CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals for Catalyst Preparation

All chemicals used in catalyst preparation and analytical procedures were described as followed:

1. Aluminium oxide C (Al_2O_3) was obtained from Degussa AG.
2. Titanium oxide P25 (TiO_2) was obtained from Degussa AG.
3. Cerium (IV) Oxide (CeO_2), 99.9%, < 5 micron, was obtained from Aldrich.
4. Cerous nitrate hexahydrate ($Ce(NO3)_3 \cdot 6H_2O$, 99%, was obtained from Aldrich.
5. Silver Nitrate ($AgNO_3$), assay 99.9%, was obtained from Carlo Erba.
6. Hydrogen tetrachloroaurate (III) trihydrate ($HAuCl_4.3H_2O$), ACS, 99.99%, was obtained Alfa Aesar A Johnson Matthey Company.
7. Titanium (IV) butoxide or Tetrabutyl orthotitanate ($C_{16}H_{36}O_4Ti$), AR grade, was obatined from Fluka Chemie A.G.
8. Methanol (CH_3OH), AR grade of 99.8%, was obtained from Labscan.
9. Nitric acid (HNO_3), AR grade of 65%, was obtained from Labscan.
10. Urea (($NH_2)_2CO$), RPE grade, was obtain from Carlo Erba.
11. Hydrochoric acid (HCl) was obtained from Labscan.
12. Ammonium solution

3.1.2 Reactant Gases for Reaction and TPD Experiment

All reactant gases were obtained from Thai Industrial Gas Co., Ltd. as shown below:

1. Helium (HP grade)

2. 30% Ethylene balance with Helium

3. 15% Oxygen balance with Helium

4. Oxygen 97%

TPD reactant gases were obtained from Air Product Co., Ltd. as followed:

1. Nitrogen (HP grade)

2. 8% Oxygen in Helium

3.2 Catalyst Preparation Procedures

3.2.1   Incipient Wetness Method

3.2.1.1 Silver Catalysts

Silver catalysts were prepared by the incipient wetness method using aluminum oxide (fumed alumina, Degussa C, 85-115 m^2/g) with aqueous silver nitrate (Carlo Erba, 99.9%) solution to achieve nominal silver loadings of 10, 12, 14 and 16% wt. After impregnation, the catalyst precursors were dried at 110°C over night followed by calcination in air at 500°C for 5 h. After that, each catalyst was sieved in order to select grain sizes in the range of 212-425 µm for the activity studies.

With the above procedure, Ag on TiO_2 (Degussa P25, 60 m^2/g) and Ag on CeO_2 (Aldrich, 7 m^2/g) were prepared with aqueous silver nitrate solution to achieve nominal silver loadings of 10, 12, 14, 16% wt.

3.2.1.2 Gold-silver Catalysts

For the preparation of gold-silver on alumina catalyst, a silver catalyst with nominal 14% wt Ag loading was prepared and dried at 110°C for 2 h. Then, 18 g of this catalyst was divided into six aliquots. Five of these aliquots were impregnated with appropriate amounts of aqueous gold precursor ($HAuCl_4$, Alfa) solution, to achieve nominal gold loadings of 0.1, 0.3, 0.5, 0.7 and 1.0% wt. The sixth aliquot was impregnated with pure distilled water, without any precursor salts. After that, the six catalyst samples were dried at 110°C over night followed by calcination in air at 500°C for 5 h. The catalysts were sieved in order to select grain sizes in the range of 212-425 µm for the activity study.

3.2.1.3 Gold Catalysts

Au catalysts on different supports of TiO_2 (Degussa P25), CeO_2 (Aldrich) and CeO_2 (sol gel-urea hydrolysis) were prepared with aqueous gold precursor ($HAuCl_4$, Alfa) solution with a nominal gold loading of 1% wt. Then, the catalyst precursors were dried at 110°C over night followed by calcination in air at 500°C for 5 h. After that, each catalyst was sieved in order to select grain sizes in the range of 212-425 μm for the activity studies.

3.2.2 Deposition Precipitation Method

Au/TiO$_2$ catalysts were prepared by deposition-precipitation of $Au(OH)_3$ on titanium dioxide (Degussa P-25) in the aqueous solution at a constant pH of 8. An amount of $HAuCl_4$ with 1% wt Au was dissolved in distilled water under continuous stirring and heating at 70°C. This solution pH was maintained at 8 by gradually adding 1 M ammonium solution into the aqueous solution. Then the calculated amount of TiO_2 support was added into the mixed solution. The mixed solution was still maintained at pH 8 for 1 h. The resultant residue was washed several times until the conductivity was constant, then dried at 110°C over night, and finally calcined at 400°C for 5 h (Tsubota *et al.*, 1995, and Uphade *et al.*, 2000).

