



## CHAPTER III EXPERIMENTAL

### 3.1 Equipments

- High pressure packed-bed continuous flow reactor system consisting of;
  - Mass flow controller (Brooks instrument 5850E)
  - High pressure liquid pump (Water 515 HPLC)
  - Back pressure regulator (SIEMENS)
  - ¾" O.D. stainless steel reactor
  - Tubular furnace with a temperature controller
- Gas chromatograph (Agilent 7890)
- X-ray diffractometer (Bruker AXS/D8 advance)
- Thermogravimetric/derivative thermogravimetric analyzer (TG-DTA, Perkin Elmer/Pyris Diamond)
  - Temperature programmed reduction apparatus (TPR)
  - Temperature programmed oxidation apparatus (TPO)
  - Surface area analyzer (SAA, Quantachrome/Autosorb1-MP)
  - UV light source (11-W low-pressure mercury lamp, Philips)
  - UV cut-off filter (B-48S/ATG)
  - Stirring hot plate
  - Oven (Carbolite CWE 1100)

### 3.2 Chemicals

- Beef fat (from PTT Public Company Limited)
- Palladium(II) nitrate dehydrate ( $\text{Pd}(\text{NO}_3)_2$ )
- Palladium chloride ( $\text{PdCl}_2$ )
- Titanium dioxide ( $\text{TiO}_2$ , Degussa P-25)
- Tetraisopropyl orthotitanate (TIPT,  $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ )
- Laurylamine hydrochloride (LAHC,  $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2\cdot\text{HCl}$ )
- Acetylacetone (ACA,  $\text{CH}_3\text{COCH}_2\text{COCH}_3$ )
- n-Dodecane ( $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$ , 99.9 % purity, Merck)

- Acetone ( $\text{CH}_3\text{COCH}_3$ , 99 % purity, LabScan)
- Methanol ( $\text{CH}_4\text{O}$ , 99 % purity, Merck)
- Distilled water
- Pyridine ( $\text{C}_5\text{H}_5\text{N}$ , 98 % purity, Carlo Erba reagente puro)
- N,O-bis(trimethylsilyl)-trifluoro acetamide (BSTFA,  $\text{C}_8\text{H}_{18}\text{F}_3\text{NOSi}_2$ , 99 % purity, ACROS)
- Eicosane ( $\text{C}_{20}\text{H}_{42}$ , 99 % purity, ACROS)

### 3.3 Gases

- Hydrogen ( $\text{H}_2$ , HP grade, 99.99 % purity)
- Helium (He, HP grade, 99.99 % purity)
- Nitrogen ( $\text{N}_2$ , HP grade, 99.99 % purity)
- Air (HP grade, 99.99 % purity)

### 3.4 Experimental Procedures

#### 3.4.1 Catalyst Preparation

The preparation of 1 wt% Pd/TiO<sub>2</sub> supported catalyst was performed by 4 different techniques.

1) Incipient wetness impregnation (IWI) using commercial P-25 TiO<sub>2</sub> support denoted as P25-IWI.

2) Incipient wetness impregnation (IWI) using TiO<sub>2</sub> support synthesized via a combined sol-gel process with surfactant-assisted templating method denoted as SG-IWI.

3) Photochemical deposition (PCD) using commercial P-25 TiO<sub>2</sub> support denoted as P25-PCD.

4) Photochemical deposition (PCD) using TiO<sub>2</sub> support synthesized via a combined sol-gel process with surfactant-assisted templating method denoted as SG-PCD.

5) Combined single-step sol-gel process with surfactant-assisted templating method (SATM) denoted as SSSG.

#### 3.4.1.1 Preparation TiO<sub>2</sub> Support by Sol-gel Method

Nanocrystalline mesoporous TiO<sub>2</sub> was synthesized via a combined sol-gel process with surfactant-assisted templating method, consisting of the following steps:

a) ACA was first introduced into the TIPT with the TIPT to ACA molar ratio equal to unity.

b) The mixed solution was gently shaken until homogeneous mixing.

c) Afterwards, a 0.1 M LAHC aqueous solution with pH of 4.2 was added to the ACA-modified TIPT solution, in which the molar ratio of TIPT to LAHC was tailored to a value of 4.

d) The mixture was continuously stirred at 40 °C overnight to obtain transparent yellow 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 overnight to eliminate the solvent, which is mainly the distilled water used in the preparation of LACH aqueous solution.

g) The dried gel was finally calcined at 500 °C to remove the LAHC and consequently produce the desired mesoporous TiO<sub>2</sub> catalysts.

