CHAPTER III
EXPERIMENTAL

3.1 Equipment and Materials

3.1.1 <u>Equipment</u>

1) Gas chromatographs (Shimadzu, GC-17A and GC-14B)

2) Scanning electron microscope (Hitachi, Tabletop TM3000)

3) Surface area analyzer (Quantachrome, Autosorb-1MP)

4) TPR analyzer (SRI model 110 TCD detector)

5) TPO analyzer (SRI model 110 FID detector)

6) Transmission electron microscope (JEOL, JEM-2010)

7) X-ray diffractometer (Rigaku, SmartLab)

8) X-ray fluorescence spectrometer (Panalytical Axios, PW 4400)

9) X-ray photoelectron spectroscope (AXIS ULTRA DLD)

10) Thermogravimetric and differential thermal analyzer (Perkin Elmer/Pyris Diamond)

3.1.2 <u>Materials</u>

1) Gases: all of which were supplied by Praxair (Thailand) Co., Ltd.

- Helium (He, 99.99 % purity)
- Hydrogen (H_2, 99.95 % purity)
- Nitrogen (N_2, 99.99 % purity)
- Oxygen (O_2, 99.70 % purity)

2) Chemicals

- Nickel (II) nitrate hexahydrate (97 % purity, Sigma-Aldrich.)
- Cerium (III) nitrate hexahydrate (99 % purity, Sigma-Aldrich.)
- Zirconium oxide chloride octahydrate (99 % purity, Merck.)
- Urea (99 % purity, Fluka Chemie A.G.)
- Acetic acid, (99.7 % AR grade, RCI Labscan.)
- Ethanol (96 % AR grade, RCI Labscan.)

3.2 Experimental Procedures

3.2.1 Catalyst Preparation

3.2.1.1 $Ce_{0.75}Zr_{0.25}O_2$ Support

$Ce_{0.75}Zr_{0.25}O_2$ support was prepared via urea hydrolysis method form salt solutions of $Ce(NO_3)_3 \cdot 6H_2O$ (99.00 %) and $ZrOCl_2 \cdot 8H_2O$ (99.00 %). Support was prepared in the form of mixed oxide solid solution with empirical formula: $Ce_{1-x}Zr_xO_2$, in order to obtain $Ce_{0.75}Zr_{0.25}O_2$, the ceria-to-zirconia molar ratio was determined from the volume proportion of each metal salt aqueous solution (0.1 M) added. Then, 0.4 M of urea solution was added with a volume ratio of salt to urea solution equal to 2:1. The mixture was kept at 100 °C for 50 h, then cooled down to room temperature following with filtration and washed with ethanol in order to separate a gel support from the solution. Afterwards, it was dried overnight in an oven at 110 °C followed by calcination at 500 °C for 4 h.

3.2.1.2 $Ce_{0.75}Zr_{0.25}O_2$ Supported Nickel Catalyst: Impregnation

The $Ce_{0.75}Zr_{0.25}O_2$ support (as prepared in Section 3.2.1.1) was impregnated with an aqueous solution of $Ni(NO_3)_3.6H_2O$ at 15 wt% Ni. The support was heated at 50-60 °C on a hotplate while impregnated to prevent the support from forming slurry. The impregnated support was dried at 110 °C overnight and then calcined at 500 °C for 4 h. The resultant catalyst was ground and sieved to a particle size of 180-250 μm (60 - 80 mesh).

3.2.2 Catalyst Characterization

3.2.2.1 BET Surface Area

BET surface area was determined by N_2 adsorption at -196 °C using a Quantachrome Autosorb-1MP. Prior to the analysis, the samples were out gassed to eliminated volatile adsorbents on the surface at 250 °C for 12 h. The quantity of gas adsorbed onto or desorbed from a solid surface were measured at 5 equilibrium vapor pressure (P/P_o) values of 0.1115, 0.1615, 0.2115, 0.2615, and 0.3115 by the static volumetric method (Equation 3.1). The adsorption data were calculated using Brunauer–Emmett–Teller (BET) method as shown in Equation 3.2:

$$\frac{P/P_0}{W\left(1 - P/P_0\right)} = \frac{1}{W_m C} + \frac{C-1}{W_m C}\left(P/P_0\right)$$

