CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1   Tetraisopropyl orthotitanate (TIPT, $Ti(OCH(CH_3)_2)_4$)

3.1.2   Cerium (IV) diammonium nitrate ($(NH_4)_2Ce(NO_3)_6$)

3.1.3   Laurylamine hydrochloride (LAHC, $CH_3(CH_2)_{11}NH_2 \cdot HCl$)

3.1.4   Acetylacetone (ACA, $CH_3COCH_2COCH_3$)

3.1.5   Hydrochloric acid (HCl)

3.1.6   Hydrogen peroxide (H_2O_2)

3.1.7   *tert*-butanol (C_4H_9OH)

3.1.8   Cyclohexene (C_6H_{10})

3.1.9   Cyclohexene oxide ($C_6H_{10}O$)

3.1.10 Cyclohex-2-ene-1-ol or 2-cyclohexen-1-ol

3.1.11 Cyclohex-2-ene-1-one or 2-cyclohexen-1-one

3.1.12 (1S,2S)-*trans*-1,2-cyclohexanediol

3.1.13 Dodecane

3.1.14 Distilled water

3.2 Equipment

3.1.15 Gas chromatograph with flame ionization detector (HP, GC 5890)

3.2.2   X-ray diffractometer (Bruker AXS, D8 Advance)

3.2.3   Surface area analyzer (Quantachrome, Autosorb-1)

3.2.4   Scanning electron microscope (Hitachi, S-4800)

3.2.5   Transmission electron microscope (JEOL, JEM 2100)

3.2.6   Thermogravimetric differential thermal analyzer (Perkin Elmer, Pyris Diamond)

3.3 Methodology

<u>Synthesis of Mesoporous-Assembled TiO_2-CeO_2 Mixed Oxide Nanocrystal Catalysts by a Sol-Gel Method</u>

a. A specified amount of ACA was introduced into TIPT. The mixed TIPT/ACA solution was then gently shaken until homogeneous mixing

b. The LAHC/$(NH_4)_2Ce(NO_3)_6$ solution was separately prepared by adding an appropriate amount of $(NH_4)_2Ce(NO_3)_6$ to a 0.1 M LAHC aqueous solution with continuously stirring at room temperature.

c. The LAHC/$(NH_4)_2Ce(NO_3)_6$ solution was then slowly added to the TIPT/ACA solution while stirring continuously to obtain various TiO_2 and CeO_2 molar concentrations (various x values in $xTiO_2$-$(1-x)CeO_2$), where the molar ratios of $(TIPT+(NH_4)_2Ce(NO_3)_6)$-to-LAHC and $(TIPT+(NH_4)_2Ce(NO_3)_6)$-to-ACA were 4:1 and 1:1, respectively.

d. The mixture was kept continuously stirring at 40 °C for 8 h to obtain transparent sol.

e. Then, the sol-containing solution was placed into an oven at 80 °C for a week in order to obtain complete gel formation.

f. The gel was dried at 80 °C for 2 d and was calcined at different temperatures for 4 h.

