CHAPTER II

THEORY AND LITERATURE REVIEW

2.1. Definition of Ziegler-Natta catalyst

A Ziegler-Natta catalyst can be defined as a transition metal compound bearing a metal-carbon bond able to carry out a repeated insertion of olefin units. Usually, though not necessarily, the catalyst consists of two components (a transition metal salt; most frequently halide) and a main-group metal alkyl (activator) which serves the purpose of generating the active metal-carbon bond [1].

Since Ziegler and Natta discovered this catalyst in 1954, the development of more efficient and more catalysts have been relentless and still in progress today. The first generation catalyst, catalyst based on $TiCl_3/AlCl_3$ or $TiCl_3/AlEt_2Cl$ give polypropylene containing 90% isotactic index. However, the removal of catalytic (deashing) and separation of the atactic polymer fraction were required. In the second generation catalyst, Lewis base introduced into the catalyst and it gave higher activity and % isotactic index. A drastic development was achieved with the third generation catalysts which composed of $TiCl_4$ supported on $MgCl_2$ with Lewis base as and electron donor, leading to highly active catalyst and isotactic index. In the fourth and fifth generations new types of internal and external Lewis bases such as diesters, diethers and silane were used.

At the same time, sixth generation catalyst approach to homogeneous stereospecific catalysts (metallocene catalyst) combined with methylaluminoxane (MAO) were able to provide highly stereoregular isotactic or syndiotactic polypropylene in extremely high yield.

2.2. Heterogeneous Ziegler-Natta catalyst [1, 11]

Early the use of titanium-aluminium alkyl catalysts to produce polyethylene grew at a slower step than the chromium oxide on silica catalysts. The main difficulty with the catalysts was that the yield of polymer per unit catalyst in low pressure processes was so low that the catalyst residuals in polymer had to be extracted. When the market demand for a low molecular weight, narrow MWD resin was sufficient to motivate the study in this system.

The advance in titanium-aluminium alkyl catalysts resulted from attempts to form supported catalyst on a variety of materials. Although many of this new supported catalysts no longer consisted of titanium tetrachloride or alkyl halide alone. The initially supported catalysts were transition metal compounds reduced in the presence of SiO_2, Al_2O_3, SiO_2/Al_2O_3, ZnO_2, TiO_2, and MgO.

In the mid-1960s the research on supported catalyst system began to reach achievement. Possibly stimulated by Cabot's 1960 patent (BP 969,761) Solvay, Hoechst, Mitsui, Montecatini, and B. F Goodrich came out with a series of patents acting with supporting halotitanium species on hydroxymagnesium halide (Mg(OHCl)). However, the exact structural features of the support in promoting the desired polymer yield and properties were not clear. The accepted reaction of this system is:

$$ClMgOH + TiCl_4 \longrightarrow ClMgOTiCl_3 + HCl \qquad \text{e.q. 2.1}$$

After 1968, $MgCl_2$ has been almost invariably used for all supported catalysts because it allows the catalysts the high activity and can control stereospecificity.

$MgCl_2$ has two crystalline phases, the commercial α form and the less stable β from. The α form have the layer structure of the $CdCl_2$ type and shows a cubic close-packed stacking (ABC…ABC…) of double chloride layers with interstitial Mg^{2+} ions in sixfold coordination that similar to the γ-$TiCl_3$. The β form, on the contrary, shows a hexagonal close packing like that of α $TiCl_3$.

2.2.1. Catalysts based on magnesium chloride with transition metal compounds

Some of the most promising catalysts, especially for propylene polymerization, have resulted from the use of magnesium chloride as supports. An early patent in 1960 described the use of milled $MgCl_2$ with electron donor in propylene polymerization. However, there were the discoveries by Montecatini-Edison Co. and Mitsui Petrochemicals Ind. that catalysts, prepared from $MgCl_2$, $TiCl_4$ and electron donors, and activated by a mixture of trialkylaluminum and an electron donor, could polymerize propylene with a high yield (> 50 kg PP/g Ti) and with good stereospecificity (isotactic index = 90%). This has set the scene for much of the present explosion in catalyst development. The initial patents described basic routes for catalyst preparation. (Table 2.1)

Table 2.1 Magnesium chloride based catalysts

Catalyst preparation	Company	Date	Patent number
-$TiCl_4$ ball milled with $MgCl_2$	Montecatini	1968	BP 1,286,867
-Reaction of $MgCl_2$ with halogenated titanium compound	Montecatini	1969	BE 744,221
	Montecatini	1969	BE 747,846
-$TiCl_4$ reacted with $MgCl_2.nROH$	Mitsui	1968	JP 46-34092
or $MgCl_2.nH_2O$ or	Mitsui	1968	US 3,642,746
$MgCl_2$.Lewis base	Mitsui	1968	JP 46-34093
-Reaction of a magnesium dihalide electron donor adduct ($MgCl_2.6C_2H_5OH$) with a titanium compound	Hoechst	1969	BE 755,185

2.2.2. Catalysts based on magnesium alkoxide with transition metal compounds

Active catalysts for ethylene polymerization have been prepared by reacting titanium tetrachloride with magnesium alkoxides. The original structure of the alkoxide is usually destroyed during reaction and new species of increased surface area are produced. Some typical examples are listed in Table 2.2.

