



CHAPTER III EXPERIMENTAL

3.1 Materials

The bio-ethanol used for the catalytic dehydration of ethanol was obtained from Saphip Company Limited at the concentrations of 40-50%, 95%, and 99.5% ethanol.

3.2 Equipment

1. Bench-scale U-tube reactor with electrical furnace
2. Syringe pump
3. Ice-water cooling system
4. Agilent Technologies 6890, Gas chromatography (GC)
5. Perkin Elmer/Pyris Diamond (Thermogravimetric/Differential Thermal Analysis, TG/DTA)
6. Thermo Finnigan Sorptomatic 1990 (Surface Area Analyzer)
7. Oxford/6111 (Scanning Electron Microscope, SEM)

3.3 Chemicals

1. Magnesium hydrogen phosphate tri-hydrate ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$)
2. Gamma Alumina ($\gamma\text{-Al}_2\text{O}_3$) from NanoScale Corporation, USA
3. He gas (High purity grade, 99.99% purity)
4. Quartz wool

3.4 Methodology

3.4.1 Catalyst Preparation

The preparation of $\text{MgHPO}_4/\gamma\text{-Al}_2\text{O}_3$ catalyst was accomplished based on the procedure described in Kojima *et al.* (1981). MgHPO_4 was physically mixed

in the proportion of 0.5 wt% with γ -Al₂O₃ obtained from NanoScale Corporation company, USA. Then, the resulting mixture was dried in an oven at 110 °C for 3 hours and subsequently calcined in a furnace at 600 °C for 3 hours with the heating rate of 10 °C/min. Before the MgHPO₄/γ-Al₂O₃ catalyst was used in the catalytic reaction process, it was pelletized using a hydraulic pelletizer. Then, the pellets were crushed and sieved for 20-40 mesh.

3.4.2 Catalytic Reaction Process

The reaction process used in this study was shown in Figure 3.1. The catalytic dehydration process was performed in an isothermal fixed bed reactor at the atmospheric pressure. The U-tube reactor was made of S316 stainless steel with 10 mm I.D. and heated by an electrical furnace. A catalyst sample sieved for 20-40 mesh was loaded into the reactor and held in place by using quartz wool support. After that, the catalyst bed was heated up to a desired reaction temperature in a stream of helium prior to reaction. The temperature of catalyst bed was controlled by using thermocouple in a range of 370 °C to 460 °C. The bio-ethanol solution (40-50%, 95%, and 99.5% ethanol) obtained from Saphip Company Limited was fed by using a syringe pump into the catalyst bed at LHSV of 1.0 h⁻¹. The reaction products were passed through an ice-water cooling system where water was condensed. The gaseous products leaving from an ice-water cooling system were analyzed by an online analysis of gas chromatograph.

3.4.3 Products Analysis

The gaseous products mainly consisting of ethylene, and small amount of ethane propylene, C₄ and ethanol were analyzed by an online analysis of gas chromatograph (Agilent Technologies 6890 Network GC system, using HP-PLOT Q column: 30 m x 0.32 mm ID and 20 μm film thicknesses, and DB-WAX column : 30 m x 0.32 mm ID and 20 μm film thicknesses). The gas chromatograph was provided with a thermal conductivity detector (TCD) and a flame ionization detector (FID), and helium was used as the carrier gas.

