



CHAPTER III

EXPERIMENTAL

In this chapter, materials associated with the experiments in this research work are described. Several catalyst preparations and characterization techniques, and the experimental set-up are discussed. The coke investigation of spent catalyst is also described.

3.1 Materials

The bioethanol with a concentration of 99.5 % used for aromatic production was obtained from Supthip Company Limited.

3.2 Chemicals and Solvents

The chemical reagents and solvents used in this research were:

1. Aluminiumsulfate decaoctahydrate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$)
2. Ammonium hydroxide (28v/v %)
3. Deionized water
4. Bentonite clay
5. Catalyst from NanoScale Corporation, Gamma alumina ($\gamma\text{-Al}_2\text{O}_3$)
6. Catalyst from Tosoh Co., Ltd., $\text{NH}_4\text{-ZSM-5}$ zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 40$)
7. Magnesiumhydrophosphate trihydrate ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$)
8. Gallium(III)nitrate hexahydrate ($\text{Ga}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$)
9. Zincnitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)
10. Helium gas

3.3 Equipment

1. Bench-scale U-tube reactor
2. Electrical furnace
3. Syringe pump
4. Oven
5. Agilent Technologies 6890, Gas chromatography (GC)
6. Sieves, Mesh 20 - 40
7. A grinder machine
8. A hydraulic pellet
9. Hot & Stirrer plate (Cole Parmer)
10. Condensing flask
11. Thermo Finnigan/Sorptomatic 1990 (Surface Area Analyzer)
12. Varian GC-3800 simulated distillation gas chromatograph (SIMDIST GC)
13. High-performance liquid chromatography (HPLC), IP 391 standard
14. Gas chromatography, UOP 744 standard

3.4 Experimental Procedures

3.4.1 Catalyst Preparation

3.4.1.1 *Catalyst for Catalytic Reaction in Bed #1*

MgHPO₄-added activated alumina (MgHPO₄/Al₂O₃) catalyst was prepared for the catalytic dehydration of ethanol to ethylene using kneading method (Kojima *et al.*, 1981). The commercial alumina from NanoScale Corporation was firstly dried in an oven at 110°C overnight. After that, the dried alumina was added by 0.5 wt% of MgHPO₄ and kneaded for 2 hours at room temperature. Then, the resulting mixture was dried again at 110°C at least 3 hours and subsequently calcined in a furnace at 600°C for 3 hours with the heating rate of 5 °C/min. At the end, the calcined catalyst was pelletized, ground and sieved to 20 - 40 mesh particles.

3.4.1.2 Catalysts for Catalytic Reaction in Bed #2

A commercial $\text{NH}_4\text{-ZSM-5}$ (Tosoh company, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 40$) was initially calcined in air at $500\text{ }^\circ\text{C}$ for a period of 5 hours to obtain the acid form called H-ZSM-5 zeolite catalyst. The nitrate solution of gallium and zinc was used as the source of Ga and Zn, respectively. 2.0 wt% Ga was loaded on the calcined H-ZSM-5 support by the incipient wetness impregnation technique. After impregnation, the wet catalyst was dried at $110\text{ }^\circ\text{C}$ in an oven for a few hours, followed by calcination at $600\text{ }^\circ\text{C}$ for 5 hours. Then, the calcined sample was hydraulically pressed to the pellet. Subsequently, the pressed sample was ground and sieved to 20 - 40 mesh particles before it was loaded into the reactor. Also, the same impregnation technique was performed for the preparation of 2.0 wt % Zn containing H-ZSM-5 support.

For hybrid catalysts, the preparing procedures can be divided into two steps. The first step was the synthesis of Zn-containing co-catalysts, which were prepared by heterogeneous co-precipitation. A liquid mixture of soluble zinc nitrate (hexahydrate) and aluminiumsulphate (decahydrate) for the $\text{ZnO}/\text{Al}_2\text{O}_3$ co-precipitate was prepared with Zn/Al ratio equal to 1.0, or 50 mol %-Zn. The solution was kept at $50\text{ }^\circ\text{C}$ and adjusted to $\text{pH } 7.5 \pm 0.5$ by the dropwise addition of ammonium hydroxide (28 v/v%) under stirring condition. Then, the stirring was maintained for 2 hours at $50\text{ }^\circ\text{C}$ and kept without agitation for 70 hours at room temperature. The resulting solution was washed to remove most of the soluble ammonium salts, dried in an oven at $110\text{ }^\circ\text{C}$ for 3-5 hours, and subsequently calcined at $550\text{ }^\circ\text{C}$ for 10 hours. Mixed oxides of co-catalysts were finally obtained. After that the co-catalysts were crushed and sieved to 20 - 40 mesh particles.