Treatment of solid $Mg(OR)_2$ or $Mg(OR)Cl$ wherein, R is alkyl group (sometimes prepared in a preliminary stage, for example, from Grignard + $Si(OR)_4$) with interal donor and excess $TiCl_4$ diluted in aromatic or halogenated solvents. In this case, $MgCl_2$ is obtained from the reaction between the Mg compound and $TiCl_4$ and its by-products (Ti-alkoxides) are eliminated during the treatment and the following washings.

$$3Mg(OR)_2 + 2TiCl_4 \longrightarrow 3MgCl_2 + 2TiCl(OR)_3 \qquad \text{e.q. 2.2}$$

Table 2.2 Magnesium alkoxide based catalysts

Catalyst preparation	Company	Date	Patent number
-$TiCl_4$ reacted with $Mg(OR)_2$ or a complex magnesium alkoxide	Hoechst	1968	US 3,644,318
	Hoechst	1969	BE 758,994
	Solvay	1969	BE 743,325
-Reaction of magnesium alkoxide and an acid halide with a tetravalent titanium compound	Hoechst	1971	BE 780,530
	Solvay	1971	NL 216,195

2.2.3. Catalysts based on magnesium alkyl with transition compounds

The reactions between magnesium alkyls and titanium compounds have been used as a means of preparing highly active catalyst systems. Stamicarbon et al have prepared highly active catalysts using $AlEt_2Cl$, Bu_2Mg, and $TiCl_4$. Shell International Research has used the reduction of $TiCl_4$ with organomagnesium compounds to prepare highly active catalysts for ethylene polymerization. These catalyst systems have been extensively investigated by Howard and co-workers, as well as by Radenkov et al. Characterization studies have revealed that the catalysts contain appreciable amounts of magnesium chloride and they have nodular structures. The size of the primary particles was believed to be less than 0.05 μm.

The reaction of MgR_2 or $MgRCl$ (optionally dispersed on SiO_2, Al_2O_3 or other carriers) with Lewis base (alcohol) is shown below.

$$MgR''_2 + R'OH \longrightarrow Mg(OR')_2 + 2R''H \qquad \text{e.q. 2.3}$$

Where R' and R" can be the same or different alkyl groups.

After that, the reaction with chlorinating agents to form active $MgCl_2$, followed by hot treatment with internal donor and excess $TiCl_4$ as the following.

$$Mg(OR')_2 + Ph(COCl)_2 \longrightarrow MgCl_2.Ph(COOR')_2 \qquad \text{e.q. 2.4}$$

$$Mg(OR')_2 + HCl \longrightarrow MgCl_2 + 2R'H \qquad \text{e.q. 2.5}$$

$$Mg(OR')_2 + Ph(COCl)_2 + TiCl_4 \longrightarrow MgCl_2.TiCl_4.Ph(COOR')_2 \qquad \text{e.q. 2.6}$$

2.2.4. Catalyst based on magnesium hydrocarbyl carbonate with transition metal compounds

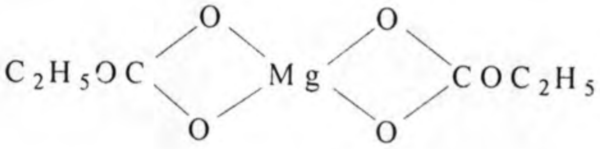
Magnesium hydrocarbyl carbonate based catalyst is prepared by the reaction of carbon dioxide and a magnesium dihydrocarbyloxide (Mg(OR)(OR'))

$$Mg(OR)_2 + nCO_2 \longrightarrow Mg(OR)_{2-n}(OCOOR)_n \qquad n = 1.2 \qquad \text{e. q. 2.7}$$

Where R and R' are alkyl or aryl groups which groups can be the same or different groups. However, the most preferable is magnesium dialkoxides. The alkoxide groups contain from 1 to 8 carbon atoms such as magnesium ethoxide, magnesium isopropoxide, magnesium di-n-butoxide, ethoxy magnesium isobutoxide, and magnesium diphenoxide. Magnesium ethoxide is the most preferable for prepared magnesium hydrocarbyl carbonate.

$$Mg(OEt)_2 + nCO_2 \longrightarrow Mg(OEt)_{2-n}(OCOOEt)_n \qquad n = 1,2 \qquad \text{e.q. 2.8}$$

The reaction of $Mg(OEt)_2$ with carbon dioxide is an exothermic reaction. The temperature of the mixture begins to increase as carbon dioxide is fed to the slurry of $Mg(OEt)_2$ in ethanol. The proposed structure of magnesium hydrocarbyl carbonate is shown below (according to US patent number 6,429,270 B2).



