CHAPTER III
EXPERIMENTAL PART

3.1 Chemicals

Polymerization grade ethylene, *UHP* grade nitrogen and *UHP* grade mixed gas ($H_2/N_2 \sim 10$ %vol) were supplied from Cryogenic gas, Michigan. They were dried by passing through a column of oxygen-moisture trap (MATHESON, model# 6427-2S). Tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) solution (11 wt% in toluene), trityl tetrakis(pentafluorophenyl)borate ($[CPh_3]^+[B(C_6F_5)_4]^-$), and *N,N*-dimethylaniline tetrakis(pentafluorophenyl)borate ($[HNMe_2Ph]^+[B(C_6F_5)_4]^-$) were obtained from Albemarle. Two silica gel supports donated by W.R. Grace Company, Maryland, had a surface area of 309 m^2/g, and pore volume of 1.62 cc/g for Sylapol^{TM} 948 and a surface area of 300 m^2/g, and pore volume 1.15 cc/g for Davisil^{TM}. Bis(cyclopentadiene) zirconiumdichloride (Cp_2ZrCl_2), triisobutylaluminum (TIBA, solution 1.0 M in toluene), triethylaluminum (TEA, 25 % in toluene), Chlorotriphenylmethane ($ClCPh_3$), and *N,N*-dimethylaniline (NMe_2Ph) were purchased from Aldrich. Toluene (Aldrich, anhydrous grade, $H_2O <$ 0.001%) was purified by refluxing with sodium for 48 h, then degassed by distillation under N_2 with CaH_2 reflux, and stored over 3A molecular sieves before use. Hexane was degassed by bubbling with N_2 and stored over 3A molecular sieves before use.

3.2 Experimental Apparatus

3.2.1 Glove Box

Regarding to the use of air-sensitive chemicals, anhydrous and anaerobic conditions are commonly required for all of the catalyst preparations in a glove box (O_2 and $H_2O <$ 1 ppm). In this study, the anaerobic glove-box was constructed of flexible PVC vinyl. All seams of the glove-box were sealed together using a radio frequency welding technique. The glove-box with a tubular aluminum frame supported was hold on a ¾" plywood base and covered with foam. The glove-

box had two entrances, one of which was used to install large equipments. After large equipment had been installed, this entry port was sealed with a large plastic disc and taped. The other entrance was the airlock, and was used to enter the glove-box on a routine basis. Further instructions for operating the glove box appear in Appendix A. Two catalyst boxes were supplied with the glove-box to ensure an anaerobic environment. The glove-box's atmosphere was free from oxygen by using palladium catalyst to remove oxygen. It should be noted here that hydrogen gas was also introduced into the glove box in order to eliminate the oxygen through the reaction of hydrogen and oxygen with having the palladium as catalyst.

During normal operation, oxygen could enter the glove-box by diffusion and other means. When the oxygen content in the glove-box exceeded the acceptable level, the spent catalyst had to be rejuvenated by heating it in a sterilizing oven for 4 h at 125 – 200 °C. The reactivated catalyst was then cooled down for 30 min before reusing in the glove-box. Generally, it was found that it took about twice a week to rejuvenate the spent catalyst. After a number of times for catalyst regeneration by heating, it was found that the palladium coating appeared to chip from the alumina pellets. When the pellets had as much as a third of white alumina surface, it was the time to replace new catalyst.

The catalyst used as oxygen scavenger has a thin layer of palladium chloride on the surface of alumina pellet. The catalyst provides reaction sites for oxygen and hydrogen to form water. The alumina in the catalyst absorbs the water which is driven off during catalyst rejuvenation. Without the presence of hydrogen, the catalyst will not be able to remove oxygen. Hence hydrogen was supplied by feeding the mixed gas having 10 % hydrogen with nitrogen into the glove-box by two methods:

(1)   The chamber was manually vacuumed and so it was refilled by 10 % hydrogen about half way. This procedure was done regularly once a day in case there was no any experiment going on.

(2)   During conducting experiments, 10 % hydrogen was introduced into the glove-box daily.

The flow of hydrogen gas was kept at the minimum flow rate to ensure having a low hydrogen concentration in the chamber for safety purpose as well as to

have a positive pressure which could prevent air leak through any small pinholes or cracks.

Since a significant amount of heat can be generated from the exothermic reaction of hydrogen and oxygen, it is strongly recommended to purge the air present in the glove box with 10 % hydrogen for a while in order to minimize the oxygen content before placing the catalyst in the glove box.

