CHAPTER II

LITERATURE REVIEW

2.1 Polymerization of olefins

Until 1953, processes for olefin polymerization were based on a radical process at high pressures and high temperatures. Polymerization of ethylene under these conditions (2000-3000 bars; 150-230°C) yields low-density polyethylene (LDPE, **Figure 2.1**), a low melting, highly branched polyethylene, containing both long- and short chain branches [8]. With propylene only atactic, low molecular weight material can be obtained. Ziegler found that ethylene could also be polymerized using $TiCl_4$ and alkylsaluminium. The process yields linear polyethylene (HDPE, **Figure 2.1**) with a high molecular weight. Natta proved that the same type of catalyst also polymerizes propylene [9]. The resulting polymer mixture is predominantly isotactic with additional polymer fractions that are of a lower stereoregularity or atactic. Copolymerizations of ethylene with 1-hexene/1-octene with the titanium Ziegler catalysts result in copolymers in which the degree of incorporation of the α-olefin varies over the molecular weight distribution. Upon reaction of a vanadium compound, e.g. $V(acac)_3$ (acac = acetylacetonato) or VCl_4, with an alkylaluminium cocatalyst a catalyst for the production of EP (copolymer of ethylene and propylene) and EPDM (ethylene-propylene-diene elastomers) is obtained [10]. The (homogeneous) system shows high (initial) activity, but is rapidly deactivated [11]. An important advantage is that the comonomers are randomly incorporated in the polymer over the full range of the molecular weight distribution.
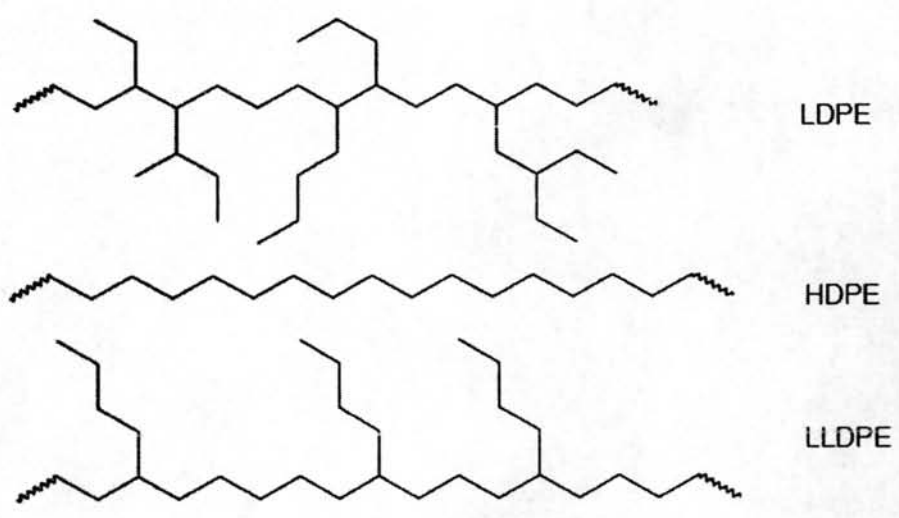
Figure 2.1 Examples of polyethenes: LDPE, HDPE and
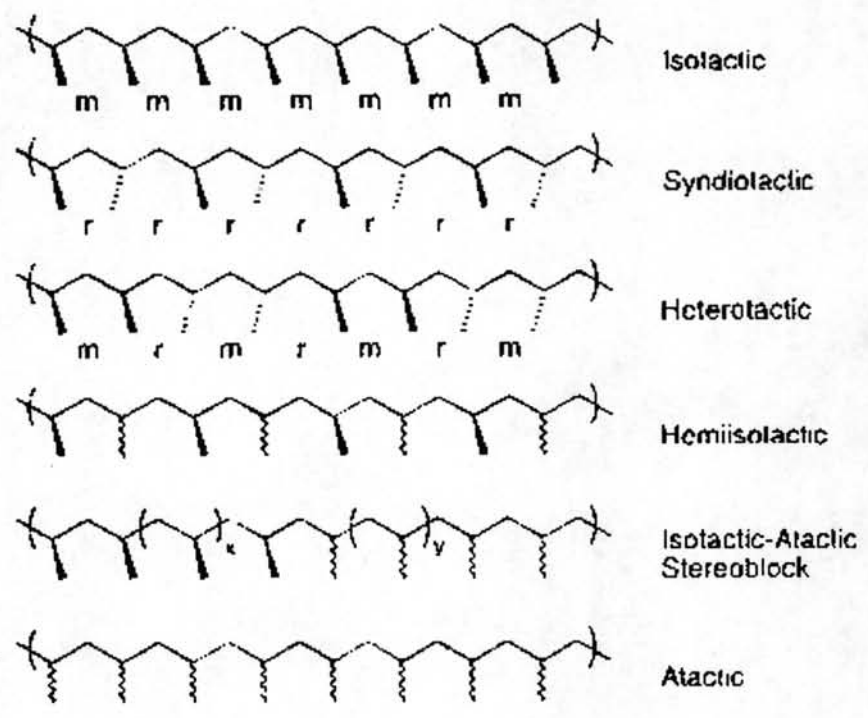LLDPE (copolymer of ethene and 1-hexene)

Figure 2.2 Common polymer tacticities [24]

The heterogeneity of Z-N (Ziegler Natta)systems and Phillips/Union Carbide type catalysts makes them very attractive for industrial application, and most polyolefin materials are still produced by means of heterogeneous catalysts[12]. These heterogeneous systems combine high activity with an easy processability of the resulting product mixture and good polymer particle morphology. The catalyst systems contain various types of active sites with different geometries and activities, which often leads to polymers with broad or polymodal molecular weight distributions or to mixtures of different types of polymers (e.g. mixtures of atactic and isotactic polypropene) [13]. Many improvements on the classical Z-N type catalysts have been made over the last 30 years, and modern Z-N systems allow a much better control of polymer properties. Most of these improvements were achieved by empirical methods [14].

In 1957 the first articles on homogeneous titanium-based olefin polymerization were published by Breslow and Newburg [15] and by Natta, Pino and co-workers [16]. When reacting Cp_2TiCl_2 with Et_2AlCl (DEAC) under conditions similar to those used with Z-N systems, a catalyst that polymerizes ethylene is obtained. The first homogeneous systems showed a low activity, when compared to classical Z-N systems and were also not active in polymerization of higher olefins. In contrast to heterogeneous systems, homogeneous catalysts have a single type of well-defined active sites. Although heterogeneous catalysts are in general industrially more practical, a higher control of properties of the catalyst, and more detailed kinetic and mechanistic studies are possible with well-defined molecular catalysts ("single site" catalysts) [17].

2.2 Mechanisms of homogeneous, catalytic olefin polymerisation

The geometric and electronic structure of the active species affect the properties of the resulting polymer, such as molecular weight, molecular weight distribution, region and stereoselectivity (for the homopolymerization of α-olefins) and the incorporation of other monomers. (for copolymerizations).
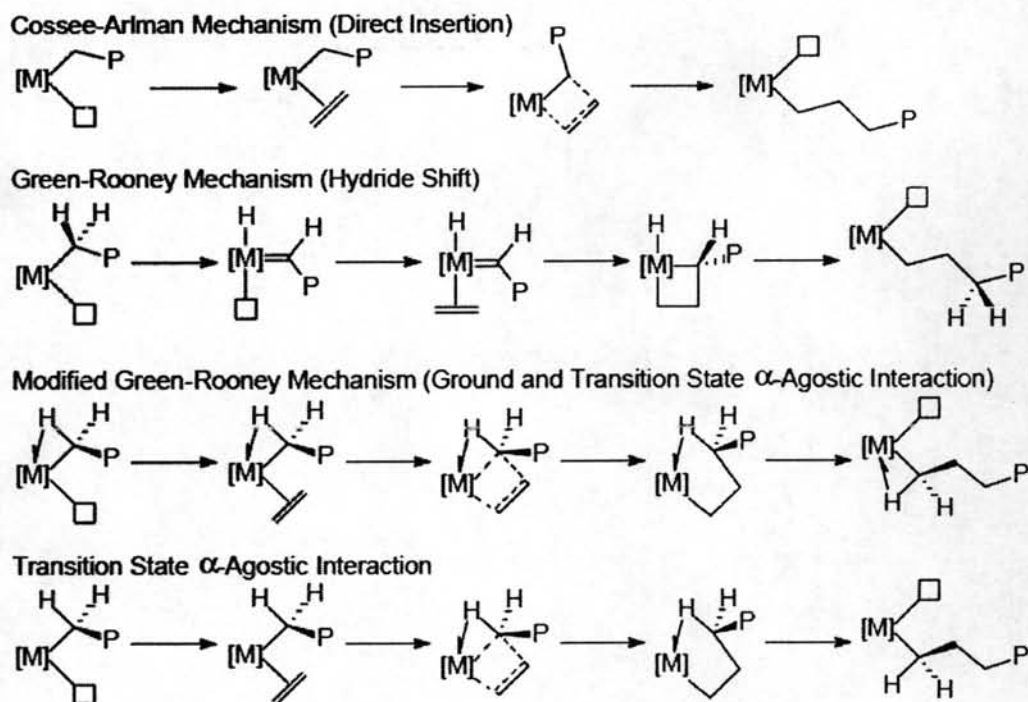
Cossee-Arlman Mechanism (Direct Insertion)

Green-Rooney Mechanism (Hydride Shift)

Modified Green-Rooney Mechanism (Ground and Transition State α-Agostic Interaction)

Transition State α-Agostic Interaction

Figure 2.3 Scheme of migratory insertion mechanism, in which the metal-bound alkyl group migrates to the alkene

It is now generally accepted that this active species is an electron deficient, preferably cationic metal alkyl species. For heterogeneous systems the active sites are at dislocations and edges of the crystals, for homogeneous catalysts the active site is enclosed by a set of ancillary ligands. The cationic metal species are electronically balanced by a preferably weakly nucleophilic, weakly coordinating counter anion. Cossee and Arlman were the first to propose a mechanism for catalytic olefin Polymerization [18]. They proposed that the polymer chain is growing via a *cis*-insertion of the olefin into a metal-carbon bond ,migratory insertion mechanism, in which the metal-bound alkyl group migrates to the alkene shown in **Figure 2.3**

2.2.1 Chain transfer - molecular weight and molecular weight distribution

Besides chain growth, chain transfer processes are also important in olefin polymerization. The rate of chain growth over chain transfer determines molecular weight and molecular weight distribution of the resulting polymer, which

are important factors for material and processing properties. These rates are determined by the catalytic centre and its surrounding ligand (and sometimes by the cocatalyst), and they provide essential information about the polymerization mechanism.