#### 3.4.1.2 Metal (Palladium) Loading

1 wt% palladium supported titania catalyst was prepared by 2 different methods according to the following procedure:

##### i) Incipient Wetness Impregnation

a) TiO<sub>2</sub> supports were impregnated with the aqueous solution of metal precursors (Pd(NO<sub>3</sub>)<sub>2</sub>).

b) After impregnation, the catalysts was dried at 110 °C overnight and subsequently calcined at 500 °C for 4 h.

c) After drying, TiO<sub>2</sub> supports were initially sieved to the particle size 20/40 mesh.

*ii) Photochemical Deposition*

a) TiO<sub>2</sub> supports were initially dispersed in distilled water and ultrasonicated for 20 min.

b) Then, a desired amount of palladium chloride, methanol, and distilled water were added to obtain 50 vol% aqueous methanol solution.

c) The mixture was magnetically stirred and irradiated for 4 h by a set of low-pressure Hg lamps (16 lamps, TUV 11 W Pl-s, Phillip).

d) After the irradiation, the Pd-deposited catalyst powders were recovered by filtration, washed with hot distilled water, and dried at 80 °C.

*3.4.1.3 Combined Single-step Sol-gel Process with Surfactant-assisted Templating Method (SATM).*

1 wt% palladium supported titania catalyst was prepared by combining between the support preparation and the metal loading together, consisting of the following step:

a) ACA was first introduced into the TIPT with the TIPT to ACA molar ratio equal to unity.

b) The mixed solution was shaken until homogeneous mixing.

c) Afterwards, a 0.1 M LAHC aqueous solution with pH of 4.2 was added to the ACA-modified TIPT solution, in which the molar ratio of TIPT to LAHC was tailored to a value of 4 in order to control the porosity of the TiO<sub>2</sub>.

d) The mixture was continuously stirred at 40 °C overnight to obtain transparent yellow sol.

e) A required amount of palladium chloride solution for the desired Pd loading of 1 wt% was incorporated into the aged transparent sol solution.

f) The resultant mixture was further aged at 40 °C for 30 min to acquire a homogeneous solution.

g) The gel was then formed by placing the sol-containing solution in an oven at 80 °C for a week for complete gel formation.

h) Afterwards, the gel was dried at 80 °C overnight.

i) Finally, the dried gel was calcined at 500 °C for 4 h to remove the LAHC template, and subsequently the desired catalyst was achieved.

### 3.4.2 Catalyst Characterizations

#### 3.4.2.1 Thermogravimetry and Differential Thermal Analysis (TG-DTA)

Simultaneous thermogravimetry and differential thermal analysis (TG-DTA) was used to study the thermal decomposition behavior of the catalysts and to obtain their suitable calcination temperatures. The catalyst of 1-5 mg was heated from 50 °C to 900 °C with a heating rate of 10 °C/min in a static air atmosphere.

#### 3.4.2.2 Atomic Absorption Spectroscopy (AAS)

Atomic absorption spectroscopy (GBC, Avanta PM) was used to determine the concentration of a particular element in a sample. Chemical element will absorb ultraviolet light when they are excited by heat. Each element has a characteristic wavelength that will be absorbed. The AAS instrument seeks for a particular element by focusing a beam of UV light at a specific wavelength through a flame and into a detector. The sample of interesting element is aspirated into the flame. If the element is present in the sample, it will absorb some of the light, thus reducing its intensity. The instrument measures the change in intensity. A computer data system converts the change in intensity into an absorbance. As a concentration increases, an absorbance increases. A standard calibration curve is constructed by standard solutions at various concentrations

#### 3.4.2.3 X-ray Diffraction (XRD)

Rigaku X-ray diffractometer system (RINT-2200) with a Cu tube for generating CuK $\alpha$  radiation (1.5406 Å) and a nickel filter, operated at a generator voltage of 40 kV and a generator current of 30 mA, was used to obtain XRD patterns of the catalysts. The scan speed of 5° (2 $\theta$ )/min with scan step of 0.05 (2 $\theta$ ) was used for the continuous run in 5° to 50° (2 $\theta$ ) range. Due to the specific chemical composition and crystallographic structure of each material, XRD is an efficient analytical technique used to identify and characterize unknown crystalline materials. Matching of the reference substance's diffraction pattern and sample's

diffraction pattern is the main principle of the technique. If they have the same pattern, the same crystallite phase was shown.