Moisture in the glove-box was removed by using silica-gel as desiccant. For the best control, a large quantity of the desiccant was placed on a large pan to ensure having a large contact surface to remove the moisture effectively. Placing desiccant in front of inlet-fan of each catalyst box was desirable. After the color of silica-gel was changed from blue to violet, it means its pores became saturated with water vapor and had to be rejuvenated. The spent silica-gel desiccant was rejuvenated at 125 – 200 °C for 4 h.

Nitrogen and the mixed gas supplied into the glove-box were purified by passing through an oxygen/moisture trap column. This would control the level of oxygen and moisture in the feed stream to be less than 50 ppb. The purified gas streams were directly connected to the airlock and the glove-box's chamber.

3.2.2 Reactor

The reactor used as a prototype of ethylene polymerization process in this study which was made of 316 stainless steel was purchased from Pressure Products Industries, as shown in Figure 3.1. The specifications for this reactor system are as follows:

|	
Part number	LC-5s-B-S1-14S16G-0-000
Serial number	99U-00043
Reactor pressure rating	2 000 psig at 650 F
Minimum design temperature	- 20 F

The reactor consisted of a reaction vessel, teflon liner, dynamic magnetic mixer, heating tape style heater, pressure gauge, internal cooling U-coil, a safety head with a rupture disc, and three inlet-valve. The dynamic magnetic mixer, which was used to drive the agitator, was belt driven by a motor mounted on the stand.

The flow diagram of the polymerization process in this study is shown in Figure 3.2. The system was designed to operate as a semi-batch type reactor process for ethylene polymerization. The reactor had two inlet-valves that were used for supplying nitrogen and charging chemical compounds. The other outlet-valve was connected to a vacuum pump for removing all of gaseous compounds from the reactor chamber.

Before each operation, it was started to check pressure-leak of the reactor before introducing chemical reactants. The reactor had to be assembled and torqued properly. All joints were carefully checked to have proper torque and the rating safety device was verified. Next, the reactor was pressurized with nitrogen to the expected working pressure. The tightness of the system seals was recharged again.
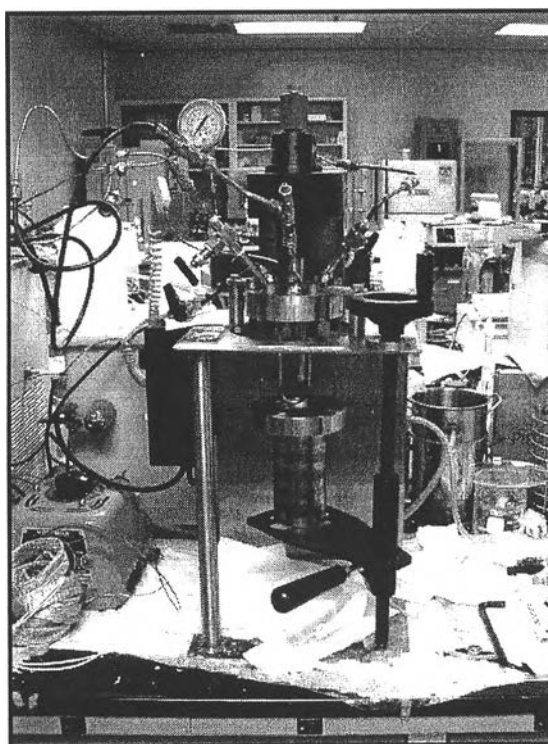
**Figure 3.1** 316-SS Reactor (PPI-500 ml model) used in this study.
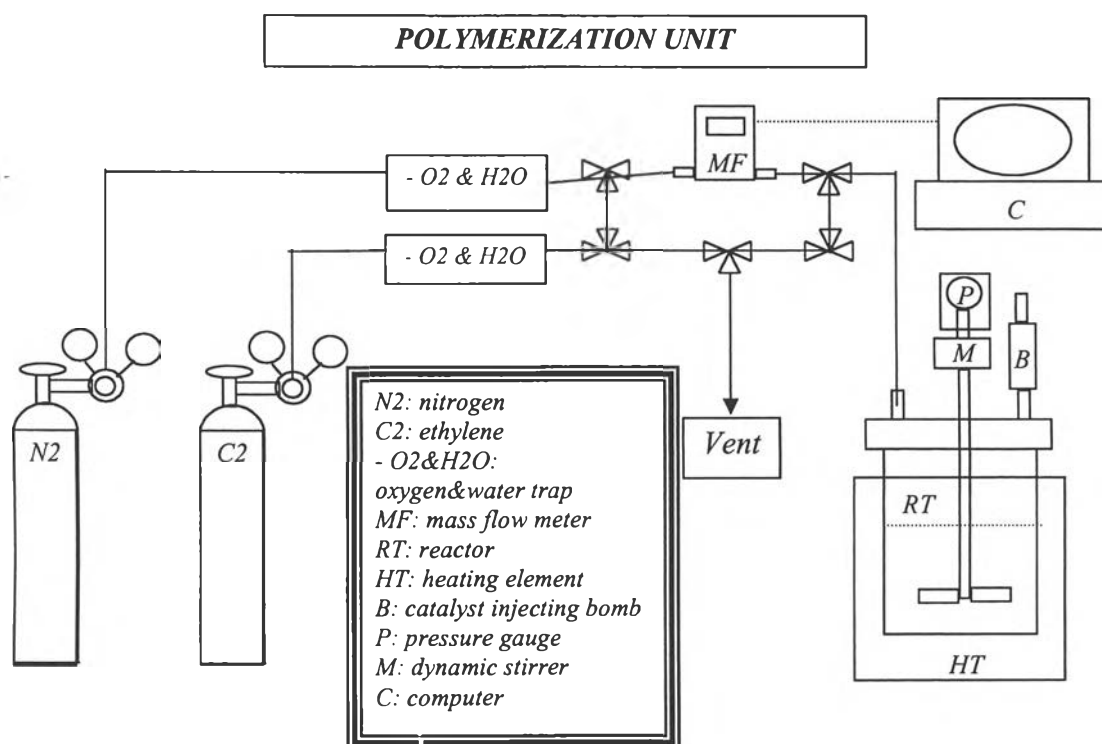
**Figure 3.2** Experimental setup of ethylene polymerization unit.