For chain transfer several mechanisms have been revealed, which include termination reactions by β-H, β-CH$_3$ and H-transfer to monomer (**Figure 2.4**) chain transfer to aluminum (e.g. when an aluminum activator or scavenger is used, (**Figure 2.5**), and σ-bond metathesis between the M-alkyl bond and a C-H bond of an alkene or a solvent molecule. Also chain transfer between catalyst active sites has been suggested (in a dual site ethene/1-hexene copolymerisation).

In industrial polyolefin production, often chain transfer agents such as H$_2$ are added to the polymerizing mixture to gain a better control of polymer molecular weights.[19] In absence of alkylaluminium the main mechanism for chain transfer is via β-H abstraction. Two different mechanisms for β-H abstraction have been observed (**Figure 2.4**), which differ in the rate determining step (r.d.s.) of the chain transfer. In both cases polymers are obtained with olefinic end-groups. When the β-H transfer to monomer is rate determining (route 1, **Figure 2.4**), the rate of chain termination increases with increasing olefin concentration . Since also the chain growth (rate of insertion) is 1st order in olefin, molecular weights are independent of monomer concentration for these systems. When the rate determining step is the β-H transfer to metal (route 2, **Figure 2.4**) the rate of termination is independent of monomer concentration (0 th order in olefin), and molecular weights · increase with increasing monomer concentration. When MAO or other alkyls aluminium are present in the reaction medium, another mechanism of chain transfer can be observed. Especially in MAO with a high Me$_3$Al (TMA) content a considerable amount of chain transfer to aluminum may occur although this
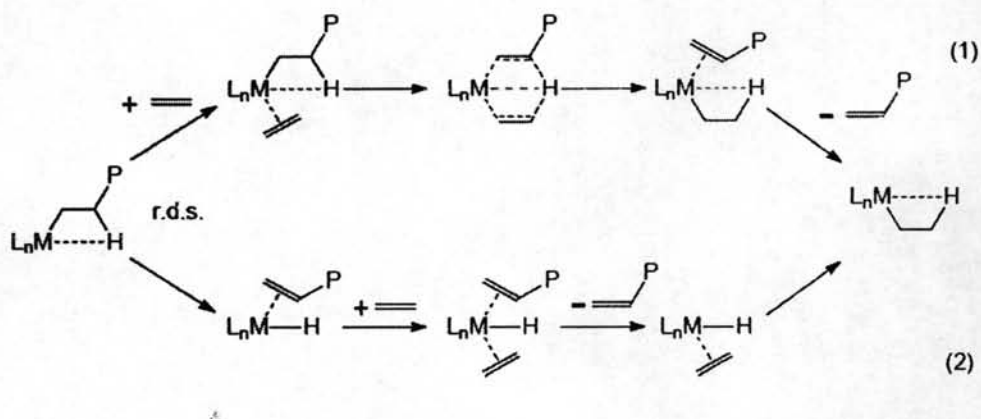
Figure 2.4 Scheme of termination reactions by β-H, β-CH$_3$ and H-transfer to monomer
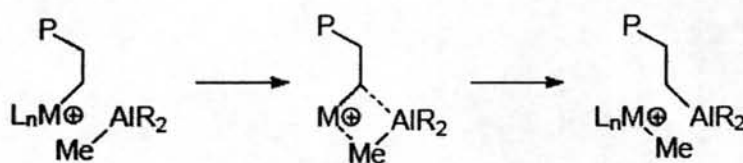

Figure 2.5 Scheme of chain transfer to aluminum

transmetallation has also been observed in TMA-free MAO.[20] As opposed to the mechanisms responsible for chain transfers to monomer, which give olefinic end groups, chain transfers to aluminum give, after hydrolysis, polymers with aliphatic end groups.

2.3 Background on polyolefin catalysts

Polyolefins can be produced with free radical initiators, Phillips type catalysts, Ziegler-Natta catalysts and metallocene catalysts. Ziegler-Natta catalysts have been most widely used because of their broad range of application. However, Ziegler-Natta catalyst provides polymers having broad molecular weight distribution (MWD) and composition distribution due to multiple active sites formed [21].

Metallocene catalysts have been used to polymerize ethylene and α-olefins commercially. The structural change of metallocene catalysts can control composition distribution, incorporation of various comonomers, MWD and stereoregularity [22].

2.3.1 Catalyst structure

Metallocene is a class of compounds in which cyclopentadienyl or substituted cyclopentadienyl ligands are π-bonded to the metal atom. The stereochemistry of biscyclopentadienyl (or substituted cyclopentadienyl)-metal bis (unibidentate ligand) complexes can be most simply described as distorted tetrahedral, with each η^5-L group (L = ligand) occupying a single co-ordination position, as in **Figure 2.6** [23].
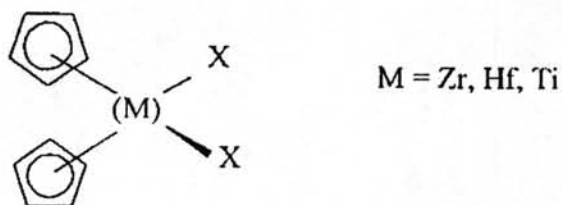

M = Zr, Hf, Ti

Figure 2.6 Molecular structure of metallocene

Representative examples of each category of metallocenes and some of zirconocene catalysts are shown in **Table 2.1** and **Figure 2.7**, respectively.

Table 2.1 Representative Examples of Metallocenes [23]

Category of metallocenes	Metallocene Catalysts
[A] Nonstereorigid metallocenes	1) Cp_2MCl_2 (M = Ti, Zr, Hf) 2) Cp_2ZrR_2 (M = Me, Ph, CH_2Ph, CH_2SiMe_3) 3) $(Ind)_2ZrMe_2$
[B] Nonstereorigid ring-substituted metallocenes	1) $(Mc_5C_5)_2MCl_2$ (M = Ti, Zr, Hf) 2) $(Me_3SiCp)_2ZrCl_2$
[C] Stereorigid metallocenes	1) $Et(Ind)_2ZrCl_2$ 2) $Et(Ind)_2ZrMe_2$ 3) $Et(IndH_4)_2ZrCl_2$
[D] Cationic metallocenes	1) $Cp_2MR(L)^+[BPh_4]^-$ (M = Ti, Zr) 2) $[Et(Ind)_2ZrMe]^+[B(C_6F_5)_4]^-$ 3) $[Cp_2ZrMe]^+[(C_2B_9H_{11})_2M]^-$ (M = Co)
[E] Supported metallocenes	1) Al_2O_3-$Et(IndH_4)_2ZrCl_2$ 2) $MgCl_2$-Cp_2ZrCl_2 3) SiO_2-$Et(Ind)_2ZrCl_2$

$Cp_2ZrCl_2(1)$ $Cp^*_2ZrCl_2(2)$ $Me_2SiCp_2ZrCl_2(3)$ $(Ind)_2ZrCl_2(4)$

$Et(Ind)_2ZrCl_2(5)$ $Me_2Si(Ind)_2ZrCl_2(6)$ $Ph_2C(Cp)(Flu)ZrCl_2(7)$
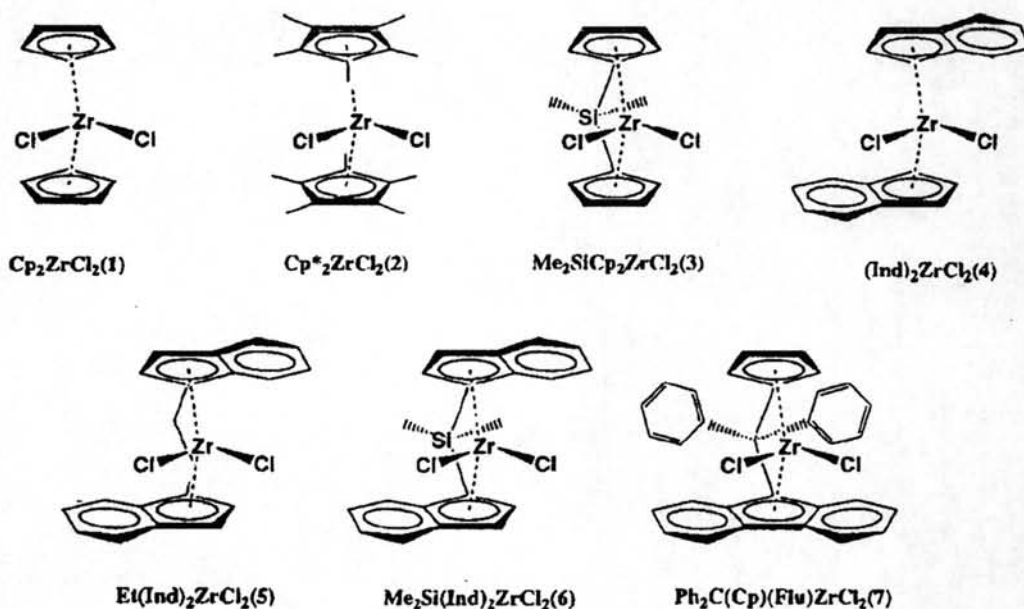
Figure 2.7 Some of zirconocene catalysts structure [24]

