

Chapter III

Theory

High density polyethylene (HDPE) is a major commodity thermoplastic used for a variety of applications such as containers, and packaging film. Because of its industrial importance, this extraordinary polymer has been manufactured since early 1965. The production of HDPE continues to be a very active area of technology. In recent years, the world wide recession, reduced and varying demands, overcapacity, and fierce price competition have caused polyolefin manufacturers to modify the existing facilities to interchangeably manufacture a variety of resins. Now, improved catalysts and processes have been developed to produce HDPEs with desired properties at a lower manufacturing cost.

3.1 General Concepts of Ziegler-Natta Catalyst

Ziegler-Natta catalysts are formed by reacting a metal alkyl (or hydride) and a transition metal salt, such as $AlEt_3 + TiCl_3$, under an inert atmosphere. Binary mixtures have usually been used; however more than one metal alkyl or transition metal salt can be present. It has been manifested that there is a definite advantage to have a ternary or quaternary system in only a few cases. Organic and inorganic molecules are added to modify some aspects of the polymerization; hydrogen, for example, is added to terminate chain growth process.

The patent literature usually claims all metal alkyls (hydrides) of group I to III base metals and transition metal salts of group IVB to VIIB, including Sc, Th and U. This definition is too broad when applied in the laboratory. In practice, only a few group IB to IIIB metal alkyls are effective. Aluminum alkyls have been overwhelmingly preferred. The most studied transition metal salts were based on Ti, V, Cr, Co and Ni metals.

Just because a metal alkyl or a transition metal salt forms an active catalyst for a particular monomer. In practice, the choice of a particular combination of a metal alkyl and a transition metal salt is largely governed by the monomer structure. For example, Ziegler-Natta catalysts based on group VIII transition metal salts, such as $AlEt_2Cl + CoCl_2$, readily polymerize dienes but not ethylene or α -olefins. On the other hand, the catalysts based

other hand, the catalysts based on group IVB, VB, and VIB transition metal are active for both dienes and α -olefins, such as Ti-, V-, and Cr- based catalysts. A particular catalyst: $(C_5H_5)_2TiCl_2$, in combination with an aluminum alkyl, polymerizes ethylene but not propylene.

Ethylene is polymerized by a substantially larger number of catalysts than are propylene and higher α -olefins. While all catalysts which are active for polymerization of α -olefins are also active for polymerization of ethylene, but the reverse is not true[47].

Sometimes an exchange reaction occurs between the transition metal and the metal alkyl to generate a new transition metal salt. When $Ti(OR)_4$ and $AlEt_2Cl$ are reacted, for example, the exchange shown in Eq.3.1 takes place.



The real catalyst may be the end product of this exchange rather than the starting mixture; at an Al/Ti ratio of 4, $\beta-TiCl_3$ is formed.

The notation " Ziegler-Natta Catalyst " has been adopted in this thesis. The reader may have noted that the literature contains a variety of other designations for this catalysts, including Ziegler catalyst, Ziegler-type catalyst, Natta catalyst, coordinated-anionic catalyst, mixed metal complex catalysts, etc. In the initial period after Ziegler's discovery, the catalysts was reported by his school to polymerize ethylene (and copolymerize ethylene and propylene) contained the transition metal in the highest oxidation state, e.g., $TiCl_4$ and VCl_4 [48]. These were named as Ziegler catalysts. Later, Natta discovered that polypropylene of greater isotacticity was produced if preformed lower oxidation state transition metal salts were used, such as $TiCl_3$ and VCl_3 . While he referred to these as modified Ziegler catalysts or Ziegler-type catalysts, others, in order to separate them from Ziegler catalysts, designated as Natta catalysts. Particular catalysts developed by other laboratories sometimes assumed the names of that company to denote a special modification of the catalyst.

Some researchers chose to refer to all of the above as Ziegler-type catalysts, others used the name Ziegler-Natta catalysts so as to include the large number of catalyst discovered and elucidated later, not only by the Natta school, but also by other researchers worldwide. The latter nomenclature has been favored in more recent years. It

means that the active catalyst contains a metal alkyl (or hydride) and a transition metal salt regardless of additional modifications, such as the presence of third component, support of the catalyst, and in situ synthesis of catalyst component.

3.2 The Role of $MgCl_2$ as Support for Ethylene Polymerization Catalysts.

$MgCl_2$ has a layer structure. Using the Artman-Cossee technique it was found that three different types—one single and two double vacancies of $MgCl_2$ —can be distinguished on the surface of a magnesium dichloride crystal. The free vacancy places are responsible for the interaction with $TiCl_4$ and Lewis base[49].

$MgCl_2$ has been found to be the ideal support, its host lattice can support chiral titanium-active sites. This has been widely attributed to near isomorphism of $MgCl_2$ and $TiCl_3$ crystals. There are two crystal forms of $MgCl_2$: the cubic close-packed form, which is very similar to the structure of $\alpha-TiCl_3$; and the hexagonal close-packed form, which is very similar to the structure of $\alpha-TiCl_3$.

Crystals of both $TiCl_3$ and $MgCl_2$ consist of two planes of chlorine atoms sandwiching a plane of metal atoms. The titanium atoms occupy two-thirds of the octahedral sites in $TiCl_3$ which the magnesium atoms occupy all the sites. The dimensions of the layers are similar in the two compounds. Furthermore, through a mechanical treatment, $MgCl_2$ can be partially distorted by a $\pm 60^\circ$ rotation of the Cl-MgCl triple layers. A similar distortion of $TiCl_3$ can be effected by ball-milling.

There are three faces of $MgCl_2$ crystalline of interest. The (100) plane has four coordinate exposed Mg atoms. The (110) face of $MgCl_2$ and the (100) face of $TiCl_3$ are very similar both having five-coordinated metal atoms at the surface. Both basal planes (001) of $TiCl_3$ are occupied entirely by Cl atoms; there are no exposed metal atoms. It will be shown that the dimeric Ti_2Cl_6 epitactically placed on the (110) face of $MgCl_2$ is the most likely candidate for stereospecific active sites.

$MgCl_2$ also has desirable morphology as a support for the new generation of olefin polymerization catalyst. It is a highly porous polycrystalline material probably due to a large number of uniformly distributed microcracks. It is sufficiently resistant to rupture by mechanical manipulation and used in gas phase polymerization, but it is weak enough so that it is broken down during polymerization. The porous morphology permits the

diffusion of monomer into the interior of the catalyst particles and replicates it to the polymer.

A third desirable characteristic of $MgCl_2$ is its low electronegativity among metal halides. The supports with electronegativities less than that of $TiCl_3$ are thought to promote the coordination of monomer to titanium via π -back donation. Soga et al. [50] has shown that $MgCl_2$, $MnCl_2$ and $CoCl_2$, which have lower electronegativity than $TiCl_3$, can increase productivity of olefin polymerization. In contrast, highly electronegativity metal halides retard the polymerization.

In conclusion, $MgCl_2$ is a rather inert chemical so it can be left in the polymer without a deashing process.