After the co-catalyst ($\text{ZnO}/\text{Al}_2\text{O}_3$ co-precipitate) had already been prepared, 5 wt% of the co-catalyst was mixed together with 75 wt% H-ZSM-5(40) powder at room temperature by mechanical mixing method. 20 wt% bentonite clay used as the binder was incorporated and intimately mixed with the mixture of catalyst. Then, the resulting mixture was dried at $110\text{ }^\circ\text{C}$ for a few hours and consecutively activated in air at $550\text{ }^\circ\text{C}$ for 10 h.

3.4.2 Catalyst Characterization

3.4.2.1 *Surface Area Analyzer (SAA)*

The Brunauer-Emmett-Teller (BET) technique was performed to determine the specific surface area, the total pore volume and the pore size of catalyst, using Thermo Finnigan/Sorptomatic 1990 which is based on the physical adsorption of nitrogen gas. The sample was initially outgassed to remove the humidity and volatile adsorbents adsorbed on the catalyst surface under vacuum at 300°C at least 18 hours prior to analysis step. The specific surface area and the pore size of catalyst were obtained from the twenty-two-point nitrogen adsorption and desorption isotherm plot. The pore size distribution was calculated using the BJH method.

3.4.3 Catalytic Activity Testing

The conversion of ethanol to aromatic hydrocarbons was carried out at LHSV = 1.0 h⁻¹ under atmospheric pressure flow system. The U-tube fixed-bed continuous flow reactor (10 mm i.d. and 45.8 cm length) was designed to charge the two beds of catalysts which separately located on the top-left hand side and the bottom-right hand side as shown in Figure 3.1. An electric furnace was performed to heat the reactor to the desired temperature of each catalytic zone controlling by independently-temperature controller. At the upper zone of reactor was the place of catalytic Bed #1. Three grams of MgHPO₄/Al₂O₃ catalyst was retained by quartz wool support on the center of the zone. The bed of catalyst was activated at 370 °C for 1-2 hours in the helium steam prior to reaction to preheat the catalyst.

At the lower zone of reactor was the place of catalytic Bed #2. Each of catalysts; pure H-ZSM-5, Ga₂O₃/H-ZSM-5(40), ZnO/H-ZSM-5(40), and hybrid catalyst (ZnO-Al₂O₃/H-ZSM-5), containing 3.0 g was packed on the center of the zone, and held in place by using quartz wool as a support as well. Similarly, the bed of catalyst was heated up to 500 °C for 1-2 hours in flowing helium before reaction to preheat the catalyst. The liquid ethanol was fed by a syringe pump into the reactor. However, prior to entry the reactor, the liquid ethanol was preheated to vaporize and mixed with helium gas at a ratio 1:1, with helium flowing at a rate of 27 ml/min. The effluent gas obtained from reaction was passed through the condensing flask to col-

lect the condensable products. The non-condensable products were passed out from the condensing flask to online gas chromatography later.