Composition and types of metallocene have several varieties. When the two cyclopentadienyl (Cp) rings on either side of the transition metal are unbridged, the metallocene is nonstereorigid and it is characterized by C_{2v} symmetry. The Cp_2M (M = metal) fragment is bent back with the centroid-metal-centroid angle θ about $140°$ due to an interaction with the other two σ bonding ligands [25]. When the Cp rings are bridged (two Cp rings arranged in a chiral array and connected together with chemical bonds by a bridging group), the stereorigid metallocene, so-called ansa-metallocene, could be characterized by either a C_1, C_2, or C_s symmetry depending upon the substituents on two Cp rings and the structure of the bridging unit as schematically illustrated in **Figure 2.8** [23].
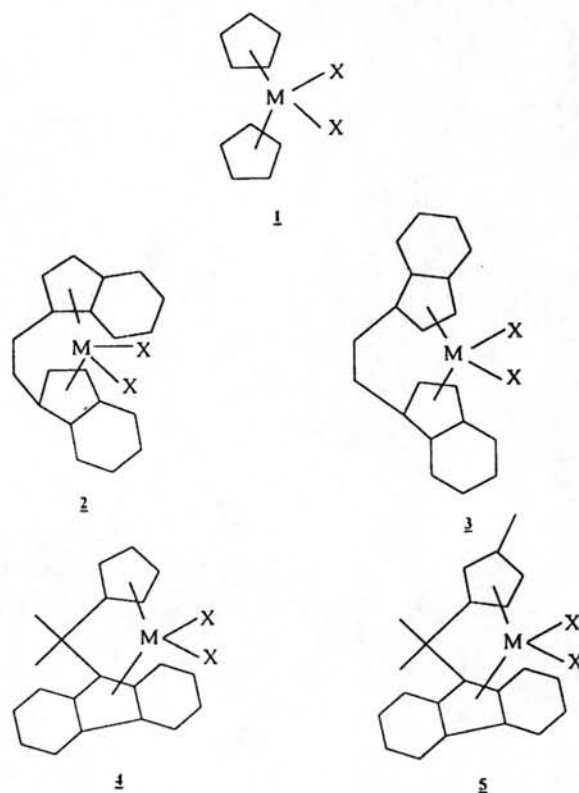
Figure 2.8 Scheme of the different metallocene complex structures [23]. Type 1 is C_{2v}-symmetric; Type 2 is C_2-symmetric; Type 3 is C_s-symmetric; Type 4 is C_s-symmetric; Type 5 is C_1-symmetric.

2.3.2 Polymerization mechanism

The mechanism of catalyst activation is not clearly understood. However, alkylation and reduction of the metal site by a cocatalyst (generally alkyl aluminum or alkyl aluminoxane) is believed to generate the cationic active catalyst species.

First, in the polymerization, the initial mechanism started with formation of cationic species catalyst that is shown below.

Initiation

$$Et(Ind)_2ZrCl_2 + Al(CH_3)_3 \longrightarrow Et(Ind)_2ZrClMe + Al(CH_3)_2Cl$$

Propagation proceeds by coordination and insertion of new monomer unit in the metal carbon bond. Cossee mechanism is still one of the most generally accepted polymerization mechanism (**Figure 2.9**) [26]. In the first step, monomer forms a complex with the vacant coordination site at the active catalyst center. Then through a four-centered transition state, bond between monomer and metal center and between monomer and polymer chain are formed, increasing the length of the polymer chain by one monomer unit and generating another vacant site.
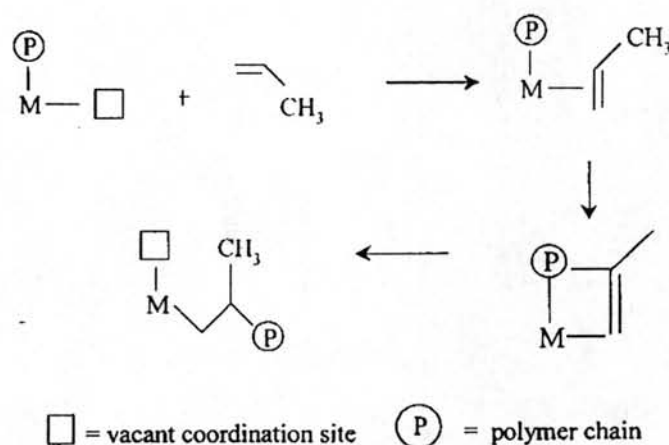

☐ = vacant coordination site   Ⓟ = polymer chain

Figure 2.9 Cossee mechanism for Ziegler-Natta olefin polymerization [26].

The trigger mechanism has been proposed for the polymerization of α-olefin with Ziegler-Natta catalysts [27]. In this mechanism, two monomers interact with one active catalytic center in the transition state. A second monomer is required to form a new complex with the existing catalyst-monomer complex, thus trigger a chain propagation step. No vacant site is involved in this model. The trigger mechanism has been used to explain the rate enhancement effect observed when ethylene is copolymerized with α-olefins.
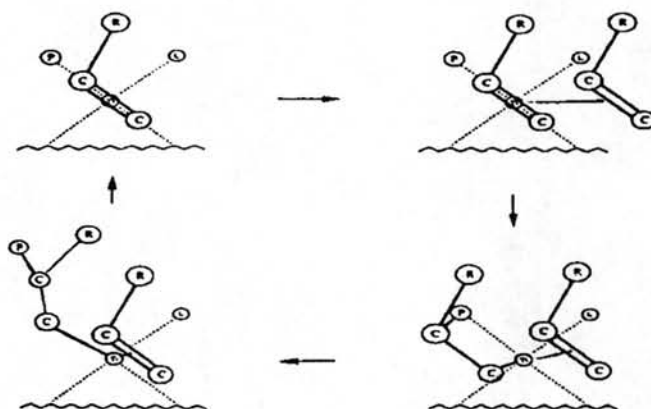

Figure 2.10 The propagation step according to the trigger mechanism [27].

After that , the propagation mechanism in polymerization shown in
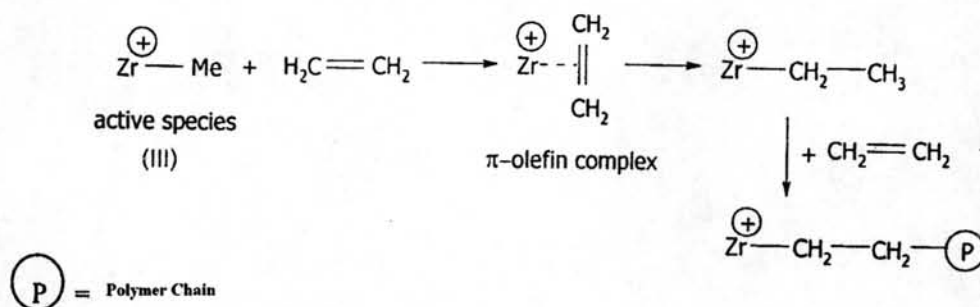
Figure 2.11

Propagation

Figure 2.11 Propagation mechanism in polymerization

Finally, the termination of polymer chains can be formed by 1) chain transfer via β-H elimination, 2) chain transfer via β-Me elimination, 3) chain transfer to aluminum, 4) chain transfer to monomer, and 5) chain transfer to hydrogen (**Figure 2.7-2.11**)[23]. The first two transfer reactions form the polymer chains containing terminal double bonds.
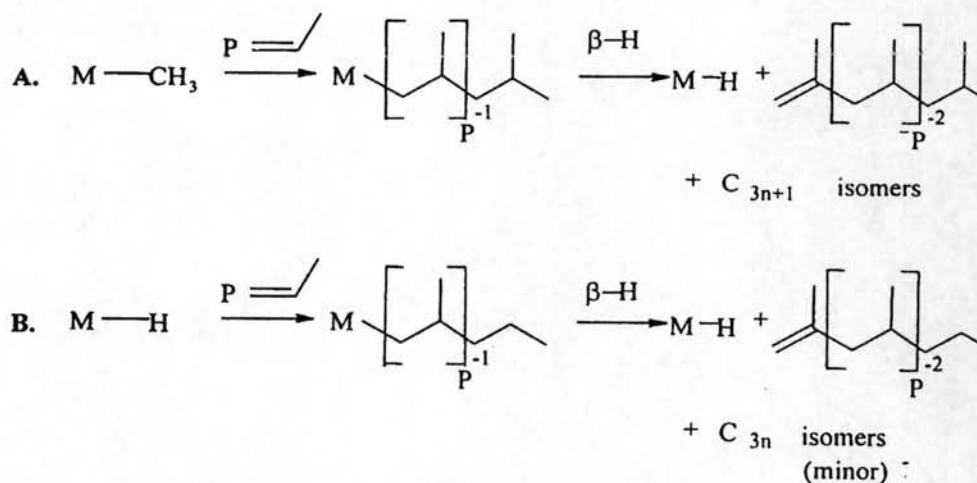

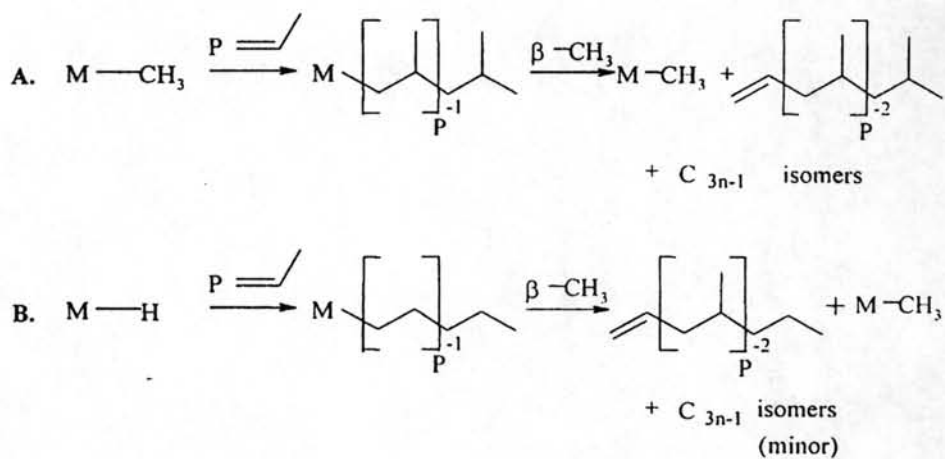**Figure 2.12** Chain transfer via β-H elimination [23]

