CHAPTER III

EXPERIMENTAL

3.1 Gases

- Hydrogen (H_2, HP grade, 99.99 % purity) was used for the catalyst activity testing, and FID detector.
- Nitrogen (N_2, HP grade, 99.99 % purity)) was used for the catalyst activity testing.
- Helium (He, HP grade, 99.99 % purity) was used as carrier gas for gas chromatograph and for temperature-programmed desorption (TPD) measurement.
- The zero grade air was used for FID detector.
- 5 vol.% oxygen balance in helium was used for the temperature-programmed oxidation (TPO) measurement.
- 2 vol.% propylene balance in helium was used for the temperature-programmed desorption (TPD) measurement.

All gases mentioned above were supplied from TIG, Thailand.

3.2 Chemicals

- Glycerol ($C_3H_8O_3$, reagent grade) was obtained from Fisher Chemical, UK.
- Cyclohexane was obtained from Labscan, Thailand.
- The commercial ZSM-5 zeolite (SiO_2/Al_2O_3 = 23,30,50,80 and 280) were obtained from Zeolyst, USA.
- Tetraethyl orthosilicate ($SiC_8H_{20}O_4$) was obtained from Aldrich, USA.

3.3 Equipment

- 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 5890) equipped with a capillary HP-INNOWAX column.
- Gas chromatograph (Shimadzu GC-17A) equipped with a capillary HP-PLOT/Al_2O_3 "S" deactivated column.
- X-ray diffractometer (Bruker AXS/D8 advance)
- X-ray Fluorescence Spectroscopy (XRF)
- Surface area analyzer (SAA, Quantachrome/Autosorb1-MP)
- Temperature programmed desorption apparatus (TPD) connected to an online MS detector (MKS Cirrus).
- Temperature programmed oxidation apparatus (TPO)

3.4 Experimental Procedure

3.4.1 Silylation Preparation

In this study, the silylation was performed on HZSM-5 catalysts by chemical liquid deposition (CLD). The modified catalysts were obtained by impregnating 0.5 mL of tetraethyl orthosilicate (TEOS) per gram catalyst in 20 vol. % of TEOS in cyclohexane at room temperature for 12 h, dried at 110 °C for 2 h and then calcined at 550 °C for 5 h. The silylated catalyst was noted as 0.5CLD20/ HZSM-5.

3.4.2 Catalytic Activity Testing

The pure glycerol (>99.99%) was fed together with a H_2 carrier at a flow rate giving a molar ratio of H_2/glycerol of 10:1. The reaction was carried out at temperatures of 400 °C, pressure of 300 psig and W/F from 0.07 to 1 h (mass of catalyst/mass flow rate of organic). The liquid products, including water, were collected in a cold trap after accumulating for 3 h and then analyzed by gas chromatography using a Agilent 5890 equipped with a capillary HP-INNOWAX column. Non-condensed products passed through the back-pressure regulator, went to vent, and were not quantified, but some samples were analyzed by gas chromatography using Shimadzu GC-17A equipped with a capillary HP-

PLOT/Al_2O_3 “S” deactivated column. The schematic of the experiment set up is shown in Figure 3.1.

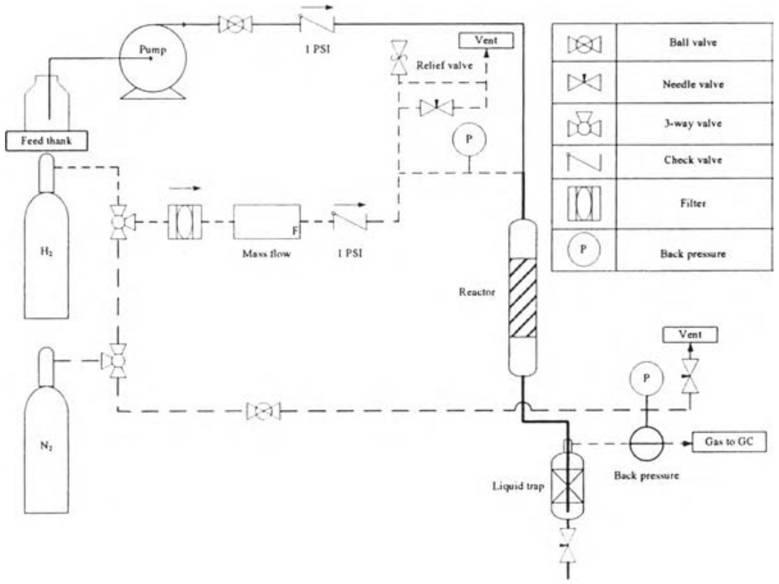

Figure 3.1 A schematic flow diagram of experimental setup.

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

The conversion of feed and selectivity is defined as follows;

$$\text{Conversion (\%)} = \frac{n_{\text{Feed,i}} - n_{\text{Feed,o}}}{n_{\text{Feed,i}}} \times 100$$

$$\text{Molar carbon yield(\%)} = \frac{n_{\text{Product.o}}}{n_{\text{Feed,i}}} \times 100$$

$$p\text{-Xylene selectivity in xylenes (\%)} = \frac{\text{moles of carbon in } p\text{-xylene}}{\text{moles of carbon in Xylenes}} \times 100$$

where $n_{\text{Feed,i}}$ and $n_{\text{Feed,o}}$ are the number of moles of carbon in glycerol at the input and output, respectively; $n_{\text{Product,o}}$ is the number of moles of carbon in the product at the output.

