CHAPTER III
EXPERIMENTAL

The experimental section consists of four parts: chemicals, catalyst synthesis methods, characterization techniques, and catalytic activity testing.

3.1 Chemicals

All chemical reagents used in this work were analytical grade and used as received without further purification. Aluminium oxide C (Al_2O_3, 85-115 m^2/g), hydrophilic fumed silica 90 (SiO_2, 75-105 m^2/g), hydrophilic fumed silica 380 (SiO_2, 350-410 m^2/g), hydrophilic fumed mixed oxide 90 (MOX 90) (1 wt.% Al_2O_3 C physically mixed with 99 wt.% SiO_2 90), hydrophilic fumed mixed oxide 380 (MOX 380) (1 wt.% Al_2O_3 C physically mixed with 99 wt.% SiO_2 380), and titanium oxide P25 (TiO_2, 35-65 m^2/g) were obtained from Degussa AG. α-Al_2O_3 (0.109 m^2/g) was supplied by Fluka. $Al_2O_{3,Acid}$, $Al_2O_{3,Neutral}$, $Al_2O_{3,Fused}$, gold chloride trihydrate ($HAuCl_4 \cdot 3H_2O$), and tin chloride ($SnCl_2$) were supplied by Aldrich. Nano $SrTiO_3$ was obtained from Wako. Silver nitrate ($AgNO_3$) was supplied by S.R. Lab. Tetraisopropyl orthotitanate (TIPT, $Ti(OCH(CH_3)_2)_4$), magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$), calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$), strontium nitrate ($Sr(NO_3)_2$), barium nitrate ($Ba(NO_3)_2$), copper nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$), palladium chloride ($PdCl_2$), and laurylamine (LA, $CH_3(CH_2)_{11}NH_2$) were purchased from Merck. Acetylacetone (ACA, $CH_3COCH_2COCH_3$) was obtained from S.D. Fine-Chemical. Analytical grade Hydrochloric acid (HCl) and ethanol (C_2H_5OH) were purchased from Labscan. The TIPT, $Mg(NO_3)_2 \cdot 6H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$, $Sr(NO_3)_2$, and $Ba(NO_3)_2$ were used as Ti, Mg, Ca, Sr, and Ba precursors for synthesizing mesoporous-assembled TiO_2, $MgTiO_3$, $CaTiO_3$, $SrTiO_3$, and $BaTiO_3$ nanocrystal supports, respectively. The LA was used as a structure-directing surfactant behaving as both mesopore-forming and gelation-assisting agent. The ACA was used as a modifying agent. The $AgNO_3$, $HAuCl_4 \cdot 3H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Ba(NO_3)_2$, $PdCl_2$, and $SnCl_2$ were used as Ag, Au, Cu, Ba, Pd, and Sn precursors, respectively, to be loaded on the studied supports.

3.2 Catalyst Synthesis Methods

3.2.1 Sol-Gel Method

3.2.1.1 Mesoporous-assembled TiO$_2$ support

The mesoporous-assembled TiO$_2$ support was synthesized by a sol-gel process with the aid of a structure-directing surfactant. Firstly, the TIPT and ACA were mixed together. The mixed TIPT/ACA solution was gently shaken until homogeneous mixing. A quantity of 60 ml of distilled water and 0.5 ml of HCl were added consecutively in a separate beaker, followed by the LA surfactant. Afterwards, the mixture was stirred until clear solution was obtained. Next, the LA solution was poured into the TIPT/ACA solution. The final mixture was kept continuously stirred until obtaining homogeneously transparent sol. Then, the sol-containing solution was placed in an oven at 80 °C for a week in order to obtain complete gel formation. After that, the gel was dried at 80 °C to eliminate the solvent for 2 d, which was mainly the distilled water used in the preparation of the LA solution. Finally, the dried gel was calcined at 500 °C (Part I) or 650 °C (Part II) to remove the LA surfactant and to consequently produce the desired mesoporous-assembled TiO$_2$ support.