The flow chart of the synthesis procedure of mesoporous-assembled TiO_2-CeO_2 nanocrystal catalysts is shown in Figure 3.1.
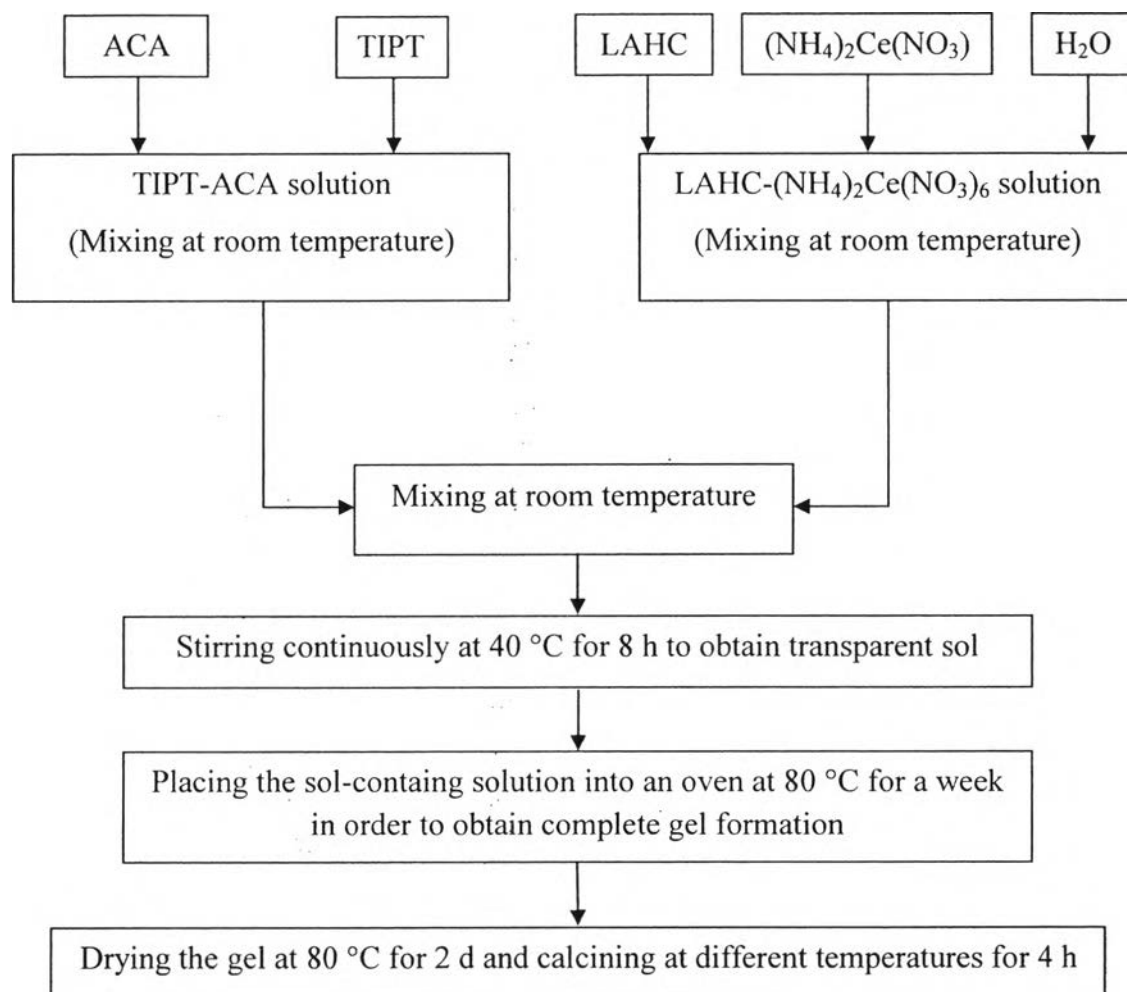

Figure 3.1 Procedure for synthesis of mesoporous-assembled TiO_2-CeO_2 mixed oxide catalysts.

3.4 Catalyst Characterizations

3.4.1 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) was used to identify phases present in the sample. The crystalline structure and the mean particle size of the catalyst were analyzed by using of a Bruker AXS system (D8 Advance) with a copper tube for generating CuKα radiation (1.54056 Å) and a nickel filter. It was also possible to achieve a relative analysis by the intensity of the peak. For the same crystalline substance, the higher intensity of the peak indicates the higher content of that phase.

The XRD patterns were obtained at a generator voltage of 40 kV and generator current of 30 mA. The goniometer parameters were divergent slit = 1° (2θ); scattering slit = 1° (2θ); and receiving slit = 0.3 mm. The scan speed of 1° (2θ)/min with scan step of 0.02 (2θ) was used for the continuous run in 20° to 70° (2θ) range. The sample was ground to the fine homogeneous powder and held in a beam direction in a thin-walled glass holder. The signal was sent to the online computer to record and analyze. The crystallite size was then calculated from the XRD pattern using Schener formula. The Scherrer equation as expressed in Equation 3.1 shows the relationship between the crystallite size (D_b) and the broadening (B_d) of the diffraction line corresponding to the Bragg angle (θ) and X-ray wavelength (λ).

$$D_b = \frac{K \cdot \lambda}{B_d \cdot \cos \theta} \qquad (3.1)$$

where:

D_b = Crystallite size (Å)

K = Scherrer constant, 0.9

λ = X–ray wavelength (Å)

B_d = Full width at half maximum of peak at 2θ (radian)

θ = Bragg angle of the reflection (radian)

3.4.2 Surface Area Analysis (SAA)

Autosorb-1 gas sorption system (Quantachrome Corparation) was used to measure the specific surface area, mean mesopore diameter, and total pore volume of the catalysts. The equipment measurement was based on Brunauer-Emmet-Teller (BET) equation. This technique was done by calculating the physical multi-layer adsorption of nitrogen. Volatile adsorbents on the surface was eliminated by heating under vacuum at 150 °C for at least 4 h prior to the analysis. Nitrogen gas with the cross-sectional area of 1.62×10^{-19} m^2/molecule was adsorbed on the catalyst surface at liquid nitrogen temperature (-196 °C). The surface area was calculated from the 44-points nitrogen adsorption. The mean mesopore diameter and total pore volume were obtained at P/P_0 ratios close to unity. The results were analyzed by Autosorb Anygas Software version 2.1 using the BET equation, as shown in Equation 3.2.