3.2.3 Sol Gel Method

3.2.3.1 Au/TiO$_2$ sol gel

The nominal 1% wt Au/TiO$_2$ with sol-gel technique was prepared under nitrogen atmosphere and at ambient temperature (297 K). Solutions were divided into two parts. A first solution was prepared by dissolving of 21.15 ml of tetrabutoxytitanium(IV)(TBOT) in 79.28 ml methanol (AR grade). A second solution was the mixture of 4.5 ml distilled water, 0.34 ml nitric acid (65 wt %) and 19.83 ml methanol. The second solution was added to the first solution with vigorous stirring and in a closed, initially nitrogen flushed system resulting in formation of gel. The resulting translucent gel was then aged for 2 h to increase the rigidity of the gel network by successive polycondensation reaction. After this first ageing process, the corresponding titania gel was redispersed with 46.92 ml methanol and homogenized for 10 min under vigorous stirring. The solution became opaque.

Afterwards, the Au precursor solution containing 0.1 g $HAuCl_4 \cdot H_2O$, 0.58 ml water and 7.74 ml methanol was added and then the mixed solution was aged for 19 h under vigorous stirring. Finally, it was dried overnight and calcined at 500°C for 5 h at air atmosphere (Schneider *et al.*, 1994).

3.2.3.2 CeO₂ Urea Hydrolysis

The CeO_2 support was prepared by hydrolysis of cerous nitrate hexahydrate solution with urea solution. For the first solution, 6.5135 g of $Ce(NO_3)_3 \cdot 6H_2O$ was dissolved in 150 ml of distilled water. Next, the second solution was prepared by dissolving 1.2012 g of urea $(NH_2)_2CO$ in 50 ml of distilled water. Then, these two solutions were mixed in a 250 ml pyrex bottle with a screw cap. This mixture was placed in an oven at 100°C for 50 h. After equilibration, the precipitate was washed with hot distilled water (80°C) for 4 to 5 times and finally, it was washed with ethanol. The resulting precipitate was dried over night at 110°C and calcined at 500°C for 4 h.

3.2.3.3 Au/CeO₂ Urea Hydrolysis

1%wt Au/CeO_2 single step sol gel with urea hydrolysis method was prepared by adding $HAuCl_4$ of 0.0447 g into the mixture of the two prepared solution and following the same procedure as described above.

3.3 Catalyst Characterization

All catalysts were characterized by atomic adsorption spectrophotoscopy (AAS), diffuse reflection infrared Fourier transform spectroscopy (DRIFTS), X-ray diffraction (XRD) at The Petroleum and Petrochemical College (PPC) and scanning electron microscopy (SEM), scanning transmission electron microscopy (STEM), transmission electron microscopy (TEM), temperature programmed desorption (TPD), and X-ray photoelectron spectroscopy (XPS) at EMAL, The University of Michigan. The details were described as below:

3.3.1 Atomic Adsorption Spectrophotoscopy (AAS)

A Varian Spectr AA-300 was employed to determine the compositions of gold and silver in the catalysts prepared. Figure 3.1 illustrates a photo of the AAS unit used in this work.
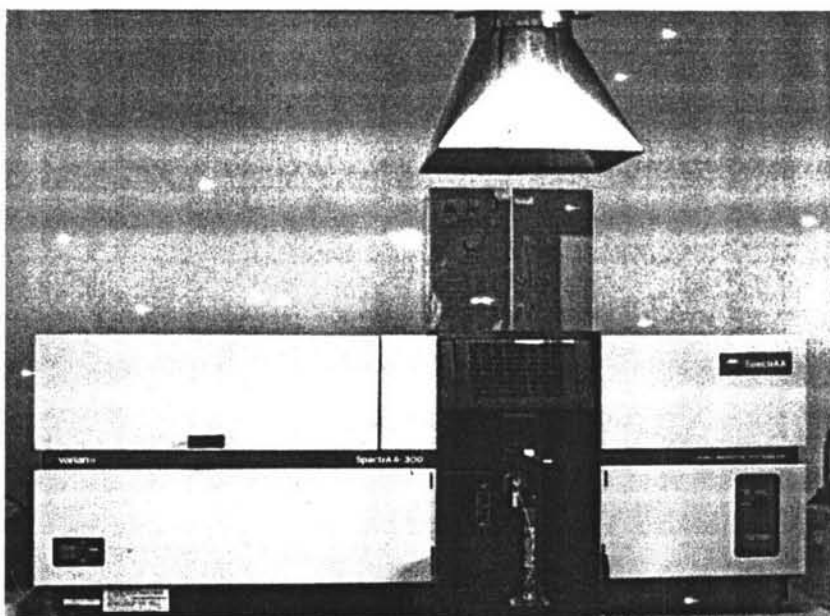

