



CHAPTER II

LITERATURES SURVEY

2.1 History of Metallocenes

Polyolefin plastics, such as polyethylene and polypropylene, are nowadays in their mature phase, with consumption of about 40 million tons per year, and could appropriately afford as commodity. They have been protagonist of an exciting innovation through a continuous development of new processes and products. The most important factor governing the growth of polymerization industry in the future years is likely to be its effect on the environment. Nowadays, novel catalysts have to be developed carefully considering the whole life cycle, from conception to destruction, with the aim of keeping the whole process environmentally benign at every step. In addition, each process involved should be carried out in an energy efficient manner. Highly active catalysts can produce polyolefins and provide an economical and high efficient process. Besides, the environmental problems have to be concerned and taken into consideration that the residual transition metals or else materials in final polyolefin products should be minimized (Razavi, 2000).

Most of the polyolefins are currently manufactured with Ziegler-Natta catalysts, titanium chloride combined with alkylaluminum (Malhotra *et al.*, 1997). These commercial heterogeneous catalysts exhibit very high activity for ethylene and propylene polymerization and high isospecificity in propylene polymerization through more than 45 years of study and development of the catalysts. What seems to be lacking, however, is high catalytic productivity and precise control of polymerization (Sinclair and Wilson, 1994).

Since metallocene catalyst was first discovered over 40 years ago, this was originally referred to as sandwich molecules (Kaminsky, 1999). No potential applications were found until 1976 when Walter Kaminsky of the University of Hamburg discovered that one metallocene acted as an effective catalyst for the ethylene polymerization (Britovsek *et al.*, 1999). He found that the small additions of water greatly increased the metallocene catalysts' activity when trimethyl aluminum (TMA) was used as the co-catalyst. Subsequent studies showed that this activity was

resulted from the formation of methylaluminoxane (MAO) by the hydrolysis of TMA. This particular metallocene, however, had poor activity and uncontrollable stereochemistry for the polymerization of propylene. The metallocene was not of much interest to the scientific world until 1984 when Kaminsky and Hans Brintzinger of Konstanz University found that another metallocene could produce highly stereoregular polypropylene (Britovsek *et al.*, 1999; Gupta *et al.*, 1994 and Kaminsky, 1999).

Since the 1950's and 60's, the development of the conventional Ziegler-Natta catalysts has been indisputably contributed to industrial polymerization of olefin. Ziegler-Natta catalysts not only can speed up the rate of reaction, but also they provide stereochemical control. Until the metallocene catalysts have come out recently, there is another alternative way for mass production of polyethylene and polypropylene. The significant difference between the Ziegler-Natta catalysts and the metallocene catalysts is the distribution of active sites. The Ziegler-Natta catalysts have many sites, not all of which are stereospecific. Hence, the resulting polymers are branched and have a broad distribution of molecular weight. On the other hand, the metallocene catalysts are single sited that can produce polymers with having linear structure, stereoregular, and narrow distribution of molecular weight. The metallocene catalysts can essentially polymerize with up to 10 times the stereospecificity of Ziegler-Natta catalysts (Britovsek *et al.*, 1999).

The stereospecificity of a polymer is described by its tacticity. Tacticity is the stereochemistry of the substituents on a polymer's backbone (Figure 2.1). From previous studies, it is shown that the metallocene catalyst can keep a polymer almost 100% homotactic (Soga and Shiono, 1997). In addition metallocene can polymerize almost any olefin regardless of molecular weight or steric hindrance. It is also applied to produce bulky polymers such as polystyrene and polycycloolefins that now have new industrial potential as well as new properties (Malhotra and Coville, 1997). Another advantage of metallocenes is that the molecular weight of the polymer produced can be more precisely controlled than with the Ziegler-Natta catalysts (Möhring *et al.*, 1994). These aforementioned factors are what truly shape a polymer. Polymer's physical properties (e.g. stiffness, density, transparency, melting point, etc.) vary dramatically with its molecular weight, molecular weight

distribution, and its tacticity. For example, atactic polystyrene is the material used to make disposable Styrofoam cups. These cups are notably delicate; that crush easily and melt from that flame of a match. In contrast, syndiotactic polystyrene is crystalline. It has a melting point of 270 °C and can compete commercially with such polymers as nylons and polyesters (Malhotra *et al.*, 1997).

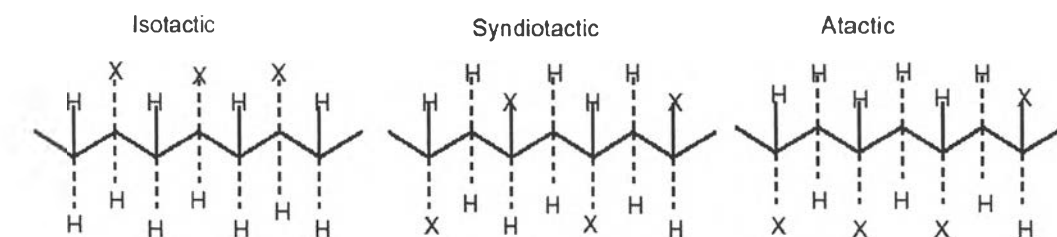


Figure 2.1 Tacticity of polymer chain (X = alkyl chain).

2.2 Characteristics and Functions of Metallocenes

The name “metallocene” was first coined in the early 1950s as a more elegant replacement for the term “iron sandwich” describing dicyclopentadienyliron, a compound of iron and cyclopentadiene (C_5H_5)₂Fe or Cp₂Fe. The aspect description of metallocene is the term “sandwich molecule” (Figure 2.2), as the molecule contains a metal ion which is sandwiched between two flat cyclopentadiene rings (Cp or C₅H₅) (Huang and Rempel, 1995).

Metallocene catalysts are organometallic coordination compounds in which one or two cyclopentadienyl rings or substituted cyclopentadienyl rings (e.g. indene, fluorene) are bonded to a central transition metal atom (Figure 2.3) (Hamielec and Soares, 1996). The cyclopentadienyl ring of a metallocene is singly bonded to the central metal atom by a π -bond. Consequently, the formal valence of the ring-metal bond is not centered on any one of the five carbon atoms in the ring but equally on all of them. The most common metals used in metallocene catalysts for olefin polymerization are Zr, Ti, and Hf. In addition, several works were conducted to find out other effective metals such as Sc, Y, Sm, Yb, Lu and other lanthanides for metallocene development (Huang and Rempel, 1995). The nature and number of the

rings and substituents, type of transition metal, and its substituents, the type of the bridge, if present, and the co-catalyst type directly governs the catalytic behaviors of these organometallic compounds towards the polymerization of linear and cyclic olefins and diolefins.

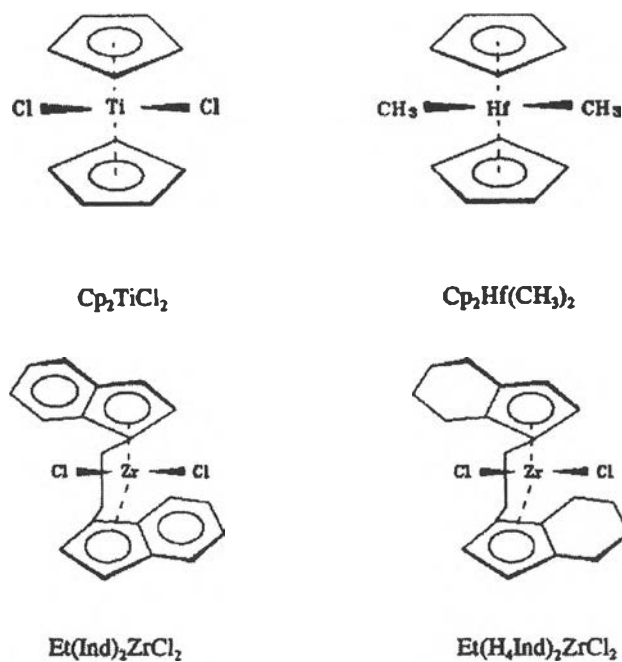


Figure 2.2 The structure of metallocene catalysts (Huang and Rempel, 1995).

Different metallocene catalysts acquire different reactions because the symmetry of the metallocene affects the structure of the polymer. In order to achieve isotacticity, the metallocene needs bridging between two cyclics. Without the bridge, the cyclic groups would spin around the metal atom independent of each other and rotate randomly between stereospecific and nonstereospecific configurations. The metal atom itself is usually bonded to chlorine ions (Hamielec and Soares, 1996).

The remarkable differences can be identified with the traditional titanium based Ziegler-Natta catalyst. Among the former ones, it has to be mentioned that both titanium and metallocene based catalysts give rise to insertion polymerization, that can be classified as a coordinated ionic reaction with the transition metal bearing

a partial positive charge and it occurs through a cis coordination of the olefin on the catalytic site (Cam and Giannini, 1992).

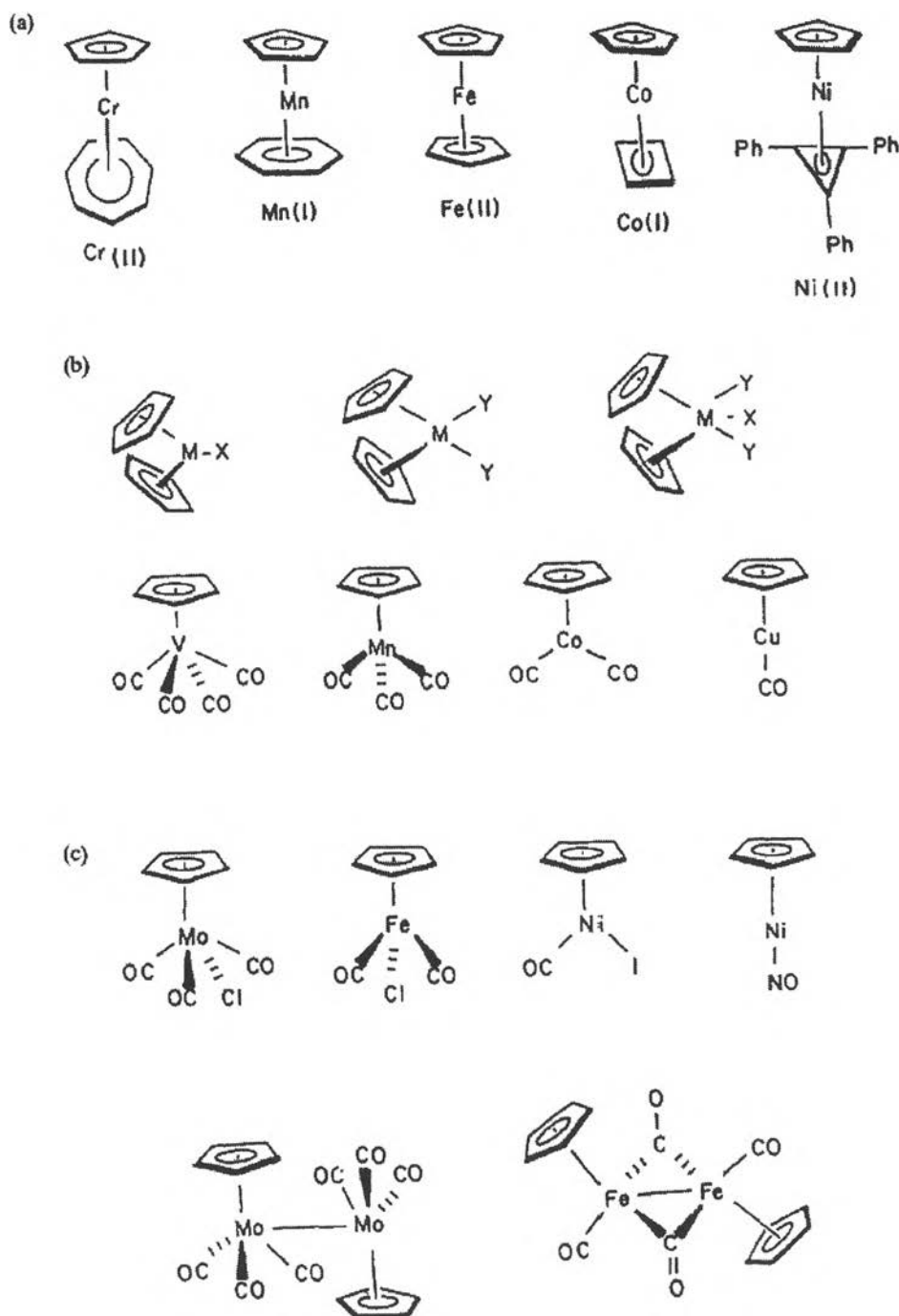


Figure 2.3 (a) Metallocenes with parallel cyclopentadienyl rings, (b) bent metallocenes, (c) monocyclopentadienyl metallocenes (Huang and Rempel, 1995).

A type of transition metal is considerably the first factor of various catalytic performance of metallocenes for ethylene and propylene polymerization. The activity of hafnocene is normally lower than its zirconocene. It can be attributed that the different concentrations of active center afford different carbon-metal bond strength (Möhring and Coville, 1994).