Figure 2.13 Chain transfer via β-CH₃ elimination [23]
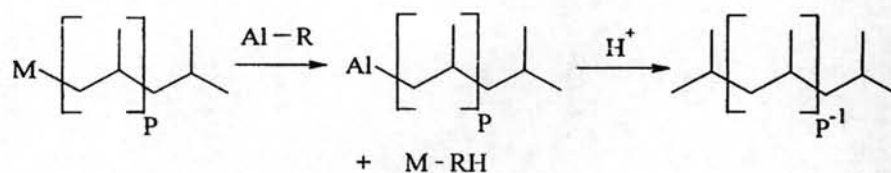
Figure 2.14 Chain transfer to aluminum [23]

Figure 2.15 Chain transfer to monomer [23]

Figure 2.16 Chain transfer to hydrogen [23]

2.3.3 Cocatalysts

Metallocene catalysts have to be activated by a cocatalyst. The most common types of cocatalysts are alkylaluminums including methylaluminoxane (MAO), trimethylaluminum (TMA), triethylaluminum (TEA), triisobutylaluminum (TIBA) and cation forming agents such as $(C_6H_5)_3C^+(C_6F_5)_4B^-$ and $B(C_6F_5)_3$ [28].

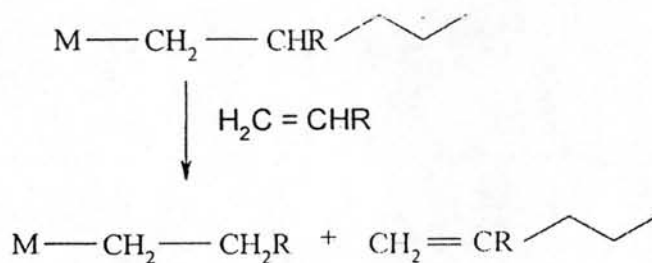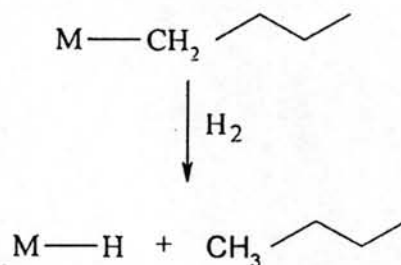Among these, MAO is a very effective cocatalyst for metallocene. However, due to the difficulties and costs involved in the synthesis of MAO, there has been considerable effort done to reduce or elimination the use of MAO. Due to difficulties in separation, most commercially available MAO contains a significant fraction of TMA (about 10-30%) [29]. This TMA in MAO could be substantially eliminated by toluene-evaporation at 25°C.

Indeed, the difficulties encountered to better understand the important factors for an efficient activation are mainly due to the poor knowledge of the MAO composition and structure. Several types of macromolecular arrangements, involving linear chains, monocycles and/or various three-dimensional structures have been successively postulated. These are shown in **Figure 2.17**. In recent work, a more detailed image of MAO was proposed as a cage molecule, with a general formula $Me_{6m}Al_{4m}O_{3m}$ (m equal to 3 or 4) [30].
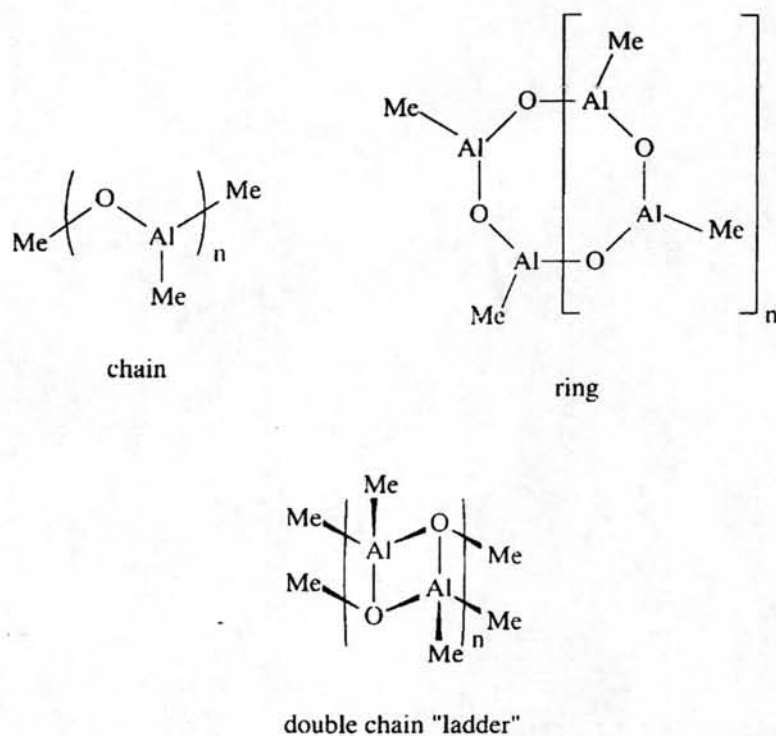
chain

ring

double chain "ladder"

Figure 2.17 Early structure models for MAO [30]

In the case of rac-Et(Ind)$_2$ZrMe$_2$ as precursor, the extracted methyl ligands do not yield any modification in the structure and reactivity of the MAO counter-anion, thus allowing zirconium coordination site available for olefin that presented in **Figure 2.18** [31].
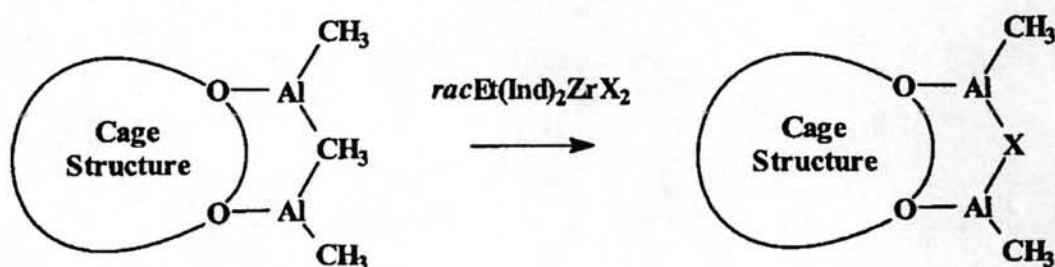

Figure 2.18 Representation of MAO showing the substitution of one bridging methyl group by X ligand extracted from racEt(Ind)$_2$ZrCl$_2$ (X = Cl, NMe$_2$, CH$_2$Ph) [31].

Cam and Giannini [32] investigated the role of TMA present in MAO by a direct analysis of Cp$_2$ZrCl$_2$/MAO solution in toluene-d$_8$ using ^{1}H-NMR. Their observation indicated that TMA might be the major alkylating agent and that MAO acted mainly as a polarization agent. However, in general it is believed that MAO is the key cocatalyst in polymerizations involving metallocene catalysts. The role of MAO included 1) alkylation of metallocene, thus forming catalyst active species, 2) scavenging impurities, 3) stabilizing the cationic center by ion-pair interaction and 4) preventing bimetallic deactivation of the active species.

The homogeneous metallocene catalyst cannot be activated by common trialkylaluminum only. However, Soga et al.[33] were able to produce polyethylene with modified homogeneous Cp$_2$ZrCl$_2$ activated by common trialkylaluminum in the presence of Si(CH$_3$)$_3$OH. Their results show that for an "optimum" yield aging of the catalyst and Si(CH$_3$)$_3$OH mixture for four hours is required. However, MWD of the produced polymers is bimodal although the polymers obtained in the presence of MAO have narrow MWD.

Ethylene/α-olefins copolymers with bimodal CCD were produced with homogeneous Cp_2ZrCl_2 with different cocatalysts such as MAO and mixture of TEA/borate or TIBA/borate [34]. It seemed that the active species generated with different cocatalysts have different activities and produce polymers with different molecular weights.

2.3.4 Catalyst activity

The ethylene polymerization rate of the copolymerization reaction with the catalyst system SiO_2/MAO/rac-Me_2Si [2-Me-4-Ph-Ind]$_2ZrCl_2$ was studied by Fink et al. [35]. The temperature was varied from 40 to 57°C. Small amount of hexene in the reaction solution increased the polymerization rate. The extent of the "comonomer effect" depended on the polymerization temperature. At 57°C the maximum activity of the ethylene/hexene copolymerization was 8 times higher than the homopolymerization under the same conditions. At 40°C the highest reaction rate for the copolymerization is only 5 times higher than that for the ethylene homopolymerization. For the polymer properties of the ethylene/α-olefin copolymerization, the molecular weights of the polymers decreased with increasing comonomer incorporation. Ethylene/hexene copolymers produced by a metallocene catalyst also have the same melting point and glass transition temperature.

Series of ethylene copolymerization with 1-hexene or 1-hexadecene over four different siloxy-substituted ansa-metallocene/methylaluminoxane (MAO) catalyst systems were studied by Seppala et al. [36]. Metallocene catalysts rac-Et[2-(t-BuMe$_2$SiO)Ind]$_2ZrCl_2$ (1), rac-Et[1-(t-BuMe$_2$SiO)Ind]$_2ZrCl_2$ (2), rac-Et[2-(i-Pr$_3$SiO)Ind]$_2ZrCl_2$ (3) and rac-Et[1-(i-Pr$_3$SiO)Ind]$_2ZrCl_2$ (4) were used. The effects of minor changes in the catalyst structure, more precisely changes in the ligand substitution pattern were studied. They found that series of polymerization with siloxy-substituted bis(indenyl) ansa-metallocene are highly active catalyst precursors for ethylene-α-olefins copolymerizations. The comonomer response of all four catalyst precursors was good. Under the same conditions the order of copolymerization ability of the catalyst was rac-Et[2-(i-Pr$_3$SiO)Ind]$_2ZrCl_2$ > rac-Et[2-

(t-BuMe$_2$SiO)Ind]$_2$ZrCl$_2$ and rac-Et[1-(i-Pr$_3$SiO)Ind]$_2$ZrCl$_2$ > rac-Et[1-(t-BuMe$_2$SiO)Ind]$_2$ZrCl$_2$. These catalysts are able to produce high molecular weight copolymers.

