

CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Polyethylene Sources

- Commercial polyethylene films were purchased from D.M. Plaspec Co. Ltd

3.1.2 The Chemical Reagents for Catalyst Preparations

- Zirconium (IV) hydroxide ($Zr(OH)_4$) containing 88.8 % ZrO_2 was purchased from Aldrich Chemical Co. Inc. (USA)
- Zirconium oxide (ZrO_2) was used as catalysts and catalyst supports. It was purchased from Riedel-deHaen.
- Ammonium sulfate (NH_4SO_4) was purchased from Asia Pacific Speciality Chemical Limited
- Ethylene glycol (EG) was purchased from Farmitalia Carlo Erba(Barcelona).
- Acetonitrile (CH_3CN) was obtained from Lab-Scan Company Co., Ltd.
- Sodium hydroxide was purchased from Merck Com pany Co., Ltd. (Germany)

3.1.3 The Carrier Gas Used in Pyrolysis Study

- High purity nitrogen was purchased from Thai Industrial Gas Co., Ltd., (TIG).

3.1.4 Gas Sampling Bag

- Dual- Valve Tedlar PVF Gas sampling Bags of size (3.8 Liters) were purchased from Cole-Parmer

3.1.5 Standard Fluid for GC Calibrations

- Refinery gas test sample (Agilent P/N 5080-8755) was supplied from Agilent Technologies (manufactured for Agilent by Scott Special Gasses), and
- 99.0% n-pentane (C₅H₁₂) and 99.0% n-hexane (C₆H₁₄) were supplied from Labscan, Analytical Reagent, with 0.626 g/cm³ and 0.659 g/cm³ density, respectively.
- ASTM Method D2887 Column Test Mixture was provided by ULTRA Scientific. This ULTRA standard TM solution was gravimetrically prepared, and the analyte concentrations were verified using high-resolution gas chromatography and/or high performance liquid chromatography.

3.2 Catalyst Preparation

3.2.1 Synthesized ZrO₂

3.2.1.1 *Precursor Preparation (Sodium glycozirconate)*

The synthetic method of sodium glycozirconate is started by mixing 11.4 mol of zirconium hydroxide (Zr(OH)₄) and 200 mol% sodium hydroxide equivalent to zirconium dioxide mixed together in 35 ml of ethylene glycol (EG). The reaction was occurred at the boiling point of ethylene glycol (~200 °C) under nitrogen atmosphere to remove water as a by-product along with ethylene glycol from the system. The reaction was complete after 12 hours, and the resulting solution was clear. The reaction mixture was cooled, and 2-5 % of dried methanol in acetonitrile was added. The product precipitated out as a white solid. The solid was filtered off, washed with acetonitrile (3 x 5 ml), and dried under vacuum (0.1mmHg) at room temperature.

3.2.1.2 *Zirconia Preparation*

The sol-gel process was carried out at 25 °C Sodium glycozirconate was first dissolved in water using different hydrolysis ratio (h=H₂O/alkoxide molar ratio). The obtained zirconia based gels were soaked and

washed in water to remove the sodium. The separated gel was oven dried at 80 °C for 12 h and then calcined at different temperatures for 7 h. The sodium ion was removed by washing with water.

3.2.2 Super Acid Preparation

The solid super acids $\text{SO}_4^{2-}/\text{ZrO}_2$ were easily prepared by impregnating the synthesized and commercial ZrO_2 with $(\text{NH}_4)_2\text{SO}_4$ solution followed by calcinations at 550 °C for 2 hours in a furnace. The amounts of SO_4^{2-} in $\text{SO}_4^{2-}/\text{ZrO}_2$ were varied from 0 to 8 wt%.

3.2.2 Super Basic Preparation

The solid super basic $\text{KNO}_3/\text{ZrO}_2$ were prepared by using the impregnation technique which is the synthesized and commercial ZrO_2 were grind with KNO_3 at vary weight ratio followed by adding water of 0.5 ml/g. The catalyst were dried at 110 °C for 12 h. The amounts of K^+ in this catalyst were varied from 0 to 30 wt%.

3.3 Pyrolysis Studies

PE film was cut into $1 \times 1 \text{ mm}^2$ approximately and loaded into a semi-batch reactor with or without catalyst. Before the reaction began, nitrogen gas was flown through the reactor to get rid of the remaining air at a flow rate of 30 ml/min for half an hour. Then, the reactor was heated from room temperature to 500 °C at a heating rate of 10 °C/min, held at 500 °C for 1 hour. (See the reactor and reactor system in Figure 3.1) The pyrolyzed products were calssified into three groups: gases (products which were not condensable at ice-NaCl cooling temperature), liquid hydrocarbons and residues. The amount of gaseous products was calculated by subtracting the weight of liquid products, residues and catalyst from the total weight of PE film sample and fresh catalyst initially loaded to the reactor. Pyrolysed gas products were characterized via Gas Chromatograph in an Agilent Technologies HP 6890N gas chromatograph equipped with FID and a capillary

column, HP-PLOT Q with 20 μm coating thickness, 0.32 mm i.d. and 30 m length, using refinery gas (gas mixtures) for calibration. The temperature program of the column oven was as follows: temperature constant at 70°C for the first 8 min and increased to 200°C with a heating rate of 20°C/min and kept at this temperature for 20 min. Pyrolysed liquid products were performed by Simulated Distillation Gas Chromatography (DGC) (ASTM-D 2887) in a Varian CP-3800 gas chromatograph equipped with FID and a capillary column, WCOT fused silica 15 m long \times 0.25 mm i.d., using ASTM Method D2887 Column Test Mixture for calibration. The temperature program of the column oven was as follows: the initial temperature at 30°C and increased to 320°C with a heating rate of 20°C/min and kept at 320°C for 8.50 min.