The steric and electronic factors of the substituents on Cp ligands affect the catalyst activities. Steric and electronic effects are always mixed and the overall effect on catalyst activity is dependent on the balance of the two Cp rings. The previous works have reported the effects of alkyl substitution on the Cp ring for several zirconocenes and the order of the activity was found to be $(\text{MeCp})_2\text{ZrCl}_2 > (\text{EtCp})_2\text{ZrCl}_2 > \text{Cp}_2\text{ZrCl}_2 > (\text{Me}_5\text{Cp})\text{ZrCl}_2 > (\text{Me}_5\text{Cp})_2\text{ZrCl}_2$ (Möhring et al., 1994). These results were further interpreted to mean that single alkyl substituents could increase the activity by electron donation enhancement of coordinated anionic propagation, whereas very bulky substituents decreased the activity of ethylene polymerization due to steric hindrance (Möhring and Coville, 1994). The effect of the bridge was purposed, the C-bridge being shorter than the Si-bridge, the Cp ligands thus forming a wider angle. The activity of ethylene polymerization was found Si-bridge higher than C-bridge (Soga and Shiono, 1997).

2.3 Activator Compounds

2.3.1 Methylaluminoxane (MAO)

Since the discovery of a cocatalyst, namely methylaluminoxane (MAO) by Water Kaminsky, the activity of ethylene polymerization has been dramatically increased when zirconocene derivatives are reacted with MAO. The activation mechanism and the structure of MAO are not completely understood. MAO does not readily form a crystalline solid. Indirect methods, otherwise X-ray crystallography, have to be carried out for deducing the structure. Among the methods that frequently have been applied are NMR, freezing point depression, complexation and extraction with ethers and chemical analysis (Harlan *et al.*, 1995). Based on previous works, some crucial information of MAO can be given as follows (Ystenes *et al.*, 2000):

1. The molecular weight of MAO is roughly 800-1200.

2. There is a dynamic exchange of methyl groups in solution.
3. There are 2 or 3 different methyl groups.
4. There probably is more than one type of MAO molecule.
5. Removing TMA from MAO gives an Me/Al ratio of ca. 1.5.

Aluminoxanes, in general, are understood as species containing an oxygen bridge binding two aluminum atoms. Any other groups such as alkyl, aryl, halide or alkoxy can then be the pendent ligand bonded to the aluminum atoms. Aluminoxane is obtained from the controlled hydrolysis of organoaluminum compounds. For methylaluminoxane, the careful hydrolysis of trimethylaluminum (TMA) by crystal water of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{Al}_2(\text{SO}_4)_3 \sim 14\text{-}18\text{H}_2\text{O}$ is proved to be the most effective laboratory method of obtaining uniform products in high yield. Technically, MAO is made from the direct reaction of TMA with water (Harlan *et al.*, 1995).

Despite the unique effectiveness of MAO as a cocatalyst, it still remains a “black box”. Depending on the nature of the hydrated salt (for H_2O source) used for the MAO synthesis and the exact MAO synthetic reaction conditions, MAO-activated metallocenes may exhibit widely different activities in olefin polymerization (Chien and Wang, 1988 and 1990). The MAO structure can hardly be elucidated directly because of the multiple equilibria present in MAO solutions, and the residual TMA in MAO solutions appears to participate in equilibria that can further interconvert into various MAO oligomers (Kaminsky, 1994 and Siedle *et al.*, 1991). There are two types of TMA present in typical MAO solutions: “free-TMA” and “associated-TMA” as show in equation (2.1).



It is difficult to reduce the $\text{CH}_3:\text{Al}$ ratio to less than 1.5 by evaporation of volatile components because vacuum-drying removes only the free TMA, while the associated TMA can only be removed chemically (Kaminsky, 1994). It was found that cryoscopic MAO molecular weight decreased after AlMe_3 addition according to a linear relationship, which is caused by disproportionation reactions

(Chien and Wang, 1988). The residual TMA is also important for the solubility of MAO in aromatic hydrocarbons. The agreement appears to be that the MAO oligomers are fluxional molecules with a dynamic equilibrium among them, which change their size and structure. However, recent in-situ FTIR spectroscopy investigations did not indicate any obvious reaction between TMA and MAO (Ystenes *et al.*, 2000). Harlan *et al.* (1995) reported that the aluminoxane has three-dimensional cage compounds with four-coordinated aluminum centers and not those containing coordinatively unsaturated three-coordinated aluminum centers (Figure 2.4), as has been traditionally proposed. Other attempts to elucidate the MAO structure are the help of size exclusion chromatography, NMR, mass balance and phase separation experiments (Togni and Halterman, 1998). Nevertheless, in the light of its complicated and unresolved structural features, MAO is usually represented for the sake of simplicity as having linear chain or cyclic ring structures, containing three-coordinated aluminum centers (Figure 2.5).

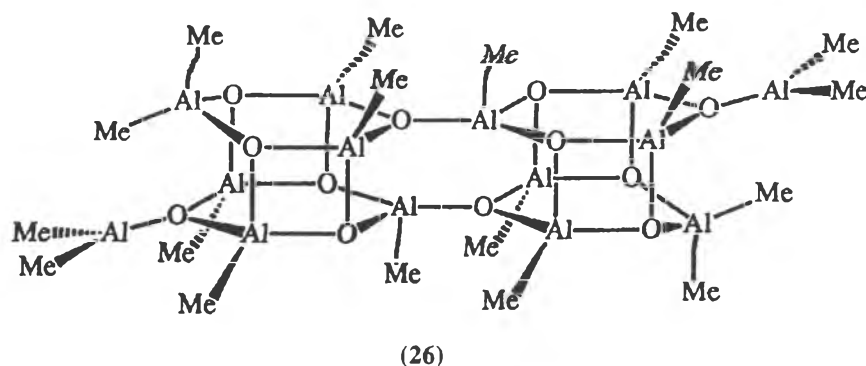


Figure 2.4 MAO structure in three-coordinated aluminum (Togni *et al.*, 1998).

The role of MAO as co-catalyst is not clearly addressed and many functions have been attributed. MAO has been proposed as being responsible for the alkylation of the catalyst, stabilization of the cationic metallocene alkyl by acting as a counter-ion and the prevention of bimolecular reduction of the catalyst (Kaminsky, 1994 and 1995). This would account for the large amount of MAO required for good polymerization activity and chain transfer capabilities (Kaminsky, 1995). MAO also

scavenges impurities such as water and oxygen from the reaction medium (Harlan *et al.*, 1995; Ystenes *et al.*, 2000). It has also been proposed that the most important function of MAO is in the formation of the active species. This zirconocene cation or active center is thus stabilized by a so-called “crown-aluminoxane” complex (Togni and Halterman, 1998).

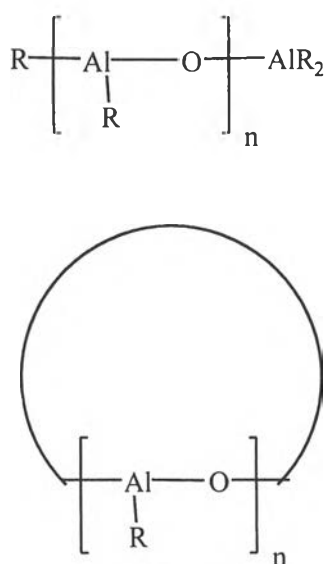


Figure 2.5 The structure of MAO; linear and cyclic (Ystenes *et al.*, 2000).

Conventional MAO has very low solubility in aliphatic solvents as well as poor storage stability in solution, which considerably limits its utility. Other more soluble and commonly used aluminoxanes are ethylaluminoxane and isobutylaluminoxane, which are synthesized by the partial hydrolysis of triethylaluminum (TEA) and triisobutylaluminum (TIBA), respectively (Wang *et al.*, 1999 and 2000). However, these alkylaluminoxanes do not perform as well as MAO in metallocene-mediated olefin polymerization. Furthermore, commercial modified methylaluminoxane (MMAO) available from Akzo-Noble (Figure 2.6) and prepared by controlled hydrolysis of a mixture of trimethylaluminum and triisobutylaluminum, exhibit improved solution storage stability and improved solubility in aliphatic solvents and can be produced at a lower cost while providing good polymerization efficiency (Wang *et al.*, 1999 and 2000).

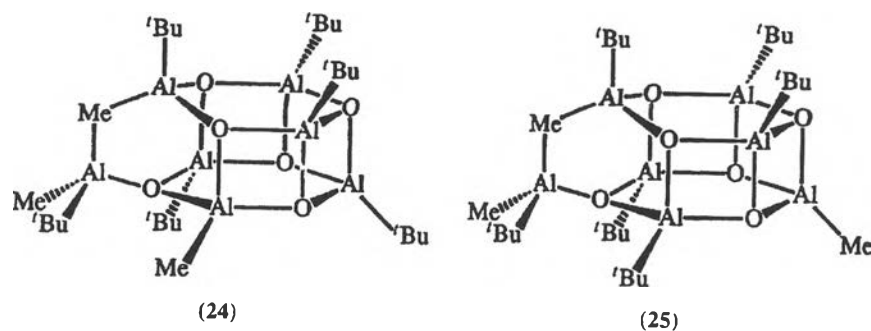
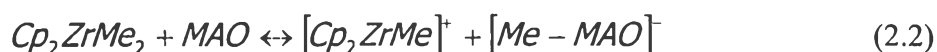


Figure 2.6 The modified structure of MAO with triisobutylaluminum (Togni and Halterman, 1998).

Despite the success of MAO in promoting high activity of metallocene-mediated olefin polymerization, it also exhibits disadvantageous features. High MAO:catalyst precursor ratios (100 to 10000:1) are generally required for obtaining acceptable polymerization activity and relatively stable kinetic profiles (Kaminsky *et al.*, 1994 and 1995). It has been suggested to use of UV-Vis spectroscopy to follow the activation with Al/Zr and catalyst stability over time (Albizzati and Galimberti, 1998). Furthermore the activity of Cp_2ZrCl_2/MAO catalyst often seems to increase indefinitely with the Al/Zr ratio. This effect is usually discussed on the assumption of an equilibrium between an inactive metallocene precursor and its catalytically active form (Kaminsky, 1994).



In addition this raises issues of the high cost of this co-catalyst and the high ash content (Al_2O_3) of the product polymer. Poor control over polymer morphology may be another matter of concern when polymerizations are carried out other than in the solution phase processes. Finally, the intrinsically complicated structural features of MAO as well as the superstoichiometric quantities of MAO required in the activation process prevent full characterization of the catalytically active species (Kaminsky, 1994 and 1995 and Togni and Halterman, 1998). The overall activation

process and the nature of the resulting active species are therefore not well understood. Consequently there is a great need to develop new co-catalyst systems which can provide equivalent or even greater catalytic activity and, at the same time, allow isolation and characterization of the active species for a better fundamental understanding of cationic transition metal-mediated coordination polymerization.

2.3.2 Organoboranes

Jordan (1991) presented the first knowledge to open the possibility to synthesize and isolate cationic metallocene complexes of group IV to be useful for ethylene polymerization in the absence of an aluminum co-catalyst. Zirconium cations were generated by using one-electron oxidants, it could then be trapped in the presence of labile ligands L. Such the complex $[\text{Cp}_2\text{ZrR}(\text{THF})]^+[\text{BPh}_4]^-$, the THF partly dissociated from it in CH_2Cl_2 solution and it catalyzed ethylene polymerization within low activity.

The organoboranes are well popular materials in applications of olefin polymerization, were triggered by Marks and Lamanna research groups (Siedle *et al.*, 1993 and Yang *et al.*, 1994). They independently discovered that the combination with group 4 metallocene alkyls, strongly Lewis acidic promoter such as tris(pentafluorophenyl) borane, $\text{B}(\text{C}_6\text{F}_5)_3$, trityl tetrakis(pentafluorophenyl)borate ($[\text{CPh}_3]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$), and *N,N*-dimethylaniline tetrakis(pentafluorophenyl)borate ($[\text{HNMe}_2\text{Ph}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$), provides highly effective co-catalysts for activating metallocene and relating metal alkyls for yielding highly efficient olefin polymerizations (Bochmann, 1996, 1997 and 1999). The synthesis of $\text{B}(\text{C}_6\text{F}_5)_3$ was first reported in 1964 by Massey and Park, (1964). This compound allows isolation of crystallographically characterizable cationic metallocene complexes. Other kinds of organoboranes, such the trityl cation (CPh_3^+) are powerful alkyls and hydride-abstracting or oxidizing reagents. Ammonium cation (HNMe_2Ph^+) can be ready to cleave metal-alkyl bond via facile protonolysis (Bochmann and Lancaster, 1994).

In application, organoboranes have a few advantages over the use of MAO that the borane and borate activators typically yield high productivity catalysts. Organoboranes are also non-pyrophoric materials and can substitute the use of excess MAO to achieve high catalytic activity. The required amount of organoborane in

polymerization processes is essentially stoichiometric activator/metallocene ratios (Kaminsky, 1996).

