

CHAPTER I

INTRODUCTION



1.1 Background

The developments of metallocene have been challenged in many fields of research groups along the past decade. Metallocene catalysts have many advantages over conventional Ziegler-Natta or chromium catalysts. There are main features that distinguish metallocene catalysts from the conventional catalysts used in the polyolefin industry: they can polymerize almost any vinyl monomer irrespective of its molecular weight or steric hindrance; they produce extremely uniform polymers and copolymers of narrow molecular weight distribution and narrow compositional distribution; they can control vinyl unsaturation in the polymer produced; and they polymerize α -olefins with very high stereoregularity to give isotactic or syndiotactic polymers. Metallocene is well defined organometallic transition metals compounds with only one active site for the polymerization reaction (single-site catalysts), while conventional catalysts are formed by complex chemical reactions leading to the formation of chemically ill defined multiple active centers (Britovsek *et al.*, 1999). Each of them comes with its own ability for polymerization, transfer and termination rates, producing polymers with heterogeneous molecular and chemical composition. In contrast, single-site catalysts produce very homogeneous polymers with narrow molecular weight distribution (MWD), polydispersity of about 2 (Figure 1.1), and narrow chemical composition distribution (CCD) (Huang and Rempel, 1995 and Malhotra *et al.*, 1997).

The new generation of single-site catalysts can really impact the polyolefin industry if they can be used as dropped into large capacity production plants and produced resins that can be processed in the existing equipment without major modifications. Both requirements should be achieved at a favorable cost and performance balance with respect to conventional polyolefin technologies. There are two important issues involving in using metallocene catalysts. The single-site catalysts technology is currently facing, namely, development of methods for supporting the new single-site catalysts suitable for dropping into slurry and gas-

phase processes and the development of polyethylene with better properties and good processibility.

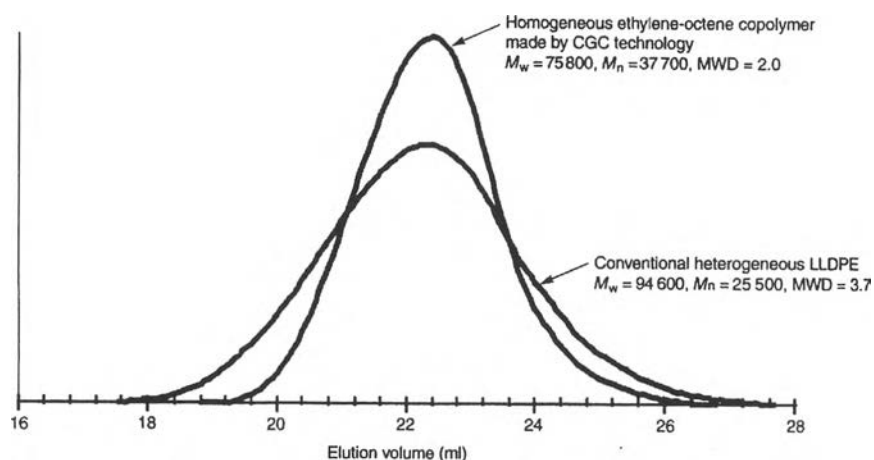


Figure 1.1 Comparison of molecular weight distribution of polymer product for conventional Ziegler-Natta catalyst and metallocene catalyst (Huang and Rempel, 1995).

1.2 Motivation

For the successful substitution of existing heterogeneous polymerization, the metallocene catalyst requires heterogenization by the attachment of the catalyst on a suitable support. Homogenous metallocene catalysts do not allow control of polymer particle morphology which, in the case of less soluble polymers, can lead to serious reactor fouling (Cam and Giannini, 1992). In heterogeneous catalysts the growing polymer tends to form replicas of the original catalyst particle to give free-flowing powders which are easy to separate and process (Ribeiro *et al.*, 1997). Heterogenized catalysts prepared by reacting metallocenes with Lewis acidic supports such as Al_2O_3 or $MgCl_2$ followed by activation with aluminum alkyls, by covalent attachment of metallocenes, and by ion exchange with crystalline silicates have been reported (Bochmann, 1999). In most cases, heterogenization is carried out by impregnating dehydroxylated high surface area silica with methylaluminoxane (MAO) and the

