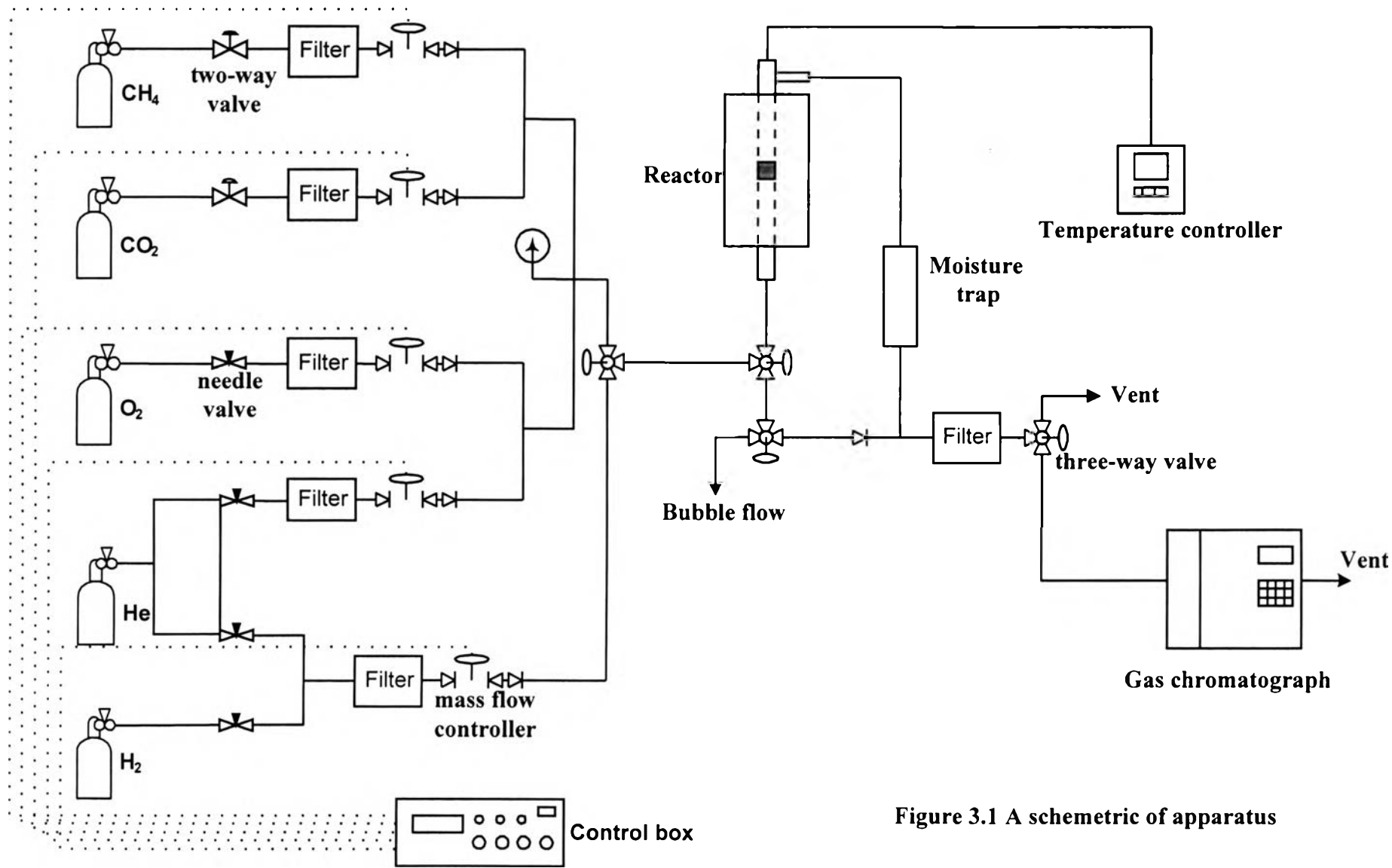


Figure 3.1 A schematic of apparatus

3.1.2 Reaction

A 4-mm-inside-diameter quartz reactor used as a catalytic reactor was loaded with 0.02 g of catalyst. The catalyst was held in place with quartz wool, approximately 0.02 g at the bottom and 0.02 g on the top of the catalyst, plugged at the center of the reactor. The reactor was placed in a tubular furnace, which was controlled by an OMRON temperature controller (Model E5C5) using a K-type thermocouple. A variable autotransformer (Type 3PN1520), obtained from the Staco Energy Product Co. was used to control the electrical current to the temperature controller with the maximum variation of ± 5 °C at steady state. The exiting gas was fed through a moisture trap, packed with silica gel, to remove water from the reaction before going to the gas analytical instrument.

3.1.3 Analytical

The product gases leaving the reactor were analyzed for H₂, CO, CH₄, and CO₂ by a Hewlett Packard (HP 5890 series II) gas chromatograph (GC) using the Hayesep DB 100/120 packed column, 4m x 1/8in, stainless steel with a thermal conductivity detector (TCD). A 6-port valve was used for the sample injection and nitrogen gas (99.99%, Thai Industrial Gas Public CO., Ltd.) was used to drive the auto-sampling valve. Helium was used as a carrier gas at a flow rate of 15 ml/min. The injector temperature, oven temperature, and detector temperature were set at 110, 120, and 130 °C, respectively. Samples were taken from the reactor effluent and analyzed every 15 minutes. The detector output was fed to an on-line computer running the HP Chemstation to automatically evaluate data and report the results.

