



## CHAPTER III EXPERIMENTAL

### 3.1 Materials and Equipment

#### 3.1.1 Chemicals

##### *Catalyst synthesis*

- Tetraisopropyl orthotitanate (TIPT,  $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ )
- Acetylacetone (ACA,  $\text{CH}_3\text{COCH}_2\text{COCH}_3$ )
- Laurylamine hydrochloride (LAHC,  $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2\cdot\text{HCl}$ )
- Hydrochloric acid (HCl)
- Cerium (IV) diammonium nitrate  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$
- Distilled water

##### *Epoxidation reaction*

- Cyclohexene ( $\text{C}_6\text{H}_{10}$ )
- *tert*-butanol ( $\text{C}_4\text{H}_9\text{OH}$ )
- Hydrogen peroxide ( $\text{H}_2\text{O}_2$ )

##### *Characterization*

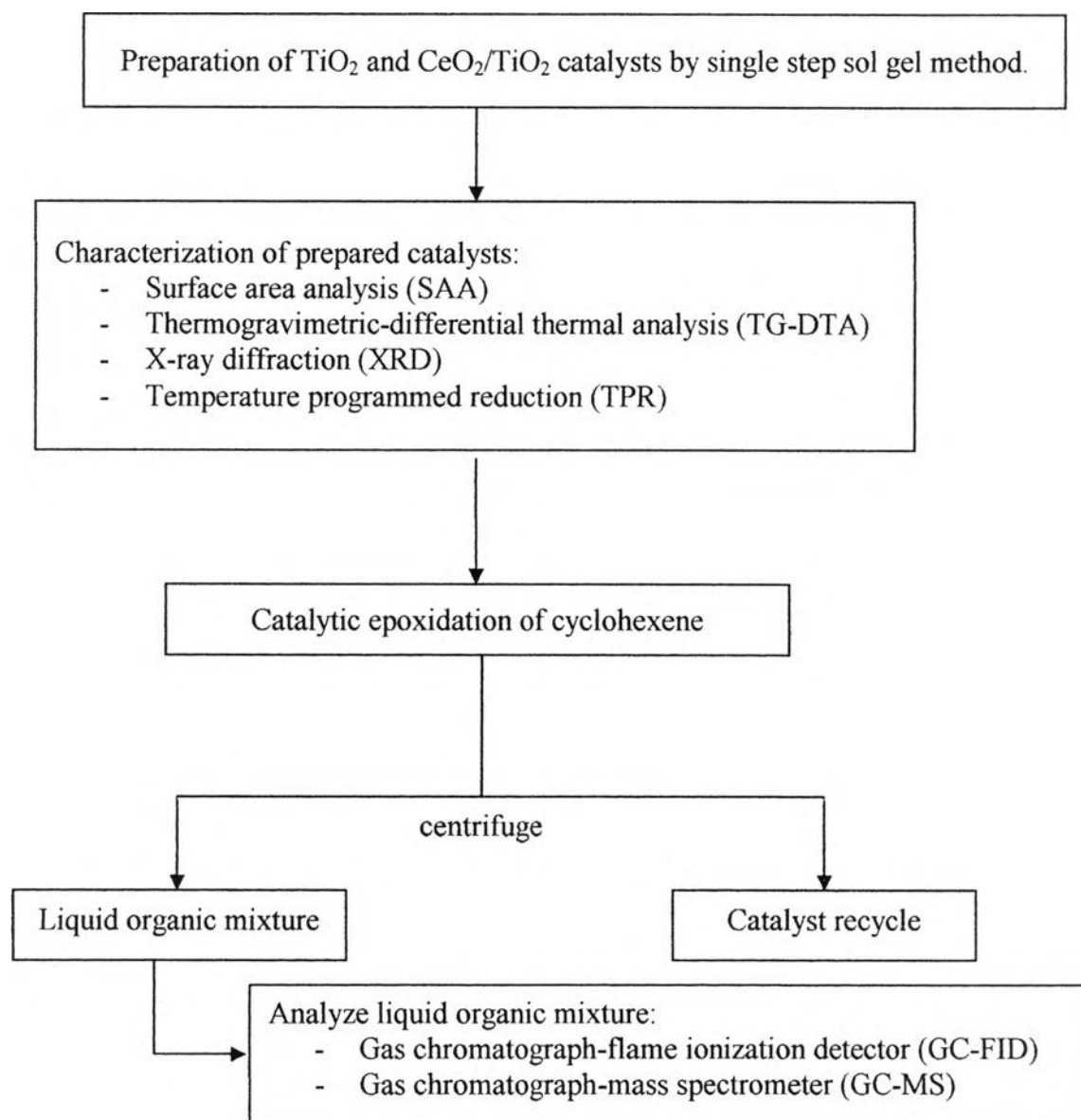
- Helium
- Hydrogen
- Air
- Cyclohexene oxide ( $\text{C}_6\text{H}_{10}\text{O}$ )
- Cyclohex-2-ene-1-ol or 2-cyclohexen-1-ol
- Cyclohex-2-ene-1-one or 2-cyclohexen-1-one
- (*1S,2S*)-*tran*-1,2-cyclohexanediol