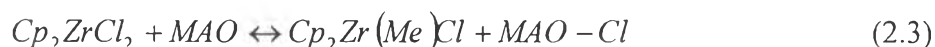
Over the past few years, many research groups have issued a number of new development of effective $B(C_6F_5)_3$ activators, including bifunctional boranes. In recent, Piers group synthesized bis(pentafluorophenyl) borane $[HB(C_6F_5)_2]_2$ by reduction of monomeric chloroborane with $Me_2Si(Cl)H$, which also serves as the solvent for the reaction, in a quantitative yield (Bochmann, 1997). Bochmann and Lancaster (1994) reported that $(Me_3SiCp)_2MMe_2 / [CPh_3]^+[B(C_6F_5)_4]^-$ ($M = Ti, Zr, Hf$) gave new cationic catalysts, the ethylene polymerization activity increased in the order $Ti < Hf < Zr$. The activity of the Zr complex was comparable to that of Cp_2ZrCl_2/MAO system. They also found that the activity increased with temperature, with corresponding to the decrease in polymer molecular weight. These results suggest that highly active cationic metallocene catalysts are closely connected with the nature of the cation-anion tight ion pairing. Exxon applied the metallocene/organoboranes type catalysts to a high pressure process to produce LLDPE. $Me_2Si(H_4-Ind)ZrMe_2 / [HNMe_2Ph]^+[B(C_6F_5)_4]^-$ and $Me_2Si(H_4-Ind)HfMe_2 / B(C_6F_5)_3$ catalyst systems had good heat stability when compared with MAO system, so that these catalysts showed higher activity than MAO systems at high temperatures. TOSOH studied the effect of metallocene structure on catalyst performance with $B(C_6F_5)_4$ activated catalysts and found that $Ph_2C(Cp)(Flu)ZrCl_2 / [HNMe_2Ph]^+[B(C_6F_5)_4]^- / Bu_3Al$ produced high molecular weight polyethylene with good activity (EXXON, 1993). For ethylene-1-butene copolymerization, high molecular weight VLDPE was synthesized with high activity at high temperatures. $Et(Ind)_2ZrCl_2 / [HNMe_2Ph]^+[B(C_6F_5)_4]^- / Bu_3Al$ produced ethylene-1-hexene copolymer with a higher MFR value (MFR = 60). This result is nearly the same as that Bujadoux received from the MAO-activated catalysts, which indicates that the metallocene structure mainly govern the catalyst performance for copolymerization in a high-pressure process (Togni and Halterman, 1998).

2.4 Activation of Metallocenes

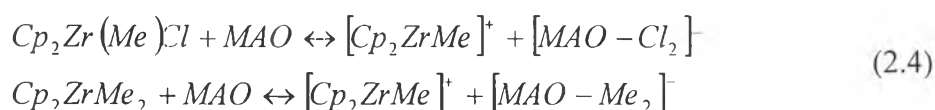
2.4.1 The Activation of Metallocenes with MAO

The function of MAO is a co-catalyst for Cp_2ZrX_2 ($Cp = C_5H_5$, $X = Me, Cl$) in metallocene-type olefin polymerization. The commonly accepted mechanism involves the metal atom losing its chloride ions. The active center is a zirconocene cation (Cp_2ZrMe^+), an intermediate which has been postulated for the last three decades. Evidence for this comes from the formation, isolation and ethylene polymerization ability of Cp_2ZrMe^+ complexes. The activation mechanism of the general system, Cp_2ZrCl_2/MAO , can be anticipated as follows (Kaminsky, 1994);

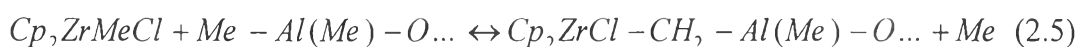
The first step is to alkylate the zirconocene metal fragments by ligand exchange. This reaction is very fast and takes place within seconds even at $-60^\circ C$:



Second, most importantly, MAO abstracts the second chloride to generate a formally cationic zirconocene moiety. Alternative use of a dialkylzirconocene, the MAO acts to abstract the alkide:



In this single site catalyst, nearly every zirconocene atom is active, forming the same active center. Some evolution of methane is taken place simultaneously with the mixing of metallocene and methylaluminoxane. This brings that formation of $Zr-CH_2-Al$ bonds as a side reaction which leads to seemingly inactive species.



Studies on zirconocene dichloride/MAO systems using an NMR and a combined IR/NMR or an X-ray structure of a neutral dimethylzirconocene/aluminoxane adduct $\{(\text{Cp}_2\text{ZrMe}(\text{m-OAlMe}_2))_2\}$ provided some evidences supporting these mechanisms (Harlan *et al.*, 1995). Aside from alkylating the metallocene dihalide, abstracting a chloride or alkide with the formation of a $[\text{Cp}_2\text{ZrMe}]^+$ cation also act as scavenger for impurities. The co-catalytic function of MAO is probably best described as establishing a stabilizing environment for the metallocene cation or cation-anoin pair in the form of a host-guest or “crown-aluminoxane” complex (Ystenes *et al.*, 2000). The formulation of metallocene cations as the active species is based on the work of Dyachkovskii and coworkers on the synthesis of isolable active cations for olefin polymerization (Togni and Halterman, 1998).

Furthermore, X-ray photoelectron spectroscopy studies on $\text{Cp}_2\text{ZrR}_2/\text{MAO}$ ($\text{R} = \text{Cl}, \text{Me}$) also suggested the formation of cationic species. While in the heterogeneous Ziegler-Natta systems, Ti(III) constitutes the active species, reduction of Cp_2ZrCl_2 with the formation of Zr(III) does occur with MAO but is negligible during the first few hours, according to an EPR-study (Ystenes *et al.*, 2000).

Although it is known very little about the structure of the active site, it is proposed that the Zr moiety is sandwiched between MAO chains as shown in Figure 2.7(A) (Albizzati and Galimberti, 1998). It has been explained that MAO acts as a Lewis base and coordinates to Zr through its oxygen atoms (Figure 27(B)) (Albizzati and Galimberti, 1998). The sandwich view of the active is supported by the large excess amount of MAO required for catalytic activity (Kaminsky, 1995). The polymerization rate is proportional to $[\text{Zr}][\text{Al}]^4$ and at low MAO concentrations the activity falls off rapidly because there is no longer enough MAO available to separate the Zr centers. It has been shown that with ^{14}CO radiolabeling and at Al/Zr ratios in excess of 1000, all the Zr molecules have active centers (Albizzati and Galimberti, 1998).

An understanding of chain transfer processes is important for polymer MW control. The chain length of polymer formed is determined by the relative rates of propagation (insertion) and chain termination (by chain transfer) (Kaminsky,

1994). Two major means of chain transfer to terminate the polymerization process are shown in Figure 2.8.

- (1) A dominant β -H elimination process, which is the main determinant of chain length.
- (2) A chain transfer to aluminum in MAO complex.

As the Zr concentration in the reaction increases, polymer MW decreases, that can be indicative of a bimolecular reduction in deactivation mechanism (Resconi *et al.*, 1990).

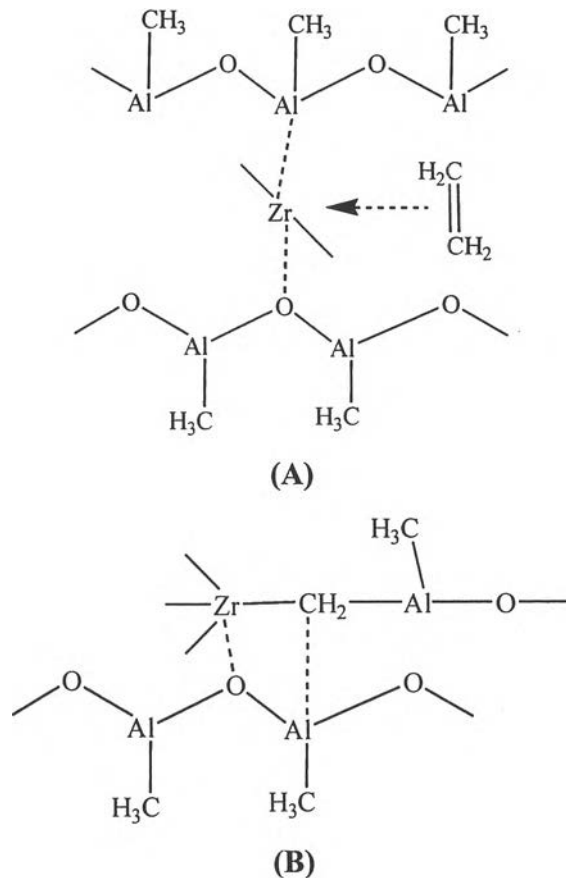


Figure 2.7 (A) The inserticn of ethylene monomer to active center, (B) The coordination between active Zr and O in MAO.

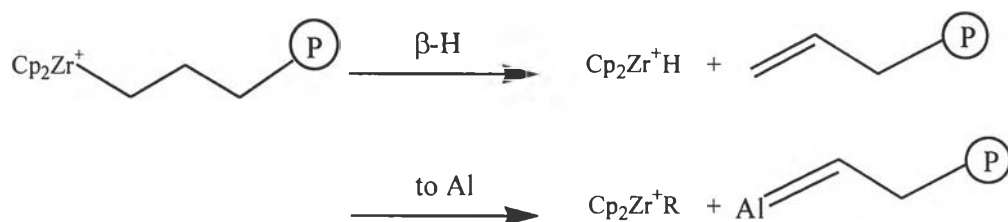


Figure 2.8 The models for chain transfer: β -H elimination process and chain transfer to aluminum in MAO.

The monomer will then attach itself to the metal ion with a specific orientation. This is the step that governs the polymer its stereospecificity. The monomer is held stereospecifically and then another monomer is inserted repeatedly resulting in growing polymer chain, which is also held by the metal atom. In theory, the metal atom has two hands; the first hand holds the chain that is being formed, and the second hand grabs the monomer. The second hand then passes the monomer to the first hand to be added to the chain. The chain grows out from the catalyst, meaning that the monomers are added from the inside of the catalyst (Giannetti *et al.*, 1985).

Very few investigations of cyclopentadienyl ring substituent effects on the polymerization mechanism and kinetics have been reported (Resconi *et al.*, 1990). The substituent effects on chain transfer and stereoregularity for Me₂Si-bridged Zr complexes have been studied (Kaminsky, 1994 and Togni and Halterman, 1998). Increasing the electron density at the metal increases the polymerization rate and the rate of chain transfer. This is illustrated by the methyl exchange reactions between Cp₂ZrMe₂ derivatives and different co-catalysts (Albizzati and Galimberti, 1998).

The type of aluminoxane has influenced the efficiency of the metallocene/ aluminoxane catalytic system (Wang *et al.*, 2000). Therefore, MAO is used as the important co-catalyst which is an effective activator for the group 4B metallocenes in homogeneous polymerization system. The use of MAO cocatalyst boots up the catalytic activity by tremendous orders of magnitude when compared with the active alkylaluminum cocatalysts. There are some other aluminoxanes

which are able to activate the metallocenes, such as ethylaluminumoxane (EAO) and isobutylaluminumoxane (iBAO). However, MAO is much more effective than those ethyl and isobutyl analogues and is most preferred in practice.

2.4.2 The Activation of Metallocenes with Organoborane

The concept of the generation of positive charge at the transition metal atoms as chain-propagating species has stimulated the development of rational routes to organoborane compounds. The reactions of metallocene dialkyls with electrophiles which generate very weakly coordinating anions have proved a particularly successful strategy for the generation of highly active, MAO-free polymerization catalysts (Figure 2.9).

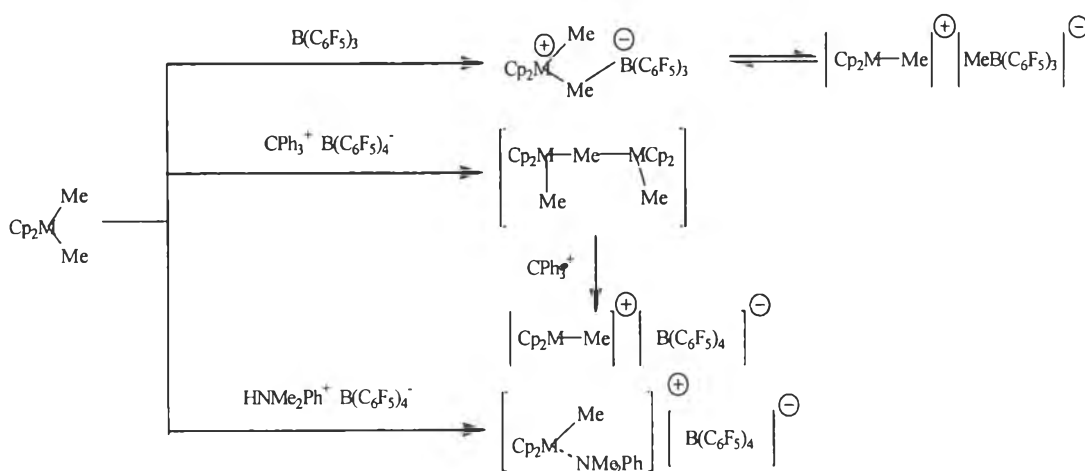


Figure 2.9 The activation of metallocene with borane compounds (Bochmann *et al.*, 1996).