2.3.5 Copolymerization

By adding a small amount of comonomer to the polymerization reactor, the final polymer characteristics can be dramatically changed. For example, the Unipol process for linear low density polyethylene (LLDPE) uses hexene and the British Petroleum process (BP) uses 4-methylpentene to produce high-performance copolymers [37]. The comonomer can be affected the overall crystallinity, melting point, softening range, transparency and also structural, thermochemical, and rheological properties of the formed polymer. Copolymers can also be used to enhance mechanical properties by improving the miscibility in polymer blending [38].

Ethylene is copolymerized with α-olefin to produce polymers with lower densities. It is commonly observed that the addition of a comonomer generally increases the polymerization rate significantly. This comonomer effect is sometimes linked to the reduction of diffusion limitations by producing a lower crystallinity polymer or to the activation of catalytic sites by the comonomer. The polymer molecular weight often decreases with comonomer addition, possibly because of a transfer to comonomer reactions. Heterogeneous polymerization tends to be less sensitive to changes in the aluminum/transition metal ratio. Chain transfer to aluminum is also favored at high aluminum concentrations. This increase in chain transfer would presumably produce a lower molecular weight polymer. In addition, some researchers observed the decrease, and some observed no change in the molecular weight with increasing aluminum concentration [39].

The effect of polymerization conditions and molecular structure of the catalyst on ethylene/α-olefin copolymerization have been investigated extensively. Pietikainen and Seppala [40] investigated the effect of polymerization temperature on catalyst activity and viscosity average molecular weights for low molecular weight

ethylene/propylene copolymers produced with homogeneous Cp_2ZrCl_2. Soga and Kaminaka [41] compared copolymerizations (ethylene/propylene, ethylene/1-hexene, and propylene/1-hexene) with $Et(H_4Ind)_2ZrCl_2$ supported on SiO_2, Al_2O_3 or $MgCl_2$. Broadness of MWD was found to be related to the combination of support types and types of monomers. The effect of silica and magnesium supports on copolymerization characteristics was also investigated by Nowlin *et al.* [42]. Their results indicated that comonomer incorporation was significantly affected by the way that support was treated based on the reactivity ratio estimation calculated with simplified Finemann Ross method. However, it should be noted that Finemann Ross method could be misleading due to linear estimation of nonlinear system.

Copolymer based on ethylene with different incorporation of 1-hexene,1-octene, and 1-decene were investigated by Quijada [43]. The type and the concentration of the comonomer in the feed do not have a strong influence on the catalytic activity of the system, but the presence of the comonomer increases the activity compared with that in the absence of it. From ^{13}C-NMR it was found that the size of the lateral chain influences the percentage of comonomer incorporated, 1-hexene being the highest one incorporated. The molecular weight of the copolymers obtained was found to be dependent on the comonomer concentration in the feed, showing that there is a transfer reaction with the comonomer. The polydispersity (Mw/Mn) of the copolymers is rather narrow and dependent on the concentration of the comonomer incorporation.

Soga *et al.* [44] noted that some metallocene catalysts produce two-different types of copolymers in terms of crystallinity. They copolymerized ethylene and 1-alkenes using 6 different catalysts such as Cp_2ZrCl_2, Cp_2TiCl_2, Cp_2HfCl_2, $Cp_2Zr(CH_3)_2$, $Et(Ind\ H_4)_2ZrCl_2$ and i-Pr(Cp)(Flu)ZrCl$_2$. Polymers with bimodal crystallinity distribution (as measured by TREF-GPC analysis) were produced with some catalytic systems. Only Cp_2TiCl_2-MAO and $Et(H_4Ind)_2ZrCl_2$-MAO produced polymers that have unimodal crystallinity distribution. The results seem to indicate that more than one active site type are present in some of these catalysts. However, it is also possible that unsteady-state polymerization conditions might have caused the

broad distributions since the polymerization times were very short (5 minutes for most cases).

Marques *et al.*[45] investigated copolymerization of ethylene and 1-octene by using the homogeneous catalyst system based on $Et(Flu)_2ZrCl_2$/MAO. A study was performed to compare this system with that of Cp_2ZrCl_2/MAO. The influence of different support materials for the Cp_2ZrCl_2 was also evaluated, using silica, $MgCl_2$, and the zeolite sodic mordenite NaM. The copolymer produced by the $Et(Ind)_2ZrCl_2$/MAO system showed higher molecular weight and narrower molecular weight distribution, compared with that produced by Cp_2ZrCl_2/MAO system. Because of the extremely congested environment of the fluorenyl rings surrounding the transition metal, which hinders the beta hydrogen interaction, and therefore, the chain transference. Moreover, the most active catalyst was the one supported on SiO_2, whereas the zeolite sodic mordenite support resulted in a catalyst that produced copolymer with higher molecular weight and narrower molecular weight distribution. Both homogeneous catalytic systems showed the comonomer effect, considering that a significant increase was observed in the activity with the addition of a larger comonomer in the reaction medium.

The effect of different catalyst support treatments in the 1-hexene/ethylene copolymerization with supported metallocene catalyst was investigated by Soares *et al.* [46]. The catalysts in the study were supported catalysts containing SiO_2, commercial MAO supported on silica (SMAO) and MAO pretreated silica (MAO/silica) with Cp_2HfCl_2, $Et(Ind)_2HfCl_2$, Cp_2ZrCl_2 and $Et(Ind)_2ZrCl_2$. All the investigated supported catalysts showed good activities for the ethylene polymerization (400-3000 kg polymer/mol metal.h). Non-bridged catalysts tend to produce polymers with higher molecular weight when supported on to SMAO and narrow polydispersity. The polymer produced with Cp_2HfCl_2 supported on silica has only a single low crystallinity peak. On the other hand, Cp_2HfCl_2 supported on SMAO and MAO/silica produced ethylene/1-hexene copolymers having bimodal CCDs. For the case of Cp_2ZrCl_2 and $Et(Ind)_2ZrCl_2$, only unimodal CCDs were obtained. It seems that silica-MAO-metallocene and silica-metallocene site differ

slightly in their ability to incorporate comonomer into the growing polymer chain, but not enough to form bimodals CCDs.

Soares *et al.* [47] studied copolymerization of ethylene and 1-hexene. It was carried out with different catalyst systems (homogeneous $Et(Ind)_2ZrCl_2$, supported $Et(Ind)_2ZrCl_2$ and in-situ supported $Et(Ind)_2ZrCl_2$). Supported $Et(Ind)_2ZrCl_2$: an $Et(Ind)_2ZrCl_2$ solution was supported on SMAO. It was used for polymerization of ethylene and 1-hexene. In-situ supported $Et(Ind)_2ZrCl_2$: an $Et(Ind)_2ZrCl_2$ solution was directly added to SMAO in the polymerization reactor, in the absence of soluble MAO. Homogeneous $Et(Ind)_2ZrCl_2$ showed higher catalytic activity than the corresponding supported and in-situ supported metallocene catalysts. The relative reactivity of 1-hexene increased in the following order: supported metallocene $\approx$ in-situ supported metallocene < homogeneous metallocene catalysts. The MWD and short chain branching distribution (SCBD) of the copolymer made with the in-situ supported metallocene were broader than those made with homogeneous and supported metallocene catalysts. They concluded that there are at least two different active species on the in-situ supported metallocene catalyst for the copolymerization of ethylene and 1-hexene.

Soares *et al.* [48] investigated copolymerization of ethylene and 1-hexene with different catalysts: homogeneous $Et(Ind)_2ZrCl_2$, Cp_2HfCl_2 and $[(C_5Me_4)SiMe_2N(tert-Bu)]TiCl_2$, the corresponding in-situ supported metallocene and combined in-situ supported metallocene catalyst (mixture of $Et(Ind)_2ZrCl_2$ and Cp_2HfCl_2 and mixture of $[(C_5Me_4)SiMe_2N(tert-Bu)]TiCl_2$. They studied properties of copolymers by using ^{13}C-NMR, gel permeation chromatography (GPC) and crystallization analysis fractionation (CRYSTAF) and compared with the corresponding homogeneous metallocene. The in-situ supported metallocene produced polymers having different 1-hexene fractions, SCBD and MDW. It was also demonstrated that polymers with broader MWD and SCBD can be produced by combining two different in-situ supported metallocenes.

In addition, Soares *et al.*[49] studied copolymerization of ethylene and 1-hexene with an in-situ supported metallocene catalysts. Copolymer was produced

with alkylaluminum activator and effect on MWD and SCBD was examined. They found that TMA exhibited the highest activity while TEA and TIBA had significantly lower activities. Molecular weight distributions of copolymers produced by using the different activator types were unimodal and narrow, however, short chain branching distributions were very different. Each activator exhibited unique comonomer incorporation characteristics that can produce bimodal SCBD with the use of a single activator. They used individual and mixed activator system for controlling the SCBDs of the resulting copolymers while maintaining narrow MWDs.

2.4 Metallocene catalysts

2.4.1 Olefin polymerization with metallocene catalysts

The modern organometallic chemistry has begun when apply metallocene complexes with Group IV metals to new technologies and production of new materials. Metallocene compounds are becoming an important grade of catalysts for the synthesis of organic molecules and polymers. Metallocene catalysts are operated in all living industrial plants that are presently used for polyolefin manufacture revolutionize the technology for the production of these polymers [50].