3.3 The preparation of high activity catalysts

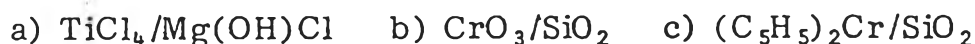
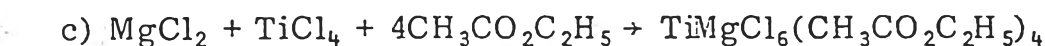
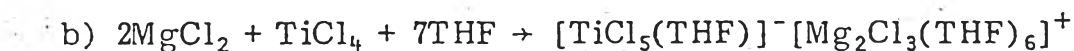
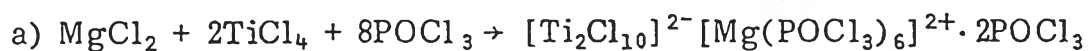
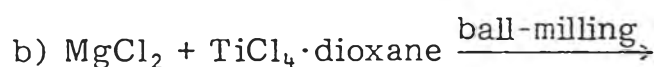
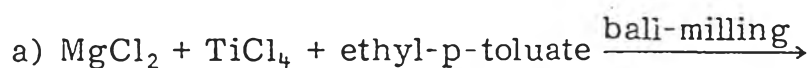
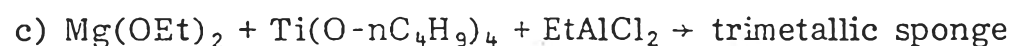
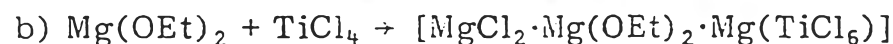
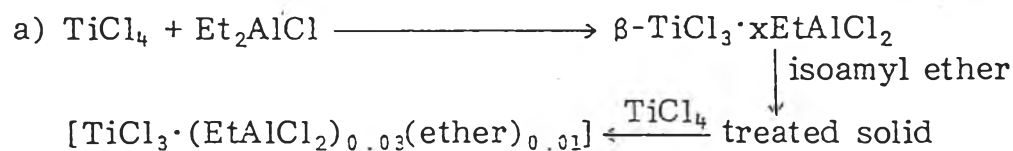
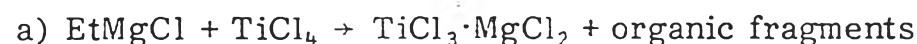
The efficiency of olefin polymerization catalysts can be improved by several methods. The data usually available in the patents are not authoritative to develop a rigorous classification relating to catalytic efficiency. It is based on operational methods to prepare the catalysts. These classes are distinguished by the mode of formation of a precursor composition containing a transition metal compound. The operational classes for compounds of transition metals are chemical anchoring to the surface of a substrate, formation of bimetallic complexes, insertion into defects of a substrate, formation of high surface area sponge, and formation of solid solution by cocrystallization. Table 3.1 illustrates examples of each class[51].

The operational methods used to improve catalyst productivity appear to have a common basis for their effectiveness. The provided techniques to expose and isolate the loading amount of transition metal compound, either in a solid matrix or a bimetallic to complex, have been highly effective. The methods stabilize the transition metal centers to provide the higher polymerization efficiency of many catalysts.

3.3.1 Chemical Anchoring to Surface of Substrate

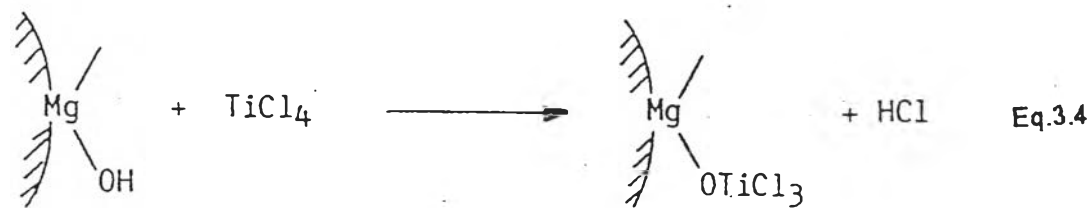
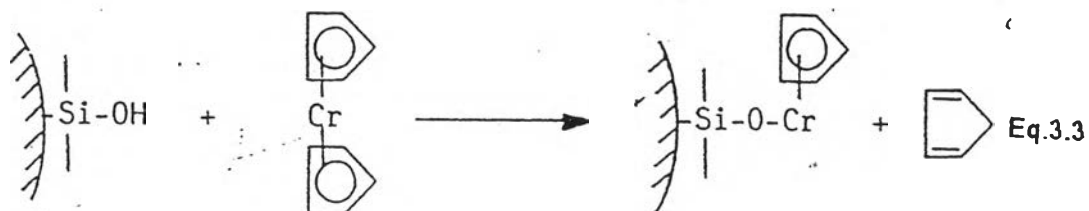
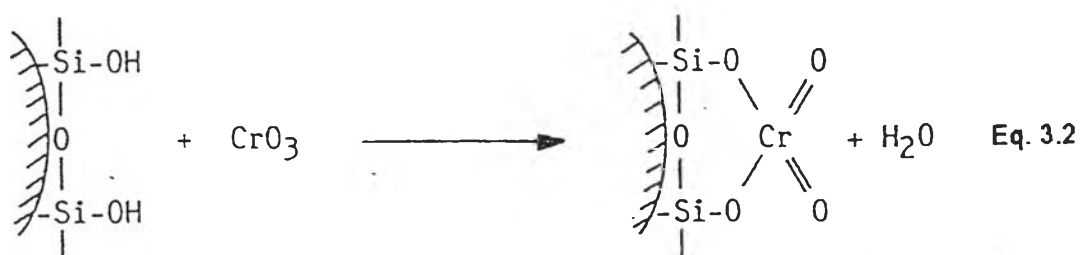
In chemical anchoring, a chemical reaction takes place between surface groups on the substrate and the transition metal compound to form a new surface composition(Eqs.3.2-3.4). Chemical attachment of the compound to the support provides

Table 3.1 Operational Methods to High Activity Catalysts [51]

1. Chemical Anchoring to Surface of Substrate2. Formation of Bimetallic Complexes3. Insertion into Defects of Substrate4. Formation of High Surface Area Sponge5. Formation of Solid Solutions by Cocrystallization (Cocrecipitation)

an anchoring device to prevent destruction of the potentially active sites by metal interaction. The heating temperature to the support can have a significant effect on the polymerization activity of the catalyst [52].

High surface area silica supports have proven particularly attractive with Cr-based catalysts, probably because such high surface areas provide an efficient means to isolate active centers. At chromium loading with the $\text{CrO}_2/\text{SiO}_2$ catalyst, chromium efficiency was at a maximum. Each chromium loading atom was assumed to be an active site.



3.3.2 Formation of Bimetallic Complexes

Bimetallic complexes containing at least one atom of Mg, Mn, or Ca and at least one atom of Ti, V or Zr, when reacted with organometallic compounds of the metals belonging to one of Groups IA-III A of the Periodic table, are claimed as highly active catalyst in the polymerization of olefins.

The complexes have the general formula $M_m M' X_{2m} Y_n E$,
 where $M = \text{Mg, Mn, Ca}$,
 $m = \text{a number from 0.5 to 2}$,

M = Ti, V, Zr,

X = Cl, Br, I,

Y = one or more atoms or groups of atoms selected from atoms of halogen,
-NR₂, -OR, -SR and others of a similar nature,

n = a number from 0.5m to 20 m,

E = electron donor compounds selected from classes of compounds which included esters, alcohols, ethers, amines, nitriles and certain phosphorus compounds.

The bimetallic complexes of the general formula MMTY.nE, wherein T= oxygen, a certain anion, or a certain pair of monovalent groups, have been shown to provide, on activation, highly active catalysts. These bimetallic halides can be prepared by reacting the halide MX₂(or MT) with the compound MY' at a temperature from 25-150°C in the electron donor solvent E (in Table 3.1). Unlike the surface complexes formed by chemical anchoring to a substrate, bimetallic complexes are well-defined compound with characteristic properties. The simplicity of these bimetallic complexes offers the opportunity to identify basic requirements for achieving high polymerization activity. The product of interaction between TiCl₄, MgCl₂ and CH₃COOC₂H₅ to form MgTiCl₆(CH₃COOC₂H₅)₄, which is illustrated below[51].