(3.1)

where

W = the weight of gas adsorbed at relative pressure P_0 (g)

W_m = the weight of adsorbate constituting a monolayer of

surface coverage (g)

C = a constant that is related to the energy of adsorption in

the first adsorbed layer and magnitude of adsorbate

interaction and then the surface of the sample will be

calculated by

Surface area of sample = $\dfrac{W_m A_{nitrogen}\left(6.02 \times 10^{23}\right)}{Mw_{nitrogen}}$ (3.2)

where

$A_{nitrogen}$ = the crossed-section area of one molecule nitrogen

= 0.162 nm^2 at -196 °C

$Mw_{nitrogen}$ = the molecular weight of nitrogen (g/mol)

3.2.2.2 H_2-Temperature Programmed Reduction

Temperature programmed reduction of hydrogen (H_2-TPR) were carried out using an SRI model 110 TCD detector. The samples were pretreated in N_2 atmosphere at 150 °C for 30 min prior to running the TPR experiment, and then cooled down to room temperature with N_2 feeding. A 5 % H_2/N_2 gas was used as a reducing gas. The temperature was raised at a constant rate of 10 °C/min from room temperature to 900 °C. The amount of H_2 consumption as a function of temperature was determined from a TCD signal.

3.2.2.3 Temperature Programmed Oxidation (TPO)

Temperature Programmed Oxidation (TPO) technique was employed to analyze the amount and characteristic of the coke deposited on the spent catalyst. The spent catalyst was performed in a continuous flow of 5 % O_2 in He while the temperature will be linearly increased with a heating rate of 10 °C/min. The CO_2 produced by the oxidation of the coke species were converted to methane using

a methanizer filled with 15%Ni/Al$_2$O$_3$ and operated at 415 °C in the presence of H$_2$. The evolution of methane was analyzed using a FID detector.

3.2.2.4   X-ray Diffraction (XRD)

A Rigagu X-ray diffractometer (XRD) system equipped with a RINT 2000 wide-angle goniometer using CuK$_\alpha$ radiation (1.5406 Å) and a power of 40 kV×30 mA were used for examination of the crystalline structure. The sample was ground to a fine homogeneous powder and held on thin-walled glass plate against the X-ray beam. The intensity data was collected at 25 °C over a 2θ range of 20° to 80° with a scan speed of 5° (2θ)/min and a scan step of 0.02° (2θ).

3.2.2.5   X-Ray Fluorescence (XRF)

Ceria-Zirconia support was characterized by XRF-semi quantitative method over X-ray Fluorescence Analyzer (model: Panalytical Axios, PW 4400) in order to ensured that the support was completely synthesized and close to a desired Ce to Zr molar ratio of 3:1 and detected weight percent (wt%) of Ni metal at the catalyst surface.

3.2.2.6   X-ray Photoelectron Spectroscopy (XPS)

XPS is used for determination the surface composition, chemical state, and oxidation state of the fresh and spent catalysts. The XPS spectra were obtained by using an incident chromatic AlKα X-ray source (1253.6 eV) operated at 14.8 kV and 20 mA for excitation and a hemisphere analyzer (Thermo VG scientific). The high-resolution XPS spectra were composite average of 10 scans with a passing energy of 50 eV. The pressure in the analysis chamber was in the range of 10^{-8} Torr during data collection. The binding energy was adjusted to the C 1s peak at 285 eV. Data analysis and curve de-convolution were accomplished by using the Thermo Advantage Spectra Data Processor software.

3.2.2.7   Scanning Electron Microscopy (SEM)

SEM were carried out using a Tabletop microscope TM 3000 (Hitachi) operated at 5 kV and 15 mA and used for examination of the sample morphologies. Prior to scanning, the sample was dried overnight at 110 °C followed by Pt coating (model: E-1010) operated at 12 mA for 150 s.

