CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Catalyst Preparation Materials

(1) Aluminum isopropoxide ($Al(OC_3H_7)_3$) of 98% purity

[Fluka Co., Ltd.]

(2) Silver nitrate ($AgNO_3$) of 99.9% purity

[BDH laboratory supplies]

(3) 1,3-Butanediol anhydrous ($C_2H_4(OH)C_2H_4OH$) of 99% purity

[Aldrich chemical Inc.]

(4) Aliminum oxide, fused (α-Al_2O_3) of 99% purity

[Aldrich chemical Inc.]

3.1.2 Reactant Gases

(1) Ethylene (C_2H_4) 40 ± 1.68% in helium

[Thai Industrial Gas Public Co., Ltd.]

(2) Ultra high purity (UHP) oxygen (O_2) 20 ± 0.2% in helium

[Thai Industrial Gas Public Co., Ltd.]

(3) Ultra high purity (UHP) hydrogen (H_2) (99.999%)

[Thai Industrial Gas Public Co., Ltd.]

(4) High purity (HP) helium (He) (99.99%)

[Thai Industrial Gas Public Co., Ltd.]

3.2 Catalyst Preparation

In this study the silver supported on alumina high surface area (HSA) catalysts were prepared by the sol-gel method. The different silver loadings of 3, 5, and 10 wt% were used. The second catalyst, silver supported on low surface area (LSA) α-alumina was also prepared by the incipient wetness impregnation method. Catalysts with different silver loadings of 13, 15, 17, 20 wt% were prepared.

3.2.1 Sol-Gel Method

Fibrillar aluminum hydroxide sols were obtained by addition of alumina isopropoxide (AIP) to hot water (85^0C) in ratio of 1 g to 10 ml. And then added nitric acid in the AIP/HNO$_3$ molar ratio of 1 to 0.195. After being stirred for a while, the sol solution became a clear solution. After that the solution of silver nitrate dissolved in 1,3-butanediol with AIP/1,3-butanediol molar ratio of 1 to 4 was slowly added to the fibrillar sol solution. During mixing, the temperature of this mixed solution was controlled constantly at 85^0C and continuously heated at this temperature for an hour after the completed addition of metal salt. Then the heating was stopped and solution was stirred at room temperature for 24 hours. After vigorous stirring, the solvents were eliminated by heating to form a gel. The gel was dried at 110^0C for a day.

After that the prepared catalyst was ground by mortar and separated into two different sizes by using sieves and then the catalyst was stored in a dessiccator. The catalyst size of -70 + 120 mesh was used in the present experiment. Alumina alone was also prepared from the fibrillar aluminum hydroxide sol in the same procedure.

3.2.2 Incipient Wetness Impregnation Method

The α-Al_2O_3 (Aldrich, 99%) support was heated at 550^0C in flowing air for 2 hours before impregnation with silver. After that this support was impregnated with $AgNO_3$ (Fluka, 99.99%), which dissolved in distilled deionized water, by adding drop by drop and then dried overnight at 110^0C in an oven and the catalyst was stored in a dessiccator. The size of prepared catalyst was -200 + 325 mesh.

3.3 Catalyst Characterization

3.3.1 BET Surface Area Measurement

The surface area, total pore volume, and average pore diameter of all prepared catalyst samples were determined by using Autosorb-1 Gas Sorption system (Quantachrome Corporation), which used the Brunauer-Emmett-Teller (BET) method. It operates by measuring the quantity of gases adsorbed onto or desorbed from a solid surface at some equilibrium vapor pressures. Nitrogen gas with cross sectional area of 1.62×10^{-2} nm^2 was employed as an adsorbate at a liquefied nitrogen temperature (77 K). Before adsorption, the sample amount of 800 mg were dried and outgassed in the sample cell at 300^0C for at least 2 hours to eliminate volatile adsorbents at the surface. The results were analyzed by Autosorb ANAGAS Software version 2.10.

