

CHAPTER III

EXPERIMENTAL

In the present study of the copolymerization of ethylene/ α -olefin with the zirconia modification on supported zirconocene catalysts, the experiments were divided into four parts:

- (i) Preparation of the zirconia modified support
- (ii) Preparation of MAO/modified support
- (iii) Ethylene and α -olefins copolymerization Procedure
- (iv) Characterization of ethylene and α -olefin copolymer products and MAO/modified support

The details of the experiments are explained as follows.

3.1 Chemicals

The chemicals used in these experiments were analytical grade, but only major materials are specified as follows:

1. rac-Ethylenebis(indenyl)zirconium dichloride ($\text{Et}(\text{Ind})_2\text{ZrCl}_2$) was supplied from Aldrich Chemical Company, Inc. and used without further purification.

2. Ethylene gas (99.96%) was devolved from National Petrochemical Co., Ltd., Thailand and used as received.

3. 1-Hexene (99+%) was purchased from Aldrich Chemical Company, Inc. and purified by distilling over sodium under argon atmosphere before use.

4. 1-Octene (98%) was purchased from Aldrich Chemical Company, Inc. and used as received.

5. 1-Decene ($\geq 97\%$) was purchased from Fluka Chemie A.G. Switzerland. and used as received.

6. Methylaluminoxane (MAO) 2.667 M in toluene was donated from Tosoh Akso, Japan and used without further purification.

7. Trimethylaluminum [Al(CH₃)₃] 2.0 M in toluene was supplied from Nippon Aluminum Alkyls Ltd., Japan and used without further purification.

8. Silica gel from Fuji Silasia Chemical Ltd., (Cariact P-10, surface area 300 m²/g) was calcined at 400 °C for 6 hours under vacuum.

9. Hydrochloric acid (Fuming 36.7%) was supplied from Sigma.

10. Zirconium (IV) propoxide 70 wt% solution in 1- propanol (d = 1.058 g/mL) was supplied from Aldrich Chemical Company, Inc.

11. Propan-1-ol (n-Propanol) (d = 0.803 g/mL) was supplied from UNILAB.

12. Methanol (Commercial grade) was purchased from SR lab.

13. Toluene was devotes from EXXON Chemical Ltd., Thailand. This solvent was dried over dehydrated CaCl₂ and distilled over sodium/benzophenone under argon atmosphere before use.

14. Ultra high purity argon gas (99.999%) was purchased from Thai Industrial Gas Co., Ltd., and further purified by passing through columns packed with molecular sieve 3 A, BASF Catalyst R3-11G, sodium hydroxide (NaOH) and phosphorus pentaoxide (P₂O₅) to remove traces of oxygen and moisture.

3.2 Equipments

All types of equipments used in the catalyst precursor preparation and polymerization are listed below:

3.2.1 Cooling system

The cooling system was in the solvent distillation in order to condense the freshly evaporated solvent.

3.2.2 Inert gas supply

The inert gas (argon) was passed through columns of BASF catalyst R3-11G as oxygen scavenger, molecular sieve 3×10^{-10} m to remove moisture. The BASF catalyst was regenerated by treatment with hydrogen at 300 °C overnight before flowing the argon gas through all the above columns. The inert gas supply system is shown in Figure 3.1.