3.2 Experimental Procedure

3.2.1 Catalyst Preparation

Two catalysts, 1.5 wt% Pt supported on ZrO_2 and 1.5 wt% Pt supported on Ce-doped ZrO_2 were prepared by incipient wetness impregnation of the calcined support with a solution of the metal salt. The ZrO_2 support was prepared by calcining Zr(OH)_4 , which was obtained from the MEI chemicals, in the stagnant air at 800 °C for 4 hours. The Ce-doped support was obtained by aqueous impregnation of $\text{CeN}_3\text{O}_9 \cdot 6\text{H}_2\text{O}$ (99%, Fluka Co., Ltd.) to Zr(OH)_4 . The incipient wetness of the Zr(OH)_4 was 0.1 ml/g and the weight percent of Ce in the final materials was varied from 3%, 5%, and 7%. The materials used to prepare all supports were shown in Table 3.1. After $\text{CeN}_3\text{O}_9 \cdot 6\text{H}_2\text{O}$ was impregnated to ZrO_2 , the material was then dried at 110 °C for 12 hours, and calcined at 800 °C for 4 hours. The incipient wetness of Ce-doped ZrO_2 was 0.58 ml/g.

Table 3.1 The amounts of Zr(OH)_4 and $\text{CeN}_3\text{O}_9 \cdot 6\text{H}_2\text{O}$ used for catalyst preparation (based on 1 g of ZrO_2).

Catalyst	Zr(OH)_4 (g)	$\text{CeN}_3\text{O}_9 \cdot 6\text{H}_2\text{O}$ (g)
ZrO_2	1.2924	-
3%Ce ^a	1.2924	0.0958
5%Ce ^b	1.2924	0.1633
7%Ce ^c	1.2924	0.2333

^a 3%Ce-doped ZrO_2

^b 5%Ce-doped ZrO_2

^c 7%Ce-doped ZrO_2

Finally, the supports were impregnated with $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (99%, Merck Chemical Co., Ltd.). The catalyst was then dried at 110 °C for 12 hours, and calcined at 400 °C for 2 hours.

3.2.2 Catalyst Characterization

3.2.2.1 *Surface Area Measurement*

The surface area of catalyst was measured by a Quantachrome Corporation Autosorb-1, employing nitrogen gas at liquid nitrogen temperature (77 K). An adsorption process went on until the equilibrium was established. Before starting the analysis, 0.3 ± 0.2 g of sample was outgassed under vacuum in the sample cell at 200 °C in the flow of He (99.99%, Thai Industrial Gas Public Co., Ltd.) for at least 1 hours to eliminate any volatile adsorbates on the surface. The volume-pressure data were utilized to calculate the five point BET (Brunauer, Emmett, and Teller) surface area, total pore volume, and average pore diameter.

3.2.2.2 *X-ray Diffraction (XRD) Analyses*

X-ray diffraction technique was used to identify the internal structure, bulk phase, and composition of crystalline material. X-ray diffraction pattern is unique for each crystallite substance, so chemical identity can be assumed. Furthermore, it is possible to make a relatively quantitative analysis by comparing the intensity of the diffraction lines. For the same crystalline substance of two different samples, the higher intensity shows the higher content.

A Philips X-ray diffractometer system (PW 3020) equipped with a graphite monochromator and a Cu tube for generating a CuK radiation was used to obtain the XRD patterns. The sample was ground to a fine homogeneous powder and was held in the beam in thin-walled glass. Constructive interference was achieved with monochromatic irradiation by varying the angle of incidence (2 to 90 degrees) with the scan speed of 5

degrees/min and scan step of 0.02 degree. The digital output of the proportional X-ray detector and the goniometer angle measurements were sent to an on-line microcomputer for storage and subsequent data analysis by PC-APD version 3.5B.

3.2.3 Methane Reforming with Carbon Dioxide

All experiments were investigated using 0.02 g of fresh catalyst, less than 0.125 mm in diameter. The catalyst was heated in He at a flow rate of 15 ml/min from room temperature to 500 °C, which was the reducing temperature. The catalyst was then reduced in H₂ with the flow rate of 30 ml/min for 1 hr. After that, the system was flushed with He at a flow rate of 15 ml/min for 30 minutes at 500 °C, and heated to 800 °C prior to reaction.

After the reaction, the used catalysts were analyzed by Temperature Programmed Oxidation (TPO) analyzer to determine the amount of carbon deposited on the catalysts.

3.2.3.1 *Effects of Oxygen Addition*

The effect of oxygen addition was investigated at the CH₄:CO₂ ratio of 2 and a total flow rate of 150 ml/min. Oxygen was varied from 3-9%. Each experiment was tested at 800 °C for approximately 15 hours. The various gas compositions used were presented in Table 3.2.

3.2.3.3 *Effects of Promoter Concentrations*

This effect was investigated with constant 1.5 wt% Pt loading. The tests were conducted using Pt/ZrO₂ catalyst and three promoted catalysts with different percentages of cerium (3%, 5%, and 7% Ce). The experiments were carried out with the same gas compositions used in the effect of oxygen addition study.

Table 3.2 Gas compositions for the effects of oxygen addition study (Total flow rate 150 ml/min).

Test no.	%O₂	CH₄ (ml/min)	CO₂ (ml/min)	O₂ (ml/min)	He (ml/min)
1	0	75	37.5	0	37.5
2	3	75	37.5	4.5	33.0
3	7	75	37.5	10.5	27.5
4	9	75	37.5	13.5	24.0