3.2.1.2 Mesoporous-assembled SrTiO$_3$ support

The mesoporous-assembled SrTiO$_3$ support was also synthesized by a sol-gel process with the aid of a structure-directing surfactant. The TIPT and ACA were firstly mixed together. The mixed TIPT/ACA solution was gently shaken until homogeneous mixing. A required amount of Sr(NO$_3$)$_2$ was dissolved by 24 ml of distilled water in a separate beaker. Next, 36 ml of EtOH was mixed with the as-prepared Sr(NO$_3$)$_2$ solution until homogeneous solution was obtained. After that, the LA and 0.5 ml of HCl were added to obtain the Sr(NO$_3$)$_2$/LA/HCl solution. The Sr(NO$_3$)$_2$/LA/HCl solution was poured into the TIPT/ACA solution. The final mixture was kept continuously stirred until obtaining homogeneously transparent sol. Then, the sol-containing solution was placed into an oven at 80 °C for 4 d in order to obtain complete gel formation. Afterwards, the gel

was dried at 80 °C for 4 d to eliminate the solvents, which were mainly the distilled water and EtOH used in the preparation of the $Sr(NO_3)_2$/LA solution. The dried gel was finally calcined at 500 °C (Part I) or 400, 500, 600, 650, 700 and 800 °C (Part II) or 650 °C (Part III and IV) for 4 h to remove the LA surfactant and to consequently produce the desired mesoporous-assembled $SrTiO_3$ support.

3.2.1.3 Mesoporous-assembled perovskite titanate supports

The mesoporous-assembled perovskite titanates ($MgTiO_3$, $CaTiO_3$, and $BaTiO_3$) were synthesized by the same sol-gel process with the aid of a structure-directing surfactant as used for the synthesis of the $SrTiO_3$ support. Firstly, the TIPT and ACA at an equimolar ratio were mixed together. The mixed TIPT/ACA solution was gently shaken until a homogeneous mixture was achieved. An appropriate amount of corresponding alkaline earth nitrate ($Mg(NO_3)_2 \cdot 6H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$ or $Ba(NO_3)_2$) was dissolved in distilled water. Next, ethanol was mixed with the as-prepared alkaline earth nitrate solution. After that, 1.112 g of the LA surfactant and 0.5 ml of HCl were added to obtain the alkaline earth nitrate/LA/HCl solution. The alkaline earth nitrate/LA/HCl solution was poured into the TIPT/ACA solution, based on the alkaline earth metal-to-Ti molar ratio of 1:1 and the LA-to-(alkaline earth metal + Ti) ratio of 0.25:1. The final mixture was continuously stirred at room temperature until a homogeneous transparent sol was obtained. Then, the sol-containing solution was placed in an oven at 80 °C for 4 d to achieve complete gelation. Afterwards, the gel was further dried at 80 °C for 4 d to eliminate the solvents. Finally, the dried gel was calcined at 650 °C for 4 h to produce the desired mesoporous-assembled perovskite titanate supports.

The obtained mesoporous-assembled TiO_2, $MgTiO_3$, $CaTiO_3$, $SrTiO_3$, and $BaTiO_3$ supports prepared by the sol-gel method were impregnated with various Ag loadings by the incipient wetness impregnation explained below.

3.2.2 Incipient Wetness Impregnation

Supported silver catalysts were prepared by the incipient wetness impregnation on various aluminium oxides (Al_2O_3 C, α-Al_2O_3, $Al_2O_{3,Neutral}$, $Al_2O_{3,Acid}$,

and $Al_2O_{3,Fused}$), TiO_2 (TiO_2 P25 and TiO_2 (sol-gel)), SiO_2 (SiO_2 90 and SiO_2 380), mixed oxides (MOX 90 and MOX 380), $SrTiO_3$ ($SrTiO_3$ (sol-gel) and nano $SrTiO_3$), $MgTiO_3$, $CaTiO_3$, and $BaTiO_3$ with an aqueous silver nitrate solution to achieve various nominal silver loadings of 10, 12.5, 13.5, 15, 17.5, and 20 wt.%. After the impregnation step, the catalysts were dried at 110 °C overnight, followed by calcination in air at 500 °C for 5 h.