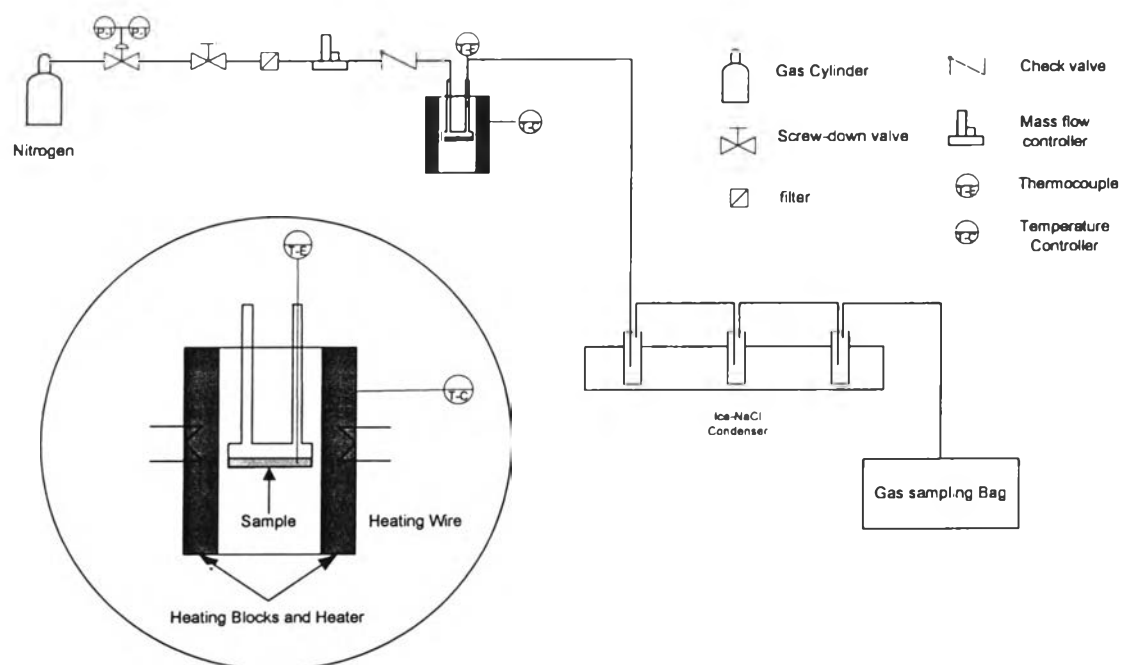


Figure 3.1 Schematic diagram of reactor and reactor system.

There were two parts of pyrolysis studies:

- the characteristic of product from non-catalytic pyrolysis, and
- effect of catalysts on pyrolysis products using
 - Superacid catalysts
 - SO_4^{2-} / Commercial ZrO_2
 - SO_4^{2-} / Synthesized ZrO_2

- Superbasic catalysts
 - KNO₃/ Commercial ZrO₂
 - KNO₃/ Synthesized ZrO₂

3.4 Testing and Characterization

3.4.1 PE Film Testing and Characterization

3.4.1.1 *Thermal Stability*

Thermal properties were examined by thermogravimetric analysis (TGA) using Du Pont Instrument TGA 2950 with the N₂ flow rate of 50 ml per min. The sample was heated from 30-900 °C with heating rate of 10 °C.

3.4.2 Catalyst Characterization

3.4.2.2 *Thermal Stability*

Thermogravimetric analysis (TGA) of catalysts was performed with the same procedure as it was accomplished on PE film by using Dupont TGA machine Model 2950.

3.4.2.2 *Crystal Structure*

Crystal structure of catalyst was characterized using a D/MAX-2200H Rigaku diffractometer with CuK α radiation on specimens prepared by packing sample powder into a glass holder. The mesoporous product was characterized at a scanning speed of 5 degree/sec. The working range was $2\theta = 5-60$

3.4.2.3 *Surface Area and Pore Size Distribution*

Surface area and average pore size were measured by BET method using a Quantasorb Jr. (Autosorb-1). The product was degassed at 250°C for 12 hours prior to analysis.

3.4.2.4 *Function Group of Catalyst*

FTIR spectroscopic analysis was conducted on a Bruker Instrument (EQUINOX55) with a scanning resolution of 4 cm⁻¹