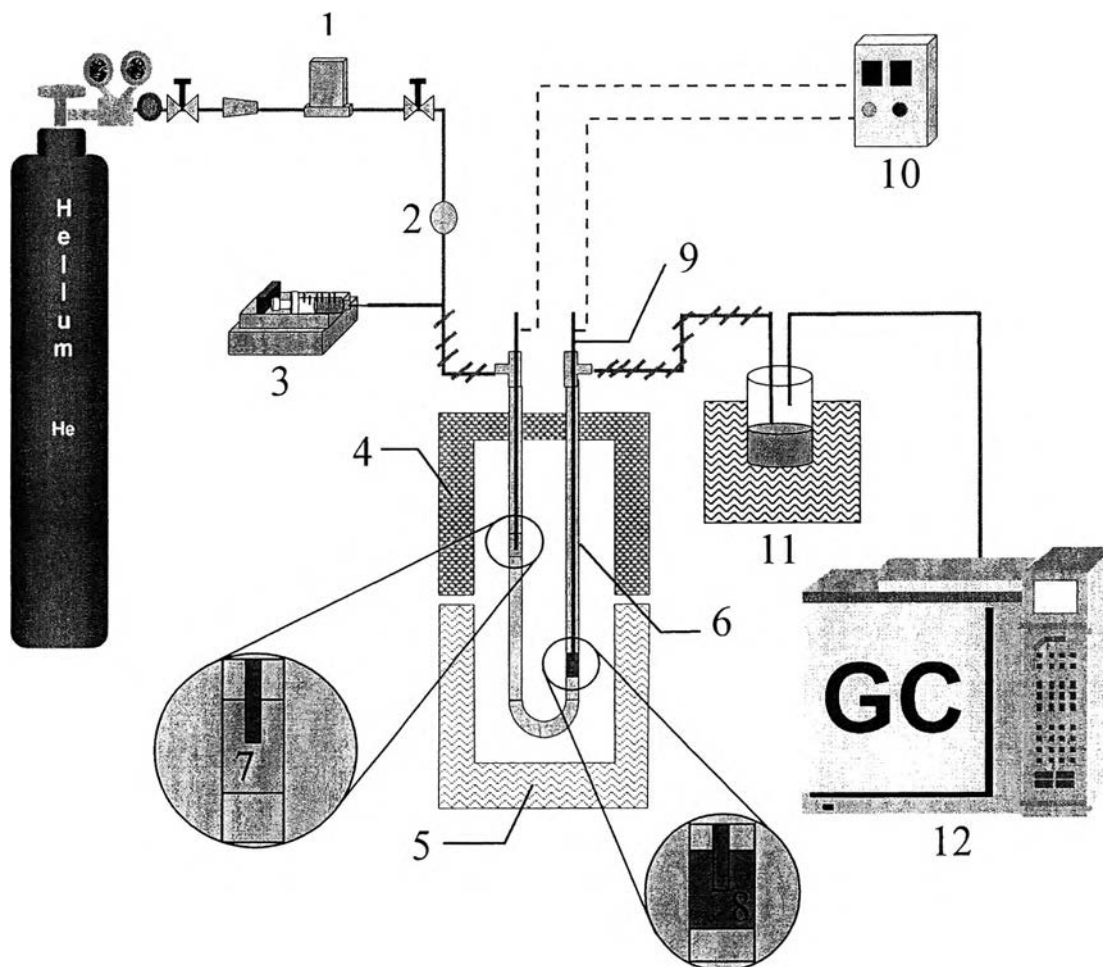


Figure 3.1 Schematic of experimental set up using two catalytic beds reactor. 1 = Flow meter, 2 = Pressure gauge, 3 = Syringe pump, 4 = Upper electric furnace, 5 = Lower electric furnace, 6 = U-tube reactor, 7 = Catalytic Bed #1, 8 = Catalytic Bed #2, 9 = Thermocouple, 10 = Temperature programmed controller, 11 = Cooling unit, 12 = Gas chromatograph.

3.4.4 Product Analysis

3.4.4.1 *Liquid Product Analysis*

The liquid products formed during the catalytic reactions were collected in the condensing flask kept at -15 °C, and oil composition was analyzed by high-performance liquid chromatography (HPLC) conformed with IP 391 standard method to examine mono-, di-, and tri-aromatic contents in oils. A gas chromatography conformed with UOP 744 standard method was also performed to determine the quantity of BTEX in oils. In addition, the Varian CP3800 Simulated Distillation Gas Chromatography (SIMDIST GC): ASTM D2887; was performed to identify the classification of petroleum fractions.

3.4.4.2 *Gaseous Product Analysis*

The gaseous products were analyzed by online gas chromatography equipped with a TCD detector (Porapak Q Column) to detect C1- C4 hydrocarbons as well as carbon dioxide, and with an FID detector (DB-WAX Column) to detect ethanol and oxygenates.