Yang *et al.* (1994) employed $\text{B}(\text{C}_6\text{F}_5)_3$ with Cp_2MMe_2 to obtain a crystallographically characterizable, polymerization catalyst. Borane abstracts a methyl group from the metallocene to give in the solid state a weakly coordinated cation-anion pair with a non-linear $\text{Zr}(\mu\text{-Me})\text{B}$ bridge to give the side-product free reaction.

Direct synthesis of metallocenium ions (Cp_2MR^+) was triggered by Jordan (1991). In their early work Lewis base (tetrahydrofuran or acetonitrile) bound

precursors were used. The compounds exhibited only slight olefin polymerization activity. Other approaches to the generation of Cp_2MR^+ can be made both directly and quantitatively, provided that the counteranion is highly resistant to electrophilic attack in the reaction between Cp_2MMe_2 and $\text{B}(\text{C}_6\text{F}_5)_3$. $\text{B}(\text{C}_6\text{F}_5)_3$ is a strong Lewis acid leading to have the zwitterionic product which becomes catalytically active for ethylene polymerization. Likewise, Cp_2MMe_2 reacts with either $[\text{CPh}_3]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ or $[\text{HNMe}_2\text{Ph}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, to yield $[\text{Cp}_2\text{MR}]^+\text{B}(\text{C}_6\text{F}_5)_4^-$. The chemistry of the active species is dominated by its desire to stabilize itself by coordination to any available electron donor, such as the methyl group of the anion.

Chien *et al.* (1991) issued the reaction between $\text{Et}(\text{Ind})_2\text{ZrMe}_2$ and $[\text{CPh}_3]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ to create the dimethyl zirconocenium cation. The application of this reaction to catalyze polymerization was found to require a highly threshold amount of $\text{Et}(\text{Ind})_2\text{ZrMe}_2$, most of which is probably consumed to scavenge impurities. $\text{Et}(\text{Ind})_2\text{ZrMe}_2$ are unstable to storage and transfer. Therefore, the analogous dichloro zirconocene ($\text{Et}(\text{Ind})_2\text{ZrCl}_2$) is more efficient and convenient to be chosen as a ternary system comprised of $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{AlR}_3/[\text{CPh}_3]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ to generate the bare cation ($\text{Et}(\text{Ind})_2\text{ZrR}^+$). Yano *et al.* (2000) reported the similar work that studied ethylene polymerization and copolymerization with various hafnocene compounds in combination with $[\text{HNMe}_2\text{Ph}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ /TIBA as co-catalyst at high temperature. They found that the activity of hafnocene catalysts depended on the alkylaluminum compound. Beck and Brintzinger (1998) found that only one methyl group is transferred to a zirconocene dichloride even by a large excess of TMA, while the uptakes of two alkyl groups, followed by alkane evolution, are observed with TEA and TIBA.

Siedle *et al.* (1998) found that the NMR results showed the loss of methane from $(\text{Me}_5\text{Cp})_2\text{ZrMe}^+$ produced by protonolysis of $(\text{Me}_5\text{Cp})_2\text{ZrMe}_2$ by Et_3NH^+ and $(\text{C}_6\text{F}_5)_3\text{BOH}^-$. They also concluded that a metal-fluorine bridge bond such as that demonstrated here may significantly affect the chemistry of highly electrophilic cations which are associated with putatively noncoordinating anions such as $\text{B}(\text{C}_6\text{F}_5)_3^-$. This concept has exploited to design new borate co-catalysts according to previous works (Strauss, 1993 and Zhou *et al.*, 2001).

A comprehensive discussion in the formation of catalytic active species for aluminoxane-free system was delivered by Yang *et al.* (1994). They reported that the reaction of metallocene dimethyls with $B(C_6F_5)_3$ gave methyl-bridge zwitterionic complexes as the product of first reaction as shown in Figure 2.10. This route offers the advantage that the product is stabilized by methyl coordination and is less polar and significantly more soluble in toluene. Several such complexes have been characterized by X-ray diffraction. The $Zr-CH_3-B(C_6F_5)_3$ bridge is comparatively weak, with rather long $Zr-C H_3$ distance which depends on the steric requirements of the Cp ligands. Two of the methyl hydrogen groups are agostically bonded to zirconium creating a complex, which is indeed an active species for ethylene polymerization. Under catalytic conditions, this complex is partly dissociated to $[Cp_2ZrMe]^+[MeB(C_6F_5)_3]$. The activity of this active species depends on the bulkiness of the Cp's ligands, the results as shown elsewhere in the previous works (Jia *et al.*, 1997).

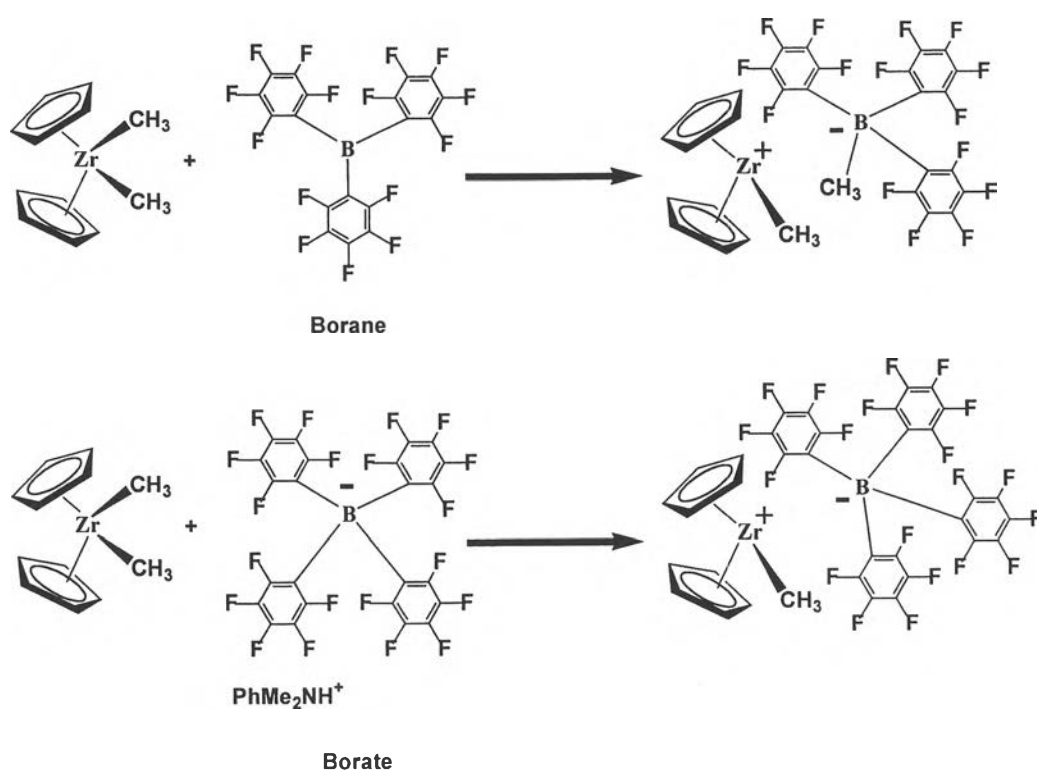


Figure 2.10 Activation of dimethyl zirconocene with borane compounds (Yang *et al.* 1994).

2.4.3 Comparison Catalytic Activations between MAO and Organoboranes

Although the activation processes of MAO and borane co-catalysts are quite similar, the characteristics of the polymers obtained with these systems process some differences. It is a wrong idea to think simply that they can be exchanged. The identity of the polymers obtained with the ionic zirconocenium-borate catalysts and with zirconocene/MAO systems is also taken as an indication that both co-catalysts have the same active form of the cationic $[\text{Cp}_2\text{ZrMe}]^+$ species.

Togni and Halterman (1998) reported that $\text{B}(\text{C}_6\text{F}_5)_3$ has much greater ability to abstract a methyl group from metallocene than MAO, while MAO has a high ability to stabilize the binuclear ionic species. A study by using UV/Visible spectroscopy showed that the coordinating ability increase in the order $\text{MAO} < [\text{MeB}(\text{C}_6\text{F}_5)_3]^- < [\text{B}(\text{C}_6\text{F}_5)_4]^- < [\text{B}(3,4\text{-(CF}_3)_2\text{C}_6\text{H}_3)_4]^-$, i.e. the lesser the coordinating ability, the higher the catalytic activity (Siedle *et al.*, 1998).

Togni and Halterman (1998) also disclosed the theoretical investigation on the formation of olefin separated ion pairs by density-function-theory calculation. From the reaction between metallocene precursors and a low molecular weight MAO model in the presence of ethylene, present the key intermediate of the polymerization mechanism. They found that a large size of the counterion does not represent a relevant feature of an efficient co-catalyst, justifying why quite small size anions like $\text{B}(\text{C}_6\text{F}_5)_3^-$ exhibit high co-catalytic activity (Massey and Park, 1964). High Lewis acidity of Al atoms present in MAO accounts for the extremely higher co-catalytic activity compared with other alkylaluminium compounds (Bochmann, 1999).

The activity of these organoboranes is comparable or even surpasses that of zirconocene/ MAO system, yet in the absence of a scavenging agent, the cationic catalysts is not very long lived. Polymerization times given are in the range of minutes. Thus, in applications of the borate-activated catalysts, higher amount of aluminum alkyls are favorable added to act as purifying agents and thereby achieve the high activity. Except trimethylaluminum is not suitable as a scavenger in this reaction, because of inactive heterodinuclear dimers which are formed in equilibrium with the monomeric cations. With TEA related heterodinuclear dimers form but dissociate more readily so that polymerization activities increase in the order $\text{Me} < \text{Et}$ (Chien *et al.*, 1994).

2.5 Catalysis of Olefin Polymerization

The elementary aspects of the catalytic processes basically involve with the initiation, propagation, and termination reactions. Several mechanistic refinements of α -olefin polymerization have been proposed. Prominent hypothesis includes (1) the trigger model, in which two monomers are coordinated to the metal as the complexes passes through the insertion transition states (Siedle *et al.*, 1998), and (2) various two-state models involving a fast propagating state and a slow propagating state for which the steady-state distribution of the catalyst between the two states depends on type of monomer (Liu *et al.*, 2001). Chain termination processes in 1-alkene polymerization play essentially a critical role in controlling polymer molecular weight and vary dramatically with the structure of the catalyst and the nature of the 1-alkene (Figure 2.11).

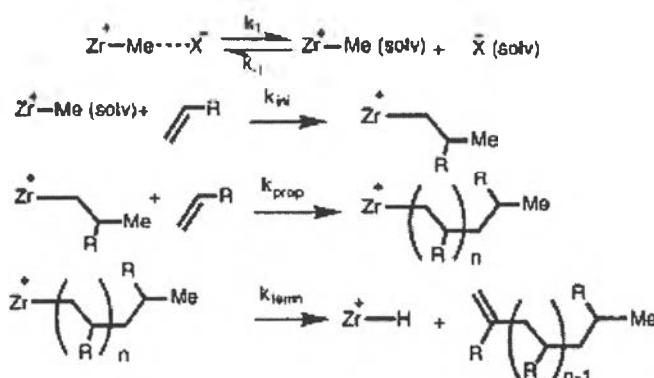


Figure 2.11 Olefin polymerization mechanism (Liu *et al.*, 2001).

The chain termination step involves with 1,2 insertion β -H transfer to yield a vinylidene end group, whereas a vinylene end group results from β -H transfer following a 2,1 insertion (or regioerror). The chain termination processes that depend on alkene concentration yield saturation-like behavior in terms of the increase of polymer molecular weight with increasing alkene concentration. Vinylidene end groups arise from unimolecular β -hydride elimination (β -H transfer to metal) after a

1,2 insertion, whereas vinylene end groups arise from bimolecular β -H elimination (chain transfer to monomer) following a 2,1 insertion of propene (Figure 2.12).