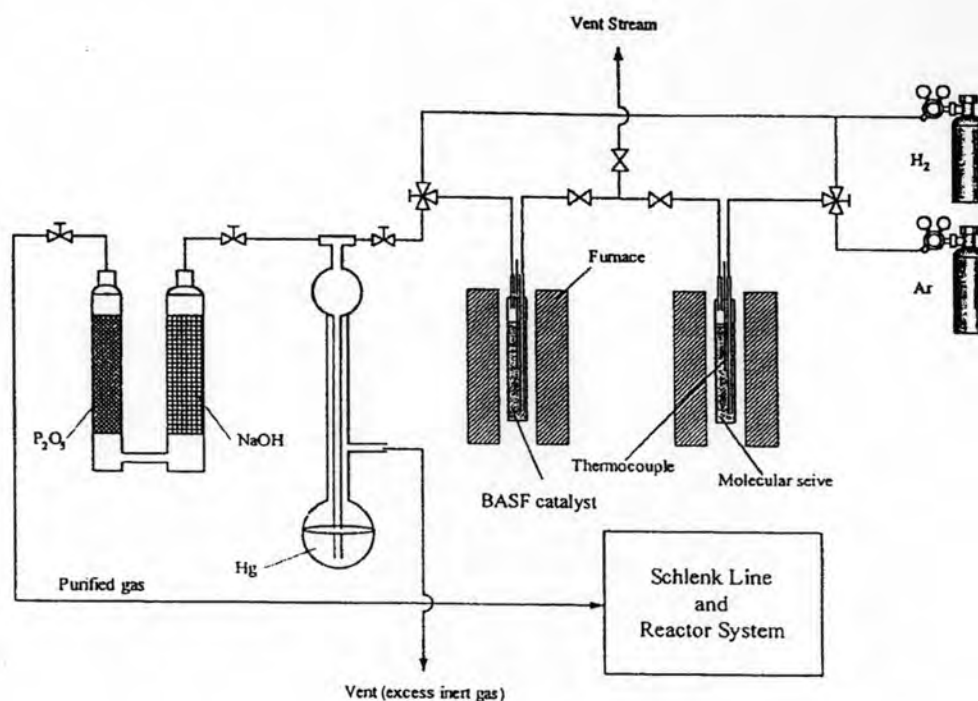


Figure 3.1 Inert gas supply system

3.2.3 Magnetic stirrer and heater

The magnetic stirrer and heater model RTC basis from IKA Labortechnik were used.

3.2.4 Reactor

A 100 ml stainless steel autoclave was used as the copolymerization reactor.

3.2.5 Schlenk line

Schlenk line consists of vacuum and argon lines. The vacuum line was equipped with the solvent trap and vacuum pump, respectively. The argon line was connected with the trap and the mercury bubbler that was a manometer tube and contain enough mercury to provide a seal from the atmosphere when argon line was evacuated. The Schlenk line was shown in Figure 3.2.

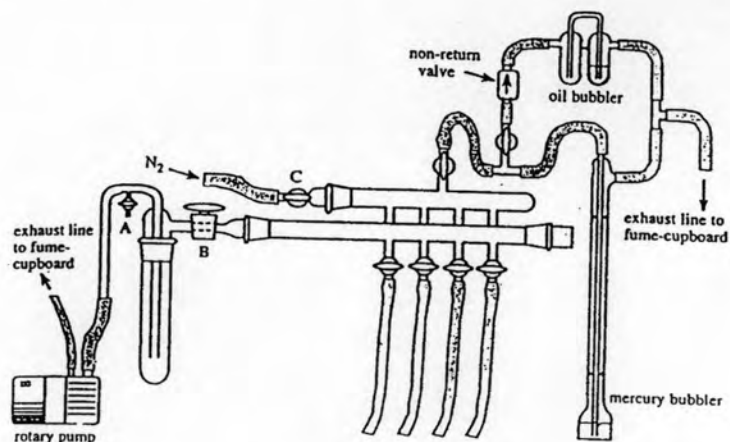


Figure 3.2 Schlenk line

3.2.6 Schlenk tube

A tube with a ground glass joint and side arm, which was three-way glass valve as shown in Figure 3.3. Sizes of Schlenk tubes were 50, 100 and 200 ml used to prepare catalyst and store materials which were sensitive to oxygen and moisture.

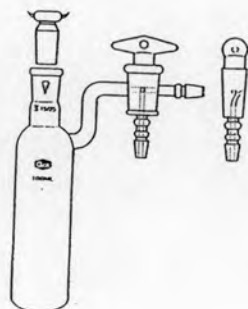


Figure 3.3 Schlenk tube

3.2.7 Vacuum pump

The vacuum pump model 195 from Labconco Corporation was used. A pressure of 10^{-1} to 10^{-3} mmHg was adequate for the vacuum supply to the vacuum line in the Schlenk line.