3.3.2 X-ray Diffraction (XRD) Analysis

The XRD was utilized to identify the internal structure, bulk phase, and composition of crystalline catalyst. A Rigaku X-ray diffractometer system (RINT-2200) equipped with a graphite monochromator and a Cu tube for generating a CuK radiation (1.5406^0A) 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 may be achieved with monochromatic irradiation by varying the angle of incidence (20 to 90 degrees). The digital output of the proportional X-ray detector and the goniometer angle measurements are sent to an online microcomputer for the storage and subsequent data analysis. Crystallites can be found from the broadening of X-ray diffraction peak, measured at one-half of the height. An estimate of the dimension of the crystallites is calculated by the Scherrer formula (Equation 3.1).

$$d = 0.89 \, \lambda / \beta \, \text{Cos} \, \theta \qquad (3.1)$$

where

d = crystallite size

λ = wavelength

θ = diffraction angle

β = peak width at the middle height

3.4 Apparatus

The experimental apparatus used in this research is shown schematically in Figure 3.1. It consists of 3 parts: (i) gas mixing system, (ii) catalytic reactor, and (iii) gas analysis instrument.

3.4.1 Gas Mixing System

This section was for mixing of reactant gases before flowing to the catalytic reactor. Mass flow controllers (Sierra Instrument, model 840) regulated the flow-rates of O_2, C_2H_4, He, and H_2. All gases were passed through the 7-micron stainless steel filters for removing the particles in the gas. All fittings and tubings were made of stainless steel having outside diameters of 1/4" and 1/8" obtained from Swagelok Co., Ltd.

3.4.2 Catalytic Reactor

The size of the quartz glass fixed-bed reactor was ID 8 x 520 mm. The catalyst sample was placed between quartz wool in the middle of the reactor, which was placed in a heating mentle equipped with a PID controller (Yamatake.Honeywell, model SDC10). A thermocouple was inserted to control the temperature of the reaction in middle of the catalyst bed.

3.4.3 Gas Analysis Instrument

The gas chromatographic analysis was carried out using a Hewlett Packard 5890 Series II model gas chromatograph (GC) equipped with both thermal conductivity detector (TCD) and flame ionization detector (FID). A sampling valve at 110^0C equipped with a 200 µl sampling loop was applied to inject the reactor effluent gas into the GC for analysis. A Porapack N packed column (80/100, 12' x 1/8") connected to TCD was used to separate H_2, O_2, CO_2, and CH_4 at 70^0C, as well as C_2H_4, C_2H_6, and C_2H_4O at 150^0C. In addition, a GS-GasPro capillary column (15m x 0.32mm) connected to FID was also used to separate CH_4, C_2H_6, and C_2H_4 at 70^0C and C_2H_4O at 150^0C. The data were collected and analyzed using a Hewlett-Packard 3396 II integrator.

3.5 Catalytic Activity Measurement

Catalytic activity measurement for selective oxidation of ethylene with oxygen over both (HSA) Ag/Al_2O_3 sol-gel catalysts and (LSA) Ag/α-Al_2O_3 catalysts were carried out at atmospheric pressure in a fixed-bed flow reactor. The procedure of the activity measurement can be described as follows:

(a) The desired amount of catalyst sample was loaded and then pretreated with different conditions such as 20% O_2 at 300^0C for 2 hours, H_2
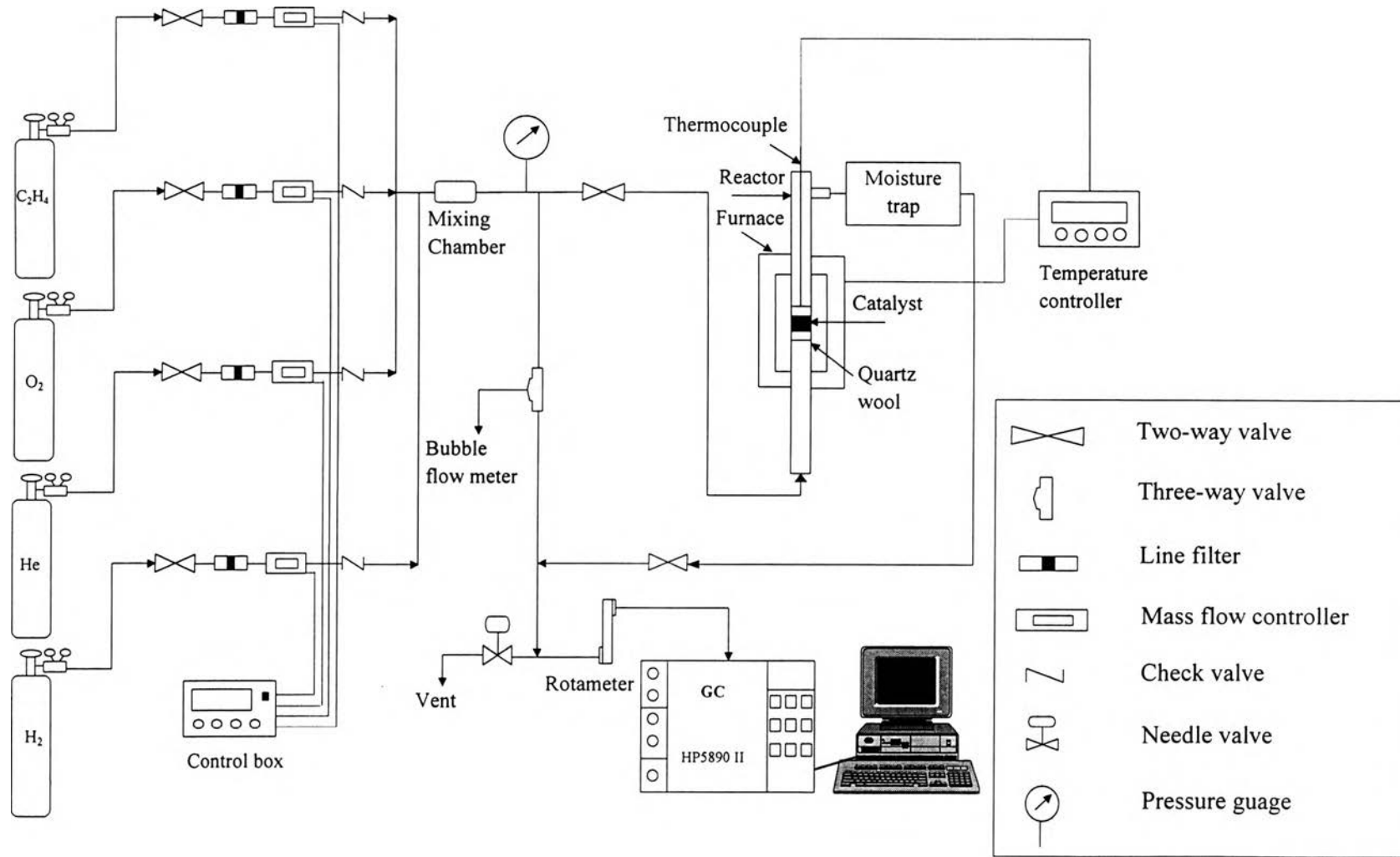
Figure 3.1 Schematic diagram of experimental setup.

at 400°C for 2.5 hours. After that cooled down to the desired reaction temperature with flowing helium.

(b) The reactant gas mixture containing desired concentrations of C_2H_4, O_2, and He was by passed to the analytical instruments in order to check the composition of the feed stream before passing through the reactor. To conduct the effect of hydrogen, 5% H_2 was fed to the feed gas stream.

(c) The mixture of reactant gases was passed through the catalyst bed at desired flow rate. Two sets of reaction temperature ranges of 100°C to 225°C at 25°C increment and 210°C to 270°C at 20°C increment were used. The composition of C_2H_4, O_2, H_2, CO_2, and C_2H_4O were measured at each temperature until the composition of these gases reached steady state.

3.5.1 Catalytic Activity Test for (HSA) Ag/Al₂O₃ Sol-Gel Catalyst

3.5.1.1 Effect of Silver Loading

The following conditions were used to determine the effect of silver loading on the catalytic activity.

Experimental Conditions	
Catalyst	3, 5, 10 wt% (HSA) Ag/Al₂O₃
Catalyst weight	0.2 g
Reactant composition (C_2H_4, O_2)	10%, 10%
Calcination of catalyst	Air (600°C, 5 hrs)
Pretreatment of catalyst	20% O_2 (300°C, 2 hrs)
Flow rate	100 ml/min
Space velocity	17,045 h^{-1}
Temperature	100 to 225°C

3.5.1.2 Effect of Hydrogen Gas

To determine the effect of hydrogen gas, the following conditions were used.