metallocene, a method that has the added advantage of allowing a reduction of the excess of MAO necessary to achieve acceptable productivities. There is no firm attachment of the metallocene to the support with such catalysts; rather the polymerization chemistry takes place in the MAO/alkene surface film along the lines known for homogeneous systems (Sinclair and Wilson, 1994).

Generally, supported metallocene catalysts are prepared by the reactions between metallocene and supports (unmodified or modified by aluminum compounds or siloxane compounds) for a given period of time, followed by successive washing and drying. To overcome the preparation complexities of traditionally supported metallocene catalysts, metallocene can be supported in situ, which eliminates the need for a supporting step before polymerization (Chu *et al.*, 2000). These catalysts have a good catalytic activity, produce polymers with a good morphology and high bulk density, and do not cause reactor fouling. Additionally, they can be activated with trimethylaluminum (TMA) alone in the absence of soluble MAO in the polymerization reactor.

As a result of the high cost of using large excesses of MAO, alternative catalysts have been developed in the absence of MAO. The key is to find a co-catalyst that would form the metallocenium cation, providing charge stabilization, being weakly coordinating, and be chemically inert so that it would not react with the highly reactive metallocene cation. It has been reported that organoboranes can fulfill this role by treating metallocene alkyls with a cation generating agent such as $B(C_6F_5)_3$, $[CPh_3]^+[B(C_6F_5)_4]^-$, or $[HNMe_2Ph]^+[B(C_6F_5)_4]^-$, to generate equilibrium concentrations of the catalytically active species metallocenium (Bochmann and Lancaster, 1992b). The activity and stability of such MAO-free cationic catalysts are strongly dependent on the weakly coordinating nature of the counteranion, with $[B(C_6F_5)_4]^-$ and $[RB(C_6F_5)_3]^-$ being particularly successful (Bochmann and Jaggar, 1992a; Bochmann and Lancaster, 1995 and Siedle and Newmark, 1995).

First, these organoboranes were developed for homogeneous metallocene catalyst systems for olefin polymerization. This can result, however, in reactor fouling, poor productivities, poor polymer bulk densities, and poor polymer particle morphologies. For these reasons, it is preferable to develop heterogeneous versions

of these organoborane co-catalysts, where the co-catalysts are deposited on a carrier, preferably an oxide such as silica gel.

Recent works (Bochmann, 1999) were studied supported organoboranes which had been modified with an alkyl aluminum compound treated with solution of a metallocene catalyst and an organoborane and then the solvent was removed. The resulting catalyst system provided a low activity heterogeneous borane catalyst system. Because there is no direct chemical bond between the catalyst, organoborane and the support, resolubilization of the catalyst may make this system unsuitable for slurry reactors.

Recently, novel in-situ activated catalyst systems showed remarkable kinetic profiles for ethylene polymerization. Their activities did not rapidly decay and showed time independent ethylene consumption when zirconocene was reacted directly with supported MAO inside the reactor. Therefore the kinetic profiles are very important in providing information about the active species and catalysis decay status in polymerization processes (Naga *et al.*, 1999).

Figure 1.2 shows that the polymerization mechanism for the in situ metallocene catalysts tentatively which can be divided as follows: (1) initial contact between support and homogeneous metallocene, (2) activation of catalytic sites, (3) exposure and activation of new sites formed by catalyst fragmentation, (4) reactivation of deactivated catalytic sites by soluble metallocenes, and (5) steady state. It seems that active sites are formed by the complexation of metallocene and MAO molecules supported on supported-MAO (SMAO), (Steps 1 and 2). Polymerization starts with the injection of ethylene, causing particle fragmentation and growth. It is reasonable to assume that additional MAO molecules supported on SMAO are exposed during this step and, therefore, activated by the metallocene molecules remaining in the solvent (Step 3). To explain the stable polymerization rates observed with this catalyst, the deactivated sites on the SMAO surface are reactivated by complexation with soluble metallocene (and possibly with TMA), leading to the dynamic equilibrium illustrated in Steps 4 and 5 as shown in Figure 1.1.