3.3 Methods of Catalyst Preparations

3.3.1 Silica Treatment

The equipment setup for calcinations of silica supports is shown in Figure 3.3. To prepare the partially hydroxylated silica, silica gel support was washed with DI-water in a 250 ml volumetric flask and dried at 50 °C under vacuum. Then, it was packed into a horizontal quartz tube and calcined at 500 °C under flowing oxygen for 6 h. After that, the temperature was decreased to 25°C with oxygen flow and the silica powder was stored under vacuum until use. Two types of silica supports (Davisil™ and Sylapol™) were used in this work. Figure 3.4 shows the morphology of these two silicas under transmission microscope.
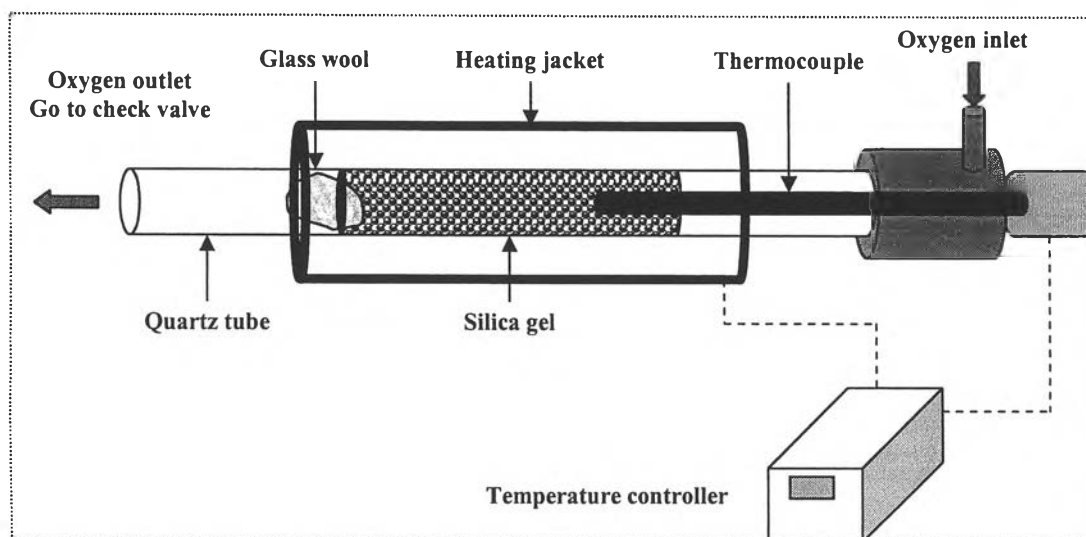
Figure 3.3 Setup of calcination unit.