$$\frac{1}{W \cdot \left(\frac{P_0}{P} - 1\right)} = \frac{1}{W_m \cdot C} + \frac{(C-1)}{(W_m \cdot C)} \cdot \left(\frac{P_0}{P}\right) \tag{3.2}$$

where:

P = Pressure of gas

P_0 = Saturated vapor pressure of the liquid at the operating temperature

W = Weight of gas adsorbed at a relative pressure, P/P_0

W_m= Weight of adsorbate constituting a monolayer of surface coverage

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

The specific surface area was calculated by Equation 3.3.

$$S = \frac{W_m \cdot A_{N_2} \cdot \left(6.02 \times 10^{23}\right)}{M_{W,N_2}} \tag{3.3}$$

where:

S = Specific surface area (m^2/g)

A_{N_2} = Cross-sectional area of one molecule of N_2

        $(1.62 \times 10^{-19}$ m^2/molecule at -196 °C)

M_{W,N_2} = Molecule weight of nitrogen (28 g/g-mol)

3.4.3 Transmission Electron Microscopy (TEM)

The transmission electron micrograph was applied for investigating the average particle size and identifying morphological structure of the synthesized catalysts. The catalyst sample was ground into fine powder and ultrasonically dispersed in ethanol. A small droplet of the suspension was deposited on a copper grid, and the solvent was evaporated prior to loading the sample into the microscope. The TEM was operated at an accelerating voltage of 200 kV in bright field modes. A beam was passed through a series of lenses to form a magnified image of a sample that is inserted in the area of the objective lenses. The image from selected area was viewed through projection onto a view of screen. However, electron beams could be easily scattered by air molecules, and TEM columns must be kept under high vacuum. Additionally, the electromagnetic lenses were used for focusing the electron beam. The elemental analysis of the catalysts was also investigated by an energy-dispersive X-ray (EDX) analyzer attached to the TEM.

3.4.4 Scanning Electron Microscopy (SEM)

The morphology of the catalysts was observed by using a scanning electron microscope (SEM) operated at 2 kV. The sample was placed on the stub and coated with gold in a sputtering device before taking the micrograph. The specimen was scanned with a narrow beam of electrons. The quantity of electrons scattered or emitted as the primary beam bombards each successive point of the specimen surface was measured by an electron detector, and was used to modulate the intensity of a second electron beam and to form an image on a screen.

3.4.5 Thermogravimetric-Differential Thermal Analysis (TG-DTA)

Simultaneous thermogravimetry and differential thermal analysis (TG-DTA) of uncalcined (dried) gel was used to obtain suitable calcination temperature for removing the LAHC surfactant. The uncalcined gel of 5-20 mg was heated from 30 to 700 °C with a heating rate of 10 °C/min in nitrogen gas with α-Al_2O_3 as the reference. Moreover, the TG-DTA was used for determination of the surface OH density (OH/nm^2) and surface OH-to-catalyst weight ratio (OH/g) of the calcined catalysts. The OH surface density of the catalysts was calculated by using the TGA weight loss and surface area, as shown in Equation 3.4 (Zou and Lin, 2004).

$$nOH/nm^2 = \alpha \left(\frac{2(wt_{T_1} - wt_{T_2})N_A}{MW_{H_2O} \times SSA \times wt_{T_1}} \right) \tag{3.4}$$

where:

wt_{T_i}	= The sample weight at the corresponding temperature T_i
MW_{H_2O}	= The molecular weight of water (18 g/g-mol)
N_A	= Avogadro's constant (6.02×10^{23} mol^{-1})
SSA	= Specific surface area (m^2/g)
α	= A calibration factor given as 0.625
nOH/nm^2	= The OH surface density (nm^{-2})

A temperature range from 100 to 120 °C has been found to be responsible for removal of physically adsorbed water; therefore, this range is not crucial for powder characterization as it depends even on humidity during sample preparation. But for a temperature range from 120 to 500 °C, it represented the weight loss by the removal of hydroxyl groups from the powder surface and possible desorption of volatile organic compounds associated with the powder surface.