Polyethylene's properties and the appropriate technology must be used to produce products which have the required properties by customer. This requires detailed knowledge and know-how of relationships among processing conditions, polymer structure and polymer properties. For catalytic polymerization processes the catalyst, mostly in combination with a cocatalyst, and the polymerization process are observed as the polymerization technology. This means that both the process and the catalyst are an integrated completion and must be well balanced in respect to each other [51]. The catalyst or catalyst system plays the key role, as polymerization behavior such activity, molecular mass regulation, copolymerization behavior, process control and polymer structure such molecular mass distribution, comonomer distribution, chain structure and polymer particle morphology such bulk density, particle size, particle distribution, in the choice of process and product properties [52]. The catalyst determines the polymerization behavior, the polymer structure and the

polymer powder morphology in heterogeneous processes. The catalyst system must appropriate the polymerization process.

2.4.2 Catalyst systems for olefin polymerization

In 1953 Karl Ziegler, who succeeded in polymerizing ethylene into high-density polyethylene (HDPE) at standard pressure and room temperature, discovered of catalysts based on titanium trichloride and diethylaluminum chloride as cocatalyst, at the Max-Planck-Institute in Mulheim. A little later, Natta, at the Polytechnical Institute of Milan, was able to indicate that an appropriate catalyst system was capable of polymerizing propene into semi-crystalline polypropene. Ziegler and Natta shared a Nobel Prize for Chemistry in 1963 for their work [53]. With this so-called Ziegler-Natta catalyst.

Ziegler-Natta catalyst has been widely used in olefin polymerization; the coordination polymerization allows the catalyst geometry around the metal center to control the polymer structure. In homogeneous polymerization, the ligand of a catalyst largely controls the geometry of an active metal center on which the polymerization reaction occurs. However, the conventional Ziegler-Natta catalysts the molecular structure of the polymers cannot be controlled well the molecular structure of the polymers because these catalysts have different nature types of catalytic sites.

Kaminsky discovered the metallocene catalyst system; it has proven to be a major breakthrough for the polyolefin industry. Metallocene catalysts show in opposite to conventional Ziegler-Natta catalytic systems, only one type of active site (single site catalyst), which produces polymers-with a narrow molar mass distribution ($M_w/M_n = 2$). The molecular structure of the metallocene catalysts can be easily changed which allows control of the structure of polyolefin produced with these catalysts. Many metallocene are soluble in hydrocarbons or liquid propene. These properties allow one to predict accurately the properties of the resulting polyolefins by knowing the structure of the catalyst used during their manufacture and to control the

resulting molar mass and distribution, comonomer content and tacticity by careful selection of the appropriate reactor conditions. In addition, their catalytic activity is 10-100 times higher than that of the classical Ziegler-Natta systems.

Metallocene, in combination with the conventional aluminum alkyl cocatalyst used in Ziegler systems, are indeed capable of polymerizing ethylene, but only at a very low activity. Only with the discovery and application of methylaluminoxane (MAO) by Sinn et al., 1980, was it possible to enhance the activity, surprisingly, by a factor of 10000. Therefore, MAO played a crucial part in the catalysis with metallocenes. Since this discovery of effective zirconocene-MAO catalyst systems for ethylene polymerization, development of the catalyst system has been conducted to achieve higher activity and to obtain higher molecular weight polyethylene. Modifications of metallocene ligand were investigated in non-bridged and bridged zirconocene catalysts [54].

The varying ligand of the metallocene can be change the different microstructures and characteristics in polyolefin. By combining different olefins and cycloolefins with one another, the range of characteristics can be further broadened. The production of polyolefin with tailored microstructures and chemically uniform copolymers has not yet been achieved by conventional heterogeneous catalysts [53]. However, extensive research has been concerned towards metallocene catalyst studying modifications of the catalyst system, which leads to specific changes in catalytic activity and product characteristics [54]. The development of metallocene catalysts has not yet been complete, and studies are required to increase the understanding of several important factors which affect catalytic performance, such as transition metal-olefin interaction, metal-alkyl bond stability, influence of other ligands, and steric effects of the other ligands.

2.5 Heterogeneous system

The new metallocene/MAO systems offer more possibilities in olefin polymerization compared to conventional Ziegler-Natta catalysts, such as narrow

stereoregularity, molecular weight and chemical composition distributions (CCDs) through ligand design. However, only heterogeneous catalysts can be practically used for the existing gas phase and slurry polymerization processes. Without using a heterogeneous system, high bulk density and narrow size distribution of polymer particles cannot be achieved. The advantages of supporting catalysts include improved morphology, less reactor fouling, lower Al/metal mole ratios required to obtain the maximum activities in some cases the elimination of the use of MAO, and improved stability of the catalyst due to much slower deactivation by bimolecular catalyst interactions. Therefore, developing heterogeneous metallocene catalysts, that still have all the advantages of homogeneous systems, became one of the main research objectives of applied metallocene catalysis.

Steinmetz *et al.* [55] examined the particle growth of polypropylene made with a supported metallocene catalyst using scanning electron microscopy (SEM). They noticed formation of a polymer layer only on the outer surface of catalyst particles during the initial induction period. As the polymerization continued, the whole particle was filled with polymer. Particle fragmentation pattern depended on the type of supported metallocene.

2.5.1 Catalyst chemistry

The nature of the active sites affects the polymer morphology, catalyst stability and activity, and the characteristics of the polymer produced. However, structure and chemistry of the active sites in supported catalysts are not clearly understood. Catalytic activities for supported metallocene are usually much lower than that of their counterpart homogeneous system. Formation of different active species, deactivation of catalyst during supporting procedure, and mass transfer resistance may contribute to decreased catalyst activity.

Tait *et al.* [56] reported general effects of support type, treatment, supporting procedure, and type of diluents on reaction kinetics and physical properties of polymer produced. Although the activities of supported catalysts are much lower

compared to homogeneous systems. The activity of catalysts increased slightly when o-dichlorobenzene was introduced in toluene

The catalytic activities of supported catalyst depended on the percentage of the incorporated metallocene was reported by Quijada *et al.* [57]. However, in the case of metallocenes supported on MAO pretreated silica, depending on how the surface bound MAO complex with the catalyst, the activity can be as high as that of homogeneous system. According to the experiment by Chein *et al.* [58], if a single MAO is attached to silica, it would complex with zirconocene and lowers its activity. On the other hand, if multiple MAOs are attached to the surface silanol, the supported zirconocene will not be further complexed with MAO and have activity.

2.5.2 Supporting methods

In the case of carriers like silica or other inorganic compounds with OH group on the surface, the resulting catalyst displayed very poor activities even combined with MAO. The reaction of metallocene complexes with the Si-OH groups might cause the decomposition of active species. Such decomposition could be suppressed by fixing MAO on the silica surface and then reacting with metallocenes [59]. Therefore, silica must be pretreated before the interaction with metallocene, to reduce the OH concentration and to prepare an adequate surface for metallocene adsorption and reaction in a non-deactivating way [60]. Metallocene immobilization methods can be divided in to three main groups. The first method is the direct support of catalyst onto an inert support. The second method involves the pretreatment of the inert support with MAO or other alkylaluminum followed by metallocene supporting. The third method, the catalyst is chemically anchored to the support, which often involves in-situ catalyst synthesis. These methods produce catalysts with distinct activities, comonomer reactivity ratios, and stereospecificities.

2.5.2.1 Direct supporting of inert material

Collins *et al.* [61] reported that Et(Ind)$_2$ZrCl$_2$, when supported on partially dehydrated silica, reacted with surface hydroxyl groups during adsorption to form inactive catalyst precursors and free ligands (**Figure 2.19**). Therefore, the activity is lower compared to the case of using dehydrated silica. **Figure 2.20** shows the proposed structure Et(Ind)$_2$ZrCl$_2$ supported on alumina. For the case of alumina, the activity of catalyst supported on dehydrated alumina in lower than the one supported on partially dehydrated alumina. The high Lewis acidity of aluminum sites on dehydrated alumina facilitates the formation of Al-Cl bonds and Zr-O bonded species when the metallocene compound is adsorbed on these sites. However, the metal sites in this case remain inactive even after MAO addition.
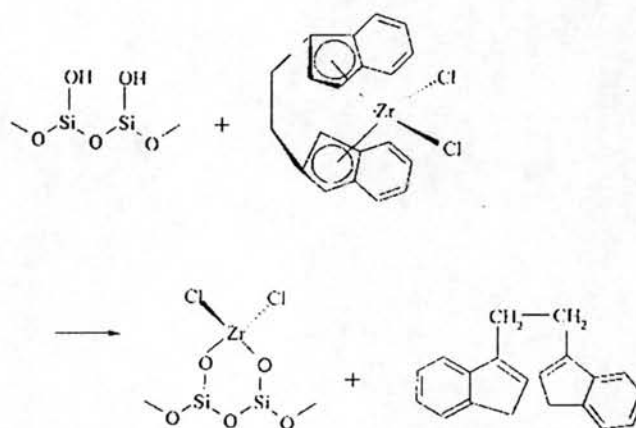

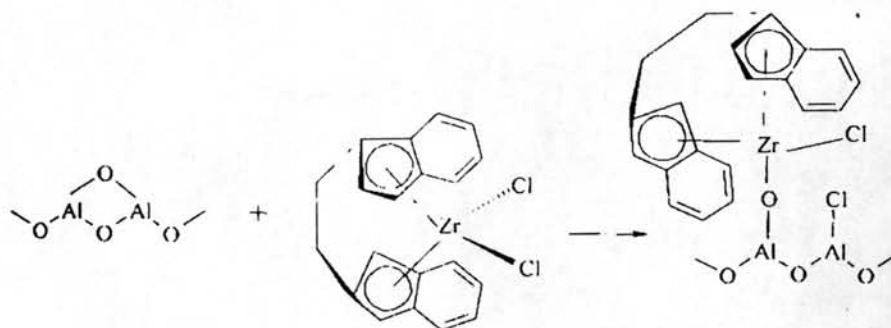**Figure 2.19** Structure of Et(Ind)$_2$ZrCl$_2$ supported on silica [39]

Figure 2.20 Structure of Et(Ind)$_2$ZrCl$_2$ supported on alumina [39]

Kaminsky *et al.* [62] proposed a possible explanation for the different behavior of metallocene supported directly on to silica, homogeneous systems, or supported onto MAO-pretreated silica. It is assumed that the supporting of metallocenes on silica takes place in three stages. First, the metallocene reacts with OH groups of the silica as shown in **Figure 2.21**.
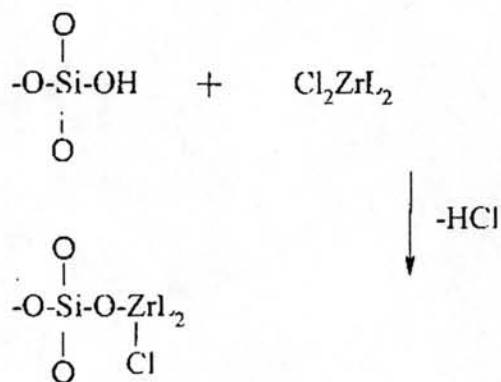

Figure 2.21 Reaction of silica and metallocene during catalyst supporting [62], where L is a ligand (Cp, Ind).