CO, CO_2, CH_4 and O_2. Since the presences of water disturb an analysis in those TCD columns, a condenser was placed before to ensure that the condensable products were totally condensed, leaving the non-condensable products to pass through a moisture trap column before being analyzed by GC-TCD. The schematic diagram of the experimental system is presented in Figure 3.2. The data of instrumental calibration are provided in Appendices A-D.
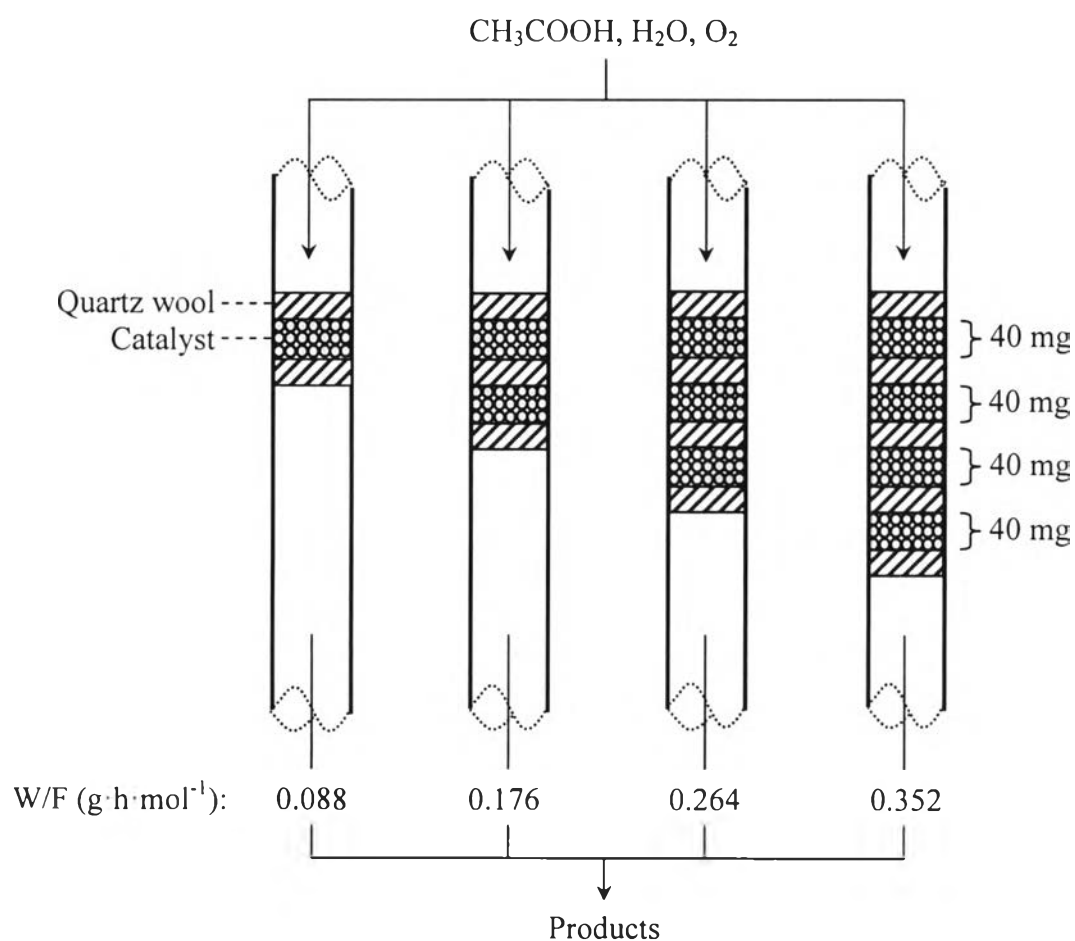