The same impregnation method used for the Ag catalyst synthesis was implemented for Au catalysts. The nominal Ag loading of 17.5 wt.% (actual Ag loading = 17.16 wt.%) on $SrTiO_3$ support was used in the preparation of bimetallic catalysts. The bimetallic catalysts were synthesized by adding the second metal precursors (Au from $HAuCl_4 \cdot 3H_2O$, Cu from $Cu(NO_3)_2 \cdot 3H_2O$, Ba from $Ba(NO_3)_2$, Pd from $PdCl_2$, and Sn from $SnCl_2$) on the as-prepared Ag catalysts with the different nominal second metal loadings of 0.25, 0.5, 0.75, 1, 1.5, and 2 wt.%. Then, the catalyst samples were dried at 110 °C overnight, followed by calcination in air at 500 °C for 5 h to produce the bimetallic catalysts.

Furthermore, the Sn-promoted on $Cu-Ag/SrTiO_3$ catalyst was prepared by further impregnation of Cu-Ag bimetallic catalyst with tin chloride precursor at the various nominal tin loadings of 0.1, 0.2, 0.3, 0.4, and 0.5 wt.%. Following the impregnation step, the catalysts were dried at 110 °C overnight and then calcined at 400 °C for 2 h to obtain the Sn-promoted $Cu-Ag/SrTiO_3$ catalyst.

3.3 Characterization Techniques

The N_2 adsorption-desorption isotherms were obtained by a Brunauer-Emmett-Teller (BET) surface area analyzer (Quantachrome, SAA-1MP) to determine the specific surface areas of all synthesized catalyst samples. Prior to analysis, each catalyst sample was outgassed at 200 °C for 8 h. The actual contents of metal loaded on the catalyst samples were analyzed by an atomic adsorption spectrophotometer (AAS, Varian, Spectr AA-300).

The crystallinity of the catalysts was examined by an X-ray diffractometer (XRD, Rigaku, RINT 2200 HV) equipped with a Ni filter and a Cu Kα radiation source (λ = 1.542 Å) operating at 40 kV and 30 mA. The catalyst samples were

scanned using a continuous scanning mode at a rate of 5° min^{-1} in the range of 2θ from 5° to 90°. The Ag crystallite size (D) was calculated from the line broadening of the corresponding X-ray diffraction peak of Ag using the Debye-Scherrer equation (Cullity, 1978; Jackson, 1991) with the full line width at half maximum of intensity and the 2θ value. as follows:

$$D = \frac{0.9\lambda}{B\cos\theta}$$

where λ is the x-ray wavelength (1.542 Å for Cu source), B is the full width half maximum (FWHM) of the diffraction peak measured at 2θ, and θ is the diffraction angle. The dispersion and surface area of the Ag particles were determined using a H_2 chemisorption apparatus (Micromeritics, ASAP 2020). The catalyst samples were reduced at 600 °C in 5 % H_2 in N_2 atmosphere before the analysis.

The catalyst surface morphologies were investigated by a field emission scanning electron microscope (FE-SEM, JEOL 5200-2AE). Prior to analysis, the samples were coated with Pt to improve their conductivity. The particle sizes of loaded metals and morphological surfaces of the catalyst samples were obtained by transmission electron microscopy (TEM, JEOL 3011 at 300 kV and JEOL 2010 at 200 kV). The specimens for TEM analysis were prepared by ultrasonically dispersing powders of the catalysts in ethanol and then placing drops of the suspension onto a grid coated with a carbon film. The existence of Ag, Au, and other second metal particles on the supports was verified by using an energy dispersive X-ray spectroscope (EDS) attached to the TEM. The metal particle sizes were determined from statistical data of the TEM images.