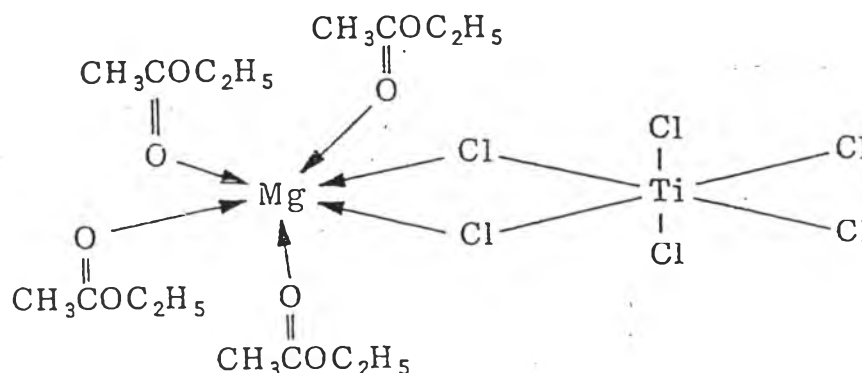


Figure 3.1 Structure of MgTiCl₆(CH₃COOC₂H₅)₄ [51].

The molecular structure of MgTiCl₆(CH₃COOC₂H₅)₄ may be described as a slightly deformed bicoctahedron. The TiCl₄ molecule has changed its coordination from tetrahedral to octahedral. Whereas, the MgCl₂ retained its octahedral coordination. The bimetallic complexes were obtained by reacting TiCl₄, VOCl₃, MoOCl₄, WOCl₄ or AlCl₃ with Be, Mg, Ca or Sr chlorides in the presence of electron donors, such as POCl₃(L) or C₆H₅POCl₂(L'). These complexes showed well-defined stoichiometry, ionic character and crystalline structure. Complexes (TiCl₆)MgL₆,

$(TiCl_5L)MgL'$ and $(Ti_2Cl_{10})MgL_8$ treated with $(i-C_4H_9)_3Al$, cocatalyst, were found very active for ethylene polymerization only.

Conclusions about the role of Mg ions in these catalysts and other high activity catalysts require the following discussion:

Titanium centers may be diluted by Mg ions, which influence the number of active centers. This dilution process can take place in several ways, including bimetallic complex formation, formation of solid solution by cocrystallization and chemical anchoring to the surface of a substrate, which may not involve Mg ions.

The process of Mg ions can stabilize active Ti centers from deactivation processes. The type of ligand on the Mg ion influences the extent of stabilization.

The presence of Mg ions enhances chain transfer processes since the average molecular weight of HDPE decreases when Mg/Ti ratio increases.

The presence of Mg ions leads to produce polyethylenes with a narrow molecular weight distribution ($M_w/M_n \sim 3-5$).

The similarity in size, coordination preference, electronic structure and electronegativity of Ti(IV), Mg(II), and Al(III) ions are reflected in structural parameters and chemical properties (Table 3.2). The similarity in size between Mg(II) and Ti(VI) and the common electronegativity and size/charge ratio for Al(III) and Ti(VI) permit an easy substitution between the metal ions in a framework. All three metal ions should fit equally well into the interstices between chloride anions in the lattice. The metal ions can react to form organometallic compound which can be stabilized by formation of adducts with electron donors. Ligand exchange and substitution of a metal ion species for another are common reaction..

Chloride ion plays an important role in many high activity Ziegler-Natta catalysts. It permits facile bridge formation between the metal centers of the catalyst framework. Alkoxide bridge probably introduces steric effects and decreases catalyst crystallinity and uniformity. Replacement of a bulky alkoxide by a chloride ion may also lead to vacancies in the catalyst lattice and increase the effectiveness surface area of the catalyst particles.

3.3.3 Insertion into Defects of Substrate

Several studies have examined the nature and performance of high activity $MgCl_2$ precursors prepared by a milling method. The primary effect of milling

Table 3.2 Geometric and Electronic Properties of Ions of Catalyst Component [51]

Ion	Radius (nm)	Size/charge	Pauling electronegativity	Electronic structure	Coordination number	Geometry
Ti(IV)	0.068	0.017	1.5	$3s^2 3p^6 3d^0$	6	Octahedral
					4	Tetrahedral
					5	Distorted trigonal bipyramidal
Mg(II)	0.065	0.033	1.3	$2s^2 2p^6$	4	Tetrahedral
					6	Octahedral
					5	-
Al(III)	0.050	0.017	1.6	$2s^2 2p^6$	4	Tetrahedral
					6	Octahedral
					5	-
Cl(-)	0.18	0.18	3.2	$3s^2 3p^6$	1	-
					2	Bent-bridging group

is to break the layered structure of the MgCl_2 crystal. The structure variation introduced by ball-milling are related with the disordered rotation of Cl-Mg-Cl triple layers. This breakage into crystallites around 10 nm occurs along the weakly bounded layers. With prolonged grinding time for MgCl_2 , each peak in the XRD pattern becomes lower and broader progressively. It indicates that the crystallite size becomes smaller and smaller during grinding.

The reduction in the crystallite of MgCl_2 during milling was greatly accelerated. The TiCl_4 diffuses to the inner layers of the MgCl_2 structure and through this diffusion makes the cleavage of the MgCl_2 crystal easier. Then the TiCl_4 adsorbed on the MgCl_2 surface is in a state of high dispersion. When ethylene molecules enter into the internal voids of MgCl_2 to polymerize ethylene, the particle disintegrates into smaller crystallites. The crystallite size can be directly correlated with the catalytic activity.

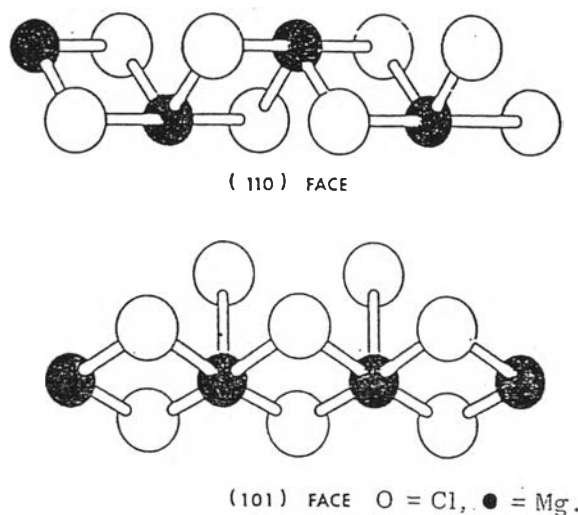


Figure 3.2 Faces of magnesium chloride after ball milling [51].

Activated magnesium halides would appear to be ideal substrates for titanium halides. The coordinatively unsaturated Mg ions located at the side surfaces and crystal edges can easily bond with titanium halides on the more probable cleavage surfaces of the crystals. The (110) and (101) faces of the Mg atoms are coordinated with four or five Cl atoms, respectively (Figure 3.2). Strongly bonded surface complexes involving halogen bridging between Ti and Mg are formed (Figure 3.3). The presence of electron donor can enhance the stability of these surface complexes. It is possible that interaction of TiCl_4 with activated MgCl_2 to form surface complexes with a formation of a $\text{Mg}[\text{TiCl}_6]$ -type ionic complex.