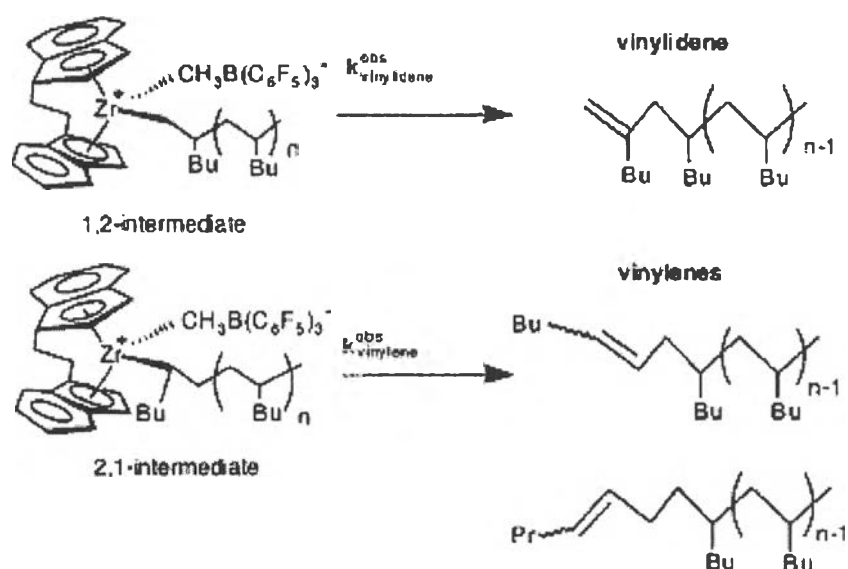
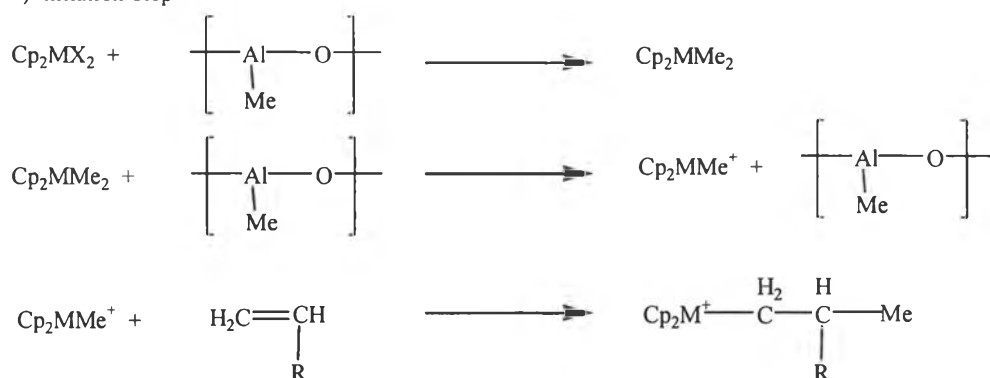


Figure 2.12 Chain transfer mechanisms (Liu *et al.*, 2001).

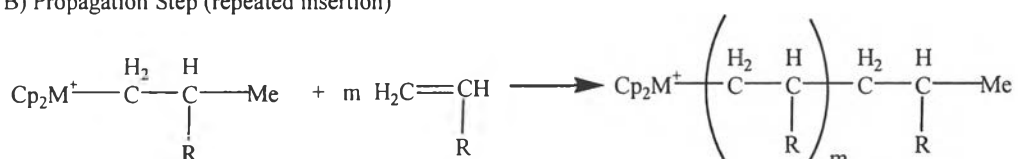
According to alternative mechanism proposed by Cossee and Arlman in 1964 (Figure 2.13), the chain propagation cycle starts with a vacant coordination site and the coordination of an olefin to this vacant coordination site at the metal. Olefin coordination is followed by the insertion of the olefin π bond into the metal-carbon σ bond of the growing polymer chain. Stereo- and region- control of vinyl olefin polymerization is thought to occur at this stage. Chain termination can occur through a number of pathways. The growing polymer chain can transfer a β -hydrogen to the metal, generating an olefin terminated polymer, and a metal hydride complex. The metal hydride complex can undergo olefin insertion, initiating growth of a new polymer chain. The polymer chain can transfer a β -hydrogen to an incoming monomer, again generating an olefin terminated polymer and a metal alkyl, which can initiate chain growth. The polymer chain can be transferred to the counteranion, generating a polymer “capped” by an organometallic functional group and a new cationic metal alkyl, which can initial chain growth. Chain growth can also be

stopped by the generation of catalytically inactive or dormant species or inactive sites. These inactive sites can be reactive by the addition of hydrogen and, in the case of propylene polymerization, by the addition of ethylene (Ewen and Elder, 1993).

A) Initiation Step



B) Propagation Step (repeated insertion)