Figure 3.1 AAS Varian Spectr AA-300 at PPC.

3.3.2 Diffuse Reflection Infrared Fourier Transform Spectroscopy (DRIFTS)

The fresh catalysts were run on DRIFTS using O_2 and C_2H_4 reactant gases at a concentration ratio of 2%:2% in a Nicolet Avatar 360 Spectrometer equipped with a DTGS detector as shown in Figure 3.2. Experiments were performed using a diffuse reflectance cell from SpectraTech, Type 0030-103 with ZnSe windows. The catalyst was placed in this cell and pretreated with O_2 at 200°C for 1 h. Then, purge with helium for 30 min. For each FT-IR spectrum, 128 scans were taken at a resolution in situ of 8 cm^{-1}. Prior to recording each spectrum, a background spectrum of the sample pretreated in situ under helium flow was obtained. After that, the mixed gas 2% C_2H_4 and 2% O_2 with helium balance was introduced into the system and the reactor was operated at the temperature that provided the maximum

yield for each catalyst obtained from the activity studies' result. The spectrum of effluent gas over the catalyst was collected every time interval of 5 min for 40 min.
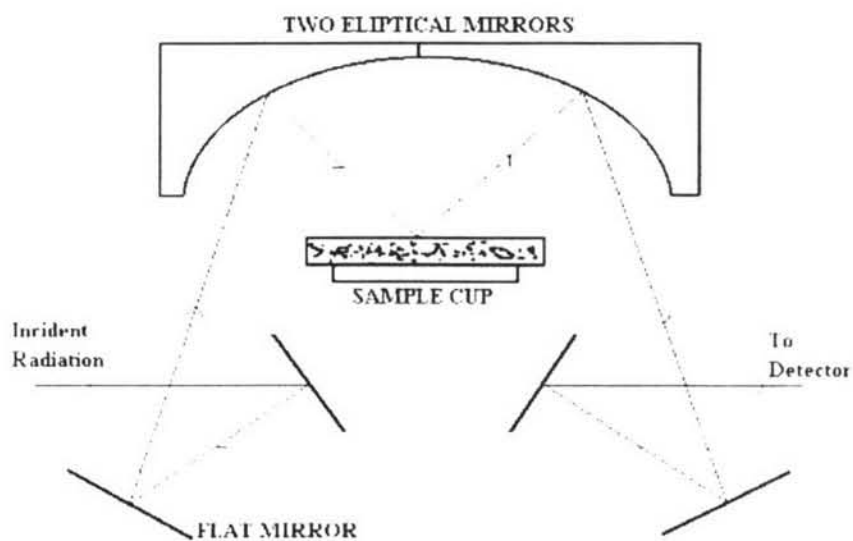

Figure 3.2 DRIFTS Nicolet Avatar 360 at PPC.

3.3.3 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) profiles of the prepared catalysts were obtained by using a Rigaku RINT 2000 diffractometer equipped with a Ni filtered Cu Kα radiation source (λ= 1.542 Å) of 40 kV and 30 mA. A photo of XRD system is shown in Figure 3.3. A catalyst sample was pressed into a hollow of glass holder and held in place by a glass window. Then, it was scanned in the range of 2θ from $20°$ to $90°$ in the continuous mode with the rate of $5°$ min^{-1}. The XRD results gave peak parameters, including the centroid 2θ, the full line width at half the maximum intensity (B), d-value and intensity. The mean crystallite size was calculated from the XRD data from X-ray line broadening, using the full line width at half maximum of intensity and the 2θ values and plugging them into the Scherrer equation (Cullity, 1956 and Matar *et al.*, 1989):

$$t = \frac{0.9\lambda}{B\cos\theta_B} \tag{3.1}$$

where   t is crystallite size (Å)

       λ is the X-ray wavelength (1.542 Å for Cu anode source)

       B is the line broadening

       θ_B is the Bragg angle

This equation works well for particle sizes of less than 1,000 Å. The broadening of diffraction lines measured at half the maximum intensity (B) is corrected by using Warren's method, which is

$$B^2 = B_M{}^2 - B_S{}^2. \tag{3.2}$$

where B_M is the breadth of the diffraction line and

       B_S is the breadth of the line from a standard.