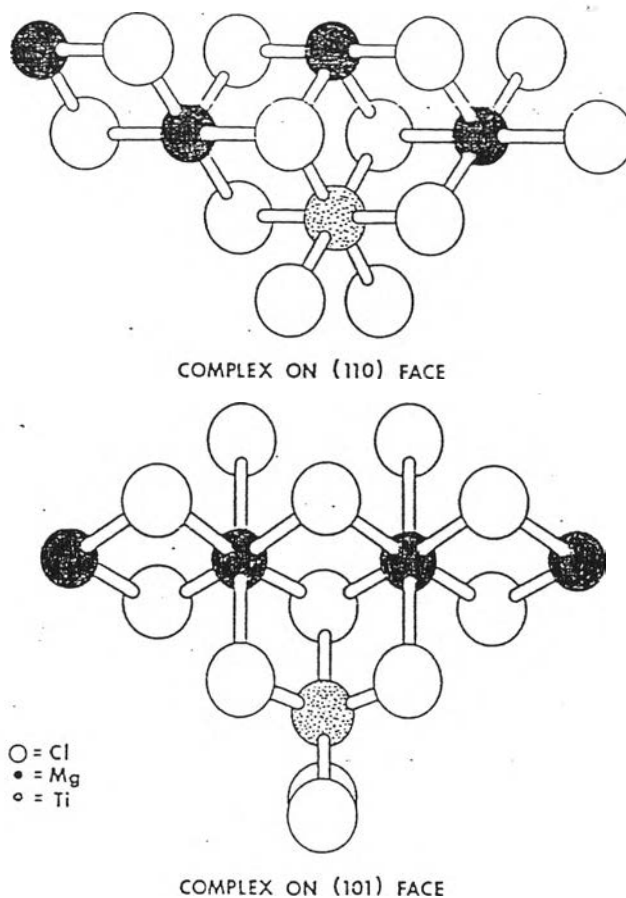


Figure 3.3 Possible complexes of TiCl_4 on face (110) and (101) of MgCl_2 [51].

3.3.4 Formation of high surface area sponge

Previously, most catalyst systems consisted of partially reduced TiCl_3 cocrystallized with AlCl_3 . Precise composition and extent of cocrystallization depend on the method of preparation and heat treatment. The effect of dry milling the TiCl_3 to increase the activity has been an important development. The catalysts can be prepared in a three-step process (Table 3.1).

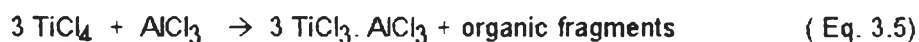
In the first step, TiCl_4 is reduced by organoaluminium compounds, Et_2AlCl . The reduced solid consists of a $\beta\text{-TiCl}_3$ based composition with aluminium compounds which has halogen and/or hydrocarbon fragments. The second step, this $\beta\text{-TiCl}_3 \cdot 1/3\text{AlCl}_3$ treatment with diisoamyl ether provides a means to remove the AlCl_3 from the solid matrix. The treated and reduced solid has the same physical form and surface area. The third step, the treated solid is reacted with TiCl_3 near 65°C to give $\delta\text{-TiCl}_3 \cdot (\text{AlR}_n\text{X}_{3-x})_x(\text{C})_y$ where C is the complexing agent, diisoamyl ether, and $0 < n > 2$, $x < 0.3$, and $0.11 > y > 0.99$. This resulting complex of $\delta\text{-TiCl}_3$ has a high surface area. Therefore, it makes the catalytic complex possess about fivefold higher activity than the conventional TiCl_3 catalyst. For the catalytic complex, the high total volume of the spherical particles is due to a particular, cellular structure (sponge) forming a network.

High activity of the bimetallic sponge catalysts based on Mg-Ti precursors can be obtained by a reaction of $Mg(OR)_2$ with tetravalent titanium halides (Table 3.1). The original structure is changed as the Mg and Ti compounds are firmly linked as a new crystalline species during the preparation. The new complexes are probably a mixture of $MgCl_2$, $Mg(OR)_2$, and Mg-Ti complexes. The final precursor (catalyst) has a much higher surface area than the original one. These high and unexpected surface areas are believed to be a major reason to the very high activity of catalysts prepared from the activated solid.

The another development of high surface area catalysts relates to the preparation and use of trimetallic sponges based on Mg-Ti-Al compounds (Table 3.1). The maximum catalytic activity in ethylene polymerization was observed using trimetallic sponges with the highest surface areas and the lowest titanium concentration. It is advantageous to isolate titanium centers from each other in the preparation step.

3.3.5 Formation of Solid Solution by Cocrystallization

In traditional Ziegler-Natta catalyst, after the reduction of $TiCl_4$ by an organoaluminum compound leads to a crystallized product of $AlCl_3$ and $TiCl_3$ [53],



with a typical content of one-third $AlCl_3$ for one $TiCl_3$.

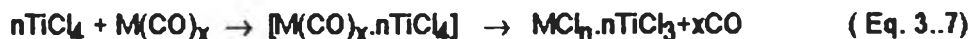
Moreover, the reduction of $TiCl_4$ by an organomagnesium compound leads to a solid solution of $TiCl_3$ in $MgCl_2$.



Cocrystallization of $MgCl_2$ with $TiCl_3$ leads to a disordered structure. This disorderness can be verified by using XRD data to compare with that of the $TiCl_3 \cdot MgCl_2$ solution with the β -structure. The treatments of these Ti-Mg complexes with an organoaluminum compound, the resultant catalysts show high polymerization activity. The high polymerization activity has been ascribed to the disorderness of $TiCl_3 \cdot MgCl_2$ structure. No remarkable X-ray lines could be assigned to either $MgCl_2$ or $TiCl_3$, which indicated a very small crystallite size must be present.

Solid solution of binary chlorides have been obtained by reacting $TiCl_4$ with $V(CO)_6$, $Cr(CO)_6$, $Mn_2(CO)_{10}$, $Mn(CO)_5Cl$, $Ni(CO)_4$, $Co_2(CO)_8$, $Fe(CO)_5$, or

$\text{Mn}(\text{CO})_6$ [54]. The reaction yield mixed chlorides of the general formula $\text{MCl}_n \cdot n\text{TiCl}_3$ where $n=2$ or 3 and M is a divalent or trivalent transition metal cation:



The binary chlorides, prepared as indicated in Eq.(3.7) have been characterized by various methods. From the obtained evidence, it showed that binary chlorides were present as solid solutions of the two constituents. The solid solution (FeTi_2Cl_8 , MnTiCl_8) with lower crystallinity exhibited high surface area values. The disorderness of crystal structure and surface area related to the ionic radius of the metals with respect to that of Ti(III). The largest surfaces were found for the binary chlorides of Fe and Mn.

Table 3.3 Catalytic Activity of Systems
Based on Binary Chlorides Containing TiCl_3 [53,54].

Binary chloride, composition	Catalyst efficiency, kg PE /g Ti	Specific activity, relative to $\text{AlCl}_3 \cdot 3\text{TiCl}_3$
$\text{MoCl}_3 \cdot \text{TiCl}_3$	1.0	0.09
$\text{NiCl}_2 \cdot 2\text{TiCl}_3$	4.2	0.38
$\text{CrCl}_3 \cdot 3\text{TiCl}_3$	9.0	0.82
$\text{CoTi}_{1.6}\text{Cl}_{6.6}$	19.1	1.74
$\text{MnCl}_2 \cdot 2\text{TiCl}_3$	22.6	2.05
$\text{FeCl}_2 \cdot 2\text{TiCl}_3$	24.0	2.18
$\text{MnCl}_2 \cdot \text{TiCl}_3$	28.1	2.55
$\text{VTi}_{1.1}\text{Cl}_{6.7}$	24.1	2.65
$\text{AlCl}_3 \cdot 3\text{TiCl}_3$	11.0	1.00
$(\text{MgCl}_2)_{1.5} \cdot \text{TiCl}_3$	132	12

Experimental conditions: n-hexane = 1000 cm^3 ; $[(i\text{-C}_4\text{H}_9)_3\text{Al}] = 40$ mmol/L; $[\text{Ti}] = 0.5\text{-}2$ mmol/L; $T = 85^\circ\text{C}$; $\text{C}_2\text{H}_4 = 5$ atm; $\text{H}_2 = 5$ atm; time = 2 h.