A   B
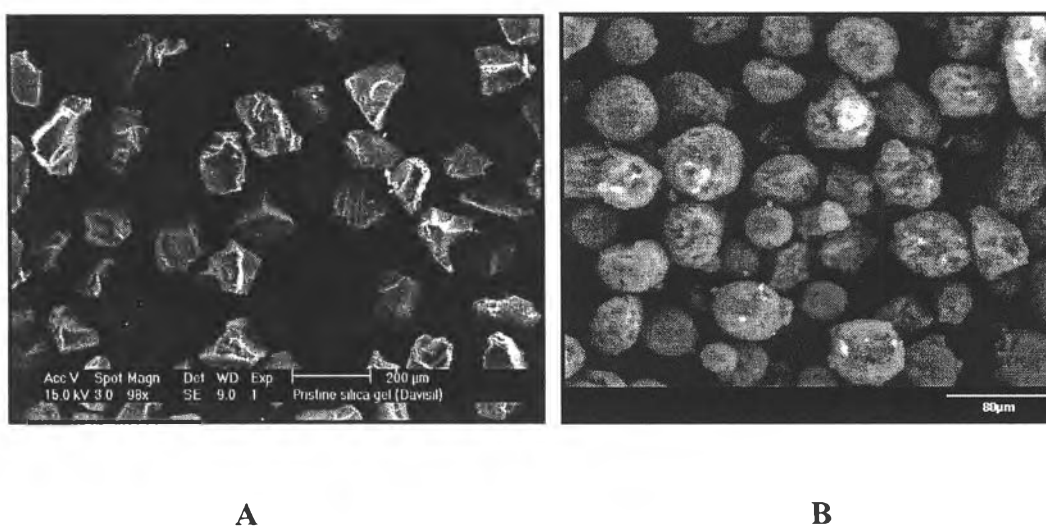
Figure 3.4 TEM micrographs of two types of silica gel used as support; (A) Davisil™ grade, (B) Sylapol™ grade.

3.3.2 Preparation Procedure of Supported Organoborane Co-catalysts

All of the catalyst preparation steps were carried out under anhydrous and anaerobic conditions in a glove box (O_2 and H_2O < 1 ppm). There were three types of catalysts prepared in these studies.

3.3.2.1 B(C₆F₅)₃-SiO₂ co-catalyst

3.3.2.1 B(C$_6$F$_5$)$_3$-SiO$_2$ co-catalyst

The treated silica gel (2 g), B(C$_6$F$_5$)$_3$ (3 ml in toluene or 0.63 mmol) and extra toluene (17 ml) were mixed together into a 100 ml volumetric flask and refluxed for 12 h. Afterwards, the solids in the mixture were allowed to precipitate overnight before collecting only the solid part with a medium fritted funnel and washing with toluene (3x5ml) and hexane (2x5ml). The precipitate was dried under vacuum for 4 h to yield 2.06 g of off-white solid.

3.3.2.2 [HNMe$_2$Ph]$^+$[B(C$_6$F$_5$)$_3$-SiO$_2$]$^-$ co-catalyst

The treated silica gel (~ 2 g) and toluene (14 ml) were mixed as slurry in a volumetric flask (100 ml) equipped with a magnetic stirrer bar. B(C$_6$F$_5$)$_3$ (1.26 mmol in 6 ml of toluene) and NMe$_2$Ph (1.26 mmol) were pre-mixed and added dropwise to the stirred slurry of silica gel. After stirring the mixture for 12 h at room temperature, the slurry was left to settle overnight. The solid part was collected with a medium fritted flask. The product was washed with toluene (3x5 ml) and hexane (2x5 ml) and then dried in vacuum for 4 h to yield 2.12 g of white solid (some mass was lost during transfer).