3.3.4 Scanning Electron Microscopy (SEM)

The surface morphology of all prepared catalysts was examined with a PHILIPS XL30FEG SEM. Each sample was prepared by dispersing the catalyst in isopropanol. The sample was vigorously shaken with hand or by a vortex mixer. Then, a drop of the suspension was placed on the SEM's stub and the solvent was allowed to evaporate at room temperature. Finally, this specimen was ready to load

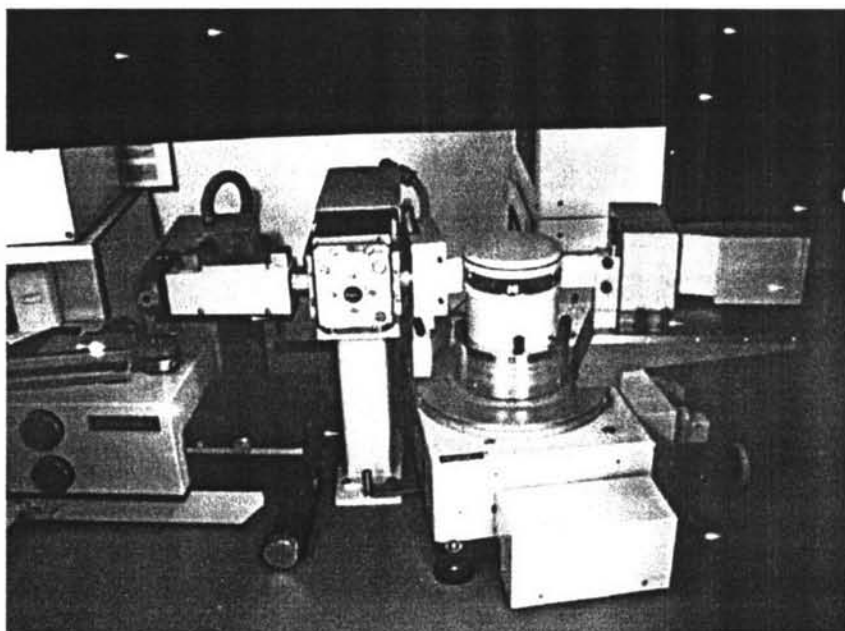in the SEM's chamber for examination. A photo of the SEM system is shown in Figure 3.4.

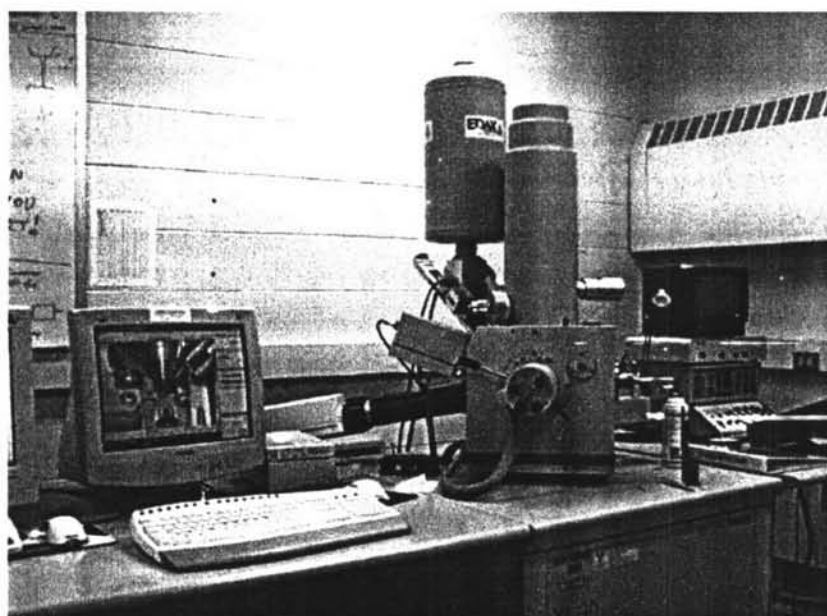**Figure 3.3** XRD Rikagu RINT 2000 at PPC.