3.4 Ethylene polymerization catalysts

Catalysts derived from the reduction of TiCl_4 by an aluminium alkyl, or using TiCl_3 prepared by hydrogen or aluminium reduction of TiCl_4 , have been used to polymerize ethylene. The relative ease of ethylene polymerization has meant that simpler catalysts can be used, but also that a wider range of catalyst types is possible. However, there are other desirable catalysts attribute to high activity; for examples, high bulk density polymer, controlled shape and particle size range also controlled molecular weight distribution. Some catalyst systems will now be discussed[55].

3.4.1 Magnesium halide supported catalysts

Catalysts based on magnesium chloride are important in the field of polyethylene. Extremely active catalysts can be prepared by milling MgCl_2 and TiCl_4 together. Polymerization is carried out by trialkylaluminium as an activator. In commercial process, these catalysts can produce polymer containing a very low ash.

More complex catalysts based on MgCl_2 have been developed; examples are given in Table 3.4. Analogous catalysts developed for polypropylene can be made by milling MgCl_2 with a Lewis base and then treating with liquid TiCl_4 . The bases are alcohols rather than esters. These catalysts have even higher activities based on transition metal component. Other advantages related to the polymer's performance in a given application; for example, the ease of blow moulding. Examples are given in the table of methods other than ball-milling for producing an active MgCl_2 . These include chlorination of a magnesium alkyl, oxide, hydroxide or alkoxide and dehydration of $\text{MgCl}_2 \cdot \text{H}_2\text{O}$ using SOCl_2 . The necessity for the elimination of oxygen containing species is not critical with polyethylene catalysts; MgO is a very effective supports.

3.4.2 Other magnesium supports

An early Solvay patent describes a catalyst produced from the reaction between MgO and TiCl_4 . $\text{Al}(\text{iBu})_3$ was an activator to produce a high activity catalyst. Methods of producing magnesium oxide include dehydration of $\text{Mg}(\text{OH})_2$ and decomposition of the metal acetate. Alcohols can be added to the support; magnesium alkoxides are effective support materials. Another suitable support is magnesium hydroxide; Table 3.5 gives examples of the use of magnesium supports in catalysts.

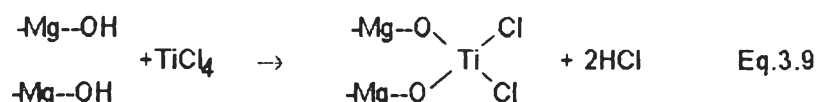
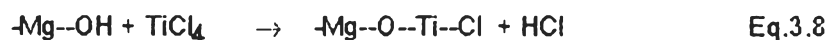
Table 3.4 Magnesium Halide Supported Catalysts [55]

<i>Assigner</i>	<i>Patent number</i>	<i>Chem. Abstr. reference</i>	<i>Application date</i>	<i>Catalyst</i>
Exxon Res. and Eng. Co. Montedison Spa	<i>Br.</i> 1 547 409	92, 7195	13/11/74	MgCl ₂ /TiCl ₄ milled with PTFE to reduce fines
	<i>Belg.</i> 842 866	86, 107 237	12/06/75	MgCl ₂ ·2AlEtCl ₂ dissolved in AlEtCl ₂ at 100 °C added to TiCl ₄ /heptane at -5 °C; used with Bu ₃ Al
Yanovskii E.A. BP Ltd. Montedison Spa	<i>U.S.S.R.</i> 630 259	90, 39 453	20/06/75	Titanium methoxychloride on MgCl ₂ ; used with Bu ₃ AlH
	<i>Br.</i> 1 554 710	92, 111 521	11/07/75	MgCl ₂ + Pr ⁱ OEt + TiCl ₄ + Ti(OPr) ₄ ; 7.68 kg (g catalyst) ⁻¹
	<i>Belg.</i> 846 314		18/09/75	Melt sprayed MgCl ₂ ·6H ₂ O treated with TiCl ₄ (+ optional electron donor)
Montedison Spa	<i>Belg.</i> 850 844		30/01/76	MgCl ₂ ·6H ₂ O treated with SOCl ₂ gives hexagonal MgCl ₂ ; treated with TiCl ₄ ; 550 kg (g Ti) ⁻¹
Soc. Chimique Charbonnage	<i>Belg.</i> 851 644	87, 185 284	25/02/76	TiCl ₃ + MgCl ₂ catalyst
Mitsui Toatsu Chem. Inc.	<i>Jpn.</i> 53 047 483	89, 75 661	12/10/76	MgCl ₂ , ZnSO ₄ , TiCl ₄ milled; treated with TiCl ₄
Asahi Kasei Kogyo	<i>Ger.</i> 2 742 585	88, 170 793	06/12/76	Mg complex + chlorosilane then treated with Ti or V compound
Mitsubishi Petrochem. KK	<i>Jpn.</i> 54 045 696	91, 40 138	17/09/77	MgCl ₂ + Ti(OBu) ₃ , then TiCl ₄ treated
Euteco Spa	<i>Fr.</i> 2 404 648	92, 23 187	30/09/77	Mg + ROH + HCl gives MgCl ₂ , then treated with TiCl ₄
Asahi Chemical Ind. KK	<i>Jpn.</i> 54 062 191	91, 124 231	27/10/77	R ₂ Mg + HSiCl ₃ treated with Ti or V compound; 117 kg g ⁻¹ h ⁻¹ atm ⁻¹
Chisso Corp.	<i>Ger.</i> 2 907 158	91, 158 364	25/02/78	Mg(OH) ₂ + AlCl ₃ milled then treated with dimethylpolysiloxane + TiCl ₄ at 110 °C
Nippon Oil KK	<i>Jpn.</i> 54 122 387	92, 77 164	16/03/78	MgO + AlCl ₃ then milled with polysiloxane + TiCl ₄ + diisopentyl ether
Union Carbide	<i>Eur.</i> 4647	92, 42 623	31/03/78	MgCl ₂ + TiCl ₄ in THF evaporated on to SiO ₂
Nippon Oil KK	<i>Jpn.</i> 54 132 689	92, 94 894	05/04/78	MgCl ₂ + 1,2-Cl ₂ C ₂ H ₄ + diisopentyl ether + TiCl ₄ ; used with Bu ₃ Al; 144 kg (g Ti) ⁻¹ h ⁻¹
Nippon Oil KK	<i>Ger.</i> 2 925 094	92, 129 652	21/06/78	MgCl ₂ + TiCl ₄ + 1,2-Cl ₂ C ₂ H ₄ + dimethylpolysiloxane milled; used with Bu ₃ Al
Idemitsu Kosan KK	<i>Jpn.</i> 55 007 803	93, 8783	30/06/78	MgCl ₂ + AlCl ₃ + EtOH, milled then treated Et ₂ AlCl then TiCl ₄ ; used with Et ₃ Al; 740 g (mmol Ti) ⁻¹ h ⁻¹
Nippon Oil KK	<i>Br.</i> 2 024 832	93, 8775	05/07/78	MgCl ₂ + C ₂ H ₄ Cl ₂ + 3TiCl ₃ ·AlCl ₃ ; used with Bu ₃ Al; 225 kg (g Ti) ⁻¹
Phillips Petroleum Co.	<i>Eur.</i> 7425	93, 27 109	24/07/78	Ti(OR) ₄ + MgCl ₂ then + R ₂ AlCl, then halide ion exchange

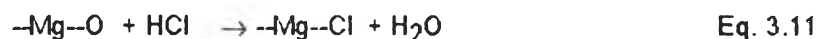
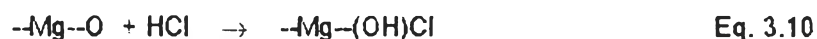
Table 3.5 Other Magnesium Supported Catalysts [55].

