

CHAPTER III

EXPERIMENTAL

Research Methodology

Research Methodology is shown in the flow diagram of Figure 3.1

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

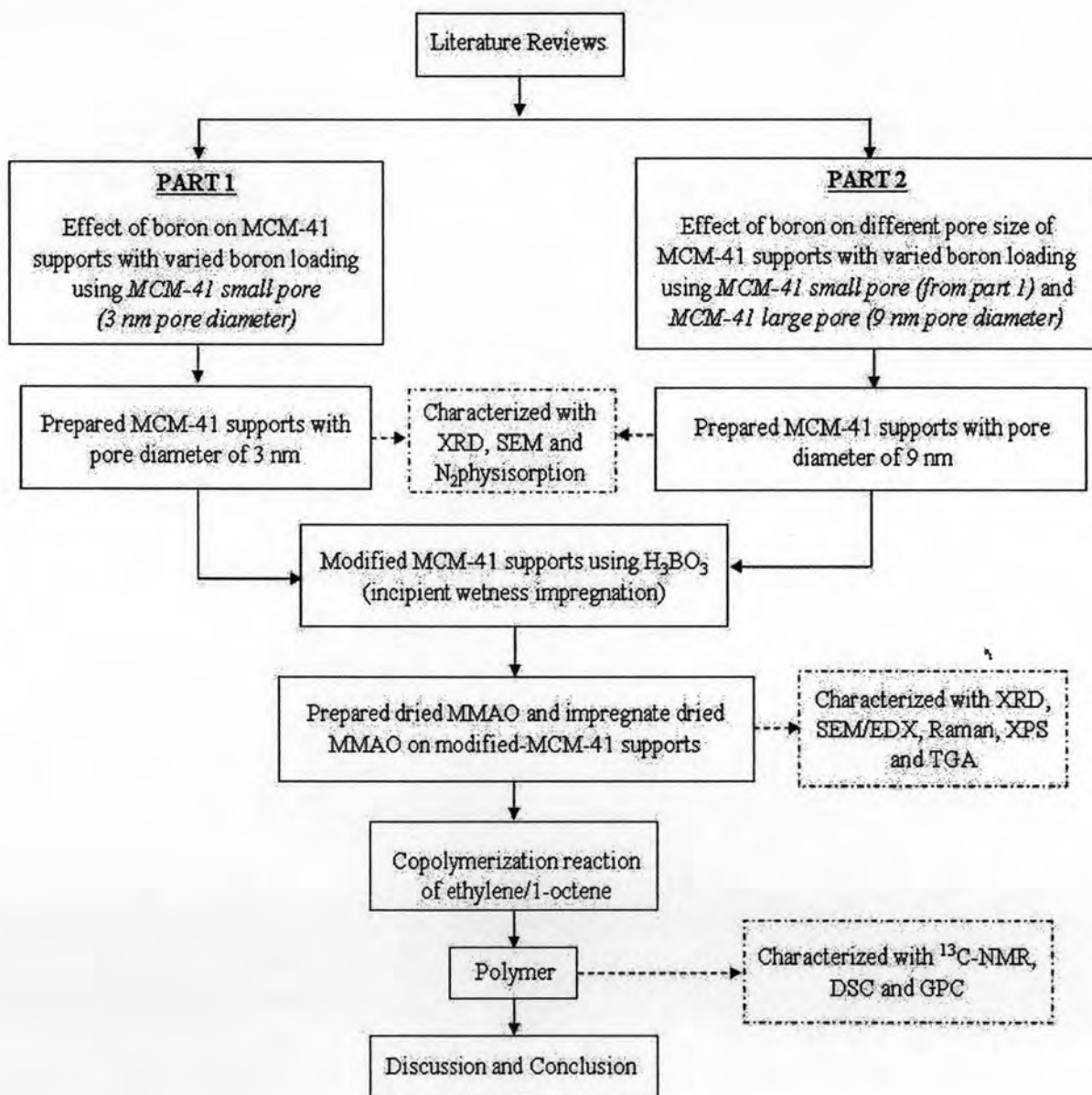


Figure 3.1 Flow diagram of research methodology

Experimental Section

The experimental is divided into four major parts:

- (i) Support and catalyst preparation,
- (ii) Ethylene and 1-octene copolymerization with the prepared support and catalyst,
- (iii) Characterization of catalyst precursor,
- (iv) Characterization ethylene and 1-octene copolymer products.