C) Chain Transfer Step (β -hydrogen transfer)



~~~~~ = polymer chain

**Figure 2.13** Polymerization mechanism for metallocene catalysts (Kaminsky, 1994).

### 2.5.1 Ethylene Polymerization

In comparison to high-density polyethylene (HDPE) produced from classical Ziegler-Natta catalysts, the metallocene catalysts can produce the HDPE with low polydispersity and total absence of branching, which in turn leads to a different rheological behavior (Malhotra *et al.*, 1997). Many research works often use ethylene polymerization as the basic model to determine the influence of catalyst concentration, co-catalyst characteristics and other aluminum alkyls, Al:Zr ratio,

temperature, steric effects etc, on the catalyst activity and the polymer parameters such molecular weight and molecular weight distribution (Cam and Giannini, 1992). In solution process of ethylene polymerization, the C-C bond forming reaction is truly homogeneous only at the very beginning. With the precipitation of polyethylene, the active complex becomes more and more embedded in the swollen, gel like polymer matrix, which represents a transfer to the heterogeneous phase (Moscardi *et al.*, 1999). This heterogeneous active complex formed leads to a diffusion-controlled reaction. The reaction rate is then controlled by the rate of diffusion of the monomer through the polymer matrix to the enclosed active center and can no longer be compared in other terms. In such a diffusion controlled polymerization, the activities of different catalysts may then appear very similar, although in reality they are not (Weickert *et al.*, 1999).

Some conclusive reviews in terms of the activity of ethylene polymerization were reported by Kaminsky and Hartmann (2000). Generally the  $\text{Cp}_2\text{ZrCl}_2$  catalyst can obtain up to 40,000,000 g PE/g Zr x h of ethylene polymerization. With different transition metals in metallocene catalysts, zirconium catalyst is more active than hafnium or titanium systems, especially, titanium complex is easily decomposed at high temperatures ( $> 50^\circ\text{C}$ ). These transition metal compounds containing some halogen show a higher activity than the systems being totally free of halogen. Besides, methylaluminoxane (MAO) is much more effective than ethylaluminoxane (EAO) or isobutylaluminoxane (IBAO). The high amount of MAO is required to maintain a very long life activity that is possibly up to 100 h of polymerization time (Kaminsky, 1994). Moreover, average molecular weight (MW) of polyethylene from metallocene catalysis can be controlled by the metallocene type and concentration, the reaction temperature or by addition of hydrogen through the hydrogenolysis reaction (Kim *et al.*, 1998 and 1999 and Cho *et al.*, 2000).

## 2.6 From Homogeneous to Heterogeneous Processes

Since the discovery of metallocene catalysts, the attractiveness of the titanocene,  $\text{Cp}_2\text{TiCl}_2\text{-AlR}_2\text{Cl}$  catalyst lay in its solubility, unlike the commercial heterogeneous Ziegler-Natta systems (Reddy and Sivaram, 1995). In comparison



with the conventional catalysts, metallocene catalysts provide higher versatility and flexibility both for the synthesis and the control of the structures of polyolefins. These were devoted for homogeneous catalysis, which are able to polymerize several olefins with high activities to yield high molecular weight polymers and copolymers. In addition, they can also produce polymer with a narrow molecular weight distribution ( $\sim 2$ ) and homogeneous chemical composition. Despite their numerous advantages, several technical problems still need to be solved before metallocene catalysts can be used widely in industry. The first main problem is the difficulty in controlling polymer morphology with soluble homogeneous catalysts and consequently their inability to be used in slurry and gas-phase processes, because they can obtain a high molecular weight of polymers. In addition, very large amount of MAO needed to achieve maximum metallocene catalytic activity is the second problem in high operating costs.

Moreover the activity of some homogeneous metallocene catalysts suffered a significant loss in during the polymerization reaction. The supported system can make them more stable. The homogenous metallocenes give polymers with narrow molecular weight distribution and consequently with a poor processability. The supported systems have the capability of producing polymers having a desired broad or bimodal MWD for good rheological and physical properties (Ribeiro *et al.*, 1997; Ciardelli *et al.*, 1998 and Chien, 1999).

In order to avoid using a high amount of MAO required, one method has been dramatically developed involving the generation of cationic metallocene complexes with the aid of noncoordinating anions (e.g. organoboranes). However this approach does not allow for any control of polymer morphology. Another possibility involves the immobilization of metallocene compounds on a support, as already commercially performed in Ziegler-Natta catalysis (Ribeiro *et al.*, 1997). For this route, the concept is to find a way to attach the metallocene to an appropriate support without losing the catalytic performance of homogeneous metallocene, such as polymerization activity, stereochemical control, ability to produce copolymers with statistical comonomer distribution etc. The heterogeneous metallocene systems also provide the good controlled morphology of polymer with a high bulk density which is good to skip the pelletization process. The development of supported metallocenes is

eligible to use them in any existing industrial gas and slurry- phase polymerization processes which do not have reactor-fouling problems (Chien, 1999).

At the earlier attempts, the inherently low activity of the  $\text{Cp}_2\text{TiCl}_2$  catalyst was adapted by supporting it on silica gel to polymerize ethylene with ethylaluminum compound as co-catalyst (Ribeiro *et al.*, 1997). This work was exploited without further incentive features rather than conventional Ziegler-Natta catalysts. Another research study was reported that the  $\text{Cp}_2\text{TiCl}_2$  catalyst was not inhibited by adsorbents (Ribeiro *et al.*, 1997). A carbon black was used to be a support for the catalyst and then presented the mirror-like the surface area of the carbon black in ethylene polymerization (Huang and Rempel, 1995).  $\text{Cp}_2\text{TiCl}_2$  was supported on 1,2-polybutadiene allowing to react with TIBA, formed a heterogeneous metallocene for ethylene polymerization, and yielded 240 g/g Ti x h (Reddy and Sivaram, 1995). Chien (1999) prepared  $\text{Cp}_2\text{ZrMe}_2$  and  $\text{CpTiMe}_3$  on  $\text{Mg}(\text{OH})\text{Cl}$  to form supported complexes catalysts for propylene polymerization, albeit with quite low activities.

Silica supported  $\text{Cp}_2\text{TiCl}_2$  catalyst with alkylaluminum gave different polyethylene products depending on the preparation procedure. When the alkylaluminum is contacted with silica prior to reacting with  $\text{Cp}_2\text{TiCl}_2$ , the polyethylene formed has a higher molecular weight and broader molecular weight distribution ( $M_w/M_n$ ) than that produced from the homogeneous catalyst. Supporting  $\text{Cp}_2\text{TiCl}_2$  on silica and reacting with alkylaluminum gives polyethylene with a bimodal distribution, one component of which has a molecular weight similar to that produced from the soluble catalyst (Zechlin *et al.*, 2000).

## 2.7 Development of Heterogeneous Metallocene Catalysts

For the supported metallocenes, several attempts have been devoted to the transformation of soluble metallocene complexes into heterogeneous catalysts by supporting them on inorganic or organic carriers. Inorganic oxide finely divided polymers, or other high surface area materials have been generally used as supports. The common inorganic supports for metallocene catalysts are silica ( $\text{SiO}_2$ ) (Zechlin *et al.*, 2000), alumina ( $\text{Al}_2\text{O}_3$ ) (Ribeiro *et al.*, 1997), magnesium chloride ( $\text{MgCl}_2$ )

(Ferreira *et al.*, 1998), and other materials such as zeolites, MgO, MgF<sub>2</sub>, CaF<sub>2</sub>, AlF<sub>3</sub>, etc. (Michelotti *et al.*, 1998), however, these support materials are not yet commercialized. The less common materials were used as support such as cyclodextrin, polystyrene, polysiloxane derivatives (Barrett and de Miguel, 1998). Silica is one of the most frequently used carriers, since it leads to good morphological features for polymer particles. The nature of the supports and the techniques used for supporting the metallocenes have crucial influences on the resulting catalytic behavior. Surface modification of the supports can also be carried out to improve the catalysts' performances (Laukkanen *et al.*, 2001). This may include reactions of the supports with organometallic compounds such as magnesium and aluminum alkyls (Lee *et al.*, 1999 and Köppl *et al.*, 2001).

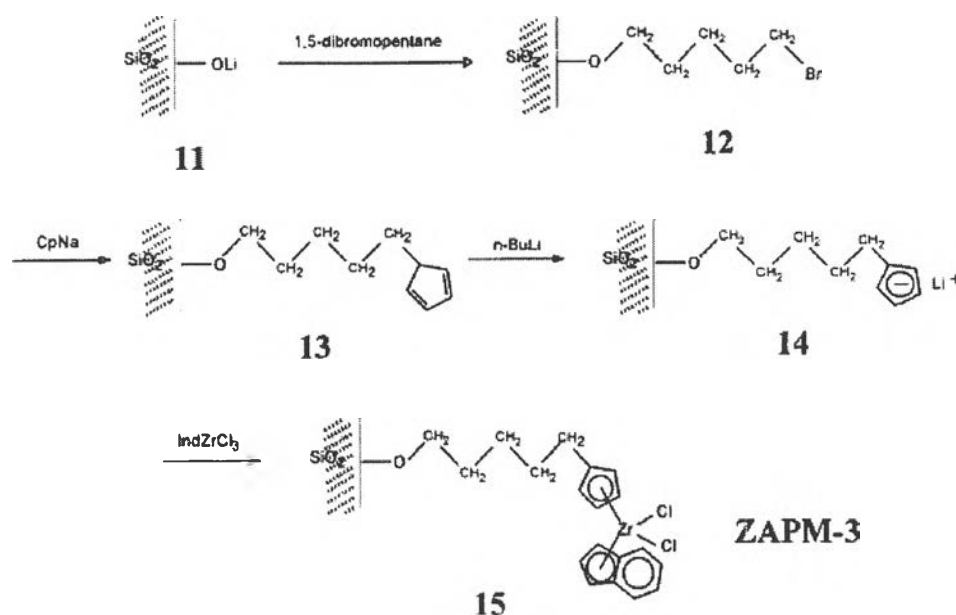
From the previous works, the main preparatory routes for supported metallocenes can be classified according to three main methodologies as follows (Ribeiro *et al.*, 1997):

**Method 1.** The first method involves direct impregnation of metallocene on a support with or without pretreatment for surface modification. It can be either (a) with mild impregnation conditions or (b) at high temperatures and long impregnation times. Generally, the dry support is reacted first with the metallocene compound in a solvent such as toluene. The solid part is then recovered by filtration and washed with a hydrocarbon solvent. The mixing temperature and the contact time are important parameters since they influence both the catalytic performances and the final properties of the polymer produced.

**Method 2.** The second method involves immobilization of MAO on the support followed by reaction with the metallocene compound. A modified version of this method involves the replacement of MAO by an aluminum alkyl. The preparation was carried out by reacting pretreated silica with a small amount of MAO under mild conditions, room temperature and 30 min. After filtration and washing with toluene, the MAO-modified SiO<sub>2</sub> support is then mixed with the metallocene and treated as described in method 1. The supported metallocene obtained can be activated by MAO and common alkylaluminums.

**Method 3.** The third method involves the synthesis of catalysts where metallocene ligands are chemically bonded to the support such as modified silica. Typical preparation for this way deals with four steps:

*Step 1* is the modification of the silica surface by addition of compounds such as  $\text{SiCl}_4$ ,  $\text{C}_2\text{H}_2\text{Br}_4$ ,  $\text{SOCl}_2$ ,  $\text{MeSiCl}_2$  or 1,5-dibromopentane. Basically the procedure is with the reaction in toluene in a reflux unit for 48 h. For example, silica is modified by 1,5-dibromopentane as shown in Figure 2.14.



**Figure 2.14** The model for modification of silica support to form a supported-metallocene catalyst (Lee *et al.*, 1999).

*Step 2* is the modification of  $\text{SiO}_2$  with immobilizing the lithium salt of the aryl derivatives such as indenyllithium, cyclopentadienyllithium, fluorenyllithium, etc. This step is generally achieved in tetrahydrofuran (THF) at a relatively low temperature.

*Step 3* is the treatment of the resulting aryl-grafted silica gel with a solution of butyllithium in hexane at room temperature to form new aryllithium derivatives.

*Step 4* is the reaction of the latter system with zirconium, titanium, or neodymium halides to yield supported metallocenes.

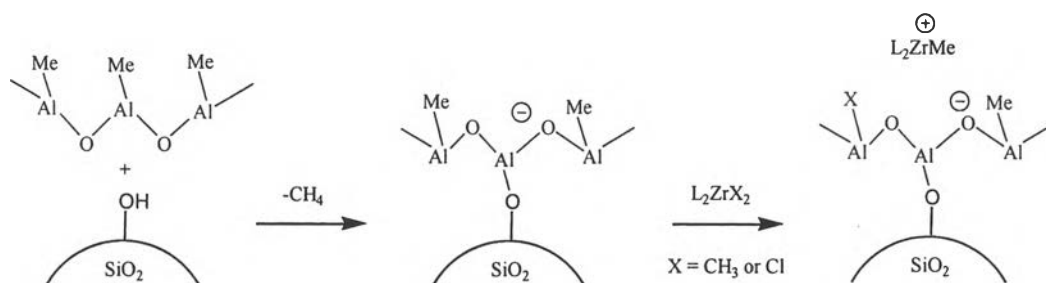
### 2.7.1 Supported MAO

From the previous categorized supported metallocenes, several works have been developed to find out an effective catalyst for producing olefin polymerization (Ribeiro *et al.*, 1997 and Chien, 1999). Due to the complicated preparations of method 3 and low efficiency of the catalyst produced by method 1, the second method has been focused for enormous movement in research and development for industrial application. The supported metallocenes developed from method 2 can provide the catalytic activity as well as those obtained from homogeneous systems and also yield the produced polymers with essentially the similar properties to those produced from the typically heterogeneous system.

Single-site catalysts activated by aluminoxane, in particular MAO, and supported on inorganic oxides form the vast majority of heterogeneous single-site catalysts for olefin polymerization. Most preparations using silica or alumina supports involve thermal or chemical pretreatment to remove residual water or hydroxyl groups which can deactivate the metallocene active sites (Chien, 1999 and Laukkanen *et al.*, 2001). This approach usually involves initial adsorption of MAO on an inorganic support with subsequent addition of the metallocene catalyst precursor in a second step, and finally followed by extensive washing with hydrocarbon solvents to ensure removal of all nonchemisorbed chemical molecules. The washed catalysts can be then used in the polymerization step, with or without additional MAO or other common aluminum alkyls introduced if necessary for achieving good activity (Figure 2.15) (Ribeiro *et al.*, 1997; Köppl *et al.*, 2001 and Liu *et al.*, 1999).