<i>Company</i>	<i>Patent number</i>	<i>Chem. Abstr. reference</i>	<i>Application date</i>	<i>Catalyst</i>
BP Ltd.	<i>Br.</i> 1 554 110	92, 216 047	06/08/75	MgO + Mg(NO ₃) ₂ + Pr ⁱ OH + TiCl ₄ + Ti(Pr ⁱ O) ₄ ; used with Et ₃ Al
BP Ltd.	<i>Br.</i> 1 559 172	92, 181 893	15/10/75	MgO + Pr ⁱ OH + TiCl ₄
Nippon Oil KK	<i>Ger.</i> 2 700 163	87, 85 533	09/01/76	EtAlCl ₂ + EtMgCl in THF; EtOH added then milled with TiCl ₄ ; used with Et ₃ Al
BP Ltd.	<i>Belg.</i> 851 908	87, 168 631	01/03/76	MgO from Mg acetate treated with TiCl ₄ then Pr ⁱ OH
BP Chemicals Ltd.	<i>Belg.</i> 854 995	88, 74 741	24/05/76	TiCl ₄ + Pr ⁱ OH treated with SnCl ₄ then added to MgO
Arco Polymers Inc.	<i>Belg.</i> 861 553	90, 6893	22/03/77	MgO treated with MeOH; refluxed with TiCl ₄ and Ti(OBu) ₄
Atlantic Richfield Co.	<i>U.S.</i> 4 167 493	91, 176 424	22/03/77	MgO + MeOH then treated with TiCl ₄ and Ti(OBu) ₄
Standard Oil Co. (Ind)	<i>U.S.</i> 4 105 846	90, 39 449	25/08/77	Mg(OEt) ₂ + Ti(OBu) ₄ then EtAlCl ₂ ; used with Et ₃ Al
Idemitsu Kosan KK	<i>Jpn.</i> 54 144 490	92, 129 646	01/05/78	Mg(OR) ₂ + X _n Si(OR) _{4-n} + TiCl ₄
BASF AG	<i>Jpn.</i> 55 000 729	92, 147 533	20/06/78	Mg(OEt) ₂ + AlCl ₃ in EtOH, dried and milled; Et ₂ AlCl added then TiCl ₄ ; used with Et ₃ Al
Idemitsu Kosan KK	<i>Jpn.</i> 55 005 920	92, 99 056	28/06/78	Mg(OR) ₂ + MgSO ₄ + TiCl ₄
Idemitsu Kosan KK	<i>Jpn.</i> 55 007 802	93, 8784	30/06/78	Mg(OH) ₂ + Al(Pr ⁱ O) ₃ then TiCl ₄ added

The surface of magnesium oxide has hydroxyl groups. TiCl_4 has been shown to react with these surface groups (Eqs. 3.8-3.9).



Gravimetric analysis suggests that HCl produced as a by-product also reacts with the surface species (Eqs. 3.10-3.11). The water produced from the last reaction can react with titanium species on the surface (Eq. 3.12). Evidence for this reaction comes from IR spectra on the analogous reaction of MgO and SiCl_4 . IR data are also available on the subsequent reaction of the surface titanium halide species with aluminium alkyl.



It was suggested that the active species is a trivalent titanium alkyl produced by reduction and subsequent alkylation reaction (Figure 3.4). For kinetic work on the same system implied encapsulation of catalyst by polymer and control, under the experimental conditions, of the polymerization by diffusion through the polymer film.

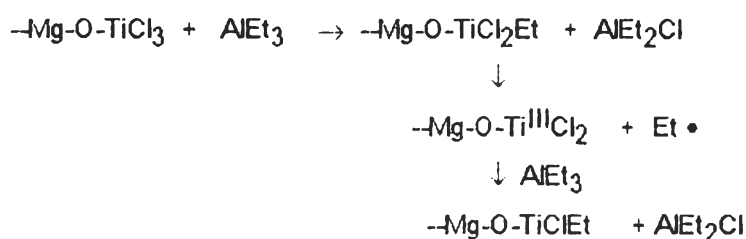


Figure 3.4 The reaction of surface titanium halides species and aluminium alkyl [55]

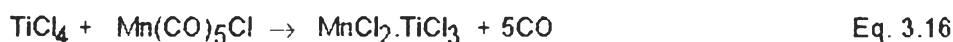
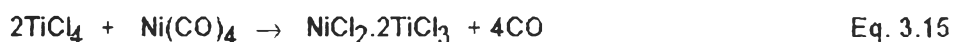
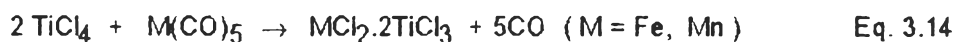
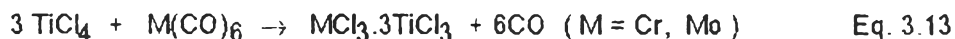
Supporting the titanium catalyst component seems to lessen the tendency for reduction by the aluminium alkyl cocatalyst. Magnesium supports such as MgCl_2 and MgO are more effective than aluminosilicate; this ability is apparently related to the chemical nature of the support rather than its surface structure. The stability of active polymerization complexes is thus increased by the support.

3.4.3 Reduced catalyst systems

For ethylene as well as propylene polymerization systems, an important class of catalysts is prepared by the reduction of a titanium(IV) compound by a metal alkyl compound. Trialkylaluminiums, alkyl halides and other mixed ligand compounds are again suitable reducing agents; however, alkylmagnesium compounds also give rise to extremely active polymerization systems. Grignard reagents, solid or soluble dialkyl magnesiums, on their own or complexed with ethers or with other metal alkyls, have all been used. Examples of catalysts are given in Table 3.6.

These catalysts give very high activities and ultra high molecular weight polymer. Reduction of TiCl_4 by magnesium alkyls generally gives rise to cocrystalline $\text{MgCl}_2\text{-TiCl}_3$ material. Reduction at relatively low temperature produces a brown product similar to $\beta\text{-TiCl}_3\text{-AlCl}_3$ solid solution. This can be transformed to purple by heating with TiCl_4 .

Evaporation of Mn into TiCl_3 produces a material of composition TiMn_3Cl_9 . Binary chlorides of TiCl_3 with other transition metal chlorides have been produced by reaction of TiCl_4 with metal carbonyl compounds. Carbonyls used include those of V, Mn, Cr, Ni, Co, Fe and Mo; reactions occur according to Eqs. 3.13- 3.16. The products are generally isomorphous with either $\alpha\text{-}$ or $\gamma\text{-TiCl}_3$. In ethylene polymerizations, good yields were achieved by $\text{Al}(\text{iBu})_3$ as cocatalyst. Activity of the catalyst decayed rapidly during the polymerization. Therefore, the overall yields were not as high as with some other systems.



3.4.4 Other supported catalysts

An active polyethylene catalyst can be made simply by the reaction of TiCl_4 with an oxide support. The interaction with surface hydroxyls is similar to that previously described for magnesia. The activity of the catalyst is low and more complicated preparation are necessary to achieve high polymer yields. Means of

Table 3.6 Reduced Catalyst systems [55].