Figure 3.1 Schematic diagram of the catalyst packing for steam reforming, partial oxidation, and autothermal steam reforming of acetic acid.
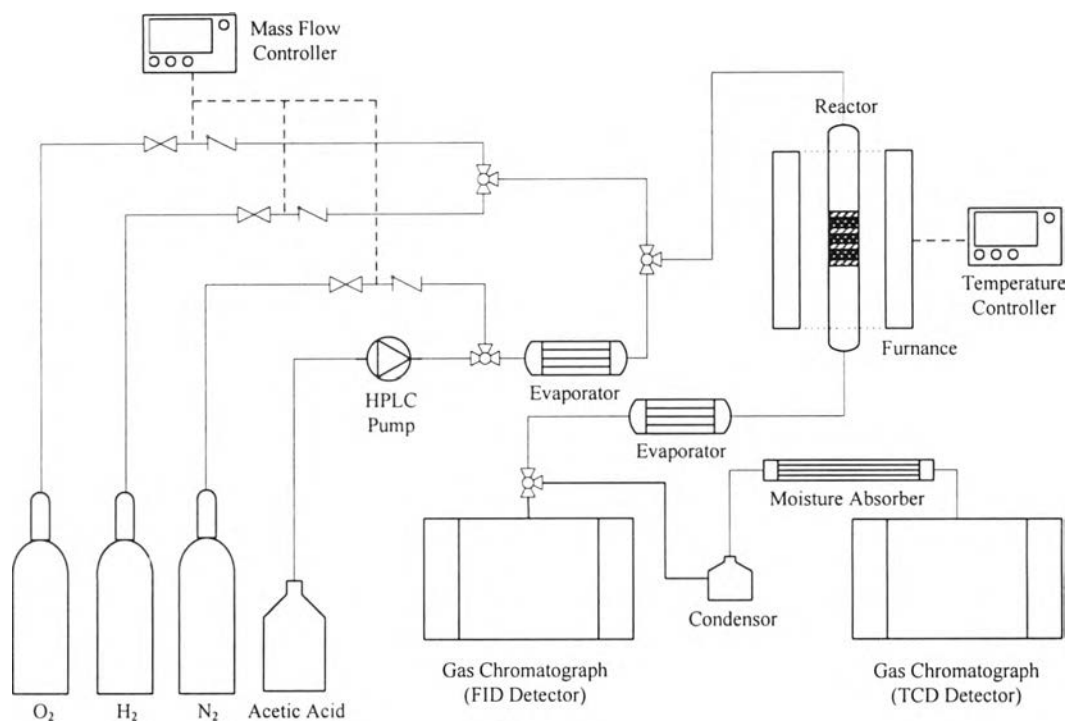
Figure 3.2 Schematic diagram of the experimental system for steam reforming, partial oxidation, and autothermal steam reforming of acetic acid.

3.2.4 Experimental Procedures

The experiments were carried out into 3 parts including steam reforming (SR), partial oxidation (POX), and autothermal steam reforming (ATR) of acetic acid. Prior to the catalytic activity testing, the SR, POX, and ATR of acetic acid were firstly performed over the bare support and quartz wool under conditions as similar to those experiments which are summarized in the following sub-sections.

Before running the reactions, the catalyst was reduced in situ with a flow of 50 % H_2 in N_2 gas at 500 °C for 2 h. Gaseous production and coke formation from each process were characterized.

3.2.4.1 Steam Reforming Conditions

Acetic acid aqueous solution with steam-to-carbon (S/C) molar ratio equal to 6 was pumped into an evaporator and vaporized at 160 °C. N_2 was applied to carried acetic acid and steam to the catalytic reactor with the total flow rate of 170 cm^3/min at a constant temperature of 650 °C. The gaseous products

were analyzed by GC-FID and GC-TCD, respectively. Then, the spent catalyst of each layer was characterized by TEM, TG-DTA, TPO, and XPS.

3.2.4.2 *Partial Oxidation Conditions*

Pure acetic acid was pumped into an evaporator and vaporized at 160 °C. N_2 was applied to carried acetic acid and then mixed with O_2 (O_2/Acetic acid molar ratio of 0.35:1) by total flow rate of 170 cm^3/min at a constant temperature of 650 °C. The gaseous products were analyzed by GC-FID and GC-TCD, respectively. Then, the spent catalyst of each layer was characterized by TEM, TG-DTA, TPO, and XPS.