#### 3.1.2 Equipments

- Gas chromatograph-flame ionization detector (HP GC 5890)
- Gas chromatograph-mass spectrometer
- X-ray diffractometer (RINT-2200)
- Surface area analyzer (Autosorb-1)
- Temperature programmed reduction system
- Oven

### 3.2 Experimental Procedure

The experimental procedures in this research can be represented by the flow diagram below. The first phase of the research experiment the synthesis of the catalysts. The various types of catalyst compositions was characterized by surface area analysis (SAA), thermogravimetric-differential thermal analysis (TG-DTA), X-ray diffraction analysis (XRD) and temperature programmed reduction analysis (TPR). The products obtained from the reaction were analyzed using the gas chromatography (GC).



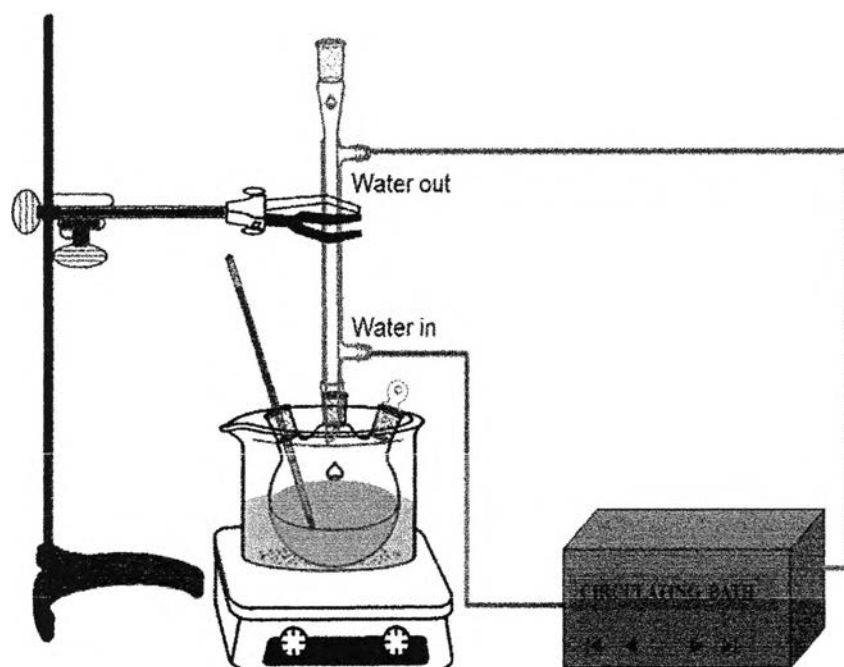
**Figure 3.1** Flow diagram of experimental procedure.