3.3.2.3 [CPh$_3$]$^+$[B(C$_6$F$_5$)$_3$-SiO$_2$]$^-$ co-catalyst

The treated silica gel (~ 2 g) and toluene (14 ml) were mixed as slurry in a volumetric flask (100 ml) equipped with a magnetic stirrer bar and then mixed with B(C$_6$F$_5$)$_3$ (1.26 mmol in 6 ml of toluene). The slurry mixture was stirred for 3 h. ClCPh$_3$ (1.26 mmol or 0.351 g) in toluene (4 ml) was added dropwise to the mixture in the dark. After stirring the mixture for 12 h at room temperature, the slurry was left to settle overnight. The solid part was collected with a medium fritted flask. The filtered solid was washed with toluene (4x10 ml) and hexane (4x10 ml) and then dried in vacuum for 4 h to yield 2.38 g of yellowish solid (some mass was lost during transfer).

3.4 Characterization Methods for Catalysts

3.4.1 Determination of Bulk Chemical Composition

Inductively Coupled Plasma Atomic Emission Spectrometer (**ICP-AES** Leeman Labs Plasma-Spec ICP, Model 2.5) was used to determine the bulk concentrations of boron and aluminum of the supported catalysts. The samples of catalyst powder were prepared by digesting in 4 N aqueous of HNO_3. A calibration curve was run prior to the samples and an independent check was run interspersed with the samples. The principle of ICP-AES technique is to vaporize a liquid sample and including all elements present by an extremely high temperature (~ 7000 °C) argon plasma, generated and maintained by radio frequency coupling. The atoms are collided with energetically excited argon species and emit characteristic atomic and ionic spectra that are detected with a photomultiplier tube. Separation of spectral lines can be accomplished in two ways. In a sequential or scanning ICP, a scanning monochromator with a movable grating is used to be the light from the wavelength of interest to a single detector. In a simultaneous or direct reader ICP, a polychromator with a diffraction grating is used to disperse the light into its component wavelength. Detectors for the elements of interest are set by the vendor during manufacture. Occasionally a scanning channel is added to a direct reader to allow measurement of an element not included in the main polychromator.

3.4.2 Examination of Surface Morphology

Scanning Electron Microscopy (**SEM**, Philips XL30FEG SEM) was used to observe the morphology of the supported catalysts. Due to the low electron emission of samples, the sample had to be sputtered and coated with carbon prior to test. Fluorine (F-K) distribution on the surface of silica support was determined by using the X-ray Energy Dispersed Spectroscopy (XEDS) detector equipped with SEM and XEDS control software.

3.4.3 Determination of Surface Chemical Composition

X-ray Photoelectron Spectroscopy (**XPS**, Perkin Elmer PHI 5400 model) was employed to identify surface species as well as to determine the binding

energy of electrons in the catalyst samples. XPS is also known as Electron Spectroscopy for Chemical Analysis (ESCA) which uses soft X-rays to produce photoelectrons from the surface layers of atoms in a solid sample. The emitted electrons are analyzed according to their kinetic energy and the spectrum produced is used to identify the elements present and their chemical states. The X-rays source is MgK (1253.6 eV) by operating at 15 kV and 300 W. The spectra were scanned at room temperature in with a resolution of 0.1 eV in the range of 0-800 eV. Samples were pressed to form a pellet under an inert gas and then placed on the sample holder. The spectra of B (1s) at 191 eV and F (1s) at 690 eV were determined at 90° angle relative to the electron detector (Kelley, 1988).

### 3.4.4 Determination of Functional Group over Silica Supports

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (**DRIFTS**) was used to investigate the changes brought about by the pretreatment with borane or alkylaluminums on the surface of silica support. The measurements were carried out under nitrogen atmosphere over the range of 4000-1500 cm^{-1}. The samples were mixed with noninfrared absorbing material, dry-KBr and placed in the sample holder-cup. The mixture ratio (sample:KBr) was 1:10 by wt. This technique involves irradiation on the powdered sample by an infrared beam where the incident radiation undergoes absorption, reflection, and diffraction by the particles of the sample. Only the incident radiation that undergoes diffuse reflectance contains absorptivity information about the sample (Niemantsverdriet, 1993).