2.3. Studies on Ziegler-Natta catalysts

The early focus was solely on productivity of Ziegler-Natta catalysts, but now fluffy bulk density, fluffy morphology, fluffy fines, catalyst kinetics, catalyst handling characteristics and comonomer incorporation efficiency are just as important. Desirable catalysts give having optimum characterization of polyethylene shown in Table 2.3.

Table 2.3 Features of the ideal ethylene polymerization catalyst

Catalyst features	Benefits
high productivity	elimination of deashing and color and stability improvement
high comonomer incorporation efficiencies	broad slate of product density
in situ branching	elimination of added comonomer
MW and MWD control	broad ranges of resin
comonomer distribution homogeneity	increasing of resin properties
high bulk densities	increasing of space-time yield
good morphology control	good handling characteristic
low cost	economic impact
no. manufacturing by-product	low environmental impact
versatility	no limitation of processes or resin grades
multiple active center	multimodal resins
carcinogen free	food packaging application

2.3.1. Replication and polymer morphology

The reasons why full control of the polymer morphology is highly desirable in polymer manufacturing can be easily understood in terms of process economics and viability. Regular polymer morphology (particle with high density, regular shape, and narrow particle size distribution) means both a high reactor throughput, good flowability, and packing, no need of further pelletization. Finally, the absence of fines prevents reactor fouling and explosion hazards during handling, and the absence of coarse particles eliminates undesirable fluidization effects.

The possibility of controlling the polymer shape, size, and PSD to some extent through the catalyst based on the fact that the polymer usually tends to duplicate, on a larger scale, the physical characteristics (shape and texture) of parent catalyst. This phenomenon, usually called "replication", is closely related to how the catalyst grain expands as the polymerization proceeds. The most recent findings on the mechanism of polymer particle growth will be:

- As soon as the polymer starts, the catalyst grain begins to disrupt into a huge number of small fragments. This process is very fast and proceeds to the crystallite dimensions or even smaller.

- The catalyst fragments, though no longer in contact with each other, are kept together and uniformly dispersed in the polymer acting as "cements"

- The fragments are spread outward as the particle grows but still remain uniformly distributed across the particle cross section. This implies that the polymer growth occurs around each fragment.

A fast and extensive catalyst "fragmentation" and uniform polymer growth rate across the particle seem, thus, to be the key features for a faithful replication.

As far as the catalyst is concerned, a proper balance between reactivities and mechanical properties appears necessary, and this is possible only if the following requirements are met:

- High surface area,

- High porosity with a large number of cracks evenly distributed throughout the mass of granule,

- High enough mechanical resistance to withstand handling, but low enough to allow breakage into microscopic particles during the polymerization,

- Homogeneous distribution of active centers and free access of monomers up to the innermost zones.

On the other hand, the polymerization conditions must be such as to avoid mass transfer limitation phenomena, which could result in an uneven polymerization rate across the particle.

The most popular among such models is perhaps the "Multigrain Model" (MGM) (see Fig. 2.1) as described below.

- Catalyst fragmentation is already complete at time zero; and

- Catalyst fragments are of uniform size and the polymer grows as a spherical globule (microparticle) around each catalyst fragment [1].

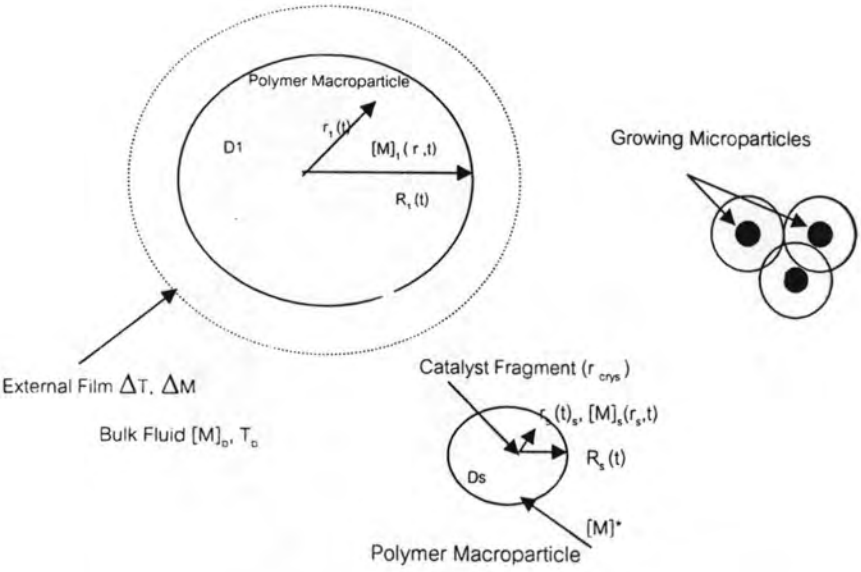


Fig. 2.1 Schematic drawing of the multigrain model.

