

## CHAPTER III

### EXPERIMENTAL

#### 3.1 Chemicals

The lists of chemicals used in this research are shown in the Table 3.1, and Table 3.2.

**Table 3.1** Chemicals used for samples preparations.

Chemical	Purity	Supplier
Zinc Oxide	Commercial Grade	Univentures PLC
Zinc Acetate	9.99%, AR Grade	Sigma-Aldrich
Lithium Carbonate	≥90.0%, AR Grade	Fluka
Sodium Carbonate	99.0%, AR Grade	Riedel-de Haën
Potassium Carbonate	99.5%, AR Grade	May& Baker
Potassium Hydroxide	98.0%, AR Grade	Ajax Finechem
Potassium Nitrate	99.5%, AR Grade	Ajax Finechem
Potassium Chloride	99.0%, AR Grade	Ajax Finechem
Methanol	≥99.9%, AR Grade	Merck
Toluene	AR Grade	Fisher Scientific
Tetrahydrofuran	≥ 99.5%, AR Grade	Fluka
n -Heptane	AR Grade	Carlo Erba
Hexane	99.0%, AR Grade	Merck
Ethyl Acetate	AR Grade	Ajax Finechem
Acetic Acid	99.5%, AR Grade	BDH Chemicals

**Table 3.2** Chemicals Standard used for GC and TLC.

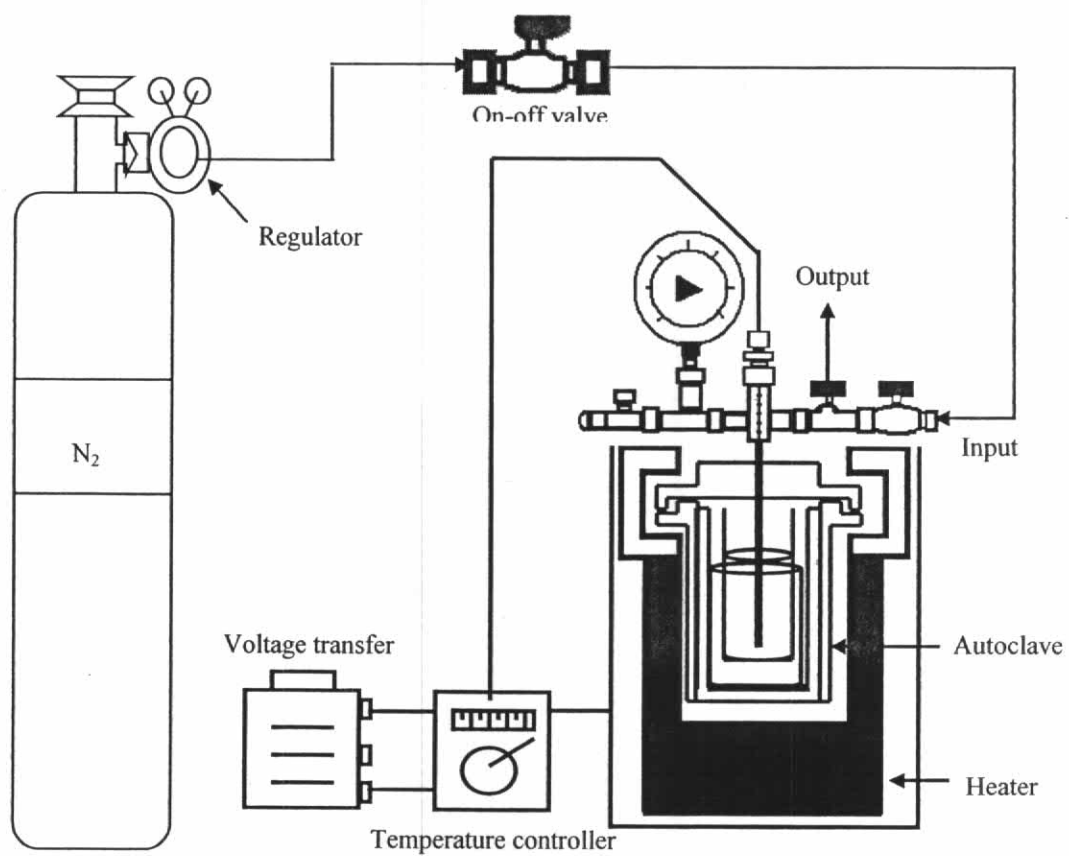
Chemical	Grade	Supplier
Monoglyceride: Monoolein	99.9%	Supelco
Diglyceride: Diolein	99.5%	Supelco
Triglyceride: Triolein	99.9%	Supelco
Free fatty acid: Oleic acid	99.0%	Sigma
Methyl ester: Methyl oleate	≥ 99.0%	Sigma
Methyl palmitate	≥ 99.5%*	Fluka
Methyl stearate	≥ 99.5%*	Fluka
Methyl oleate	≥ 99.0%*	Fluka
Methyl linoleate	≥ 98.5%*	Fluka
Methyl linolenate	≥ 99.0%*	Fluka
Methyl decanoate	99.0%*	Aldrich