The details of the experiments are explained as follows

3.1 Support Preparation

3.1.1 Synthesis of MCM-41 small pore

The MCM-41 support was synthesized according to the method described by Panpranot et al.[20] using the gel composition of CTABr : 0.3 NH₃ : 4 SiO₂ : Na₂O : 200 H₂O, where CTABr denotes cetyltrimethyl ammonium bromide. Briefly, 20.03 g of colloidal silica Ludox HS 40 % (Aldrich Chemical Company, Inc.) was mixed with 22.67 g of 11.78 % sodium hydroxide solution. Another mixture comprised of 12.15 g of CTABr (Aldrich Chemical Company, Inc.) in 36.45 g of deionized water, and 0.4 g of an aqueous solution of 25 % NH₃. Both of these mixture were stirred by agitator for 30 min, then heated statically at 100 °C for 5 days. The obtained solid material was filtered, washed with deionized water until no base was detected and then dried at 100 °C. The sample was then calcined in flowing nitrogen up to 550 °C (1-2 °C/min), then in air at the same temperature for 5 h. After preparation, the MCM-41 support having the pore diameter of 3 nm and surface area of 864m²/g was obtained [59].

3.1.2 Synthesis of MCM-41 large pore

The large pore MCM-41 with 9 nm pore diameter was prepared treating the MCM-41 small pore with 3 nm pore diameter (before calcinations) in an emulsion containing *N,N*-dimethyldecylamine (0.625 g in 37.5 g of water for each gram of MCM-41) for 3 days at 120 °C. This was washed thoroughly, dried, and calcined in flowing nitrogen up to 550 °C (1-2 °C/min), then in air at the same temperature for 5 hours After

preparation, the MCM-41 support having the pore diameter of 9 nm and surface area of 290 m²/g was obtained [59].

Table 3.1 Chemicals used in the synthesis of MCM-41 supports

Chemicals	Supplier
cetyltrimethyl ammonium bromide	Aldrich
colloidal silica Ludox HS 40%	Aldrich
aqueous solution of 25% NH ₃	BDH
30% acetic acid	Carlo Erba
sodium hydroxide	Merck
<i>N, N</i> -dimethyldecylamine	Aldrich

3.1.3 Preparation of boron modified MCM-41 [60]

B-modified MCM-41 supports were prepared by the incipient wetness impregnation on the support. The desired amount of the aqueous solution of boric acid (99.99% H₃BO₃, Aldrich Chemical Company, Inc.) was added onto the support to yield a final loading of approximately 1 and 5 wt% of B. The supports were dried overnight at 110 °C and then calcined in air at 500 °C for 4 h.

3.1.4 Preparation of catalyst precursor

3.1.4.1 Preparation of dried-MMAO

100 ml of MMAO solution in toluene was evacuated and washed with toluene (100ml) for 2 times to remove the impurity. Then continue to wash with heptane for 6-8 times to remove TMA and TIBA in MMAO to give d-MMAO as white solid.

3.1.4.2 Preparation of catalyst precursor MCM-41/d-MMAO

Calcined MCM-41 obtained is reacted with the desired amount of d-MMAO in 20 ml of toluene at room temperature for 30 minutes. The solvent was then removed from the mixture. This procedure is done for 1 times with 20 ml of toluene and 3 times of hexane to ensure the removal of impurities. Then, the solid part was dried under vacuum at room temperature.

3.2 Reaction Study

3.2.1 Chemicals and Reagents

The chemicals used in this experiment were analytical grade, but only major materials were specified as follows:

3.2.1.1 Ethylene gas (99.96%) was donated from National Petrochemical Co.,Ltd., Thailand.

3.2.1.2 Ultra high purity argon gas (99.999%) was purchased from Thai Industrial Gas Co.,Ltd.

3.2.1.3 Toluene was donated from EXXON Chemical Ltd., Thailand. This solvent was dried over dehydrated CaCl_2 and distilled over sodium/benzophenone under argon atmosphere before use.