### 3.2.1 Preparation of Mesoporous-assembled Ce/Ru/TiO<sub>2</sub> Catalyst by Single-Step Sol-Gel Method

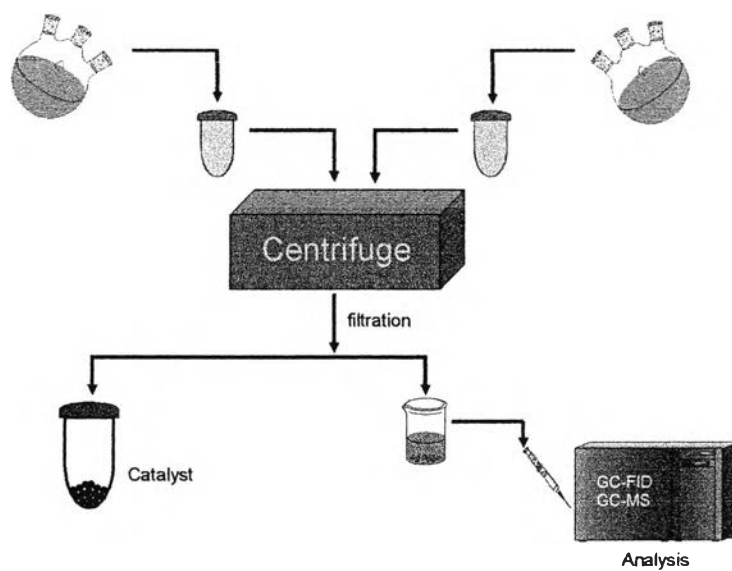
The TiO<sub>2</sub> was synthesized via the sol-gel (SG) method while the rest of the catalysts were synthesized via the single-step sol-gel (SSSG) method. A specified amount of tetraisopropyl orthotitanate (TIPT, Ti(OCH(CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub>) was introduced into acetyl acetone (ACA, CH<sub>3</sub>COCH<sub>2</sub>COCH<sub>3</sub>). The mixed TIPT/ACA solution was stirred until achieving a clear homogeneous mixture. Separately prepared, 0.1 M laurylamine hydrochloride (LAHC, CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>NH<sub>2</sub>·HCl) aqueous solution was prepared by addition of distilled water and acid while being stirred at 40 °C. For preparation by SSSG method, an appropriate amount of cerium (IV) diammonium nitrate (CAN, (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub>) and ruthenium (III) chloride hydrate (RCH, RuCl<sub>3</sub>·xH<sub>2</sub>O) was added to the LAHC solution. The molar ratios of metal precursors-to-LAHC and metal precursors-to-ACA were 4:1 and 1:1, respectively. The LAHC solution (RCH/CAN/LAHC if SSSG) was slowly poured into the TIPT/ACA solution. The mixture was kept continuously stirred at 40 °C for 8 hours to obtain a transparent sol. Then, the sol-containing solution (closed bottle) was placed into an oven at 80 °C for a week in order to obtain complete gel formation. The gel was dried (open bottle) at 80 °C for 2 days and was calcined.

### 3.2.2 Epoxidation Reaction

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<sub>2</sub>O<sub>2</sub> 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. In addition, steam treatment will be incorporated into the reactor during the reaction. The reaction will be optimized under various treatment temperatures, treatment times, and steam flow rates.



**Figure 3.2** Schematic of epoxidation reaction experiment.



**Figure 3.3** Flow diagram of catalyst separation.

### 3.2.3 Catalyst Characterization

#### 3.2.3.1 Surface Area Analysis (SAA)

Autosorb-1 Gas Sorption System (Quantachrome Corporation) will be used to measure the surface area, total pore volume, and mean pore diameter of the catalysts. The equipment measurement is based on Brunauer-Emmet-Teller (BET) equation. This technique is done by calculating the physical multi-layer adsorption of nitrogen. Volatile adsorbents on the surface will be 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  $1.62 \times 10^{-19} \text{ m}^2/\text{molecule}$  will be adsorbed on the catalyst surface at liquid nitrogen temperature (-196°C). The surface area will be calculated from the 44 points nitrogen adsorption. The mean pore diameter and pore volume will be obtained at  $P/P_0$  ratios close to unity. The result will be analyzed by Autosorb Anygas Software version 2.1 using the BET equation, as shown in Equation 3.1.