2.3.2. Activity of catalyst

The catalyst activity is the economical factor. The cost of catalysts still accounts for a large fraction of manufacturing cost of polyethylene. However, high activity can solve the problem of the catalytic residue, which causes the problems in the physical properties, flavor, taste, color of polymers. For example, the polymer use for food packaging materials must be odorless and off-taste. It is toxic to the human body and thus has limited to uses.

2.3.3. Hydrogen response of catalyst for process control

Generally, hydrogen gas is used for polymerization processes which act as a chain transfer agent. Molecular weight of polymer was controlled by adding different hydrogen concentrations. Therefore, the hydrogen response of catalysts has a relationship with the activity of catalysts and the average molecular weight of polymer.

The catalyst having low hydrogen response at high concentration of hydrogen in polymerization process was deactivated. For example, bimodal HDPE of Hostalen process, the polymer was produced in two reactors. The first reactor produced low molecular weight part mainly forming the crystalline and the second reactor was produced high molecular weight part [2]. Many researchers have revealed the method of making catalyst with high hydrogen response [13].

2.3.4. Activity and hydrogen balance

Several earlier inventors required the catalysts having a high activity or low melt flow index (MFI). For the polymerization condition which gives high MFI, a drastic drop in activity of catalysts occurs. The unique catalyst has to good activity and hydrogen response balance. Following, Garoff and co-worker [2], the equation for calculation activity balance is proposed as in equation 2.9.

$$AB = \text{Activity balance} = \frac{(A+A^*)}{2} \cdot \frac{\log(MFR_{2^*} - MFR_2)}{(A-A^*)} \qquad \text{e.q. 2.9}$$

A = activity (kg PE/g cat. h) at low MFR polymerization

A* = activity (kg PE/g cat. h) at high MFR polymerization

MFR_2 = at low MFR polymerization condition

MFR_{2^*} = at high MFR polymerization condition

2.3.5. Effect of electron donor

Roles of internal donor (aromatic monoesters: ethyl benzoate)

1. To prevent the coagulation of $MgCl_2$ particles during the milling or dissolve process, resulting in an enhancement of the effective surface area. Both monofuctional and bifuctional are essentially complexed to Mg rather than Ti. The structure of complexes could be different for the different donor types. Mono and bifuctional Lewis bases could form either 1:1 chelate complexes with tetracoordinated Mg ions on the (110) face or 1:2 complexes with adjacent pentracoordinated Mg ions on the (100) face. The possible models for donor coordination on Mg faces are shown in Figs. 2.2 and 2.3.

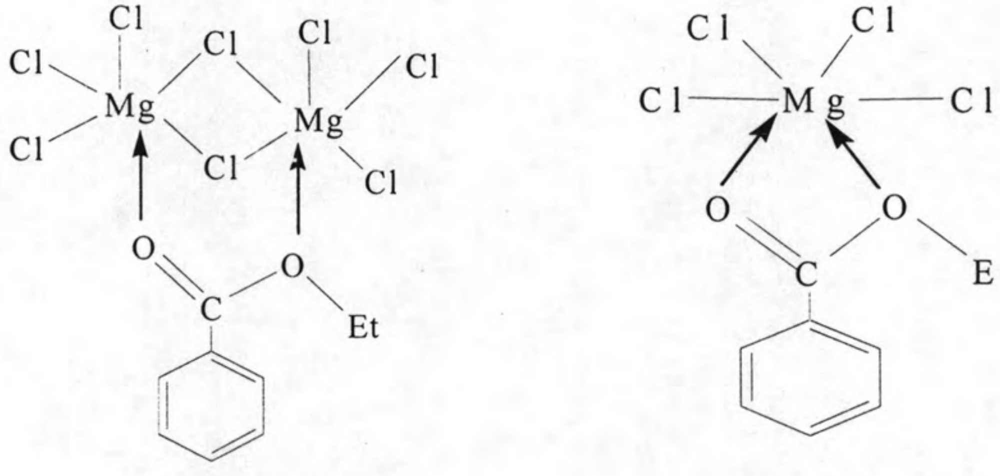
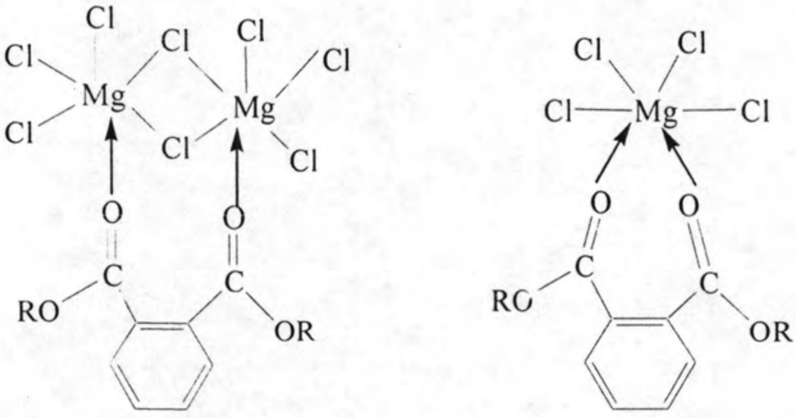