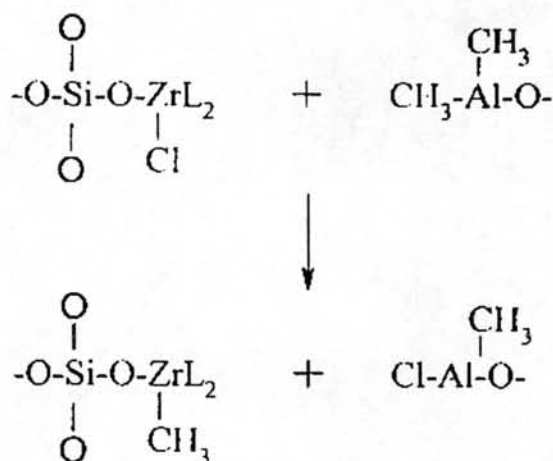The second step is the alkylation by MAO as shown in **Figure 2.22**

$$\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{-O\text{-}Si\text{-}O\text{-}ZrL_2}} \quad + \quad \underset{}{\overset{\overset{CH_3}{|}}{CH_3\text{-}Al\text{-}O\text{-}}}$$

$$\downarrow$$

$$\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{-O\text{-}Si\text{-}O\text{-}ZrL_2}} \quad + \quad \underset{}{\overset{\overset{CH_3}{|}}{Cl\text{-}Al\text{-}O\text{-}}}$$

Figure 2.22 Alkylation of supported metallocene by MAO [62]

The third step is the dissociation of the $-SiO_2\text{-}O\text{-}Zr-$ bond to an ion pair to form the cation active center $(SiO)^-(Zr)^+$. The polydispersity of polymers produced with these supported metallocenes are reported to be relatively high ($5 \approx 8$) due to different electronic and steric interactions between the silica surface and the metal active sites. The immobilization of the zirconocene on silica inhibits bimolecular deactivation processes because the active sites are separated from each other.

As a consequence less use of MAO is required, increased molecular weights are achieved due to the reduction of β-hydrogen transfer by a second zirconocene center, and polypropylene of higher isotacticity and melting point is formed.

2.5.2.2 Supporting catalyst on materials treated with alkylaluminum

When silica is pretreated with MAO, the supporting mechanism is different. The zirconocene is complexed to MAO supported on silica, which will

make the catalyst similarly to a homogeneous system. The polymers produced in this way have lower molecular weights.

Hiatky and Upton [63] reported that supporting of the aluminum-alkyl free catalysts can formed 2 complexes as shown in **Figure 2.23**, (a) deactivation through coordination of Lewis- basic surface oxides to the electrophilic metal center or (b) reaction of the ionic complex with residual surface hydroxyl groups.
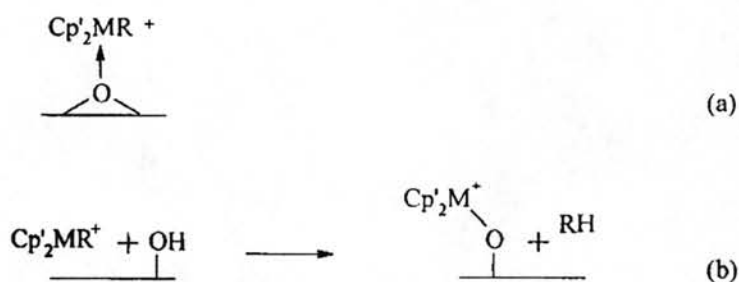
$$Cp_2'MR\ +$$
$$\uparrow$$
$$O$$

(a)

$$Cp_2'MR^+ + OH \longrightarrow Cp_2'M^+ \diagdown O + RH$$

(b)

Figure 2.23 Effect of surface hydroxyl groups on ionic metallocene catalysts [63]

However, highly active supported ionic metallocene catalysts for olefin polymerization can be prepared by pretreating the support with scavenger. It is assumed that pretreatment of the support with a scavenger serves to activate the support and compatibilize it with the ionic metallocene complex.

Lee *et al.* [64] used TMA pretreated-silica as the support for metallocene catalysts. The activity of supported catalysts showed dependency to H_2O content in silica, H_2O/TMA ratio, metallocene, and cocatalyst. The supported catalyst was also able to polymerize ethylene in the absence of MAO when common alkyl aluminum was used as the cocatalyst.

The surface aluminum and metallocene loading was studied by Santos *et al.* [65]. About 7 wt% of MAO can be supported on silica when the initial amount of MAO in mixture of silica was ca. 10 wt%. Depending on silica types, saturation of MAO supported on silica can occur at lower MAO contents.

Harrison *et al.* [66] compared a variety of silica and alumina supports with different degrees of surface hydroxylation as the supports. It was shown that as the concentration of OH groups on the surface of the support increased, more MAO could be impregnated and thus catalyst with more metallocene content could be produced. The most obvious benefit of supported catalyst with more metallocene was increased activities compared to catalysts with lower concentration of surface hydroxyl groups (increased activities both in kg PE/mol Zr/hr and kg PE /g-support/h). However, at high polymerization temperatures, leaching of catalyst from the support was observed. In lower polymerization temperatures, leaching was less significant, however, the morphology and bulk density of the polymer formed were still unsuitable for use in gas-phase polymerization.

For the case of propylene polymerization, a decrease in syndiotacticity was observed by Xu *et al.* [67] when the metallocene catalyst was supported on pretreated silica.

2.5.2.3 Chemically anchoring catalyst on support

Soga *et al.* [68] described a method to support zirconocenes more rigidly on SiO_2. The supporting steps are as follows: 1) Silica was treated with $SiCl_4$ to substitute the OH groups with chlorine atoms. 2) The resulting silica was filtered and washed with tetrahydrofuran (THF). 3) The solid was re-suspended in THF and a lithium salt of indene, dissolved in THF, was added drop-wise. 4) The resulting solid was filtered and washed again with THF. And to re-suspended solid in THF, $ZrCl_4$ 2THF dissolved in THF was added. The final solid part was separated by filtration, washed with THF and diethyl ether, and dried under vacuum. The supported catalyst produced in this way showed higher isospecificity than the corresponding homogenous system for propylene polymerization. MAO or ordinary alkylaluminums were used as cocatalysts. The yield was higher when MAO was used as the cocatalyst, but the molecular weight of the polypropylene was half of the molecular weight obtained when TIBA was used as the cocatalyst (3.4×10^5 g/mol and

7.2x10^5 g/mol, respectively). **Figure 2.24** shows the structure of the silica supported metallocenes.
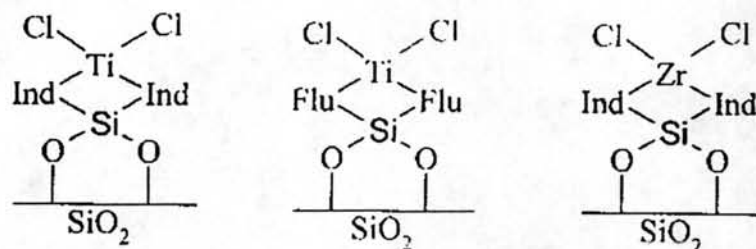

Figure 2.24 Structure of some silica supported metallocene catalysts [68]

Lee *et al.* [69] used spacer molecules in supporting metallocene catalysts onto silica to eliminate the steric hindrance near the active site caused by the silica surface (**Figure 2.25**).
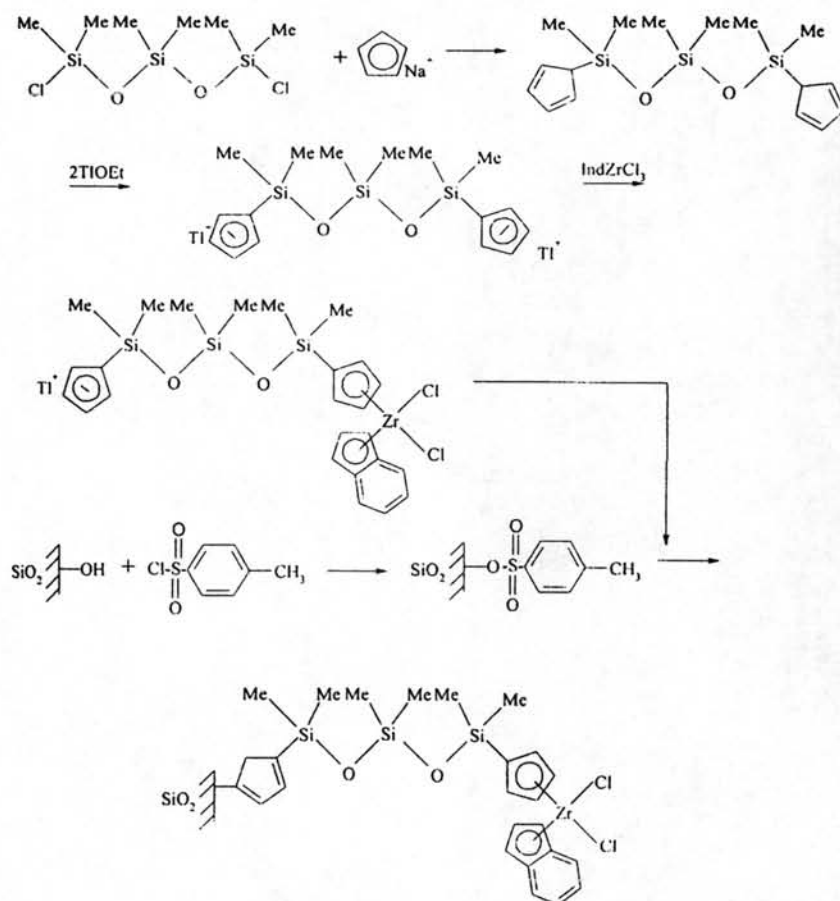
Figure 2.25 Mechanism for supporting metallocene catalysts on silica using spacer molecules [69].