For quantitative calculations of oxygen-containing liquid products, *n*-octane (C_8H_{18}) was used as the internal standard. The response factors of each product are calculated based on following formula

$$R_x = \frac{m_{is}}{m_x} \times \frac{A_x}{A_{is}}$$

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 are of reference substance x

A is peak area of internal standard

The composition of each product is calculated following formula:

$$m'_x = \frac{1}{R_x} \times \frac{m'_{is}}{m'_x} \times \frac{A'_x}{A'_{is}}$$

Where m'_x 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

3.5 Catalyst Characterization

3.5.1 Temperature Programmed Oxidation (TPO)

This technique was employed to quantify the amount and the characteristics of coke deposited on the spent catalysts during reaction and obtain information about how the coke distributes over the catalyst. TPO of the spent catalysts was performed in a continuous flow of 2 % O_2 in He while the temperature was linearly increased with a heating rate of 10 °C/min. The oxidation was conducted in a ¼″ quartz fixed-bed reactor after the spent catalyst had been dried at 110 °C overnight, weighted (10 mg), and placed between two layers of quartz wool inside the quartz tube. The sample was further purged at room temperature by flowing 2 % O_2 in He for 30 min before the TPO was stared. The CO_2 produced by the oxidation of the coke species was converted to methane using a methanator filled with 15 % Ni/Al_2O_3 and operated at 415 °C. The evolution of methane was analyzed using an FID detector. A 100 μl pulse of methane was used as the internal standard for calculating coke contents.

3.5.2 Temperature Programmed Desorption (TPD) of Isopropylamine

The acidity of parent and silylated HZSM-5 was quantified by temperature-program desorption (TPD) of isopropylamine (IPA) in a quarter inch quartz tube reactor with 50 mg of catalyst connected to an online MS detector (MKS Cirrus). First, catalyst was initially pretreated at 500 °C in a flow of He for 1 h. After the pretreatment, the sample was cooled in He to 30 °C and then 5 μl pulses of isopropylamine were injected over the sample, until the sample was saturated. The saturation of isopropylamine adsorption was confirmed by mass spectrometry (MKS Cirrus). After removal of the excess isopropylamine by flowing He for 30 min, the sample was linearly heated to 800 °C at a heating rate of 20 °C/min. The MS signal of *m/e* 44, 41, and 17 were monitored to determine the evolution of isopropylamine (IPA), propylene, and ammonia, respectively. The amount of desorbed propylene was calibrated with a 2 ml pulse of 2 % propylene in He

3.5.3 Temperature Programmed Desorption (TPD) of Water

The H_2 desorption of HZSM-5 was quantified by temperature-program desorption (TPD) of water (H_2O) in a quarter inch quartz tube reactor with

50 mg of catalyst connected to an online MS detector (MKS Cirrus). First, catalyst was initially pretreated at 500 °C in a flow of He for 1 h. After the pretreatment, the sample was cooled in He to 30 °C and then 5 μl pulses of water were injected over the sample, until the sample was saturated. The saturation of water adsorption was confirmed by mass spectrometry (MKS Cirrus). After removal of the excess water by flowing He for 30 min, the sample was linearly heated to 800 °C at a heating rate of 20 °C/min. The MS signal of *m/e* 18 was monitored to determine the evolution of water (H_2O.

3.5.4 X-ray Fluorescence Spectroscopy (XRF)

The quantitative and qualitative elemental analysis of the HZSM-5 zeolite before and after silylation were analyzed by XRF technique, Philips model PW 2400. With a primary X-ray excitation source from an X-ray tube, the X-ray can be absorbed by the atom, and transfer all of its energy to an innermost electron. During the process, if the primary X-ray has sufficient energy, electrons are ejected from the inner shell, creating vacancies. These vacancies present an unstable condition for the atom. As the atom returns to its stable condition, electrons from the outer shells are transferred to the inner shells, and the process gives off a characteristic X-ray, whose energy in the difference between the two binding energies of the corresponding shells. Because each element has a unique set of energy levels, each element produces X-rays at a unique set of energies, allowing one to non-destructively measure the elemental composition of a sample. The intensities of observed lines for a given atom vary according to the amount of that atom present in the specimen.

3.5.5 Brunauer-Emmett-Tellet Method (BET)

Surface area and micropore volume of the samples were measured using BET method on a Quantachrom/Autosorb1-MP instrument. The sample was first outgassed to remove the humidity and volatile adsorbents adsorbed on surface under vacuum at 300 °C for 12 h prior to the analysis. Then, N_2 was purged to adsorb on the surface. 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 was established. This volume-pressure data was used to calculate the BET surface area and pore volume.

3.5.6 X-ray Diffraction (XRD)

The relative crystallinities of the HZSM-5 zeolite before and after silylation was analyzed by a Rigaku X-ray diffractometer with Cu tube for generating CuKα radiation (λ= 1.5418 A°) at room temperature. The 2θ is in the range between 10 and 80 with a scanning rate of 5 °/min. This analysis is generally preformed based on the fact that an X-ray diffraction pattern is unique for each crystalline substance, chemical identity can be assumed. It is also possible to make a relatively quantitative analysis by comparing substance of different samples; the higher intensity indicates the higher content.