Figure 3.4 SEM PHILIPS XL30FLG at EMAL.

3.3.5   Scanning Transmission Electron Microscopy (STEM) and Transmission Electron Microscopy (TEM)

A JOEL 2010F transmission electron microscope operating at 200 kV equipped with energy dispersive spectroscope (EDS) was employed to identify the existence of Ag and Au particles on the catalyst surface. The catalyst samples were ground into fine powder and ultrasonically dispersed in isopropanol. A small droplet of the suspension was deposited on a honey carbon copper grid with 200 mesh sizes, and the solvent was evaporated prior to loading the sample into the microscope. Figure 3.5 shows a photograph of the TEM system.
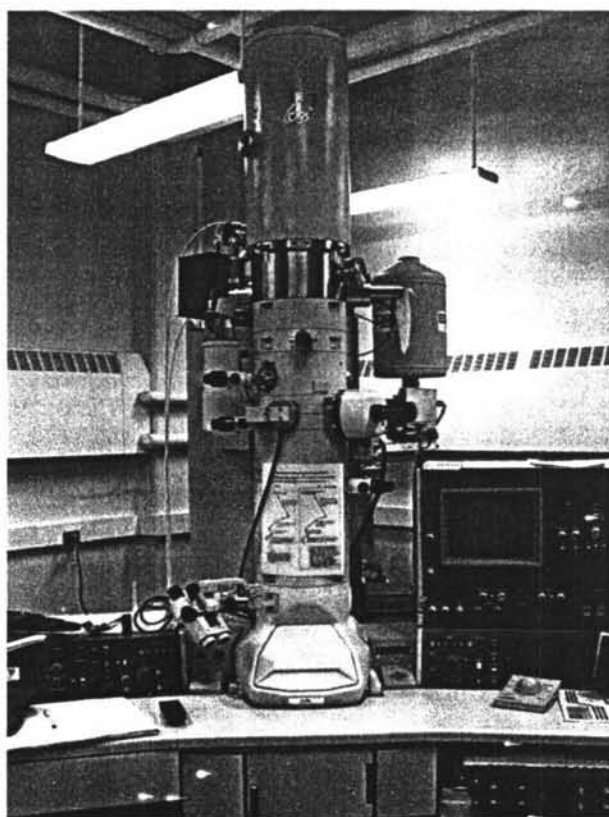

Figure 3.5 TEM JOEL 2010 F at EMAL.

3.3.6   Temperature Programmed Desorption (TPD)

The experiments were carried out by placing 100 mg of catalyst into a U-tube quartz reactor. The catalyst was pretreated in a flow of O_2 (8% O_2/N_2) at 200°C for 1 h. In an attempt to better assess the role of gold on oxygen adsorption;

two different experimental protocols were employed. In the first protocol "with cooling step", the catalyst was cooled from 200°C to room temperature under oxygen atmosphere. Then, the reactor was flushed with N_2 for 0.5 h in order to remove the gas phase of O_2. After that, the reactor temperature was ramped from room temperature to 600°C at a linear heating rate of 40°C min^{-1} in flowing N_2 (30 ml min^{-1}). In the second protocol "without cooling step", the oxygen pretreated catalyst was flushed with N_2 for 0.5 h at 200°C and then the reactor temperature was ramped linearly from 200°C to 600°C. The desorbing oxygen was detected with a thermal conductivity detector (TCD).