<i>Assignee</i>	<i>Patent number</i>	<i>Chem. Abstr. reference</i>	<i>Application date</i>	<i>Catalyst</i>
Studienges Kohle mbH	<i>U.S.</i> 4 063 009	87, 118 450	19/01/54	TiCl ₄ milled with Me ₂ Mg
Shell Int. Res.	<i>Neth.</i> 7 100 931	76, 46 721	28/07/71	BuMgBr + TiCl ₄ ; used with (octyl) ₃ Al; 31 kg (g Ti) ⁻¹
Montecatini Edison	<i>Ger.</i> 2 218 692	78, 30 535	26/10/72	BuMgCl + TiCl ₄ ; used with Et ₃ Al; 765 kg (g Ti) ⁻¹
Asahi Chem. Ind. KK	<i>Jpn.</i> 7 628 191	85, 33 704	09/03/76	Bu ₂ Mg + (HSiMe ₂) ₂ O + TiCl ₄ ; used with Bu ₃ Al; 320 kg (g Ti) ⁻¹
Dow Chemical Co.	<i>U.S.</i> 4 172 050	92, 23 181	22/04/74	Bu ₂ Mg + Et ₃ Al added to Et ₃ Al ₂ Cl ₃ , then Ti(OPr ⁱ) ₄
Phillips Petroleum	<i>U.S.</i> 4 189 554	92, 181 900	14/05/76	RMgCl + R ₂ AlCl milled, then treated with TiCl ₄
Dow Chemical Co.	<i>Belg.</i> 861 599	89, 217 818	07/12/76	Et ₃ Al ₂ Cl ₃ + Bu ₂ Mg reacted with Ti(OPr ⁱ) ₄
Arco Polymers Inc.	<i>Belg.</i> 863 474	89, 180 617	28/02/77	Ti(OBu) ₄ + R ₂ Mg·2AlR ₃ , then treated with HCl then Ti(OBu) ₄
Makhtarulin S.I.	<i>U.S.S.R.</i> 667 232	91, 57 852	10/03/77	BuMgCl + TiCl ₄
Severova N.	<i>E. Ger.</i> 130 859	—	25/05/77	TiCl ₄ + AlR ₃ + R ₂ AlOR gives high molecular weight polyethylene
Snamprogetti Spa	<i>Ger.</i> 2 828 627	90, 169 323	30/06/77	TiCl ₄ + SiO ₂ , 200 g (g Ti) ⁻¹ h ⁻¹ atm ⁻¹ ; treated with Mg vapour, 162 kg (g Ti) ⁻¹ h ⁻¹ atm ⁻¹
Soc. Chimique Charbonnage	<i>Eur.</i> 5394	92, 111 528	05/05/78	BuMgCl + 3TiCl ₃ ·AlCl ₃ used with trioctylaluminium
Nissan Chem. Ind. KK	<i>Br.</i> 2 020 672	92, 181 890	10/05/78	BuMgCl + methylhydopolysiloxane + TiCl ₄ ; used with Et ₃ Al
Phillips Petroleum	<i>Eur.</i> 5550	92, 147 526	19/05/78	Ti(OEt) ₄ + VOCl ₃ then Et ₃ Al ₂ Cl ₃ added, then TiCl ₄ added; used with Et ₃ Al
Asahi Chem. Ind. KK	<i>Belg.</i> 878 689	92, 199 058	11/09/78	TiCl ₄ + Ti isopropyl titanate; product treated with MgR ₂ ; used with Bu ₃ Al

Table 3.7 Other Supported Catalysts [55].

<i>Assignee</i>	<i>Patent number</i>	<i>Chem. Abstr. reference</i>	<i>Application date</i>	<i>Catalyst</i>
Nissan Chem. Ind. Ltd.	<i>Jpn.</i> 48 097 983	81, 64 350	25/03/72	SiO ₂ + Mg + MeOH then TiCl ₄ added; used with Bu ₃ Al
BP Ltd.	<i>Belg.</i> 845 400	87, 152 732	21/08/75	SiO ₂ + MgCl ₂ + TiCl ₄ then Pr ⁱ OH added; used with Et ₃ Al
Standard Oil Co. (Ind)	<i>U.S.</i> 4 104 199	90, 24 003	31/12/75	Hydrated magnesium stannate + Ti(OBu) ₄ + EtAlCl ₂ ; used with Et ₃ Al
BASF AG	<i>Belg.</i> 850 855	87, 118 436	03/02/76	SiO ₂ in MeOH + 3TiCl ₃ ·AlCl ₃ and manassite in MeOH; used with Et ₃ Al
Gulf Oil Corp.	<i>Belg.</i> 855 241	88, 153 301	03/06/76	ROH suspension of Mg compound evaporated on to polymer; treated with aluminium alkyl then titanium halide
Euteco Spa	<i>Br.</i> 1 553 778		19/10/76	SiO ₂ /Al ₂ O ₃ impregnated with CoSO ₄ ; treated with TiCl ₄ then Et ₃ Al
BASF AG	<i>Ger.</i> 2 721 094	90, 55 524	11/05/77	TiCl ₃ + Mg compound in ROH supported on SiO ₂ /Al ₂ O ₃
BASF AG	<i>Ger.</i> 2 721 194	90, 39 429	11/05/77	3TiCl ₃ ·AlCl ₃ on SiO ₂ or SiO ₂ /Al ₂ O ₃
American Can Co.	<i>Belg.</i> 876 583	92, 23 182	05/06/78	HDPE graft polymer + Et ₃ Al ₂ Cl ₃ then treated with MgBu ₂ + Et ₃ Al then Ti(OPr) ₄
BASF AG	<i>Ger.</i> 2 829 623	92, 181 894	06/07/78	SiO ₂ + 3TiCl ₃ ·AlCl ₃ + Mg ₆ Al ₂ (OH) ₂ Cl ₁₆ in MeOH; dried, treated with acetyl chloride; used with Et ₃ Al; 375 kg (g Ti) ⁻¹

One method of catalyst preparations is to dissolve the titanium component of the catalyst in an alcohol or an ether and then to evaporate the solvent so that it precipitates onto the carrier. Other components such as solutions of magnesium compounds can be included. In this way TiCl_4 and MgCl_2 can be put on to a support from the solution in THF. A supported version of the Grignard reduced TiCl_3 catalyst can be obtained by treatment of a support with the magnesium alkyl compound, followed by reaction with TiCl_4 . Suitable supports are MgO , ZnO , silica and alumina. Catalysts can also be produced using polymers as supports. This material can be used as a support for a catalyst made by adding sequentially a Grignard reagent, TiCl_4 and finally $(i\text{-Bu})_2\text{AlH}$. However, in a solution polymerization at high temperatures, polyethylene can diffuse away from the catalyst into solution in the reaction medium. Since the catalytic activity remains constant for a long time and reasonable yields of polymer free from catalyst residues can be produced. The properties of the polymer, including its average molecular weight, are similar in those of polymer produced using conventional catalysts.

3.4.5 Use of titanium alkoxides in catalysts

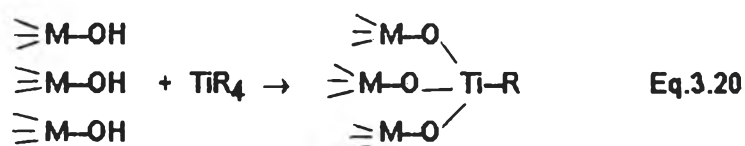
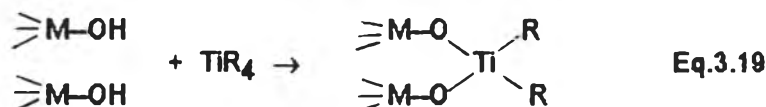
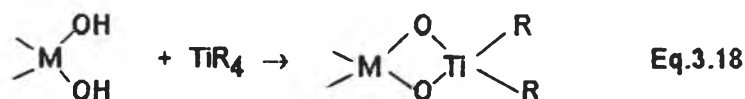
Polypropylene catalysts are characterized by the presence of their titanium component almost exclusively as halides: TiCl_4 or TiCl_3 . In the case of ethylene, high-active polymerization catalysts can also be obtained by using titanium alkoxides or alkoxychlorides. Various examples are shown in Table 3.8, and can also be found in the other tables of ethylene catalysts provided. Alkoxide complexes are used in both reduced and supported systems. The effectiveness of many catalyst supports for ethylene polymerization is probably due to the acceptability of oxygen containing titanium species as catalytic sites, these having been produced, for example, by reaction with surface hydroxyl groups.