In this thesis, supported borane ($B(C_6F_5)_3-SiO_2$) and modified-supported borane ($[HNMe_2Ph]^+ [B(C_6F_5)_3-SiO_2]^-$, and $[CPh_3]^+ [B(C_6F_5)_3-SiO_2]^-$) co-catalysts

(Figure 1.3) were prepared to avoid the excessive use of MAO for ethylene polymerization. These supported co-catalysts were exploited for “MAO-free” ethylene polymerization system that was carried out by the in-situ activation with metallocene and bis(cyclopentadienyl) zirconium dichloride (Cp_2ZrCl_2) combined with triisobutylaluminum (TIBA). TIBA was chosen as alkylating agent for Cp_2ZrCl_2 in this work. In addition, silica gel provided dramatically chemical oxide support for binding borane ($B(C_6F_5)_3$) to its hydroxylated surface. Two cationic salts of $HNMe_2Ph$, and $ClCPh_3$ were used to stabilize chemically $B(C_6F_5)_3$ on the surface of silica support in order to reduce the resolubilization of $B(C_6F_5)_3$ from the supported co-catalysts. An alkyl aluminum compound, TIBA was added for the pretreatment of silica support. This was found that the catalytic performance and control morphology of polyethylene particle could be improved.

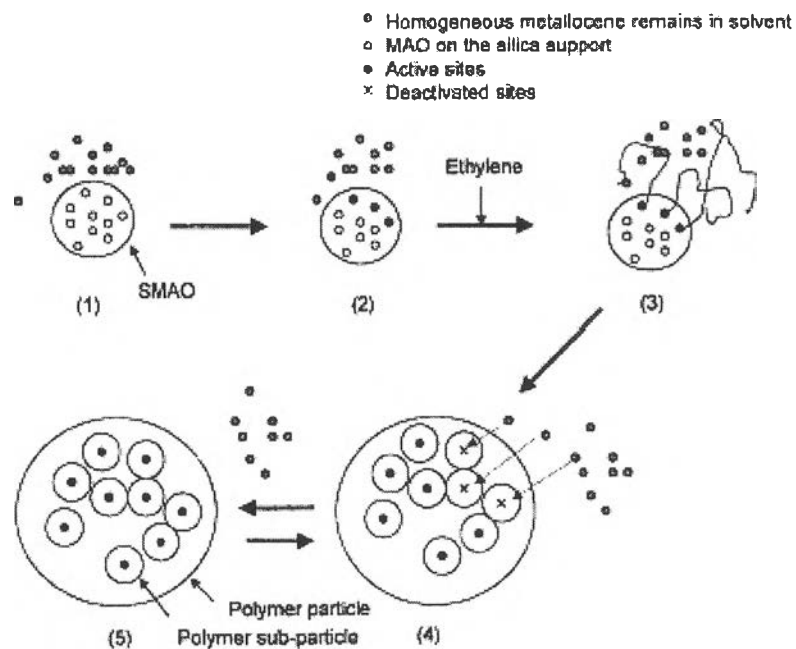


Figure 1.2 A model for the polymerization mechanism of in-situ supported metallocene catalysts: (1) initial contact between support and homogeneous metallocene, (2) activation of catalytic sites, (3) exposure and activation of new sites formed by catalyst fragmentation, (4) reactivation of deactivated catalytic sites by soluble metallocenes, and (5) steady state (Chu *et al.*, 2000).