The oxygen and ethylene uptakes of the investigated catalysts were examined using a temperature-programmed desorption (TPD) analyzer (Quantachrome, Chembet 3000). Initially, oxygen (4.99 % O_2 in He) or pure ethylene (99.99 % C_2H_4) was allowed to adsorb onto the catalyst surface at 200 °C for 2 h for the TPD experiments. Then, the catalyst samples were cooled down to room temperature in a high-purity of He stream. After that, the catalyst samples were heated from room temperature to 900 °C with a heating rate of 10 °C/min, and the desorbed gas was swept by the high-purity He at a flow rate of 20 cm^3/min. A thermal conductivity detector (TCD) was used to measure the amount of oxygen or

ethylene uptakes and the desorption profile present in the effluent. The oxidation state of the supported metal particles was analyzed by an X-ray photoelectron spectroscope (XPS, Shimadzu, Kratos). A monochromatic Al Kα source was used as the X-ray source. The relative surface charging of the samples was corrected by referencing all the energies to the C1s level as an internal standard at 285 eV (Moulder *et al.*, 1995). A thermogravimetric-differential thermal analyzer (TG-DTA, PerkinElmer, Pyris Diamond) was used to quantify the amount of coke deposited on the spent catalysts. The catalyst samples of 5-20 mg were heated from 50 to 800 °C with a heating rate of 10 °C/min in a static air atmosphere.

3.4 Catalytic Activity Testing

The ethylene epoxidation reaction on various monometallic and bimetallic catalysts was performed in a packed-bed 8-mm ID tubular reactor under 24.7 psia with different reaction temperatures from 225 to 290 °C. 30 mg of catalyst powder was initially pretreated with oxygen at 200 °C for 2 h. The feed gas was a mixture of 40 % ethylene in He, pure oxygen (HP grade), and pure helium (HP grade). Feed gas compositions of 6 % ethylene and 6 % oxygen with helium balance were regulated by mass flow controllers (Part I-III). For Part IV, the diluent gas systems (He, Ar, N_2, CH_4, and CH_4 balanced with He) were investigated their catalytic activity towards ethylene epoxidation. The feed gas compositions of 6 % ethylene and 3-7.5 % oxygen with the diluent gas balance (He, Ar, N_2, and CH_4) were used in this part. After that, the optimum percentage of oxygen (6 %) was used in the CH_4 balanced with He diluent gas. For the reaction testing experiments, the space velocity (relating the reactant gas flow rate to the reactor volume) through the reactor was maintained at 6,000 h^{-1} (the optimum space velocity in Rojluechai's work and a general range used in the industries) with total gas flow rate of 50 mL/min for all catalysts with different diluent gases. The compositions of the feed and product gases were analyzed by using an on-line gas chromatograph (Perkin Elmer, ARNEL) equipped with a 60/80 CARBOXEN 1 packed column (capable of separating carbon monoxide, carbon dioxide, ethylene, and oxygen) and a Rt-U PLOT capillary column (capable of separating EO, ethane, and propane). The CO concentration was neglected under