The behavior of this supported metallocene has been rationalized with the hypothesis that because the silica surface is essentially coated with MAO molecules, the weak ion pairs may be able to float over the surface much like in solution, leading to a similarity between this type of system and the catalyst in homogeneous system. However, the difference in MAO equivalents required, may be attributed to the fact that immobilization of the zirconocenium species may partially or completely inhibit bimolecular deactivation processes (Beck *et al.*, 1998). The supported MAO activator can also be prepared by in-situ hydrolysis of  $\text{AlMe}_3$  with hydrated silicas (Köppl *et al.*, 2001). There are other supported MAO systems

described in the literatures, such as MAO-zeolite, MAO-MCM-41 (mesoporous silica) (Rahiala *et al.*, 1999).



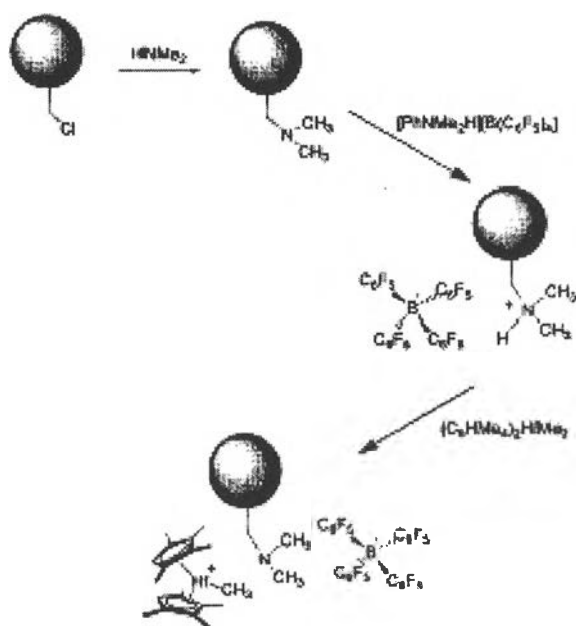
**Figure 2.15** The mechanism of supported-MAO preparation (Köppl *et al.*, 2001).

### 2.7.2 Supported “MAO-free” Borane and Borate

Borane,  $B(C_6F_5)_3$ , was first introduced to apply on the surface silanols groups of pure silica gel as strong Lewis base (Bochmann and Lancaster, 1992a and 1992b and Karl *et al.*, 1997). In the presence of tertiary amines, it can yield discrete and weakly coordinating anionic sites on the silica surface ( $-Si-O-[B(C_6F_5)_3]^- [HNMe_2Ph]^+$ ), with an associated ammonium counterion (Bochmann, 1996). The ammonium salts of these “silica-bound anions” are reported to behave much like  $[HNMe_2Ph]^+[B(C_6F_5)_4]^-$  in olefin polymerization. They can react with a variety of metallocene alkyls such as  $Cp_2ZrMe_2$  to produce cationic species weakly coordinated to the anionic silica surface. In the absence of tertiary amines in the preparation, the attachment of  $B(C_6F_5)_3$  to surface hydroxyl groups appears to be reversible under the same conditions. This results in the preferential formation of the toluene-soluble species,  $Cp_2ZrMe^+MeB(C_6F_5)_3^-$ , which is subject to leaching by washing with toluene during the synthesis. It results in significant polymerization activity loss. Siedle *et al.* (1998) demonstrated the model reactions for supported  $XB(C_6F_5)_3^-$  anions with using the reaction of  $B(C_6F_5)_3$  with water, alcohols, thiols, and polyols for preparation of adducts. Ward and Carnahan (1999) reported an alternative route to prepare silica-bound anionic  $B(C_6F_5)_3^-$  by reacting partially hydroxylated silica with  $BuLi$  followed by reaction with  $B(C_6F_5)_3$  and metathesis with  $Ph_3CCl$ .

Tian *et al.* (1999) studied the development of supported borane catalysts by treating  $B(C_6F_5)_3$ ,  $HB(C_6F_5)_2$ , and  $ClB(C_6F_5)_2$  on silica and alumina supports. They believed that the silanol group on the supports adducts a borane leading to surface-bound, silanol-borane that activates dialkylzirconocene complexes for ethylene polymerization in low MAO using. They found that the treatment of the supports with borane gave the improvement of catalytic productivity, especially for alumina support.

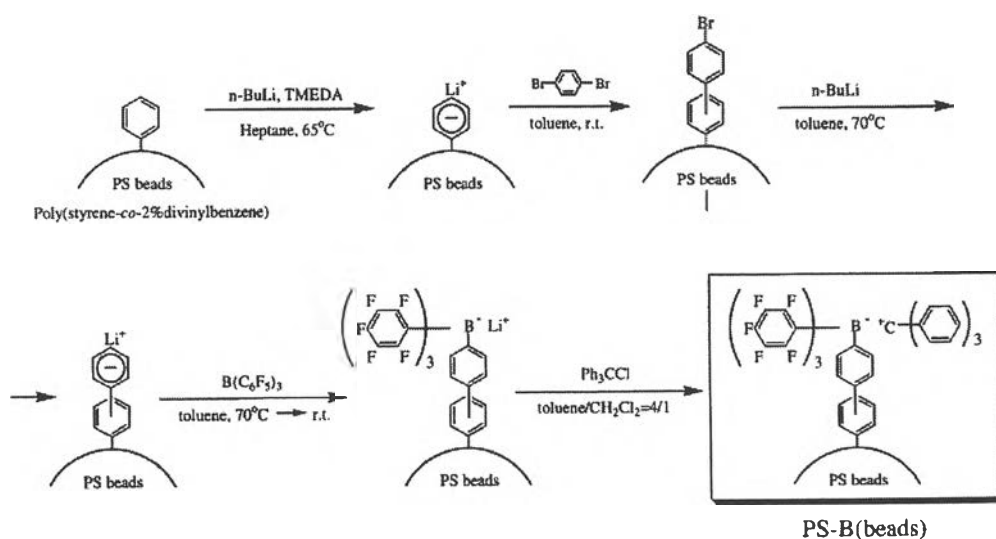
For supported borate anions, Hlatky and Upton (1996a and 1996b) reported that by reacting the activator  $[HNMe_2Ph]^+[B(C_6F_5)_4]^-$  with TEA pretreated silica in  $CH_2Cl_2$  or warm toluene, the activator can be evenly dispersed on the silica surface. The precatalyst  $Cp_2HfMe_2$  can then be activated by this supported reagent prepared by slurring in pentane. Roscoe *et al.* (1998 and 2000) presented the alternative preparation method of supported borate,  $[HNMe_2Ph]^+[B(C_6F_5)_4]^-$ , onto lightly cross-linked polystyrene (PS) resin beads (Figure 2.16).



**Figure 2.16** Sequential functionalization of chloromethylated cross-linked polystyrene (PS) resin beads with a secondary amine,  $[HNMe_2Ph][B(C_6F_5)_4]$  and a dimethylmetallocene (Roscoe *et al.* 1998 and 2000).

These supported-borate catalysts were designed to aim at functionalizing the interior of a swellable but insoluble polymer particle, which allowed a nominally heterogeneous polymerization to proceed in a microscopically homogeneous “solution-like” environment. They were not only to yield supported catalysts unusually active at low temperatures but also to generate polyethylene-co-hexene in the form of discrete, free-flowing, and millimeter-sized spheres that grow in proportion to the polymerization time.

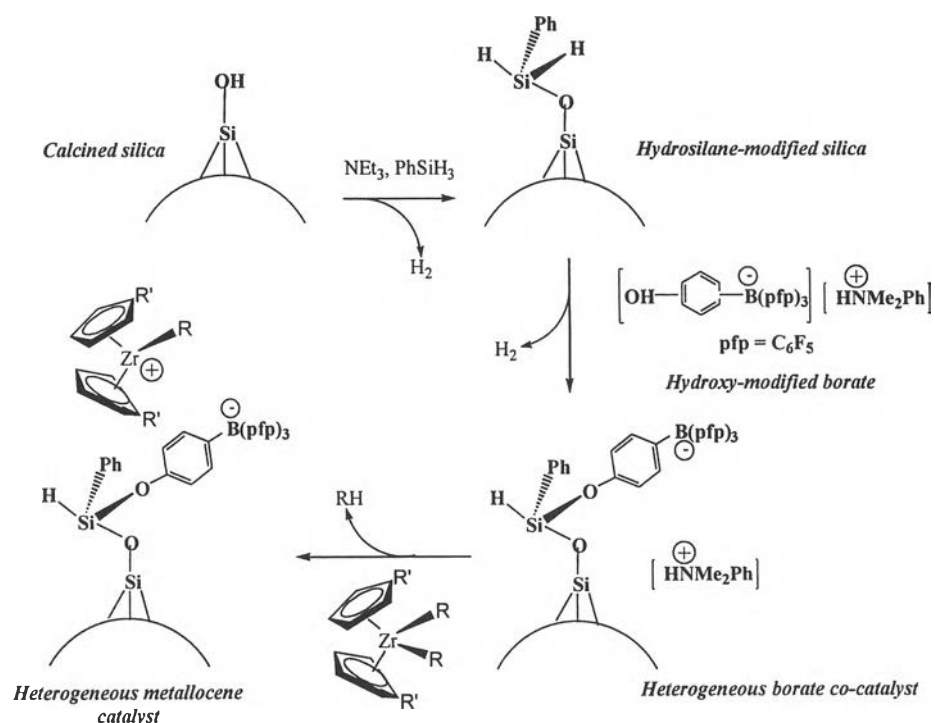
Another work to prepare polymer supported borate co-catalysts using poly(styrene-co-4-bromostyrene) (PS-B) and poly(styrene-co-2%-divinylbenzene) (PS-B beads) as the carrier was reported by Kishi *et al.* (2000). The preparation involved with the lithiation of  $n\text{-BuLi}$  on the polymer supports, the replacement of Li with  $\text{B}(\text{C}_6\text{F}_5)_3$  and followed by the reaction of  $\text{PS-B}(\text{C}_6\text{F}_5)_3$  and  $\text{Ph}_3\text{CCl}$  (Figure 2.17). The polymer supported borate catalysts were prepared by grafting the co-catalysts with *rac*- $\text{Et}[\text{Ind}]_2\text{ZrCl}_2/\text{TIBA}$  and employed for ethylene and propylene polymerizations combined with TIBA. In case of PS-B, the resulting insoluble catalysts showed very high activity for ethylene polymerization, but were not so active for propylene polymerization. The insoluble catalyst with PS-B (beads) presented low activity for both polymerizations, however, the obtained polyethylene particles replicated the sphere shape of the carrier.



**Figure 2.17** The model for synthesis of polymer supported borate co-catalyst.



Carney and coworkers developed the heterogeneous borate catalysts involved the modification of the silica surface by replacing isolated hydroxyl groups with reactive hydrosilanes (Carney and Shih, 1998). This surface modified silica was then reacted with a weak acid such as an alcohol by tethering with alkoxy-silanes borate ( $[\text{OH-Ph-B}(\text{C}_6\text{F}_5)_3][\text{HNMe}_2\text{Ph}]^+$ ). The supported product was ready to activate dialkyl-metallocenes, and dichloro-metallocene when combined with an alkylaluminum and followed by the addition of anilinium borate (Figure 2.18). This catalyst system produced polyethylene with high molecular weight, narrow molecular weight distribution and high bulk density.



**Figure 2.18** The model for synthesis modified-silica supported borate co-catalyst.

## 2.8 Surface Chemistry of Silica Support

### 2.8.1 Silica Support

The important factors influencing the immobilization of the metallocene catalysts and the fragmentation of the support during polymerization are pore size,

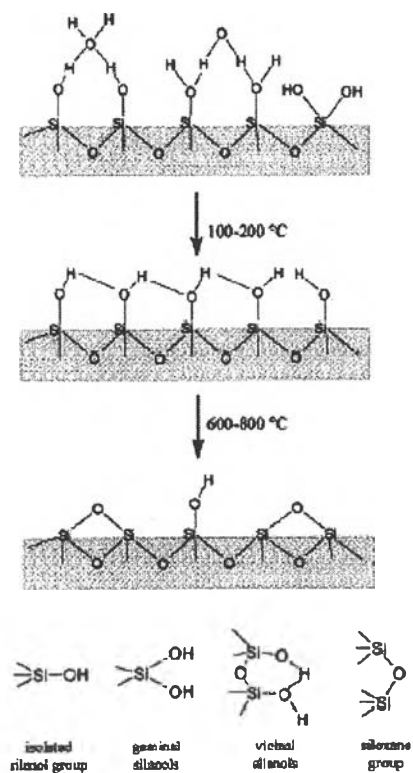
specific surface area, and chemical composition of silica support surface. The porous silica gels are prepared by neutralization of aqueous alkali metal silicate with acid (Fink *et al.*, 2000). The chemical reaction and its conditions can control pore structure and pore size distribution. The pore size distribution is essentially very narrow which ranges from 1 to 20 nm. The pores can therefore be classified as micro- and mesopores. The surface of pure silica is covered with silanol groups (OH), which is controlled by the thermal and chemical treatment during its preparation (Zechlin *et al.*, 2000).

The composition of silanol groups on the inner and outer surface of the silica gels was well analyzed by infrared spectroscopy and titration (Collins *et al.*, 1992 and Fink *et al.*, 2000). The silanol group on silica surface has a maximum concentration of 8 Brønsted acid OH groups per nm<sup>2</sup>. They are mostly found as germinal or isolated pairs and are neither very acidic nor very basic (pK<sub>a</sub> ~ 6). The hydroxylated surface is hydrophilic and easily adsorbs moisture from the air. This physically adsorbed water can be desorbed by raising the temperature to 100-200 °C. In the course of this heating a partial dehydroxylation of the silica gel takes place, reducing the number of OH group per nm<sup>2</sup> to approximately 5.5 (approximately 5 wt % silanol groups attached to 300 m<sup>2</sup>/g silica). One-half of these OH groups are germinal pairs and the other half are vicinal ones. The number of hydroxyl groups decreases continuously as the temperature is raised, until at a temperature of 600-800 °C, almost completely dehydroxylated silica with approximately 1 OH group per nm<sup>2</sup> is left. From this silanol concentration onward the surface is hydrophobic (Figure 2.19) (Fink *et al.*, 2000).

### 2.8.2 Silica for Supporting Metallocene

Porous silica gels used as supporting material for metallocene catalysts are applied in two particle patterns with different diameters. They are either irregularly formed granulates or spherical particles. The edged granulates result from grinding the filter cake which is obtained during the drying process of the silica gel production (Collins *et al.*, 1992). It is possible to obtain the desired particle size using conventional methods such as air separation or sieving processes. However, to obtain higher powder densities of these materials they are predominantly employed

as spherical particles. The granules are obtained by applying a spray-drying method or by emulsification of a silica sol in an immiscible nonpolar liquid (Fink *et al.*, 2000).



**Figure 2.19** The model for the dehydration of silica gel surface.

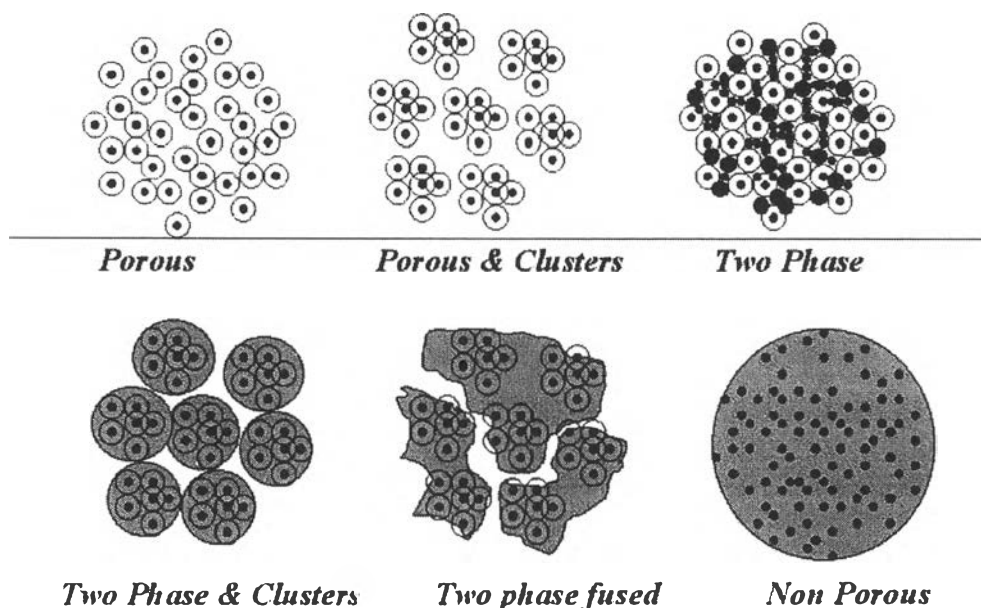
The shape of silica support is essentially able to control the morphology of the polymer particles (Ferreira *et al.*, 1998). Detailed transmission and scanning electron microscopic studies of shortly polymerized  $\text{SiO}_2$ -supported metallocene catalysts facilitated the time-resolved representation of the morphology of the various polymerization stages from the start of the reaction until the maximum activity was reached. The morphology control of the polymer is not only caused by the support, but also by its fragmentation and the resulting distribution of catalyst and co-catalyst on the support during polymerization. This was clarified by analyzing a catalytic system, the active centers of which are exclusively on the surface and the volume of which is completely free of catalysts. For this reason, the polymerization

can only take place on the outside and even after long polymerization times the support remains unfragmented and covered by the polymer. The obtained polymer morphologies are not uniform and depend on the form of the employed silica gel (Ribeiro *et al.*, 1997).

The morphology of the polymer particles may be very complex and it is one of the most important research tasks today (Liu *et al.*, 1999). At low polymerization rates, a dense polymer skin is formed around relatively large clusters, each of them consisting of a large number of microparticles. Increasing the polymerization rate by working at higher temperatures, the skin becomes thinner and it disappears completely at high polymerization rates leading to a very open macroporous structure accompanied by a fast decrease of the polymer powder bulk density. The internal structure of the polymer particle consists of interconnected pores. The morphology becomes even more complex in multi-stage processes when the physical properties differ from reactor to reactor (see Figure 2.20). Catalyst fragmentation in the very early stage of polymerization predefines the final polymer structure. This seems to be true for one-stage polymerizations without dramatic changes of the physical properties of the polymer produced over the course of polymerization. In a certain range of particle size, often nearly perfect replication of the microstructure can be expected, although integral porosity can change with increasing particle size (Weickert *et al.*, 1999).

Catalyst fragmentation depends mainly on two factors: hydraulic pressure generated by the polymer produced and rigidity of the support. If the pores of a rigid support, such silica which are too small, critical below 20 nm for silica, the pores are filled with polymer within a very short time limiting the monomer mass transfer to break the support. In comparison,  $\text{MgCl}_2$  with pores of 4 nm can be fragmented easily. Moreover, the skin around polymer particles seems to depend on the potential hydraulic pressure of the polymer flux, which is governed by the polymerization rate, and the mechanical stability of the polymer skin. A fast increase of the hydraulic pressure corresponds to a high initial polymerization rate leading to a large number of fragments whereas a low initial polymerization rate corresponds to a small number of fragments. Therefore, the accessibility of active sites, their initial activity and the monomer mass transfer must be major factors determining the

fragmentation behavior of the catalyst and the final powder morphology (Satyanarayana and Sivaram, 1993).



**Figure 2.20** The growth of polymer particle (Weickert *et al.*, 1999).

For the investigation of silica surface, Marks' group studied the relationship between the surface organometallic chemistry and catalytic properties of adsorbed actinide/ group 4 hydrocarbyls. The results obtained from CP-MAS-NMR spectroscopy showed that alkyl anion abstraction constitutes a major adsorptive pathway on dehydroxylated Lewis acidic supports. The formed cationic species are highly active heterogeneous catalysts for olefin hydrogenation and ethylene polymerization. The catalytic behavior is a strong function of the nature of the charge-compensating support material and likely the local surface topology. On hydroxylated supports,  $\mu$ -oxo adsorbate species are formed which are catalytically inactive (Dahmen *et al.*, 1988).