Fig. 2.2 Possible models for monofuction donors coordination on the (100) (a) and (110) (b) faces of $MgCl_2$.



(a) (b)

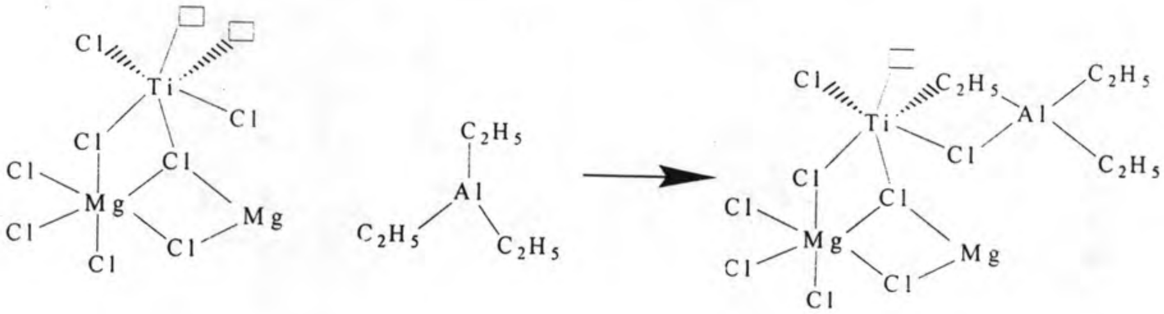
Fig. 2.3 Possible models for bifuctional donors coordination on the (100) (a) and (110) (b) faces of $MgCl_2$.

2. To prevent the formation of non-stereospecific sites by adsorbing on the $MgCl_2$ surface, where $TiCl_4$ is supported to form non-stereospecific site.

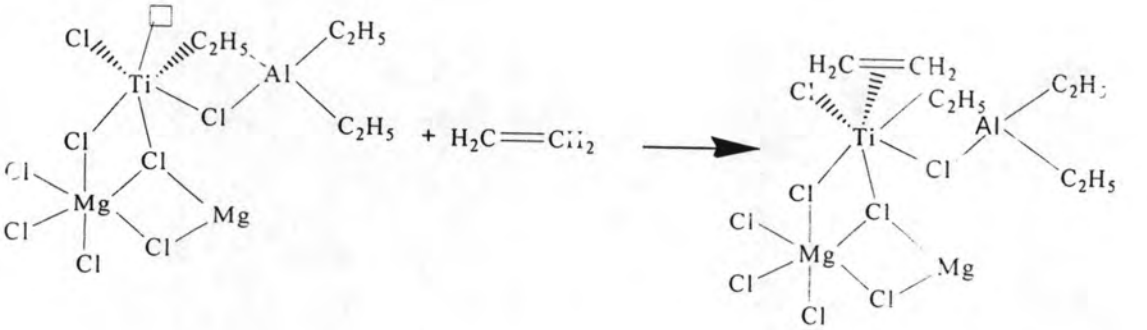
3. Formation of highly isospecific site and to be replaced by external donors in the formation of more isospecific sites.