3.2.8 Polymerization line

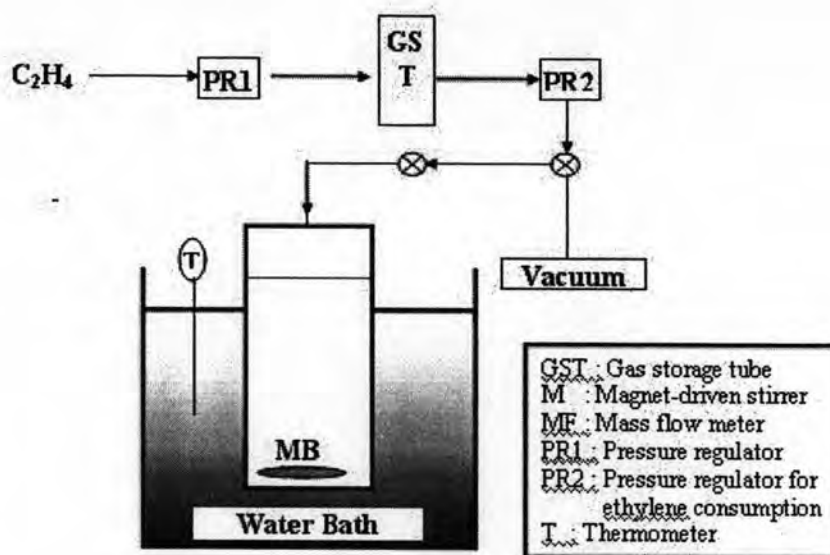


Figure 3.4 diagram of system in slurry phase polymerization

3.3 Characterizing instruments

The instruments used for characterizing catalysts and ethylene/ α -olefin copolymer products are specified below.

3.3.1 Differential scanning calorimetry (DSC)

The melting temperature of ethylene/ α -olefin copolymer products was determined with a Perkin-Elmer diamond DSC from MEKTEC, at the Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Chulalongkorn University. The analyses were performed at the heating rate

of 20 °C/ min in the temperature range of 50-150 °C. The heating cycle was run twice. In the first scan, samples were heated and the cooled to room temperature. In the second, samples were reheated at the same rate, but only the results of the second scan were reported because the first scan was influenced by the mechanical and thermal history of samples.

3.3.2 Nuclear magnetic resonance (NMR)

¹³C-NMR spectroscopy was widely used to determine comonomer incorporation and polymer structure. Comparison of the positions of peak in the ¹³C-NMR spectrum of polymer sample with characteristic led to identification of the sequence of the comonomer incorporation. The ¹³C-NMR spectra were recorded at 100°C using BRUKER Magnet System 400 MHz/54 mm, UltraShield, long hold time. Copolymer solutions were prepared using 1,2 -dichlorobenzene as solvent and benzene-d₆ for internal lock.

3.3.3 Scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX)

SEM observation with a JSM-5800 LV Scanning Microscope, Microspec WDX at Scientific Technological Research Equipment Center, Chulalongkorn University was employed to investigate the morphology of catalyst precursor and polymer. The polymer samples for SEM analysis were coated with gold particles by ion sputtering device to provide electrical contact to the specimen. EDX was performed using Link Isis series 300 program.

3.3.4 Thermal Gravity Analysis (TGA)

TGA was performed to proof the interaction between the [Al]_{MAO} and various supports. It was conducted using TA Instruments SDT Q 600 analyzer. The samples of 10-20 mg and a temperature ramping from 323 to 873 K at 5K/min were used in the operation. The carrier gas was N₂ UHP.

3.3.5 X-ray diffraction (XRD)

XRD was performed to determine the bulk crystalline phases of sample. It was conducted using a SIEMENS D-5000 X-ray diffractometer with $\text{CuK}\alpha$ ($\lambda = 1.54439 \times 10^{-10}$ m). The spectra were scanned at a rate 2.4 degree/min in the range $2\theta = 20$ -80 degrees.