\* puriss. p.a. standard for GC

### 3.2 Equipment : Autoclave Reactor for Solvothermal Synthesis

The detailed schematic diagram of the equipment used for ZnO synthesis via the solvothermal method is mainly consisted of an autoclave reactor, as shown in Figure 3.1. The reactor has the following features.

- Made from stainless steel
- Volume of 1000 cm<sup>3</sup> and 10 cm inside diameter.
- Temperature controlled through the attached thermocouple. The maximum operating temperature is 350 °C.
- Equipped with pressure gauge, in the range of 0-140 bar.
- Iron jacket was used to reduce the volume of the autoclave to be 300 cm<sup>3</sup>.



**Figure 3.1** Diagram of the reaction equipment for the catalyst preparation.

### 3.3 Samples Preparations

#### 3.3.1 Preparation of ZnO by Solvothermal Method

Preparation of ZnO by the solvothermal method was done using zinc acetate as starting material, according to the following procedure

1. About 15 g of zinc acetate was suspended in 100 ml of toluene which was as a solvent, in a test tube. The test tube was then placed into an autoclave.
2. In the gap between the test tube and autoclave wall, 30 ml of toluene was added.
3. The autoclave was purged with nitrogen. Then, the autoclave was heated to 300 °C at the rate of 2.5 °C min<sup>-1</sup> and held at that temperature for 2 hours.
4. After the reaction, the autoclave was cooled to room temperature.
5. The resulting powder was collected after repeatedly washed with methanol and centrifuge. Then, the products were dried in air.

#### 3.3.2 Preparation of ZnO Loaded with Alkali Metal Salt

The catalyst (i.e. ZnO loaded with alkali metal salt) was prepared by an impregnation method using an aqueous solution of an alkali metal compound investigated (e.g. Li<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, KNO<sub>3</sub>, KCl and KOH), according to the following procedure.

1. About 1.2 ml of the aqueous solution of the alkali metal salt with the predetermined concentration was added into about 4 g of ZnO powder. The mixture was rigorously stirred.
2. The product was dried for 12 h at room temperature.
3. The resulting powder was further dried for 24 h at 110 °C.
4. Prior to the reaction, the thus-obtained powder was calcined at 600 °C in air for 5 h, using the following conditions.

- heating up at the rate of 10 °C/min in nitrogen.
- nitrogen flow rate was 10 cm<sup>3</sup>/min.
- held in air at 600 °C for 5 h, with the air flow rate of 6 cm<sup>3</sup>/min
- cooled down to room temperature in nitrogen flow.

### 3.3.3 Transesterification of Soybean Oil

Transesterification of soybean oil, in order to synthesize methyl esters, was done, according to the following procedure.

1. A 50 ml two-necked glass flask with a water-cooled condenser was charged with 10 g (11.44 mmol, calculated from the average molecular weight of soybean oil) of soybean oil, predetermined amount of anhydrous methanol and predetermined amount of catalyst.
2. The mixture was heated to 65 °C, while it was refluxed and vigorously stirred using magnetic stirrer, the reaction was held for the required reaction period of time.
3. After the transesterification reaction was finished, the catalyst was separated from the product mixture by centrifugation at 3000 round/min for 15 min.
4. The liquid mixture was placed in a separatory funnel and was allowed to stand overnight to insure the separation of the methyl ester and the glycerol phase.
5. The glycerol phase (bottom layer) was removed and kept in a separate container. Afterwards, the excess methanol was removed from the methyl esters phase (top layer) by evaporation.