2.4. Reaction and mechanism of Ziegler-Natta catalyst [14]

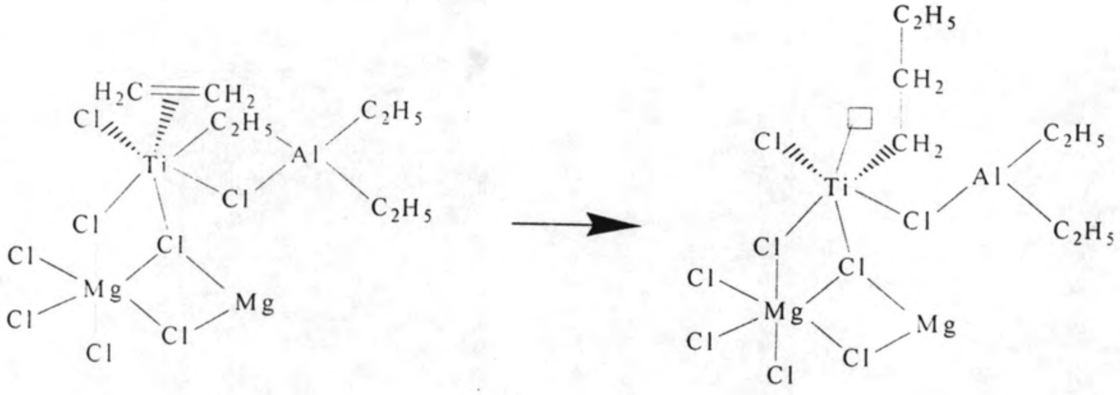
Supported Ziegler-Natta catalysts comprised $MgCl_2$ (supported catalyst), $TiCl_4$ (active species) and Al $(C_2H_5)_3$ (cocatalyst) according to following formula:



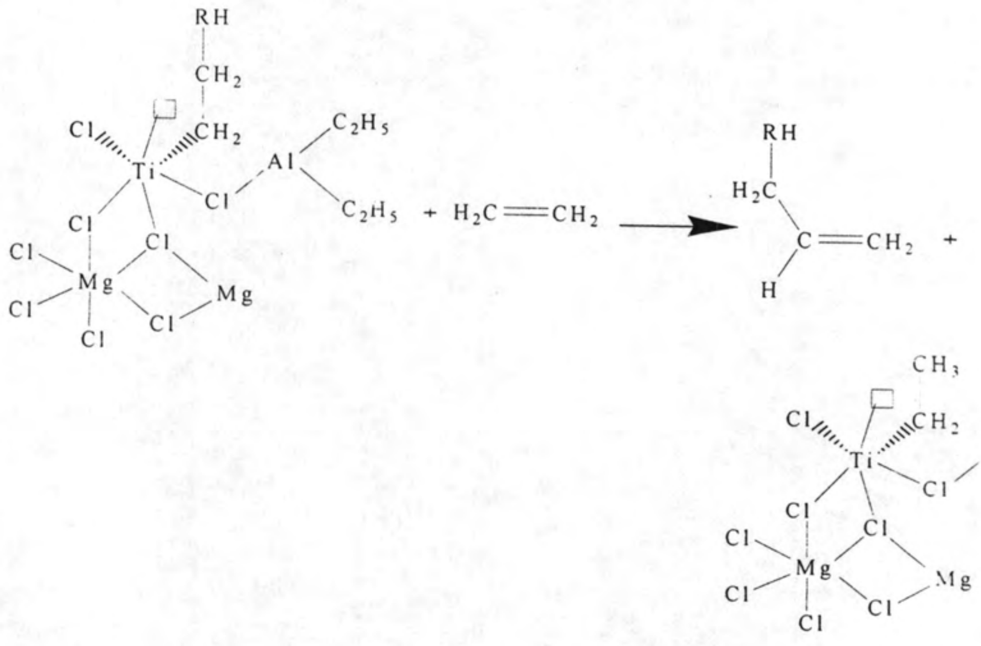
The residual compound is an octahedral Ti complex with a coordination gap that acts as an active center in which the polymer chain is initiated. This coordination gap is a vacant ligand position able to coordinate with a monomer molecule. This is the starting point for a polyethylene chain.