3.4.5 TMA Titration

The hydroxyl group content of silica supports was determined by titration with trimethylaluminum (TMA) (Collins *et al.*, 1992). The amount of CH_4 evolved is based on the stoichiometry of the equation as follows:

$$SiO_2 - OH + AlMe_3 \rightarrow SiO_2 - OAlMe_2 + CH_4 \qquad (3.1)$$
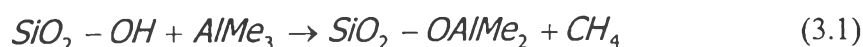
Due to spontaneous flammable reaction with air of TMA, the experiment had to be carried out in the glove-box system. Pressure was determined by a barometer. A weighed sample of calcined silica (0.06 g) was suspended by dry toluene (20 ml) in a dry volumetric flask (100 ml) connected adaptively to a sidearm U-shape (Figure 3.5) contained toluene (1 ml). The flask was sealed by rubber septa. A solution of TMA in toluene (1.0 M, 0.4 ml) was added via syringe drop by drop at constant temperature (21 °C). The mixture was vigorously stirred, and the amount of CH_4 evolved was determined by measuring the increased height of toluene in the U-tube. The silica surface hydroxyl content (mmol OH/g support) was then calculated using the ideal gas law. The experiment was repeated 3 times and the experimental error was minimized by subtracting with a blank experiment which was carried out merely with dry toluene (20 ml).
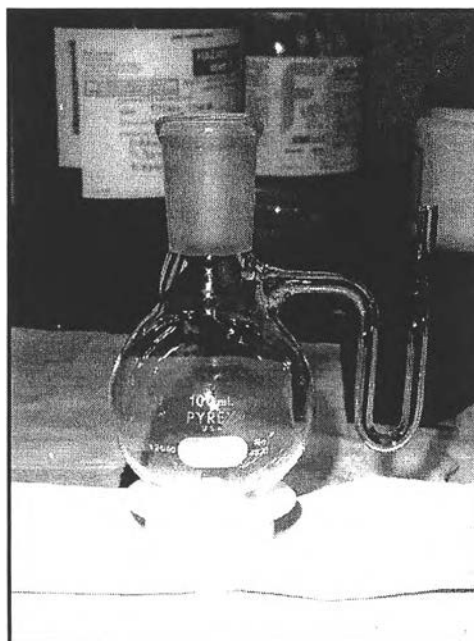

Figure 3.5 A 100 ml flask connected a U-tube sidearm.

3.5 Polymerization Procedure

The ethylene polymerization was carried out in a 500 ml stainless steel reactor (Pressure Product Industrial) equipped with a dynamic magnetic stirrer and a

Teflon liner. The polymerization temperature was controlled using a PID temperature controller (OMEGA, CN-8502) with a heating jacket and a cooling U-coil (water as coolant) inside the reactor. The temperature was measured using a thermocouple (OMEGA, K-type) immersed in a thermowell. The rate of ethylene consumption was monitored by using a mass-flow-meter (Cole-Parmer, model no. 32915-14) linked to a computer (LAB-VIEW v5.5 software) used to acquire the temperature and flow rate data as a function of time. The overall setup is schematically described in Figure 3.2 (Samson *et al.,* 1998 and Lasarov *et al.,* 2000).

Prior to each run, the reactor was dried at 150 ^{0}C under vacuum for one hour. The reactor was cooled down while flushing with pure nitrogen for several times and ethylene for the last step. The stirring speed was kept constant at 1000 rpm. All chemicals made as solutions in toluene were loaded into a cylindrical bomb (Figure 3.6) under an inert atmosphere to transfer into the reactor by N_2 overpressure. For a typical experiment, 200 ml of toluene was introduced into the reactor and the temperature was set to 40°C. For the homogeneous system, a desired amount of zirconocene and TIBA were loaded into the reactor and the reactor was pressurized with ethylene at 20 psig. After 5 min, a weighted amount of the co-catalyst, was loaded into the reactor to start the polymerization reaction. For the heterogeneous system, the prescribed amounts of zirconocene and TIBA were loaded into the reactor that was pressurized with ethylene at 20 psig. After 5 min, a weighted amount of the co-catalyst, suspended in 10 ml of toluene, was loaded into the reactor. The temperature was controlled to ±1 ^{o}C of the set point. After 30 min, the reactor was cooled down to room temperature and depressurized. 10 ml of acidic-methanol was injected into the reactor to quench the system. The final product was washed with an excess of methanol for a few times, filtered, and left in the hood for 4 days.
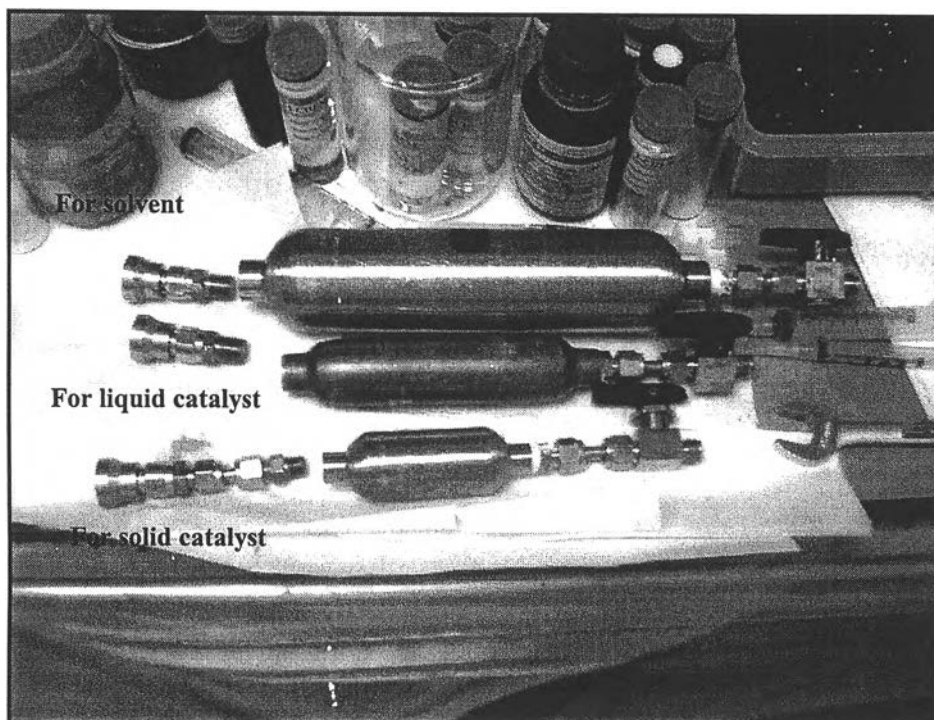
Figure 3.6 Catalyst loading tools.