## 3.4 Characterizations

### 3.4.1 Catalyst characterization

#### 3.4.1.1 X-ray diffraction (XRD)

X-ray diffraction (XRD) analysis of zinc oxide was performed by using a SIEMENS XRD D5000 diffractometer at the Center of Excellence on Catalysis and Catalytic Reaction Engineering, Chulalongkorn University, connected to a computer with Diffract ZT version 3.3 program for fully control of the XRD analyzer. The measurements were carried out by using Ni-filtered  $\text{CuK}_\alpha$  radiation. The scan was performed over the range from  $10^\circ$  to  $80^\circ$  with the resolution of  $0.02^\circ$ .

#### 3.4.1.2 Scanning electron microscope (SEM)

Scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX) were used to determine the sample morphology and elemental distribution of the samples using JEOL JSM – 35CF electron microscope at the Scientific and Technological Research Equipment Centre, Chulalongkorn University (STREC). The SEM of JEOL mode JSM-6400 was applied. After the SEM micrographs were taken, EDX was performed to determine the element distribution on the sample using Link Isis 300 software.

#### 3.4.1.3 $\text{CO}_2$ temperature programmed desorption ( $\text{CO}_2$ -TPD)

$\text{CO}_2$  -TPD was used to determined basicity of the catalyst. The continuous flows of helium ( $30 \text{ ml min}^{-1}$ ) through the 200 mg of the catalyst for 1 h at  $500^\circ\text{C}$  were employed to remove moisture and other gases (heating rate of  $10^\circ\text{C min}^{-1}$ ). Then, the catalyst was saturated with  $\text{CO}_2$  at ambient temperature (about  $25^\circ\text{C}$ ) followed by continuous flow of helium for 30 min. Then, the catalyst was heated to  $800^\circ\text{C}$  using the temperature ramp of  $10^\circ\text{C min}^{-1}$  in order to determine the  $\text{CO}_2$  desorption and the strength of the basic sites.

#### **3.4.1.4 Surface area measurement**

The specific surface area of zinc oxide particles was measured via the Brunauer-Emmet-Teller (BET) technique, using a Micromeritics ASAP 2000 instrument, using nitrogen as the adsorbate. Each sample was degassed under vacuum at  $< 10 \mu\text{m-Hg}$  at  $150^\circ\text{C}$  for 4 hours prior to  $\text{N}_2$  physisorption.

#### **3.4.1.5 Thermogravimetric Analysis (TGA)**

The prepared catalysts were subjected to a differential thermal analysis (Diamond Thermogravimetric and Differential Thermal Analyzer, STA 4094) to determine the temperature of possible decomposition and phase change in the range of  $20\text{-}1000^\circ\text{C}$ . The analysis was performed at a heating rate of  $10^\circ\text{C}/\text{min}$  under  $50 \text{ ml}/\text{min}$  flow of air.

#### **3.4.1.6 Infrared Spectroscopy Analysis (FT-IR)**

Infrared spectra of the products were also obtained using Nicolet FT-IR spectrophotometer model Impact 400. Each sample was mixed with KBr in the ratio of 1:100 and then pressed into a thin pellet. Infrared spectra were recorded at wave number in the range of  $400$  and  $4000 \text{ cm}^{-1}$ .

#### **3.4.1.7 X-ray Photoelectron Spectroscopy Analysis (XPS)**

The elemental content on the surface of the ZnO loaded with alkali metals was determined by using X-ray photoelectron spectroscopy (Amicus, using  $\text{MgK}\alpha$  radiation) at the Center of Excellence on Catalysis and Catalytic Reaction Engineering, Chulalongkorn University.

### 3.4.2 Methyl Esters Characterization by Gas Chromatography (GC)

The samples obtained from the transesterification reaction were analyzed in a Perkin-Elmer Series 8700 gas chromatograph equipped with a flame ionization detector and a capillary column OV Carbowax 20M (30m, 0.32mmID, 0.25 $\mu$ mdf). The upper layer in the separation funnel (See section 3.3.3) was dissolved in n-heptene and internal standard solutions (n- heptene: methyl decanoate at ratio of 20: 1 by weight) for GC analysis. H<sub>2</sub>, Air and He were used as carrier gas. The samples (0.5  $\mu$ l) was injected into the GC, operated with the following conditions.

- Initial oven temperature	80	°C
- Oven ramp rate	10	°C/min
- Final oven temperature	230	°C
- Injector temperature	300	°C
- Detector temperature	300	°C
- Inlet pressure	9.5	PSIG