3.5 Catalytic Epoxidation Experiments

The cyclohexene epoxidation experiments were performed in the three-necked round-bottomed flask reactor equipped with a reflux condenser and a temperature-controlling water bath. Firstly, a specified amount of catalyst, 30 mmol of cyclohexene, and 30 ml of *tert*-butanol as the solvent were added to the reactor. The mixture was stirred and heated until reaching a desired reaction temperature of 70 °C. The reaction was started by adding H_2O_2 as the oxidant to the mixture. After 5 h of reaction, the reaction was stopped. After that, the catalyst was separated by centrifugation. The filtrate was analyzed by a gas chromatograph (Hewlett-Packard 5890) equipped with a flame ionization detector (FID) for determination of product composition. The experimental schematics are shown in Figures 3.2 and 3.3.
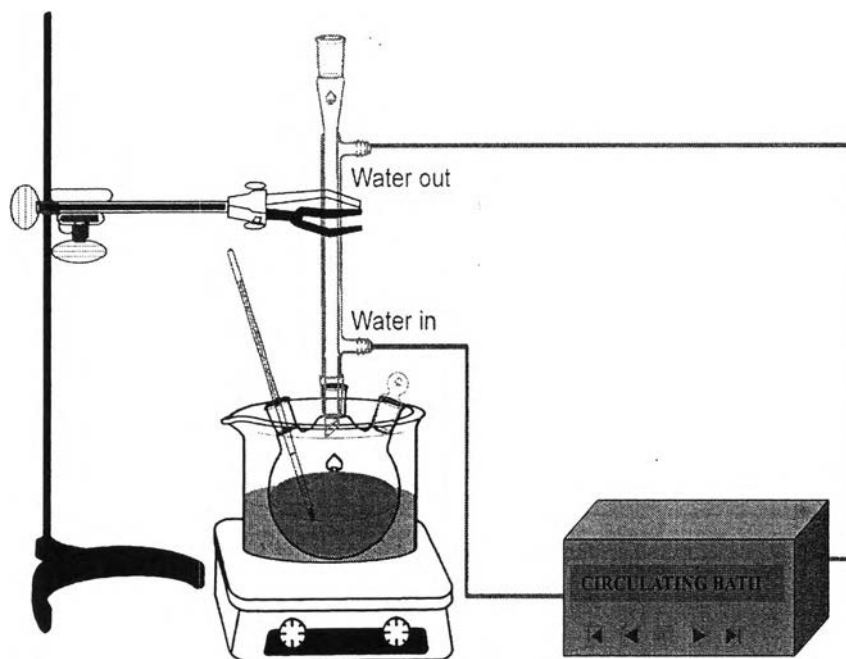

Figure 3.2 Schematic of epoxidation reaction experiment.
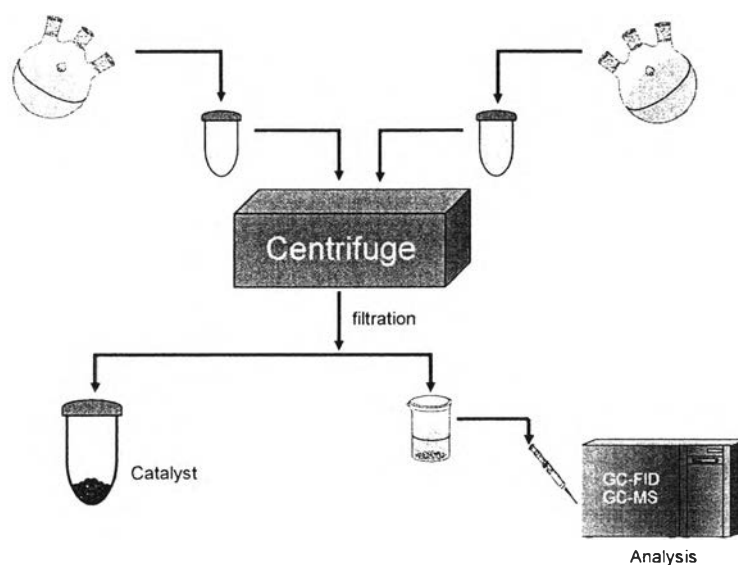
Figure 3.3 Flow diagram of catalyst separation.

Many parameters affecting the conversion and selectivity of the prepared catalysts were studied in this research, including TiO_2-to-CeO_2 molar ratio, H_2O_2-to-cyclohexene molar ratio, calcination temperature, and catalyst content.

3.6 Calculation

The conversion of the substrate and the selectivity for the products from the epoxidation reaction were calculated by Equations 3.5 and 3.6.

$$C = \frac{\text{Substrate converted (mol\%)}}{\text{Substrate used (mol\%)}} \times 100\ \% \qquad (3.5)$$

$$S = \frac{\text{A product formed (moles)}}{\text{All products formed (moles)}} \times 100\ \% \qquad (3.6)$$

where:

C	= Cyclohexene conversion (%)
S	= Product selectivity (%)
Substrate used	= Initial mol%
Substrate converted	= Initial mol% - final mol%
A product formed	= GC peak area of a product
All products formed	= ΣGC peak area of all products

The conversion was calculated on the basis of mole percentage of cyclohexene. The initial mole percentage of cyclohexene was divided by initial area percentage (cyclohexene peak area from GC) to get a response factor. The final mole percentage of cyclohexene remained in the reaction mixture was calculated by multiplying the response factor with the area percentage of the GC peak for obtaining cyclohexene after the reaction.