3.3.7   X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) spectra of the studied catalysts were recorded by using a PHI 5400 XPS with Mg Kα radiation (1253.6 eV). Copper Cu $2p_3$ (934 eV) was used to calibrate the binding energies. The analyzer was operated at 89.45 eV pass energy for survey spectra and 17.90 eV pass energy during all high-resolution core level spectra. The base pressure of the spectrometer was 3×10^{-9} torr. A catalyst sample was pressed into a pellet and the pellet was then placed on the sample holder. Then, it was kept in the load lock for out-gassing under high vacuum condition for a period of time before it was introduced into the analyzer. The spectra of Ag $3d_3$ and Ag $3d_5$ were investigated, but it was hard to identify Au spectra because of the small gold concentration. In all catalyst samples, the characteristic O1s, Al 2s, Al 2p and C1s peaks were observed. Figure 3.6 illustrate a photo of XPS unit used in this work.
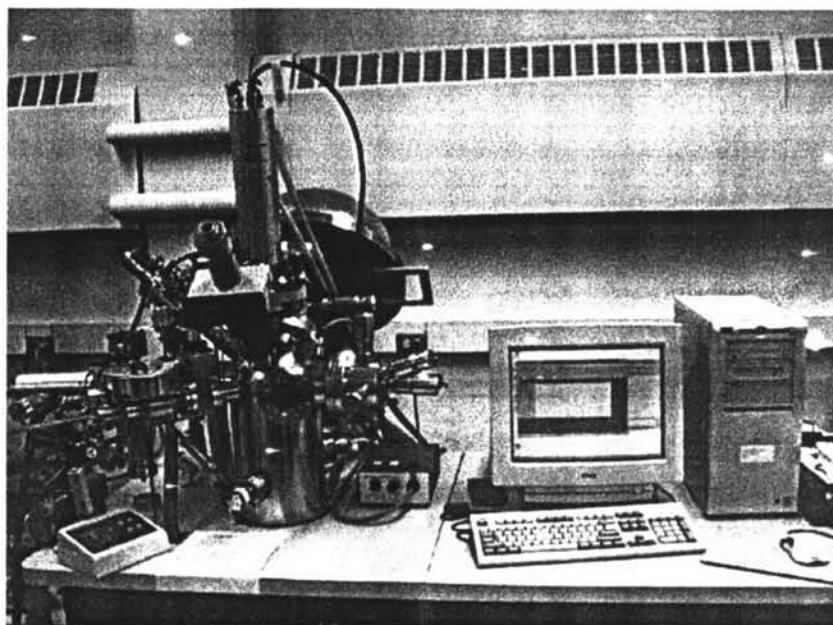
Figure 3.6 PHI 5400 XPS at EMAL.

3.4 Ethylene Epoxidation Reaction Experiment

The experimental study of ethylene oxidation was conducted in a differential reactor, which was operated at 24.7 psia. Catalyst powder of 300 mg was placed inside a Pyrex tube and secured by glass wool plugs. The tubular reactor being 10 mm in diameter was placed in a furnace equipped with a temperature controller. The catalyst was initially pretreated with oxygen at 200°C for 2 h in order to diminish some impurities and remove residual moisture from the catalyst. The feed gas was a mixture of 15% oxygen in helium, 30% ethylene in helium and pure helium (HP grade) obtained from Thai industrial gas (TIG). The flowrates of these three gas streams were regulated by mass flow controllers to obtain the feed gas composition of 6% oxygen and 6% ethylene with helium balance. The feed gas was passed through the reactor at a constant space velocity of 6,000 h^{-1} and the temperature was varied from 220 to 270°C. The compositions of the feed gases and effluent gases were analyzed by using an on-line gas chromatograph (HP5890 Series II) equipped with HaYeseb D 100/120-packed column, capable of separating carbon dioxide, ethylene and oxygen. The ethylene oxide product was calculated from the

carbon material balance with 0.25% carbon atom error (Yeung *et al.*, 1998 and Lafarga *et al.*, 2000). The presence of acetaldehyde could be ignored because it was formed in very small amounts as a result of further oxidation of acetaldehyde to carbon dioxide and water under the studied conditions. The schematic diagram of experiment setup is shown in Figure 3.7 and the system of this experiment is illustrated in Figure 3.8.

Calculations for the ethylene conversion, ethylene oxide selectivity and yield are based on the following equations:

Ethylene conversion (X) (%) $= [F\ C_2H_4\ in - F\ C_2H_4\ out][100]/[F\ C_2H_4\ in]$

Ethylene oxide selectivity (S) $= [F\ C_2H_4O\ out]\ /\ [F\ C_2H_4\ in - F\ C_2H_4\ out]$

Ethylene oxide yield (Y) $= X \cdot S = [F\ C_2H_4O\ out]\ /\ [F\ C_2H_4\ in]$

where   F C_2H_4 in   =   Inlet mass flowrate of ethylene (mole/min)

F C_2H_4 out   =   Outlet mass flowrate of ethylene (mole/min)

F C_2H_4O out   =   Outlet mass flowrate of ethylene oxide (mole/min)