3.2.4.3 *Autothermal Steam Reforming Conditions*

Acetic acid aqueous solution with S/C molar ratio equal to 6 was pumped into an evaporator and vaporized at 160 °C. N_2 was applied to carried acetic acid, steam and O_2 (O_2/Acetic acid molar ratio of 0.35:1) with total flow rate of 170 cm^3/min at a constant temperature of 650 °C. The gaseous products were analyzed by GC-FID and GC-TCD, respectively. Then, the spent catalyst of each layer was characterized by TEM, TG-DTA, TPO, and XPS.

3.2.5 Catalytic Activity Measurements

Acetic acid and oxygen conversion were defined from a ratio of reactant consumed to reactant in feed as shown in Equations 3.3 and 3.4, respectively while a C-C bond breakage conversion of acetic acid (Equation 3.5) was measured from a ratio of the gaseous single carbon compounds (CO, CO_2, and CH_4) in the product steam to the acetic acid reactant. The product yield was also calculated from a ratio of the actual product to the theoretical amount of product produced from SR, POX, and ATR of acetic acid as presented in Equations 3.6-3.12. The carbon-containing selectivity (Equations 3.13-3.16) was calculated from a ratio of interested carbon compound to the overall carbon compounds produced including CO, CO_2, CH_4, and CH_3COCH_3.

3.2.5.1 Conversions

Acetic acid (AcOH) conversion; $X_{Ac}(\%)$

$$= \frac{\text{mol AcOH,in - mol AcOH,out}}{\text{mol AcOH,in}} \times 100 \qquad (3.3)$$

Oxygen (O_2) conversion; $X_{O_2}(\%)$

$$= \frac{\text{mol } O_2\text{,in - mol } O_2\text{,out}}{\text{mol AcOH,in}} \times 100 \qquad (3.4)$$

C-C bond breakage conversion

$$= \frac{\text{mol } CH_4\text{,out} + (2 \times \text{mol CO,out}) + \text{mol } CO_2\text{,out}}{2 \times \text{mol AcOH,in}} \times 100$$

$$(3.5)$$

3.2.5.2 Yields

$$H_2 \text{ yield (\%) for SR} = \frac{\text{mol } H_2\text{,out}}{4 \times \text{mol AcOH,in}} \times 100 \qquad (3.6)$$

$$H_2 \text{ yield (\%) for POX} = \frac{\text{mol } H_2\text{,out}}{1 \times \text{mol AcOH,in}} \times 100 \qquad (3.7)$$

$$H_2 \text{ yield (\%) for ATR} = \frac{\text{mol } H_2\text{,out}}{3.3 \times \text{mol AcOH,in}} \times 100 \qquad (3.8)$$

$$CO \text{ yield (\%)} = \frac{\text{mol CO,out}}{2 \times \text{mol AcOH,in}} \times 100 \qquad (3.9)$$

$$CO_2 \text{ yield (\%)} = \frac{\text{mol } CO_2\text{,out}}{2 \times \text{mol AcOH,in}} \times 100 \qquad (3.10)$$

$$CH_4 \text{ yield (\%)} = \frac{\text{mol } CH_4\text{,out}}{2 \times \text{mol AcOH,in}} \times 100 \qquad (3.11)$$

CH_3COCH_3 yield (%)

$$= \frac{2 \times \text{mol } CH_3COCH_3\text{,out}}{\text{mol AcOH,in}} \times 100 \qquad (3.12)$$

3.2.5.3 Selectivities

$$\text{CO selectivity (\%)} = \frac{\text{mol CO,out}}{A} \times 100 \qquad (3.13)$$

$$\text{CO}_2 \text{ selectivity (\%)} = \frac{\text{mol CO}_2\text{,out}}{A} \times 100 \qquad (3.14)$$

$$\text{CH}_4 \text{ selectivity (\%)} = \frac{\text{mol CH}_4\text{,out}}{A} \times 100 \qquad (3.15)$$

CH_3COCH_3 selectivity (%)

$$= \frac{\text{mol CH}_3\text{COCH}_3\text{,out}}{A} \times 100 \qquad (3.16)$$

where A = mol CO,out + mol CO$_2$,out + mol CH$_4$,out
$+ (4 \times$ mol CH$_3$COCH$_3$,out)