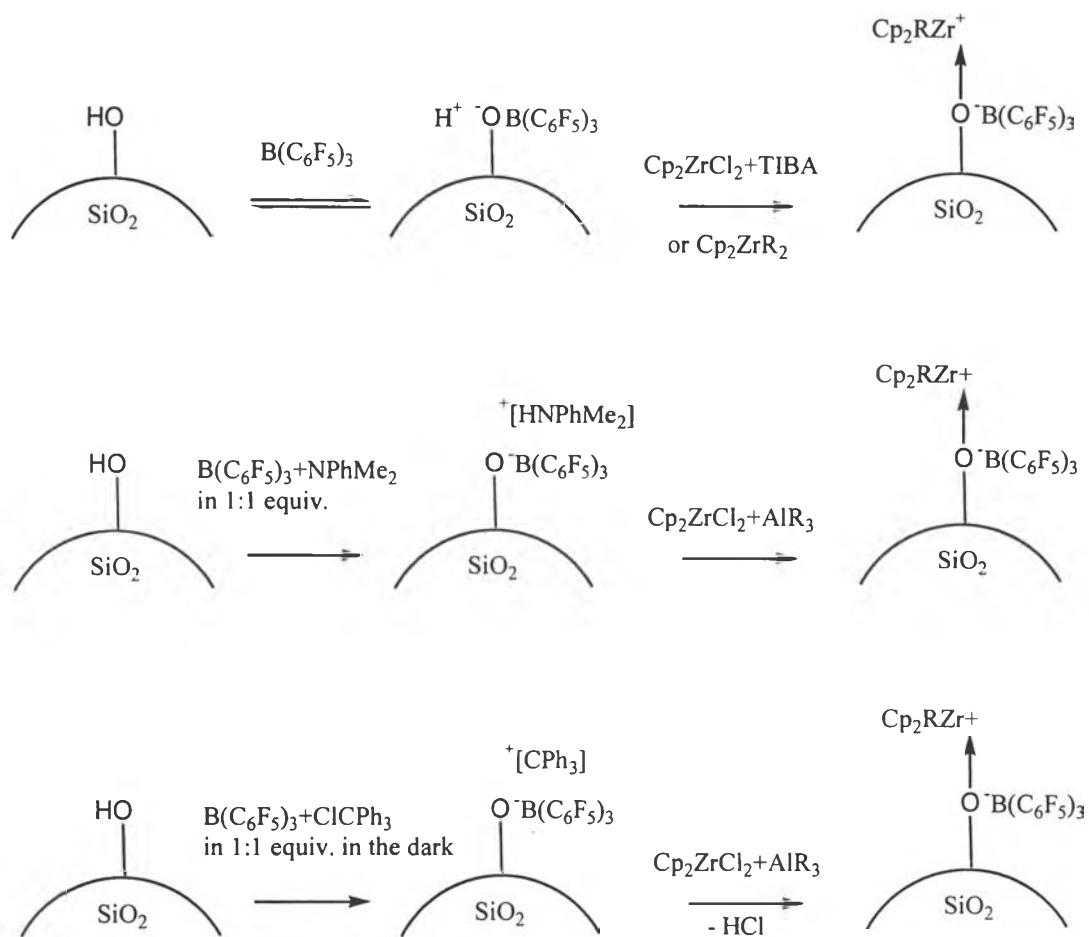


Figure 1.3 The formations of supported organoborane co-catalysts, $B(C_6F_5)_3-SiO_2$, $[HNMe_2Ph]^+[B(C_6F_5)_3-SiO_2]^-$, and $[CPh_3]^+[B(C_6F_5)_3-SiO_2]^-$ for in-situ ethylene polymerization.

1.3 Objectives

The objectives of this work could be classified into 3 categories as follows.

1. To study the in-situ activation of supported borane co-catalyst with zirconocene catalyst/ TIBA for ethylene polymerization
2. To develop the “MAO-free” supported co-catalyst by using anilinium and carbenium for preparing supported-borate silica
3. To improve the catalytic performance of supported-borane co-catalysts by pretreatment of silica support with using alkylaluminum compounds