Jezequel *et al.* (2000) used partially hydroxylated silica-alumina, alumina, and niobia, which have high Lewis acidity, to generate the zirconium cation. For comparison, they concluded that the silica support has no Lewis acidity and which presumably has no ability to extract the alkyl or the halide from the

coordination sphere of zirconium, at least by Lewis acidity. However, the addition of noncoordinating anion ( $B(C_6F_5)_3$ ) or MAO into this supported zirconocene can separate the cation from the anion to generate the active catalytic species for ethylene polymerization (Karl *et al.*, 1997). In comparison, a higher activity was found with MAO than with  $B(C_6F_5)_3$ . In particular case of the complex supported on alumina, the similar activities for both co-catalysts were found.

## 2.9 Comparisons between Homogeneous and Supported Metallocene Catalysts

From a commercial standpoint, it is most desirable that the polymers produced from supported metallocene catalysts resemble as closely as possible the characteristics of their solution-soluble counterparts, sharing narrow molecular weight distribution, random distribution of comonomers and in the case of stereospecific polymerization, high stereoregularity and melting-point.

In commercial polymer production, there are no differences in the nature of the polymer produced. Isospecific  $\alpha$ -olefin polymerization catalysts produce polypropylene with the same isotacticity whether supported or in solution, but the effect is dependent on the method of catalyst preparation. Supporting the metallocene in a first step without treatment with MAO or TMA can lead to the formation of secondary species which may broaden the molecular weight distribution or even lead to completely different products. The activities of supported metallocene catalysts are usually 10 – 60 % lower than those of their homogenous counterparts (Akimoto, 1995). Although studies are few, this may be due to deactivation of catalyst sites when contacted with the support or caused by inefficient generation of the active cationic species. It is not a general phenomenon, however, and there are cases in which supporting a metallocene has a positive effect on its activity. For example, in solution the complex  $[(C_5Me_5)CrMe(THF)_2][BPh_4]$  is only feebly active in ethylene polymerization, even in the presence of isobutylaluminum. Supporting this complex on silica leads to an almost 100-fold increase in the activity (Fink *et al.*, 2000).

An advantage of supported metallocene/aluminoxane catalysts is that the Al:M ratio, which must be 1,000 or higher for effective performance in homogeneous polymerization. The ratio can be reduced to less than 100 without

serious effect. It has been hypothesized that large excesses of alumoxane are needed to suppress bimolecular deactivation of the catalyst while the supported catalysts largely removes this pathway (Chien, 1999). Because they are less susceptible to deactivation by adventitious impurities, supported metallocene catalysts show much greater long-term stability, an important consideration when catalyst batches might be stored for several months in a plant. For example, a soluble  $\text{Me}_2\text{Si}(\text{C}_9\text{H}_{10})_2\text{ZrMe}_2/[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$  catalyst is virtually inactive after 24 h whereas the heterogenized counterpart retains a considerable portion of its original activity even after several weeks.

## 2.10 Industrial Exploitation of Metallocene Catalysts

Metallocene catalysts have been used to produce polyolefins commercially since 1991. The commercial interest centers on their use in making polyethylene and polypropylene. Polyethylene is the world's largest volume bulk plastic with annual consumption approaching 35 Mt. Polypropylene is the third ranked bulk plastic (after PVC) with annual consumption of about 17 Mt. These two polyolefins alone account 35% of all thermoplastics and elastomers (Malhotra *et al.*, 1997). In addition, metallocene can readily polymerize bulky monomers such as styrene and norbornene to make novel polymers with physical properties competitive with high performance engineering plastics such as nylon, polycarbonates and polyesters. Any technology with such broad applicability is bound to be of great interest to the plastics industry (Kaminsky and Hartmann, 2000).

After the first discoveries of metallocene, enormous research activities burst, both in the academic and in the industrial world. All the important companies active in the field of polyolefins have involved in this effort: Exxon, Hoechst, Fina, BASF, Dow, Idemitsu, Mitsui Toatsu, Mitsui Petrochemical and Montell (Malhotra *et al.*, 1997).

The commercial success of metallocene catalysts for olefin polymerization will be judged in part by their compatibility with current polymerization processes. The ability to “drop in” a new catalyst into an existing process to produce polymer efficiently without process upsets and without recourse to expensive equipment

modifications can be appreciated and accepted by polyolefin manufacturers. Metallocene catalysts have proven remarkably versatile, producing a wide range of polymer products in virtually every process in which they have been employed (Kaminsky and Hartmann, 2000).

Solution processes use homogeneous catalysts to produce polymers that can dissolve in the reaction medium. These plants may be operated at low or high pressures and temperatures. Typically they are best suited to produce polymers and copolymers with lower density and crystallinity such as VLDPE, plastomers and elastomers, as these will be soluble in the hydrocarbon solvent used or which would melt at the process temperature used. The reaction diluent is volatilized and the polymer recovered for compounding and pelletization. In slurry and bulk-monomer, or gas-phase processes, the polymer is usually to have higher density or crystallinity (e.g., high-density polyethylene, linear-low-density polyethylene, isotactic polypropylene) and is thus insoluble in the reactor diluent or fluidizing gas stream. The continuous operation of these processes suggests the use of morphologically uniform catalyst particles which can be fed into the reactor smoothly without clumping, which in turn implies fixing the solution-soluble catalyst on an insoluble carrier (Ribeiro *et al.*, 1997).

The importance of metallocene catalysts, in the view of an industrial exploitation, can be summarized as follows (Kaminsky and Hartmann, 2000):

- (1) All the traditional polyolefins can be prepared and often endowed with improved properties.
- (2) According to the regulation of metallocene structure, new polymers are produced, with new microstructure and physical-mechanical properties.
- (3) A more fruitful exploitation and even a simplification of the existing industrial processes can be envisaged.

To allow an industrial development for the metallocene based catalysis, a couple of drawbacks appeared are identified as follows:

- (1) The use of metallocene is required a large amount of MAO as co-catalyst, that is expensive.

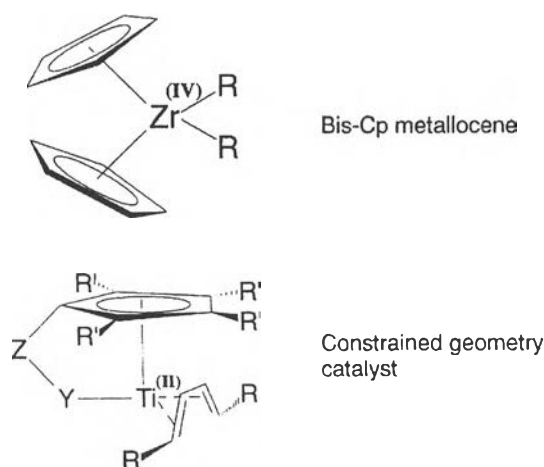


- (2) The homogeneous nature of metallocenes does not allow to use them for bulk and gas phase polymerizations.

To solve the first problem, it has been developed an alternative co-catalyst, based on MAO-free system as branched aluminum alkyl compounds. The second problem can be overcome by using supporting metallocenes on a carrier, known as heterogeneous phase based metallocenes (Kaminsky and Hartmann, 2000).

### 2.11 Polymerization Processes for Metallocene Catalysts

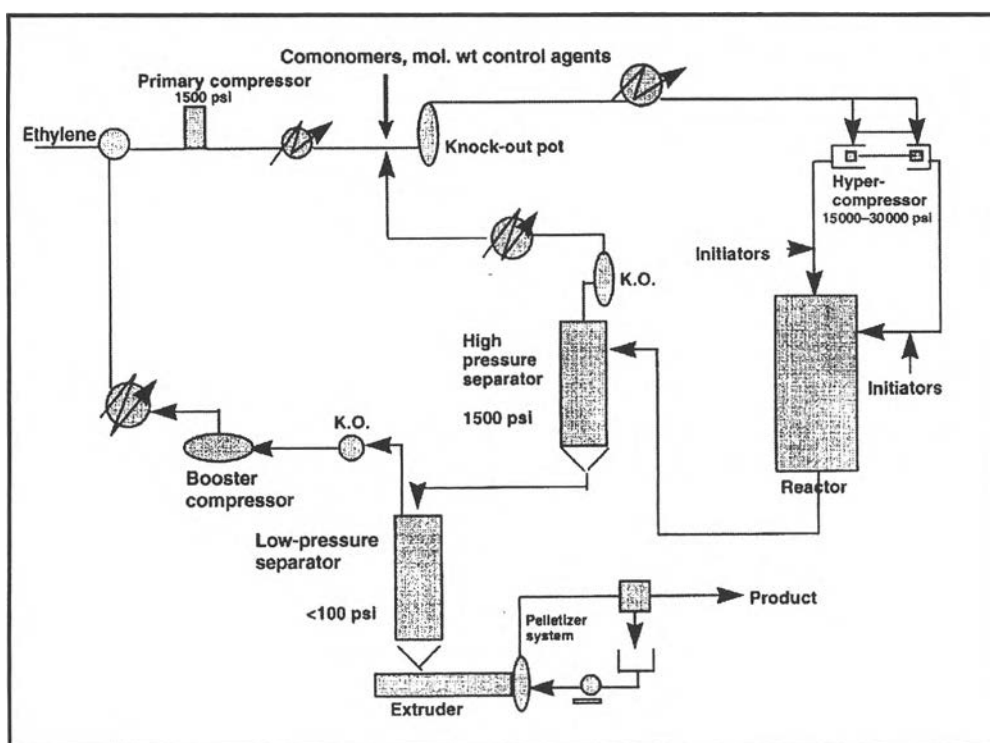
The main attribute of the metallocene catalysts is their amazingly large variety and vast versatile. Several classes of metallocenes exist and can be grouped based on their specificity and activity towards ethylene, propylene, (iso- and syndiotactic) and other  $\alpha$ -olefins. In commercial industry, two major families of high-efficiency single-site metallocene catalyst (SSC) which is an unbridged biscyclopentadienyl and a half sandwich, constrained geometry monocyclopentadienyl single-site catalyst which is known as constrain geometry catalyst (CGC) under trademark INSITE by Dow Chemical (Razavi, 2000). These two catalyst systems are illustrated in Figure 2.21.



**Figure 2.21** An unbridged biscyclopentadienyl metallocene and a constrained geometry monocyclopentadienyl metallocene.

SSC technology polyolefin copolymers can be produced by high-pressure, solution, gas-phase and slurry polymerization processes. Typical process conditions for making polyolefin copolymers in these processes are summarized as follows (Razavi, 2000):

(1) High-pressure process: Two types of commercial reactors, stirred autoclave and tube reactor, are used for the polymerization of ethylene and ethylene- $\alpha$ -olefin copolymerization at high pressure. Ethylene and an  $\alpha$ -olefin comonomer are usually compressed to at least 10,000 psi when fed into the reactor. The polymerization temperature usually exceeds 100 °C (Figure 2.22).



**Figure 2.22** Schematic diagram of the high-pressure polyethylene polymerization process.

(2) Solution process: Stirred reactors are usually used for the polymerization of ethylene and ethylene- $\alpha$ -olefin copolymerization in a solution phase. In most cases, C6-C8 hydrocarbons are used as solvent. The reactors are

operated at about 500 psi pressure and the polymerization is carried out at higher than 60 °C.

(3) Gas-phase process: In the gas-phase process, ethylene and an  $\alpha$ -olefin comonomer (1-butene or 1-hexene) are polymerized in the solid state in a fluidized bed reactor into a powder form. The polymer powder is then converted into pellet form by an extrusion process. The reactor is usually set at > 300 psi pressure and the polymerization process is generally carried out at < 90 °C.

(4) Slurry process: In the slurry process, polymers are made in stirred reactors with an organic carrier liquid such as C4-C6 hydrocarbons. The polymerization process temperature is generally < 90 °C with a reactor pressure < 300 psi. Products made in this process are in powder form and can be converted into pellets using extrusion processes.

According to the continuous and gradual expansion of the polymer particles, especially in the early stages of polymerization, it is necessary to ensure a uniform expansion and avoid overheating of the particle and melting of the polymer, which could result in the particles adhering to form sheets on the reactor walls and agitator, or large chunks which disturb fluidization or product discharge. Premature fragmentation of the polymer particles forms fine particles which can be carried into recycle lines. The catalyst should polymerize the monomer to produce a polymer product of high bulk density which mirrors the particle size distribution of the catalyst despite a 25- to 200-fold increase in volume (Kaminsky and Hartmann, 2000).

## 2.12 Industrial Polymerization Process for Supported Metallocene

The homogeneous metallocene catalysts can perform only well in solution processes. For slurry and gas phase reactors they need to be heterogenized. Supported metallocene catalysts have been run successfully in many large-scale plants, such as fluidized-bed gas-phase processes, including those with “condensed mode” operations (Razavi, 2000). Because they perform differently to conventional Ziegler-Natta catalysts, care must be taken to avoid reactor fouling and process upsets. For example, a scavenger such as TEA is injected into the reactor to remove

impurities in the feed stream (Ribeiro *et al.*, 1997). With supported metallocene catalysts, the presence of the scavenger can cause fouling. Either operating without scavenger or stopping addition soon after start-up results in improved operability and the preparation of copolymer with densities below 0.90 g/ml (Chien and Wang, 1988 and Resconi *et al.*, 1990).

The heterogenisation, if properly performed, does not harm in any performance of the metallocene catalysts and results in supported catalyst particles that can produce polymer particles with controlled morphology. In supported metallocenes, the interaction of the active species with the support, usually an inorganic carrier such as silica, is of electrostatic nature and the individual metallocenium cations and surrounding large anionic MAO are held together by cationic-anionic attractive force. No three dimensional ionic lattice as Ziegler-Natta catalysts or covalent as Phillips catalysts structures are present. In this way the active species can maintain their integrity and single site character (Razavi, 2000).

In transitioning between conventional Ziegler-Natta catalysts and metallocene catalysts, the difference in reactivity to hydrogen and comonomers makes the two systems incompatible. Polymerization by one must be stopped and the process conditions modified before introducing the second catalyst. Small amounts of a catalyst killer such as water (injected with the gas stream or added as wet silica) or methanol can be introduced to deactivate irreversibly the catalyst in the reactor. The second catalyst can be introduced after adjustment of feed streams (Razavi, 2000).