3.3.6 N_2 physisorption

Measurement of BET surface area, average pore diameter and pore size distribution of supports were determined by N_2 physisorption using a Micromeritics ASAP 2000 automated system.

3.4 Supporting Procedure

All reactions were conducted under argon atmosphere using Schlenk techniques and glove box.

3.4.1 Preparation of the zirconia –modified support

The zirconia-modified support were prepared by the sequential impregnation method as referred in [16]. The silica was used as support. First, Zr was impregnated into the support using a solution of zirconium (IV) n-propoxide (70 wt% in n-propanol, Aldrich) to produce Zr-modified supports having 1,2, and 5 wt% of Zr. The mixture was dried in oven at 100°C overnight.

3.4.2. Preparation of MAO/modified support

The modified support was heated under vacuum at 400°C for 6 hours. 2 g of calcined support was reacted with the desired amount of MAO in 10 ml of toluene at room temperature for 30 minutes. The solid part was separated and washed 5 times with

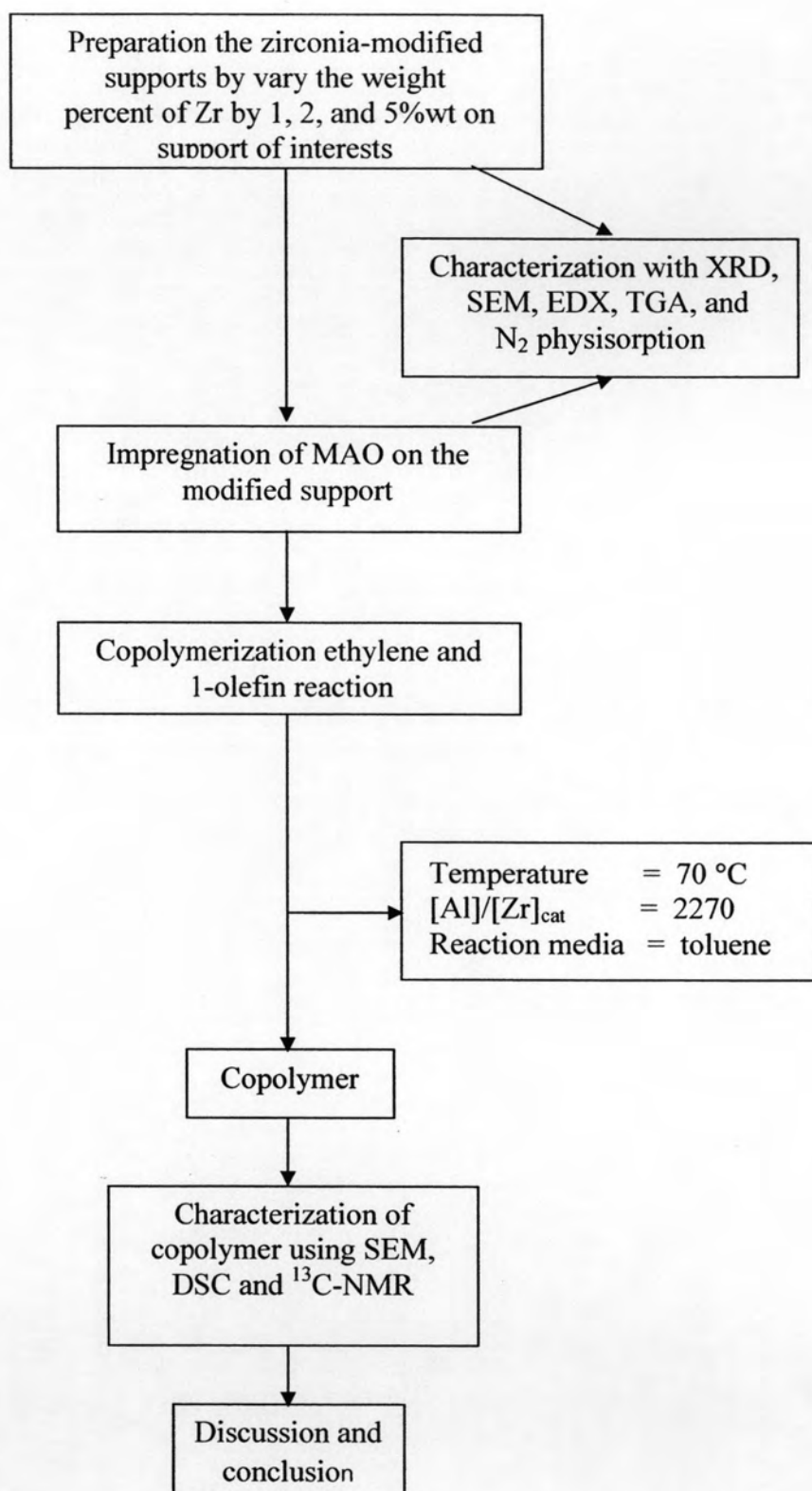
20 ml of toluene, followed by drying in vacuum at room temperature to obtain the catalyst support precursor MAO/modified support.