3.6 Characterization of Polyethylene

3.6.1 High Temperature Gel Permeation Chromatography (HT-GPC)

Molecular weight (MW) and molecular weight distribution (MWD) were determined by using High Temperature GPC equipped with three Water Ultrastyragel columns in series at 150 °C using o-dichlorobezene as solvent. The columns were calibrated with narrow molecular weight distribution polystyrene samples. Polymers with high MW show better mechanical properties than polymers with low MW. MWD is also known as the polydispersity index (PDI). Homogeneous polyethylene prepared by SSC technology tends to exhibit a narrow MWD (~ 1to 2). A narrow composition distribution is obtained for ethylene-α-olefin copolymers. The mechanical and rheological properties of polymers depend not only on their average molecular weights but also on their MWD. Polymers with a narrow MWD in general have greater dimensional stability, higher toughness, higher impact resistance, higher resistance to environmental stress cracking, and less solvent-extractable. However,

the narrow MWD of a linear homogeneous copolymer also results in poor melt processability such as low melt strength, high extruded back-pressure, high energy consumption during extrusion, etc. Especially, polymers with relatively narrow MWD with high MW will cause a higher degree of extrusion defects such as melt fracture in addition to the decreased processibility. On the other hands, polymers with broad MWD show greater flowability in molten state at high shear rate and can be easily processed. Therefore, control of MW and MWD becomes an important factor to achieve any particular application of the produced polymer resin (Cheremisinoff, 1996).

3.6.2 Scanning Electron Microscopy (SEM)

The morphology of the produced polyethylenes was determined by using SEM. Due to the low electron emission of samples, the sample had to be sputtered and coated with carbon prior to test.

3.6.3 Bulk Density Measurement

The bulk density of polyethylene produced was measured the fluffiness of a polymer by following the test method in ASTM D 1895. The definition of bulk density is the weight per unit volume of a material, including voids inherent in the polymer matrix. The term of bulk density is commonly used for materials such as molding powder and granules. It is also significant in indication of polymer performance with respect to their handling in packaging and fabrication.

The apparatus in this test method were included as followed:

(1)   A cylindrical cup (12 ml) and to weight in grams of empty cup.

(2)   A funnel opened at the bottom and installed at a constant height (15 cm above the cup).

The procedure for the measurement was begun by closing bottom-hole of the funnel with a finger. To load sample into the funnel, the bottom-hole was opened quickly and the polymer was allowed to flow freely into the cup. The excess polymer on top of the cup was immediately scraped off with using a straightedge without shaking the cup. Finally the polymer in the cup was weighted and then

calculated for density in grams of polymer per 1 ml. The test was repeated for 5 times in order to minimize error.