In addition, outlet mass flowrates of ethylene oxide were determined from the carbon balance and calculated sample was shown in Appendix C. However, the presence of ethylene oxide over catalysts was identified by DRIFTS experiment.
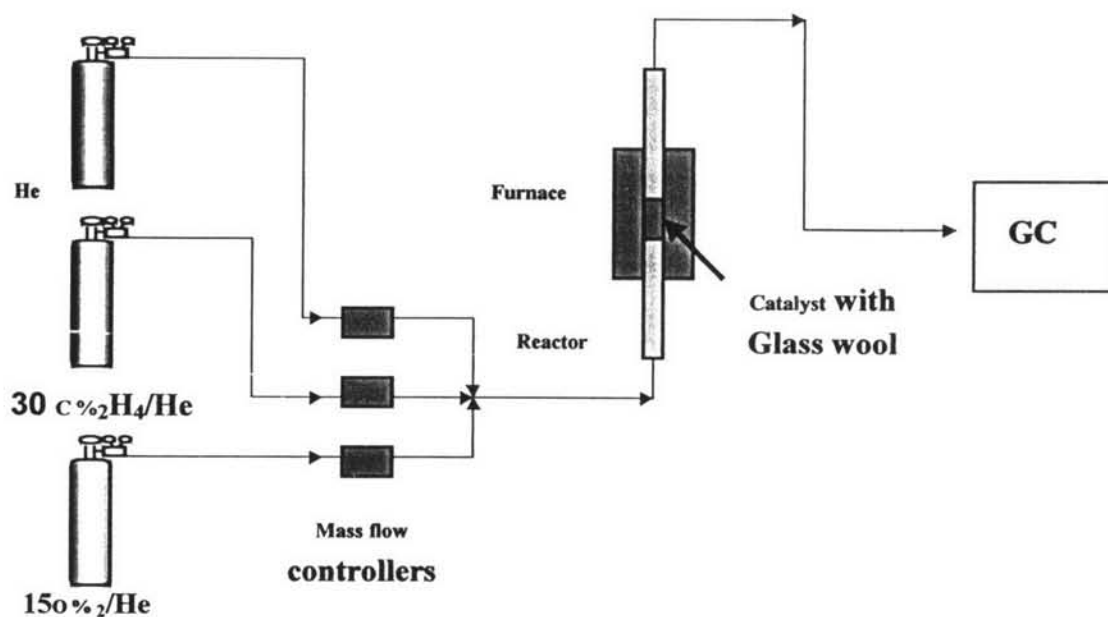

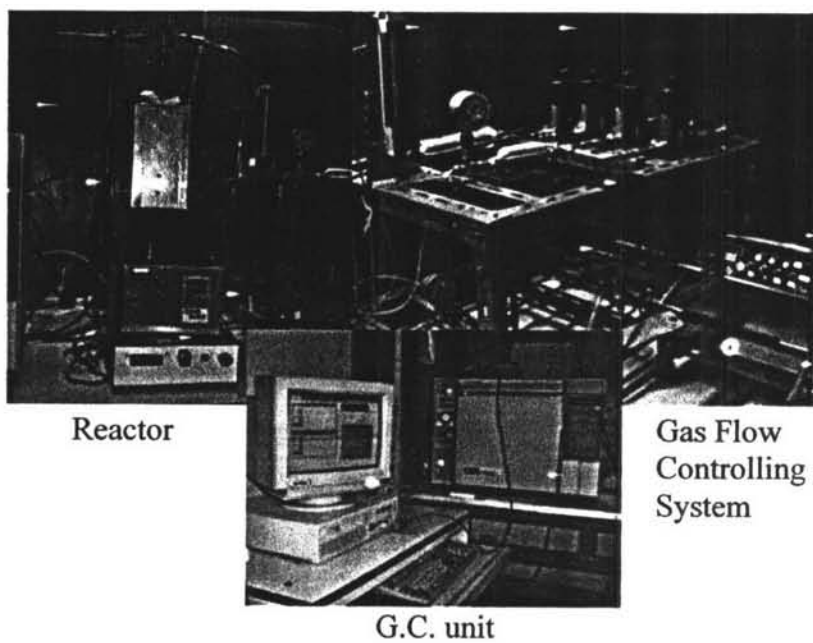**Figure 3.7** Schematic diagram of experimental setup for ethylene oxidation.

Reactor

Gas Flow
Controlling
System

G.C. unit

Figure 3.8 Experimental setup of ethylene oxidation at PPC.