#### 3.4.2.4 Hydrogen Chemisorption

This technique was used to determine the dispersion of Pd on the surface of catalysts. It was performed in a conventionally made-up system connected to a thermal conductivity detector (TCD) with 20- $\mu$ l pulses of the purified H<sub>2</sub>. Prior to the pulse chemisorption, the sample was reduced in H<sub>2</sub> atmosphere at 200 °C for 2 h. Consecutively, it was purged with N<sub>2</sub> for 1 h and cooled down to 110 °C by flowing N<sub>2</sub>. H<sub>2</sub> pulses were injected at regular interval time at 110 °C to avoid the problem of Pd hydrides formation (Castellazzi, *et al.*, 2010) until the saturation was observed. The result was detected with the TCD to determine the bound chemisorbed H<sub>2</sub>, which corresponded to H<sub>2</sub> adsorbed on the Pd surface. To calculate the Pd dispersion, a H/Pd = 1/1 stoichiometry was assumed for H<sub>2</sub> chemisorption on palladium.

#### 3.4.2.5 Brunauer-Emmett-Tellet (BET) Surface Area Analysis

The surface area of the fresh and spent catalysts was measured by BET surface area analyzer (Quantachrome/Autosorb1-MP). The sample was first outgassed to remove the humidity and volatile adsorbents adsorbed on surface under vacuum at 250 °C for 4 h prior to the analysis. Then, N<sub>2</sub> was purged to adsorb on surface, and the quantity of gas adsorbed onto or desorbed from their solid surface at some equilibrium vapor pressure by static volumetric method was measured. The solid sample was maintained at a constant temperature of the sample cell until the equilibrium is established. This volume-pressure data was used to calculate the BET surface area.

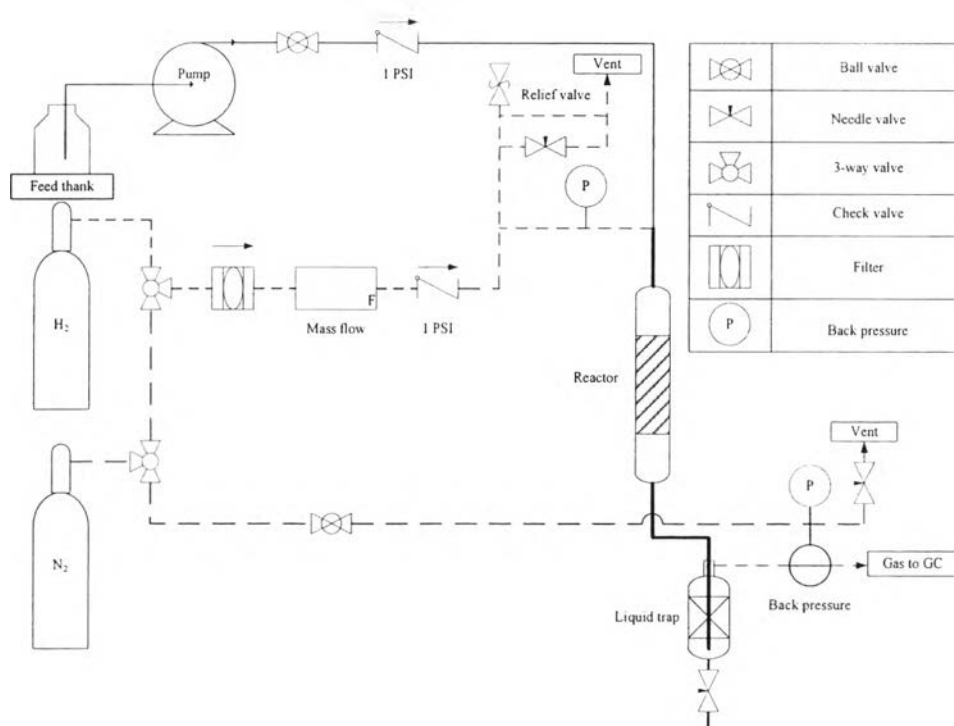
#### 3.4.2.6 Temperature Programmed Oxidation (TPO)