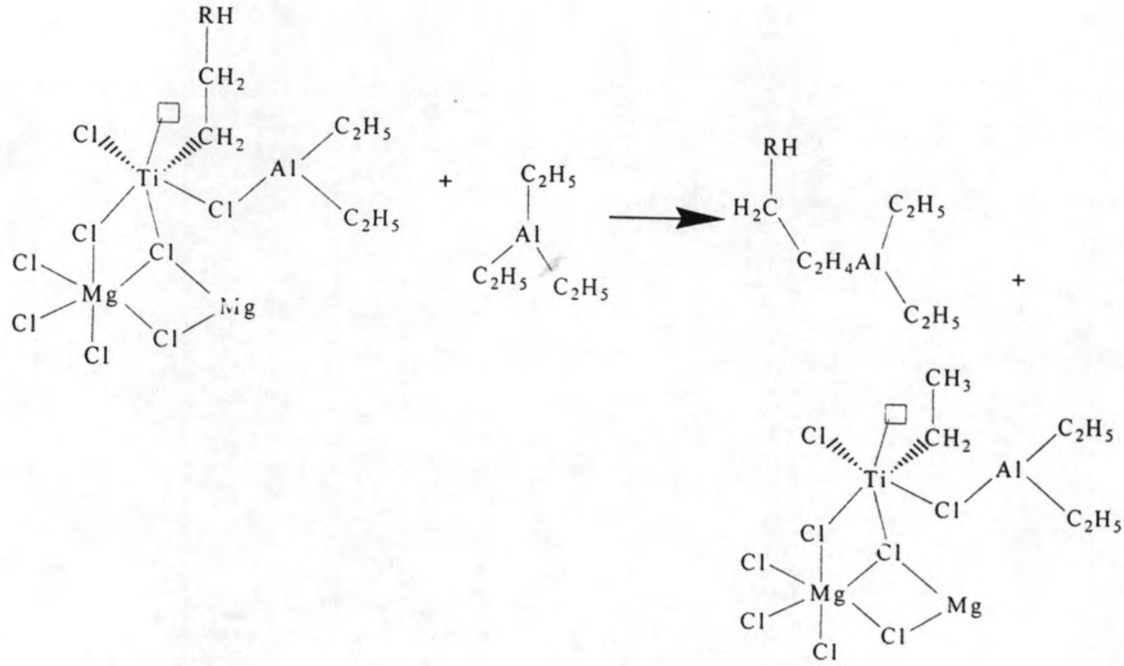


The chain propagation is an insertion process where the monomer molecular is bonded to the Ti complex and then inserted between the polymer chain and the Ti active center. This step is repeated many times.

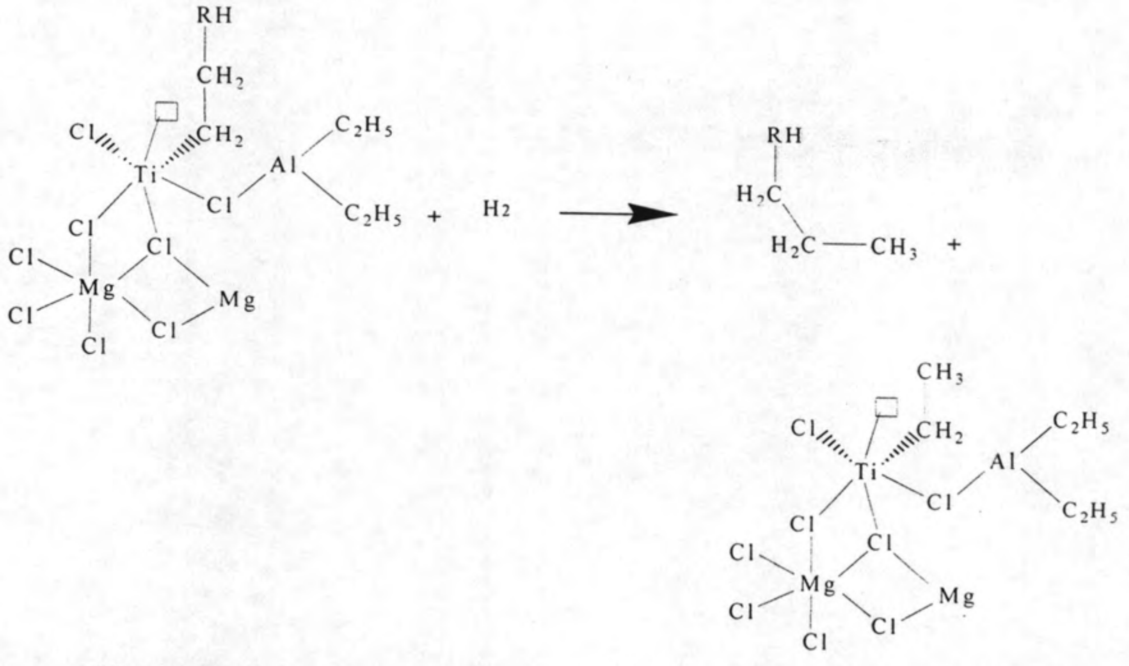


During the chain propagation step, there is also a chain transfer step that takes place in which the polymer chain is removed from Ti complex and bonded to a monomer molecule or to the Al-alkyl as shown below.





There is also a deactivation step in which the polymer chain is terminated. The normal termination step is forced by adding hydrogen, which is bonded to the Ti complex and the polymer chain is terminated and has reached the final molecular weight:



Hydrogen is used as a molecular weight controller by deactivating the Ti complex to produce a low molecular weight polymer.

2.5. Literature review

In 1984, Berthold et al. [34] prepared supported catalyst from the reaction of magnesium ethoxide with $TiCl_4$ at 90°C. The catalyst was treated at 130°C for 60 h. The catalyst had high Ti content (25.4 wt %) and produced broad MWD polyethylene (MWD = 22).