3.5 Ethylene and α -olefins Copolymerization Procedure

The ethylene and α -olefins (1-hexene, 1-octene and 1-decene) copolymerization reactions were carried out in a 100 ml semi-batch stainless steel autoclave reactor equipped with magnetic stirrer. The autoclave and magnetic bar were dried in oven at 110 °C for 30 minutes and purged with argon 5 times in glove box before use in copolymerization of ethylene and α -olefins. Toluene (to make a total volume of 30 ml), 200 mg of catalyst precursor, 3 ml of α -olefins were introduced into the autoclave in the glove box. The amount of $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ and TMA were mixed and stirred for 5 minutes at room temperature. After that, the mixture of metallocene and TMA was injected into the reactor. The reactor was frozen in liquid nitrogen to stop reaction and then the autoclave was evacuated to remove the argon. After that, the reactor was heated up to polymerization temperature and the polymerization was started by feeding ethylene gas (total pressure 50 psi) until the consumption of ethylene 0.018 mol (6 psi was observed from pressure gauge). The small amount of ethylene was used to avoid the mass transfer effect and increase the homogeneity of polymer. If the amount of comonomer remained higher than 90% after the reaction, the obtained polymer is homogeneous. The reaction of polymerization was terminated by addition of acidic methanol. The time of reaction was recorded for purposes of calculating the activity. The precipitated polymer was washed with methanol and dried in room temperature.

The various effects on the ethylene/ α -olefins copolymerization with zirconia modification on supported metallocene catalyst and optimized condition were investigated. The effects of copolymerization on production of ethylene/ α -olefins copolymer were systematically varied as follow.

Research Methodology



3.6 Characterization of Catalyst Precursor

3.6.1 Morphology and elemental distribution

Scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM and EDX) were the effective method to investigate catalyst precursor morphologies and elemental distribution throughout the sample granules, respectively. The term of morphology was referred to shape, texture or form of catalyst precursor. The EDX mapping images of the supports can provide more information about the distribution of MAO as seen for Al distribution mapping on each support.

3.6.2 Interaction between the $[Al]_{MAO}$ and various supports

Thermal Gravity Analysis (TGA) was performed to determined weight loss with temperature of catalyst precursors. The weight loss percent was referred to interaction between the $[Al]_{MAO}$ and various supports.

3.6.3 Pore size distribution of supports

Measurement of BET surface area, average pore diameter and pore size distribution of supports were determined by N_2 physisorption .

3.7 Characterization of Ethylene and α -olefins Copolymer Products

3.7.1 Chemical Structure Determination

The nuclear magnetic resonance technique was widely used for characterizing incorporated comonomer. Comparison of the position of peak in the ^{13}C -NMR spectrum of polymer sample led to identification of the sequences of the comonomer incorporation.

3.7.2 Morphology

The morphology of ethylene/ α -olefins copolymer obtained was observed with scanning electron microscopy (SEM).

3.7.3 Melting Temperature (T_m)

Differential scanning calorimetry (DSC) was an instrument designed to measure the thermal properties especially melting temperature (T_m). The melting temperature of ethylene/ α -olefins copolymers were determined from the critical point of DSC curve.