$$\frac{1}{W \cdot \left( \frac{P_0}{P} - 1 \right)} = \frac{1}{W_m \cdot C} + \frac{(C-1)}{(W_m \cdot C)} \cdot \left( \frac{P_0}{P} \right) \quad (3.1)$$

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 surface area will be calculated by Equation 3.2.

$$S = \frac{W_m \cdot A_{N_2} \cdot (6.02 \times 10^{23})}{M_{W,N_2}} \quad (3.2)$$

where:

- S = Specific surface area (m<sup>2</sup>/g)  
 $A_{N_2}$  = Cross-sectional area of one molecule of N<sub>2</sub>  
 (1.62 × 10<sup>-19</sup> m<sup>2</sup>/molecule at -196°C)  
 $M_{w,N_2}$  = Molecule weight of nitrogen (28 g/g-mol)

### 3.2.3.2 Thermogravimetric-Differential Thermal Analysis (TG-DTA)

Simultaneous thermogravimetry and differential thermal analysis (TG-DTA) of uncalcined gel will be used to obtain suitable calcination temperature for removing the LAHC surfactant. The uncalcined gel of 5-20 mg will be heated from 30 to 700°C with a heating rate of 20°C/min in nitrogen gas with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as the reference. Moreover, TG-DTA will be used for determination of the surface OH density (OH/nm<sup>2</sup>) and surface OH-to-catalyst weight ratio (OH/g) of the calcined catalysts. The OH surface density of the catalysts will be calculated by using the TGA weight loss and surface area, as shown in Equation 3.3 (Zou and Lin, 2004).

$$n\text{OH}/\text{nm}^2 = \alpha \left( \frac{2(\text{wt}_{T_1} - \text{wt}_{T_2})N_A}{MW_{H_2O} \times \text{SSA} \times \text{wt}_{T_1}} \right) \quad (3.3)$$

where:

- $\text{wt}_{T_i}$  = The sample weight at the corresponding temperature T<sub>i</sub>  
 $MW_{H_2O}$  = The molecular weight of water (18 g/g-mol)  
 $N_A$  = Avogadro's constant (6.02 × 10<sup>23</sup> mol<sup>-1</sup>)  
 SSA = Specific surface area (m<sup>2</sup>/g)  
 $\alpha$  = A calibration factor given as 0.625  
 $n\text{OH}/\text{nm}^2$  = The OH surface density (nm<sup>-2</sup>)

A temperature range from 100 to 120°C was found for removal of physically adsorbed water; therefore, this range will not be crucial for powder characterization as it depends even on humidity during sample preparation. But for a temperature range from 120 to 500°C, it represents 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.

### 3.2.3.3 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is used to identify phases present in the sample. The crystalline structure and the mean particle size of the catalyst was analyzed by using of a Rigaku X-ray diffractometer system (RINT-2200) with a copper tube for generating  $\text{CuK}\alpha$  radiation (1.54056 Å) and a nickel filter. It is 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 RINT-2200 system was used to obtain XRD patterns at a generator voltage of 40 kV and generator current of 40 mA. The goniometer parameters are divergent slit =  $1^\circ$  ( $2\theta$ ); scattering slit =  $1^\circ$  ( $2\theta$ ); and receiving slit = 0.3 mm. The scan speed of  $5^\circ$  ( $2\theta$ )/min with scan step of 0.02 ( $2\theta$ ) will be used for the continuous run in 5 to  $90^\circ$  ( $2\theta$ ) range. The sample will be ground to the fine homogeneous powder and held in a beam direction in a thin-walled glass container. The signal will be sent to the online computer to record and analyze. Scherrer equation as expressed in Equation 3.4 shows the relationship between the crystallite size ( $D_b$ ) and the broadening ( $B_d$ ) of the diffraction line corresponding to the Bragg angle ( $\theta$ ) and X-ray wavelength ( $\lambda$ ).

$$D_b = \frac{K \cdot \lambda}{B_d \cdot \cos \theta} \quad (3.4)$$

where:

$D_b$  = Crystallite size (Å)

$K$  = Scherrer constant, 0.9

$\lambda$  = X-ray wavelength (Å)

$B_d$  = Full width at half maximum of peak at  $2\theta$  (radian)

$\theta$  = Bragg angle of the reflection (radian)

#### 3.2.3.4 Temperature Programmed Reduction (TPR)

Temperature programmed reduction is used to identify the phases and interaction between the support and precursor. The objective of the TPR technique is subjecting an oxidized catalyst in a flowing reduction gas mixture atmosphere to a temperature rise. Monitoring of the H<sub>2</sub> and O<sub>2</sub> concentration in the effluent gas indicates the reduction rate. The reaction rates are used to explain the interaction between metals in the sample. The reduction reaction can be described by the following equation;



#### 3.2.3.5 Catalyst Activity Testing and Product Analysis

The filtrate (or liquid organic mixture), which is separated from the catalyst by centrifugation, is analyzed by a gas chromatograph (Agilent GC 6890) - flame ionization detector (FID) for determination of product composition. The liquid products from the cyclohexene epoxidation contain non-polar hydrocarbon. The non-polar hydrocarbon can be determined by using ZB-5 column (non-polar column), of which the composition is 5% diphenyl polysiloxane and 95% dimethyl polysiloxane. Firstly, the mixture between the standard substances and internal standard, which is dodecane, is injected into column to determine the response factor from peak area of GC. Secondly, before sample injection to GC, the liquid organic mixture has to be mixed with the internal standard. Finally, the conversion percentage and the selectivity percentage are calculated from peak area and response factor.

In this research, a gas chromatograph-flame ionization detector (GC-FID, Agilent 6890) is used as liquid product analyzer. The GC operating condition is summarized in Table 3.1.



**Table 3.1** GC conditions for the product analysis

Setting	Condition
Oven temperature	50°C for 5 min, 10°C/min to 160°C, 160°C for 5 min
Injector temperature	250°C
Detector temperature	250°C
Carrier gas	Helium 99.99% purity
Sample volume	1 µl
Column type	ZB-5 HT column (30 m × 0.32 mm ID × 0.10 µm Film Thickness)

To determine the quantity of the products, dodecane (C<sub>12</sub>H<sub>26</sub>) was used as the internal standard. The response factors of each product are calculated based on Equation 3.6:

$$R_x = \left( \frac{m_{is}}{A_{is}} \right) \left( \frac{A_x}{m_x} \right) \quad (3.6)$$

where:

$R_x$  is response factor of reference substance x

$m_{is}$  is mass in g of internal standard

$m_x$  is mass in g of reference substance x

$A_x$  is peak area of reference substance x

$A_{is}$  is peak area of internal standard

The composition (yield) percentage of each product is calculated by Equation 3.7:

$$\text{wt. \%} = \left( \frac{1}{R_x} \right) \left( \frac{m_{is}}{A_{is}} \right) \left( \frac{A_x}{m_x} \right) \times 100 \quad (3.7)$$

where:

wt.% is percentage of mass of component x in sample

$R_x$  is response factor of component x in sample

$m_{is}$  is mass in g of internal standard in sample

$m_x$  is mass in g of sample

$A_x$  is peak area of component x in sample

$A_{is}$  is peak area of internal standard in sample

The conversion percentage of the substrate and the selectivity percentage of the product in epoxidation reaction are calculated by Equations 3.8 and 3.9, respectively. Conversion of feed is defined as the weight ratio of cyclohexene converted to the initial cyclohexene, as shown in Equation 3.8. Selectivity is defined as the ratio of the weight of the product formation to cyclohexene converted (or total products produced), as shown below;

$$\text{Cyclohexene conversion (\%)} = \frac{\text{Weight of cyclohexene converted}}{\text{Initial weight of cyclohexene}} \times 100 \quad (3.8)$$

$$\text{Selectivity of product } i \text{ (\%)} = \frac{\text{Weight of product } i \text{ produced}}{\text{Weight of cyclohexene converted}} \times 100 \quad (3.9)$$