3.2.1.4 Trimethylaluminum $[\text{Al}(\text{CH}_3)_3]$ 2.0 M in toluene was supplied from Nippon Aluminum Alkyls Ltd.,Japan, and use without further purification.

3.2.1.5 Modified methylaluminoxane (MMAO) in hexane was donated from Tosoh Akzo, Japan.

3.2.1.6 *rac*-Ethylenebis(indenyl)zirconium dichloride ($\text{Et}(\text{Ind})_2\text{ZrCl}_2$) was supplied from Aldrich Chemical Company,Inc.

3.2.1.7 1-octene (98%) was purchased from Aldrich Chemical Company, Inc.

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

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

3.2.2 Experimental Equipments

All equipments, used in the catalyst preparation and polymerization, were listed as follows:

3.2.2.1 Autoclave Reactor

The autoclave is made of stainless steel with a volume of 100 ml and 3 cm inside diameter. This autoclave was used as polymerization reactor.

3.2.2.2 Calcination Line

The calcination line is used for purifying (eliminate the moisture and any impurities) the support before using.

3.2.2.3 Magnetic Stirrer and Hot Plate

The magnetic stirrer and hot plate model RCT basic from IKA Labortechnik were used.

3.2.2.4 Cooling System

The cooling system was used in the solvent distillation for condensing the freshly evaporated solvent.

3.2.2.5 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.

Special care was taken in the handling of reagents and for loading the catalyst into the reactor because most of the reagents and catalyst were very sensitive to the oxygen and moisture. In this study, the used to eliminate oxygen and moisture from the reagents and catalyst were the following:

3.2.2.6 Glove box (Argon Atmosphere)

The glove box with oxygen and moisture analyzer for transferring solid powder and liquid reagents under inert atmosphere and for storing air-sensitive reagents.

3.2.2.7 Schlenk Line

The Schlenk line consisting of a vacuum line connected to a vacuum pump and an inert gas line for purging while reagents were transferred, and a Schlenk tube for keeping reagents under inert atmosphere outside the glove box.

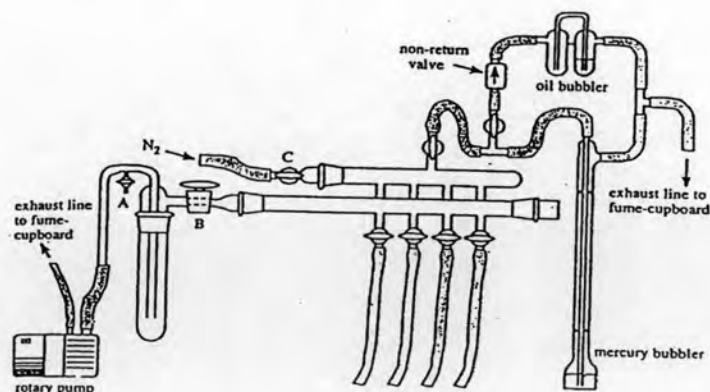


Figure 3.2 Schlenk line



3.2.2.8 Schlenk Tube

A tube with a ground glass joint and side arm, which was three-way glass valve as shown in Figure 3.2. Sizes of Schlenk tubes were 50, 100 and 200 ml used to prepare catalyst and store materials which were sensitive to oxygen and moisture.

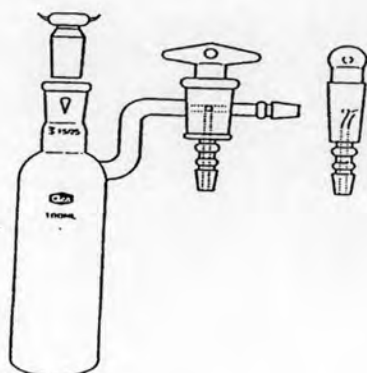


Figure 3.3 Schlenk tube

3.2.3 Polymerization

Polymerization was conducted upon the methods as follows:

The ethylene and 1-octene copolymerization reaction were carried out in a 100 ml semi-batch stainless steel autoclave reactor equipped with magnetic stirrer. In the glove box, the amount of *rac*-Et[Ind]₂ZrCl₂ and TMA were mixed and stirred for 5 min for aging. Then, toluene (to make a total volume of 30 ml) and 100 mg of dMMAO/support were introduced into the autoclave. After that, the mixture of *rac*-Et[Ind]₂ZrCl₂ and TMA were injected into the reactor. The reactor was frozen in liquid nitrogen to stop reaction and then 0.018 mol of 1-octene was injected into the reactor. The autoclave was evacuated to remove the argon. Then, the reactor was heated up to polymerization temperature (70 °C) and the polymerization was started by feeding ethylene gas (total pressure 50 psi in the reactor) until the consumption of ethylene 0.018 mol (6 psi was observed from pressure gauge). The reaction of polymerization was terminated by addition of acidic methanol. The time of reaction was recorded for purpose of calculating the activity. The precipitated polymer was washed with methanol and dried at room temperature.

3.3 Characterization

3.3.1 Characterization of MCM-41, and B modified MCM-41 and catalyst precursors using :

3.3.1.1 N₂ physisorption: Measurement of BET surface area, average pore diameter and pore size distribution of MCM-41 support were determined by N₂ physisorption using a Micromeritics ASAP 2000 automated system.

3.3.1.2 X-ray diffraction: XRD was performed to determine the bulk crystalline phases of samples. It was conducted using a SIEMEN D-5000 X-ray diffractometer with CuK_α ($\lambda = 1.54439 \text{ \AA}$). The spectra were scanned at a rate of $2.4^\circ \text{ min}^{-1}$ in the range $2\theta = 10\text{-}80^\circ$.

3.3.1.3 Raman spectroscopy: The Raman spectra of the samples were collected by projecting a continuous wave RAG laser of Nd (810 nm) through the samples at room temperature. A scanning range of $100\text{-}1000 \text{ cm}^{-1}$ with a resolution of 2 cm^{-1} was applied.

3.3.1.4 X-ray photoelectron spectroscopy: XPS was used to determine the binding energies (BE) and surface concentration of samples. It was carried out using the Shimadzu AMICUS with VISION 2-control software. Spectra were recorded at room temperature in high-resolution mode (0.1 eV step, 23.5 eV pass energy) for Al 2p core-level region. The samples were mounted on an adhesive carbon tape as pellets. The energy reference for Ag metal (368.0 eV for 3d_{5/2}) was used for this study.

3.3.1.5 Thermal Gravity Analysis: TGA was performed using TA Instruments SDT Q 600 analyzer. The samples of 10-20 mg and a temperature ramping from 30 to 600 °C at 5 °C/min were used in the operation. The carrier gas was N₂ UHP.

3.3.1.6 Scanning electron microscopy and energy dispersive X-ray spectroscopy: SEM and EDX were used to determine the sample morphologies and elemental distribution throughout the sample granules, respectively. The SEM of JEOL mode JSM-6400LV was applied. EDX was performed using Link Isis series 300 program.

3.3.2 Characterization of polymer

3.3.2.1 Gel permeation chromatography: The molecular weight and molecular weight distribution of polymer was determined using gel permeation chromatography (GPC, PL-GPC-220). Samples were prepared having approximately concentration of 1 to

2 mg/ml in trichlorobenzene (mobile phase) by using the sample preparation unit (PL-SP 260) with filtration system at a temperature of 150 °C. The dissolved and filtered samples were transferred into the GPC instrument at 150 °C. The calibration was conducted using the universal calibration curve based on narrow polystyrene standards.

3.3.2.2 Nuclear magnetic resonance spectroscopy : ^{13}C NMR spectroscopy was used to determine the α -olefin incorporation and copolymer microstructure. Chemical shift were referenced internally to the benzene- d_6 and calculated according to the method described by Randall [61]. Sample solution was prepared by dissolving 50 mg of copolymer in 1,2,4-trichlorobenzene and benzene- d_6 . ^{13}C NMR spectra were taken at 60 °C using BRUKER A400 operating at 100 MHz with an acquisition time of 1.5 s and a delay time of 4 s.

3.3.2.3 Differential Scanning Calorimeter (DSC): The melting temperature (T_m) and heat of fusion (ΔH_m) of copolymer were determined by Perkin-Elmer DSC 7. The analyses were performed at heating rate of 10 °C/min in the temperature range 30-200 °C. The heating cycle was run twice. The first scan, samples were heated and cooled to room temperature. The second scan, sample were heated at the same rate, but only the results of the second scan were reported.