Experimental Conditions	
Catalyst	5, 10 wt% (HSA) Ag/Al_2O_3
Catalyst weight	0.2 g
Reactant composition (C_2H_4, O_2, H_2)	10%, 10%, 5%
Calcination of catalyst	Air (600^0C, 5 hrs)
Pretreatment of catalyst	20% O_2 (300^0C, 2 hrs)
Flow rate	100 ml/min
Space velocity	17,045 h^{-1}
Temperature	100 to 225^0C

3.5.1.3 Effect of Calcination and Oxidation-Reduction Method

The following conditions were used to study the effect of calcination and oxidation-reduction method.

Experimental Conditions	
Catalyst	10 wt% (HSA) Ag/Al_2O_3
Catalyst weight	0.44 g
Reactant composition (C_2H_4, O_2, H_2)	6%, 12%, 5%
(1) Calcination of catalyst	Air (600^0C, 5 hrs)
Pretreatment of catalyst	20% O_2 (300^0C, 2 hrs)
(2) Calcination of catalyst	10% O_2 (40 ml/min) (500^0C, 2hrs)
Pretreatment of catalyst	H_2 (20 ml/min) (400^0C, 2.5 hrs)
Flow rate	50 ml/min
Space velocity	4,000 h^{-1}
Temperature	210 to 270^0C

3.5.2 Catalytic Activity Test for (LSA) $Ag/\alpha-Al_2O_3$ Catalyst

3.5.2.1 Effect of Silver Loading

In order to determine the effect of silver loading on the catalytic activity, the following conditions were used.

Experimental Conditions	
Catalyst	13, 15, 17, 20 wt% (LSA) Ag/α-Al$_2$O$_3$
Catalyst weight	1.07 g
Reactant composition (C$_2$H$_4$, O$_2$)	6%, 12%
Calcination of catalyst	10% O$_2$ (40 ml/min) (500^{0}C, 2hrs)
Pretreatment of catalyst	H$_2$ (20 ml/min) (400^{0}C, 2.5 hrs)
Flow rate	50 ml/min
Space velocity	4,000 h^{-1}
Temperature	210 to 270^{0}C

3.5.2.2 Effect of Reactant Molar Ratio

The following conditions were used to determine the effect of reactant molar ratio on the catalytic activity.

Experimental Conditions	
Catalyst	15 wt% (LSA) Ag/α-Al$_2$O$_3$
Catalyst weight	1.07 g
Reactant composition (C$_2$H$_4$, O$_2$)	6%, 6% (C$_2$H$_4$:O$_2$ molar ratio: 1.0)
	6%, 9% (C$_2$H$_4$:O$_2$ molar ratio: 0.67)
	6%, 12% (C$_2$H$_4$:O$_2$ molar ratio: 0.5)
	30%, 8% (C$_2$H$_4$:O$_2$ molar ratio: 3.75)
Calcination of catalyst	10% O$_2$ (40 ml/min) (500^{0}C, 2hrs)
Pretreatment of catalyst	H$_2$ (20 ml/min) (400^{0}C, 2.5 hrs)
Flow rate	50 ml/min
Space velocity	4,000 h^{-1}
Temperature	210 to 270^{0}C

3.5.2.3 Effect of Calcination and Oxidation-Reduction Method

The following conditions were used to determine the effect of calcination and oxidation-reduction method.

Experimental Conditions	
Catalyst	15 wt% (LSA) Ag/α-Al₂O₃
Catalyst weight	1.07 g
Reactant composition (C_2H_4, O_2)	6%, 12%
(1) Calcination of catalyst	Air (600°C, 5 hrs)
Pretreatment of catalyst	20% O_2 (300°C, 2 hrs)
(2) Calcination of catalyst	10% O_2 (40 ml/min) (500°C, 2hrs)
Pretreatment of catalyst	H_2 (20 ml/min) (400°C, 2.5 hrs)
Flow rate	50 ml/min
Space velocity	4,000 h⁻¹
Temperature	210 to 270°C

3.6 Catalytic Activity Calculation

In this study, the activity of catalyst is defined in the terms of percentage selectivity to ethylene oxide (EO) and yield percent of EO (Yeung *et al.*, 1998).

The selectivity to EO, S, is defined as:

$$S = \frac{(C_{C_2H_4O})_{out}}{[(C_{C_2H_4})_{out} - (C_{C_2H_4})_{in}]} * 100 \tag{3.2}$$

The yield to EO, Y, is defined as:

$$Y = \frac{(C_{C_2H_4O})_{out}}{(C_{C_2H_4})_{in}} * 100 \tag{3.3}$$

where

C is concentration of chemical compound.