By distancing the active site from the silica surface, higher catalytic activities but lower polymer molecular weights were obtained in comparison with analogous silica-supported catalysts without spacer between silica and $CpIndZrCl_2$.

Iiskola *et al.* [70] treated the surface of partially dehydroxylated silica with a silane coupling agents, $Cp(CH_2)_3Si(OCH_2CH_3)_3$, and then immobilized $CpZrCl_3$ onto cyclopentadienyl surface formed on the silica to obtain a highly active catalyst (**Figure 2.26**) for ethylene polymerization in the presence of MAO.

Depending on the calcination temperature and the modification methods, the catalysts show different

activities and produced polymers with different molecular weights. In general, when compared to homogeneous Cp_2ZrCl_2 systems, all the supported catalysts showed lower activities, but the polymers produced had higher molecular weights. On the other hand, when compared to homogeneous Cp_2ZrCl_2 systems, the activities of the supported catalysts were similar but molecular weights of polymer produced were lower and depended on the silica surface modification method used. The polydispersity index of the polymers ranged from 2.2 to 2.8.
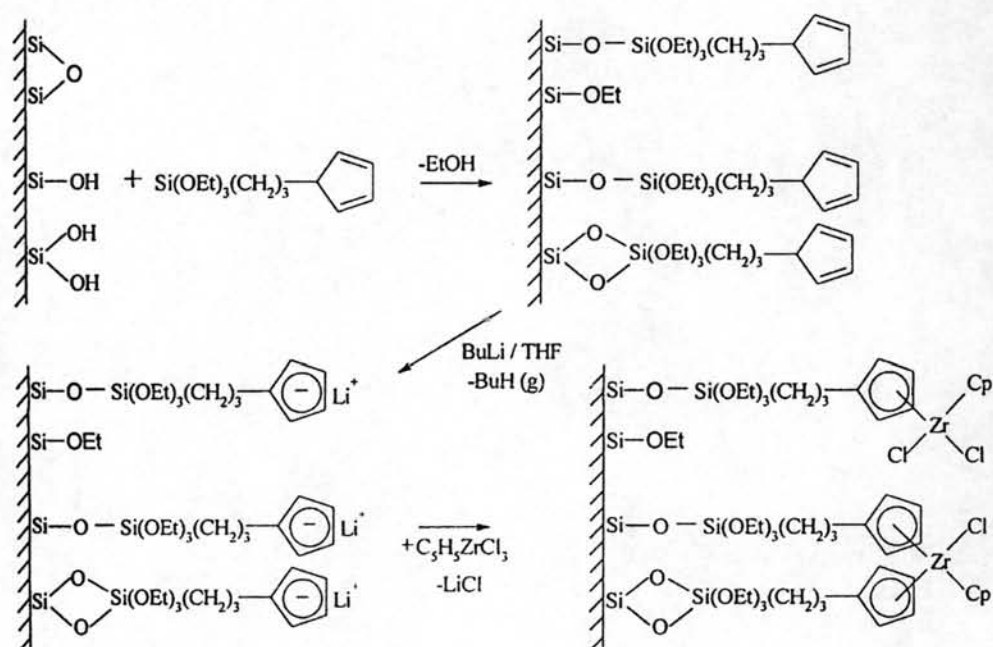

Figure 2.26 Modification of silica with $Cp(CH_2)_3Si(OCH_2CH_3)_3$ and preparation of supported metallocene catalysts [70].

2.5.2.4. Supporting on other supports

Lee and Yoon [71] studied ethylene and styrene homopolymerization initiated by cyclodexrin (CD) supported Cp_2ZrCl_2 or Cp^*TiCl_3

catalyst. The effect of CD pretreatment with MAO or TMA on catalyst behaviors was shown that either TMA or MAO could be used as cocatalyst for ethylene

polymerization while only MAO could initiate the styrene polymerization with α-CD supported catalysts.

Marques et al.[72] investigated ethylene polymerization by using Y zeolite-supported Cp_2ZrCl_2 catalysts. These system produced polyethylene with higher molecular weight and as narrow a molecular weight distribution as the homogeneous precursor, however, at relatively lower activity. The main characteristic that makes a zeolite a good support for metallocene catalyst seems to be a high Si/Al value and therefore a low Al density on the surface of the zeolite. This suggests that the presence of isolated aluminium atoms favors the fixation of zirconocene.

Moreover, Michelotti et al. [73] studied copolymerization of ethylene with higher α-olefins, such as 4-methyl-1-pentene, 1-hexene, 1-octene and 1-dodecene. The catalytic behavior of various metallocene (Cp_2ZrCl_2, Ind_2ZrCl_2, $Et(Ind)_2ZrCl_2$, and $Et(Ind)_2HfCl_2$) supported on methylalumoxane-pretreated HY zeolite (SiO_2/Al_2O_3=5.7) were compared.

Meshkova et al. [74] investigated ethylene polymerization in the presence of $ZSM-5(H_2O)/TMA-Et(Ind)_2ZrCl_2$. They found that the synthesis of MAO directly on the zeolite support and the absence of free MAO may be one of the

way of the reduction of supported zirconocene catalyst leaching. The positive temperature coefficiency of polymerization rate as well as the increase of molecular weight and melting point of PE obtained with the zeolite supported zirconocene catalyst developed in this work compared to PE produced by homogeneous zirconocene system confirms this view.

Weiss *et al.* [75] investigated the clay minerals kaolin and montmorillonite as inorganic carriers for the polymerization of ethylene and propylene with Cp_2ZrCl_2, Cp_2ZrHCl or Cp_2TiCl_2 catalyst and TMA as cocatalyst. The heterogeneous catalysts on kaolin were less active in ethylene polymerization than comparable homogeneous catalysts. But the heterogeneous catalysts on

montmorillonite are often more active in ethylene or propylene polymerization than comparable homogeneous catalysts.

Looveren *et al.* [76] studied methylalumoxane (MAO)-MCM-41 as support in the co-oligomerization of ethene and propene with $[C_2H_4(Ind)_2Zr(CH_3)_2]$. They were found that the MAO-MCM-41 was catalytically more active than the corresponding silica-based MAO derivative or the homogeneous system.

2.6 Mesoporous material

According to the definition of IUPAC, mesoporous materials are those that have pore diameters between 20 and 500 Å. Examples of mesoporous solids include silica gel and modified layered materials (4), but the pores in these materials are irregularly spaced and usually have a wide distribution of pore sizes. A considerable synthetic effort has been devoted to developing highly uniform frameworks with pore diameters within the mesoporous range. The structure of this mesoporous silicate and aluminosilicate family that has received the most attention is referred to as MCM-41

2.6.1 MCM-41

The most striking fact about the material MCM-41 is that, although composed of amorphous silica, it displays an ordered structure with uniform mesopores arranged into a hexagonal, honeycomb-like lattice. A nice example of this structure can be seen in figure 1. In this figure one looks directly inside the uniform mesopores, which are separated from each other by thin walls of amorphous silica, approximately 1 - 1.5 nm thick. The mesopores are not necessarily running in a straight way through the silica matrix, but they can be slightly curved, thereby

retaining the hexagonal ordering, as can be seen in figure 2. From the micrographs it is apparent that MCM-41 has a very large void fraction, due to the presence of the mesopores, and concomitantly a rather low density. As a result MCM-41 displays a very large specific surface area of approximately 1,000 $m^2 g^{-1}$. This property makes MCM-41 very interesting to be used as a support material for heterogeneous catalysts. Moreover, because MCM-41 exclusively contains mesopores it can both provide access to large molecules and alleviate diffusion problems, which are frequently encountered in microporous materials such as zeolites. It should be noted, however, that the one-dimensional nature as well as the relatively large length of the mesopores (usually extending over several hundreds of nanometers) could also give rise to transportation limitations.

Despite the advantages mentioned above there is one eminent drawback associated with MCM-type materials, *viz.* the rather limited stability, which is a result of the very thin, amorphous pore walls. Because of the very large mesopore surface area the pore walls are extremely reactive towards a number of agents, resulting in the collapse of the thin walls upon exposure to these agents. From a viewpoint of application the instability of silica support materials towards steam (either co-fed as a diluent or produced during catalysis), resulting in the chemical evaporation of silica, makes silicasupported catalysts inappropriate for a rather large range of processes. Furthermore, there is a notable instability of MCM-41 towards

mineralizing agents, *i.e.* hydroxide and fluoride ions, because these agents dissolve silica. As a result the stability of MCM-41 in aqueous solutions is limited to pH values ≤ 7. Moreover, the chemical affinity of the pore surface towards precursors of catalytically active phases sometimes also results in the collapse of the hexagonal framework structure. An example of this behaviour, which will be dealt with in chapters 4 and 5, is the reaction with aqueous impregnation solutions containing common molybdenum precursors, *viz.* (poly) molybdate anions. Opposed to this behaviour towards molybdenum precursors, the interaction of the MCM-41 pore surface with certain common nickel precursors is relatively weak, resulting in low dispersions of the active phase.