In 1985, Arzoumanidis and Lee [19] prepared a Ti catalyst for propylene polymerization. The support comprised the reaction of CO_2 and a magnesium ethoxide suspension in alcohol. After that the reaction product was precipitated out on the initially mixing with the inert hydrocarbon or halohydrocarbon by a chlorinating agent ($TiCl_4$, CCl_4 or diethyl aluminium chloride). It was found that to replace polar alcohol solvent by hexane or chlorobenzene needed long reaction time.

In 1987 and 1988, Nestlerode et al. [15, 16] prepared magnesium ethyl carbonate ($C_4H_{10}O_2Mg.xCO_2$, where; x = 1.2-1.3 and MW = 170) as solid particles having a uniform shape by impregnating on an inert carrier silica. CO_2 was used in solubilizing the magnesium ethoxide for controlling catalyst morphology. These supports showed excellent productivity, selectivity and morphology.

In 1993, Cohen et al. [17] prepared magnesium ethyl carbonate support from magnesium ethoxide, 2-ethyl-1-hexanol and CO_2. It shows high activity of polypropylene.

In 1994, Job (jointed with Nestlerode team) [20] reported that the contact of magnesium ethyl carbonate solution with phenolic compound could enhance catalyst acidity in the presence of electron withdrawing group on phenolic ring such as 4-nitrophenol.

In 1995, Rauleder et al. [18. 21] studied storage-stability of solutions of magnesium ethyl carbonate and magnesium methyl carbonate. They found that the characteristics of solutions were unchanged after 6 weeks storage in a tightly sealed glass bottle.

In 1997, Wagner et al. [22] prepared magnesium ethyl carbonate by using spray drying or shape-shifted technique. Fume silica was used as a carrier. By this technique, magnesium ethyl carbonate was converted to magnesium ethoxide of which size and shape of the particles can be controlled. It was found that polymer has reduced level of fine particles and high bulk density.

In 1998, Garoff et al. [2] prepared Ziegler-Natta catalyst from butyl octyl magnesium with 2- ethyl-1-hexanaol/ethyl aluminium dichloride as chlorinating agent and $TiCl_4$. The catalyst exhibited high activity and hydrogen response balance (AB = 5) suitable for bimodal polyethylene process.

In 1999, Lee and Trost [23] prepared uniform solid particles of magnesium ethyl carbonate by using emulsion system of two phases: mixture of magnesium ethyl carbonate with heptane (nonmiscible phase) and the mixture of ethanol and methanol (miscible phase). The particles were formed by adding two phase mixtures under vigorous agitation to hexane and contacting the formed particles with $TiCl_4$ and electron donor.

In 2000, Karayannis et al. [24] prepared magnesium alkyl carbonate precursor using magnesium ethoxide, 2-ethyl-1-hexanol, and CO_2 feeding at temperature of 93 °C. The mixture was precipitated with $TiCl_4$ on *in-situ* formed tetraethoxysilane carrier.

In 2001, Kang et al. [10] studied propylene polymerization with $TiCl_4$ supported on magnesium ethyl carbonate precursor. The precursor was prepared from the reaction between magnesium ethoxide suspension in ethanol with CO_2. The performance of catalyst was compared with milled-$Mg(OEt)_2$ supported catalyst. This catalyst showed good morphology but low activity (4 kg PP/(g Ti atm .h)).

In 2001, Wolf et al. [30] studied chemical species of Ziegler-Natta catalyst synthesized from $TiCl_4$ and magnesium ethoxide. The catalyst was treated at 110-130°C for 40-60 h. It was observed that the treated catalyst presented the highest catalyst activity. Thermal treatment increased Ti content and titanoxane site in the catalyst. It produced HDPE with high molecular weight.

In 2002, Morse et al. [25] prepared catalyst with the precursor of magnesium ethyl carbonate with the size of 15 μm. The catalyst had 1.5-3.5% Ti (w/w). Then, the catalyst was preactivated with triethyl aluminium and prepolymerized with propylene. The yield of polypropylene was in the range of 22-30 kg PP/g catalyst.

In 2003, [27] Job et al. disclosed the effect of chlorinating agent with the mixture of magnesium ethoxide and magnesium ethyl carbonate by using the multi-step chlorination process. The chlorinating agent used in the catalyst preparation was $TiCl_4$, $SiCl_4$, ethyl aluminium dichloride (EADC) or diethyl aluminium chloride (DEAC). It was found that the high activity was obtained using $TiCl_4$ followed by EADC.

In 2006, Zhu et al. [13] reported high activity and good hydrogen response Ziegler-Natta catalyst. It was synthesized by dissolving magnesium chloride in 2-ethyl-1-hexanol and hexamethyldisiloxane at high temperature, then added ethyl benzoate and tetraethylorthosilicate (TEOS). It was reacted with $TiCl_4$. It was found that the catalyst had high activity (41 kg/g catalyst), producing polyethylene with high MFI.