Temperature programmed oxidation (TPO) was carried out to determine the amount and characteristics of coke formed on the spent catalysts. TPO profiles of the spent catalysts were performed in a continuous flow of 2% O<sub>2</sub>/He while the temperature was linearly ramped to 800 °C with a heating rate of 10 °C

/min. The sample (30 mg) was placed in a 1/2" quartz fixed bed reactor. The CO<sub>2</sub> produced by the oxidation of coke was further converted to methane over 15% Ni/Al<sub>2</sub>O<sub>3</sub> catalyst in the presence of hydrogen at 400 °C. The methane obtained was analyzed online by a FID detector. The amount of oxidized coke was calibrated using 100 pulses of pure CO<sub>2</sub>.

### 3.4.3 Hydrodeoxygenation Experiments

The experiment was carried out in a high pressure fixed bed reactor, as shown in Figure 3.1, and the description of flow diagram is shown in Table 3.1. The catalysts were pretreated by placing in the reactor and reducing by flowing hydrogen at 500 psig for 3.5 h. The temperature was increased with a rate of 5 °C/min until reaching the reduction temperature, typically 200 °C. Then, the stream of beef fat was fed to the reactor using a high pressure pump. The flow of carrier gas and the reaction pressure were controlled by a mass flow controller and a back pressure regulator, respectively. The liquid product was collected in a condenser immersed in an ice bath at the bottom of reactor and analyzed by a gas chromatograph equipped with a FID detector.



**Figure 3.1** A schematic flow diagram of high pressure experimental setup.

**Table 3.1** Description of flow diagram

No.	Items	Functions
1	V1	On-off valve for liquid from high pressure liquid pump
2	V2	Checking valve for avoiding the backward flow of liquid from high pressure pump
3	V3	Three-way valve for switching nitrogen gas to hydrogen gas
4	V4	Checking valve for avoiding the backward flow of hydrogen or nitrogen gas
5	V5	Three-way valve for switching direction of nitrogen flow
6	V6	Needle valve for controlling pressure in back pressure regulator
7	V7	Needle valve for releasing gas from the system
8	V8	Relief valve to release to pressure overload in the system
9	V9	On-off valve for releasing the pressure from back pressure Regulator
10	V10	Metering valve for releasing the product from condenser

Production of the hydrogenated biodiesel by the deoxygenation of beef fat was conducted at temperature, pressure, and H<sub>2</sub>/feed ratio as shown in Table 3.2.

**Table 3.2** The reaction conditions for producing the renewable diesel

Parameters	Condition
Reaction temperature	325 °C
Reaction pressure	500 psig
H <sub>2</sub> /feed molar ratio	30



### 3.4.4 Product Analysis

In this research, GC/FID (Agilent 7890) was used as liquid product analyzer. The GC operating conditions are summarized as follows:

Injector temperature:	50 °C
Detector temperature:	380 °C
Carrier gas:	He
Column type:	Capillary column (DB-5HT: diameter 0.32 mm length 30 m)

The following chromatographic temperature program was used for product analysis:

**Table 3.3** The chromatographic temperature program for liquid product analysis

Step	Temperature (°C)	Rate (°C/min)	Holding time (min)
1	50	-	5
2	169	10	10
3	380	20	10

Typically, samples had to be dissolved in pyridine and silylated with *N,O*-bis(trimethyl) trifluoroacetamide, BSTFA (Acros Organics, 98+%), in order to improve the chromatographic behavior in GC analysis. The internal standard eicosane, C<sub>20</sub>H<sub>42</sub>, was added for quantitative calculations.

The calculations of conversion and product selectivity are defined as shown in equation 1 and 2, respectively. Conversion of feed is defined as the mole ratio of feed consumed to the feed input, as shown in Equation 1. Selectivity is defined as the ratio of the number of moles of the products formed to that of the feed consumed in the reaction, as shown in Equation 2.

$$\text{Conversion (\%)} = \frac{\text{moles of feed converted}}{\text{moles of feed input}} \times 100 \quad (1)$$

$$\text{Selectivity to product i (\%)} = \frac{\text{moles of product i obtained}}{\text{moles of feed converted}} \times 100 \quad (2)$$