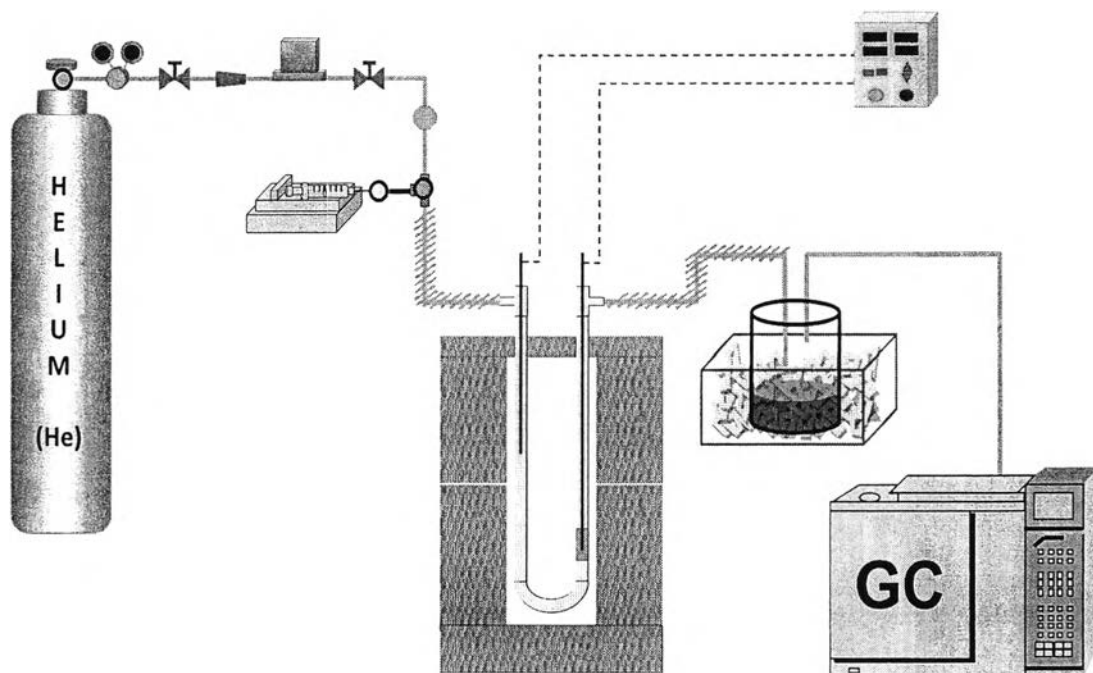


Figure 3.1 A scheme for the catalytic dehydration of bio-ethanol to ethylene process.

3.4.4 Catalyst Characterization

3.4.4.1 *Thermogravimetric/Differential Thermal Analysis (TG/DTA)*

The coke formation on spent catalysts was determined by Thermogravimetric/Differential Thermal Analysis (TG/DTA). The samples were heated from the room temperature to 800 °C with the heating rate of 10 °C/min. Nitrogen and oxygen set flow rate about 100 ml/min and 200 ml/min, respectively.

3.4.4.2 *Scanning Electron Microscope (SEM)*

The microstructure of the sample was identified by the scanning electron micrographs (JEOL/JSM 5200). The SEM uses the electrons that are backscattered or emitted from the specimen surface. The samples were placed on a stub and coated with gold by using ion sputtering device. The specimen was scanned with a narrow beam of electrons. The quantity of electrons scattering or emitting as the primary beam bombards each successive point of the metallic

specimen surface is counted by an electron detector and used to modulate the intensity of a second electron beam and forms an image on a TV screen.

3.4.4.3 Surface Area Analyzer (SAA)

The specific surface area, the total pore volume, and the pore size of catalyst were determined by Brunauer-Emmett-Teller (BET) technique and using Thermo Finnigan, Sorptomatic 1990 system. This technique was based on the physical adsorption of nitrogen gas at 77 K. Before starting characterization, the catalyst sample was out-gassed by heating under vacuum at 300 °C for 6 hours in order to remove moisture. The specific surface area and the pore size of catalyst were obtained from the twenty-two-point nitrogen adsorption and desorption isotherm plot. The pore size distribution was calculated using the BET equation as shown in Equation 1.

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

where:

W = weight of gas adsorbed at relative pressure P_0

W_m = weight of adsorbate constituting a monolayer of surface coverage

P = pressure of gas

P_0 = saturated vapour pressure of the liquid at the operating temperature

C = constant that is related to the energy of adsorption in the first adsorbed layer and magnitude of adsorbate/adsorbent interaction.

The surface area can be calculated by Equation 2.

$$A = \frac{W_m A_{\text{nitrogen}} \times 6.02 \times 10^{23}}{MW_{\text{nitrogen}}} \quad (2)$$

where:

A = surface area of sample

A_{nitrogen} = cross-section area of one molecule nitrogen (0.162 nm² at -196 °C)

MW_{nitrogen} = molecular weight of nitrogen (28 g/g-mol).