the studied conditions because it was below the detectable limit. The formation of acetaldehyde was not quantified for all synthesized catalysts because of further oxidation to carbon dioxide and water so it appeared only in trace amounts under the studied conditions (Rojluechai, 2006). The catalytic activity of each investigated catalyst was compared at 6 h of operation. The experimental data with less than 5 % error were averaged to assess the catalytic performance. Moreover, the catalytic system was operated up to 48 h (Part I and II) or 72 h (Part III and IV) over the selective catalysts or 7 d for the optimum catalyst with the best operational condition (Part IV) to observe the long-term stability of these catalysts. The schematic of experimental setup is shown in Figure 3.1.
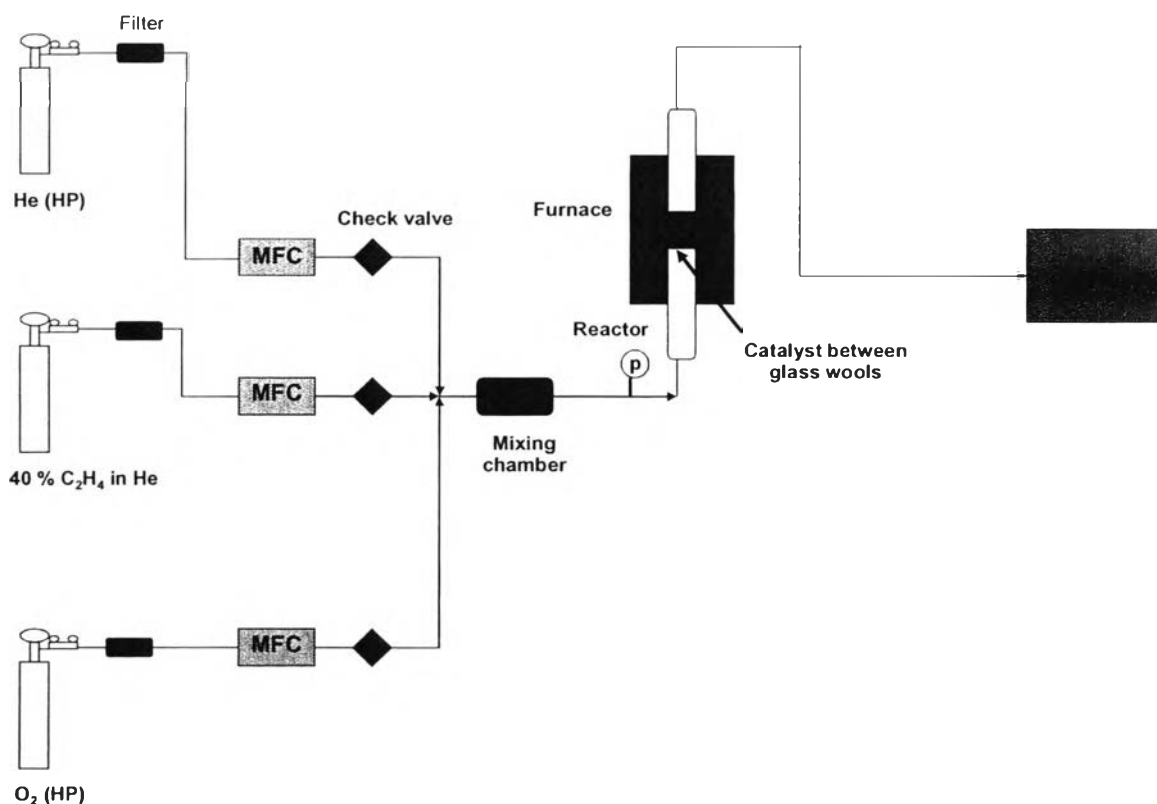

Figure 3.1 Schematic of experimental setup for ethylene epoxidation.

Ethylene conversion, EO selectivity, and EO yield were calculated using the following equations:

$$Ethylene\ conversion\ (\%) = \frac{F\ ethylene, in - F\ ethylene, out}{F\ ethylene, in} \times 100$$

$$EO\ selectivity\ (\%) = \frac{F\ EO, out}{F\ ethylene, in - F\ ethylene, out} \times 100$$

$$EO\ yield\ (\%) = \frac{F\ EO, out}{F\ ethylene, in} \times 100$$

where

F ethylene,in = Inlet mass flow rate of ethylene (mole/min)

F ethylene,out = Outlet mass flow rate of ethylene (mole/min)

F EO,out = Outlet mass flow rate of EO (mole/min)