3.4.6 Organometallic catalysts

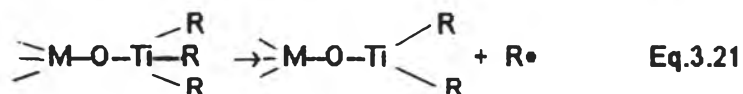
Various catalysts are used in ethylene polymerization without the necessity for an aluminium alkyl cocatalyst. These can be heterogeneous or homogenous systems. But in homogenous systems, it is often difficult to say whether the activity contributes to a soluble species from small amounts of solid or adsorbed material. However, when reacted with alumina much higher activity are gained. The activity of the soluble material could be due to adsorbed molecules on the reaction vessel. The reaction of Ti or Zr alkyl with an oxide support can occur in many ways, depending on the density of surface hydroxyl groups (Eqs. 3.17-3.20).

Table 3.8 Titanium Alkoxide Based Catalysts [55].

<i>Assignee</i>	<i>Patent number</i>	<i>Chem. Abstr. reference</i>	<i>Application date</i>	<i>Catalyst</i>
Mitsubishi Petrochem. KK	<i>Jpn.</i> 2 419 568	—	07/08/65	Ti(OBu) ₄ + Et ₃ Al ₂ Cl ₃ + orthotitanic acid
Kyawa Yuka KK	<i>Jpn.</i> 7 207 449	77, 35 260	21/08/68	Ti(OR) ₄ + R ₃ Al + CCl ₄
BP Chemicals Ltd.	<i>Br.</i> 1 484 254	89, 60 255	02/11/73	Inorganic oxide + active Mg compound + Ti(OEt) ₃ Cl
Veba Chemie AG	<i>Ger.</i> 2 600 336	87, 102 852	07/01/76	AlEt ₂ Cl + Ph ₃ SiOH treated with VOCl ₃ + Ti(OPr ⁿ) ₄
BP Chemicals Ltd.	<i>Belg.</i> 854 996	88, 51 393	24/05/76	Mg + ROH + titanium alkoxyhalide; used with Et ₃ Al
Severova N.	<i>E. Ger.</i> 133 242	—	18/08/77	TiCl ₄ + Bu ₂ AlH + Bu ₃ Al then Ti(OPr ⁿ) ₄ added
Wacker Chemie GmbH	<i>Ger.</i> 2 809 337	91, 175 976	03/03/78	EtAlH + polysiloxane + TiCl ₄ + Ti(OR) ₄ + Ti(OR)Cl ₃
Standard Oil Co. (Ind)	<i>U.S.</i> 4 199 476	93, 47 509	23/08/78	Mg(EtO) ₂ + Ti(OBu) ₄ + TiCl ₄ solution reacted with EtAlCl ₂
Standard Oil Co. (Ind)	<i>U.S.</i> 4 210 559	93, 168 885	30/10/78	Ti(OBu) ₄ + Zr(OBu) ₄ + EtAlCl ₂ ; used with Et ₃ Al; 16 kg (g Ti + Zr) ⁻¹ h ⁻¹



Silica has been dehydrated by heating, $Ti(CH_2Ph)_4$ loses on average two benzyl groups. However, a greater degree of reaction occurs using similar pretreated alumina. The effect of the support on the catalyst activity is dramatic: a solution of $Ti(Bz)_4$ has very low activity, but this is increased by a factor of 200 by supporting on the alumina surface. The molecular weight distribution is typically broad, probably indicating a variety of active sites. The catalyst activity can be increased in various ways, including heating and treatments with hydrogen and UV radiation. Reduction could occur as in Eq.3.21.



Propagation at Ti(III) can be monitored by ESR and complexation of the alkene, followed by insertion, observed in Figure 3.5. However, low valent titanium is not completely responsible for active sites since the number of these can greatly exceed the content of Ti(III). When hydrogen is in the polymerization, it is likely that the active sites are produced in the formation of metal hydride species.

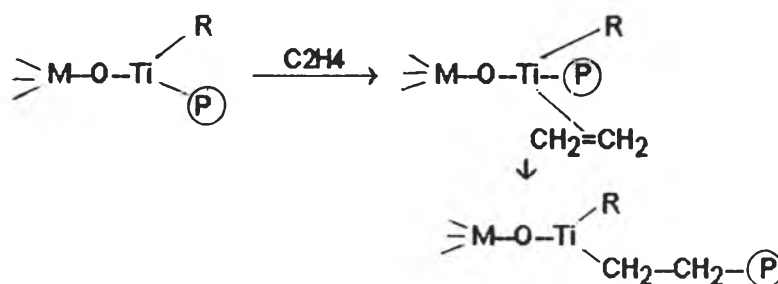
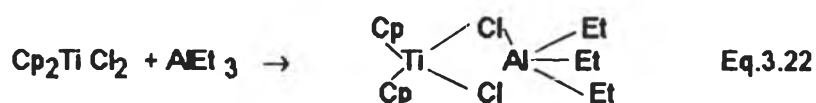


Figure 3.5 Propagation at Ti(III) of alkene [55].

3.4.7 Cyclopentadienyltitanium Catalyst

The class of catalysts has received considerable attention in academic literature. A reason of interest is the soluble nature of the catalysts, although they become heterogenous when polyethylene is formed. Catalysts derived from the compounds of bis(cyclopentadienyl)titanium(IV) have been known for approximately 25 years. $[\text{TiCl}_2\text{Cp}_2]$ becomes an active catalyst when used with alkylaluminium compounds. The two reagents combine to form a complex as in Eq.3.22.



A 2:1 (Al:Ti) complex can also be formed. Complexation is probably followed by alkylation (Figure 3.6). Propagation occurs through insertion of alkene into a metal-alkyl bond; this could be a titanium or aluminium alkyl or one bridging between the two metals. Strong evidence points toward the active site having a valency of four.

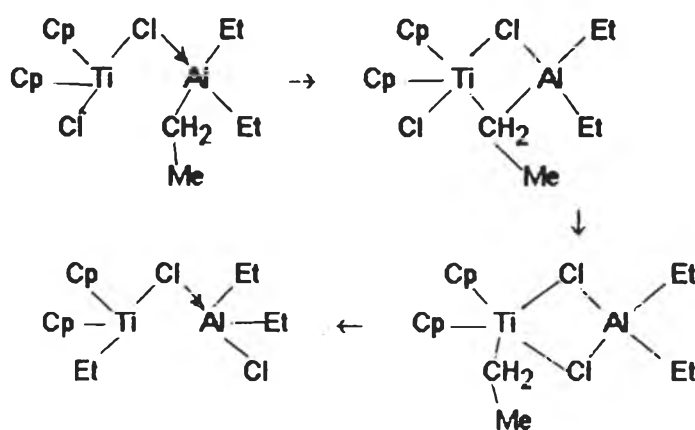


Figure 3.6 Alkylation of the complexes [55].

For example, the increase in Ti(III) content, observed using ESR, is accompanied by a reduction activity. The mechanism of the reduction is complicated (Figure 3.7); various intermediates have been detected spectroscopically

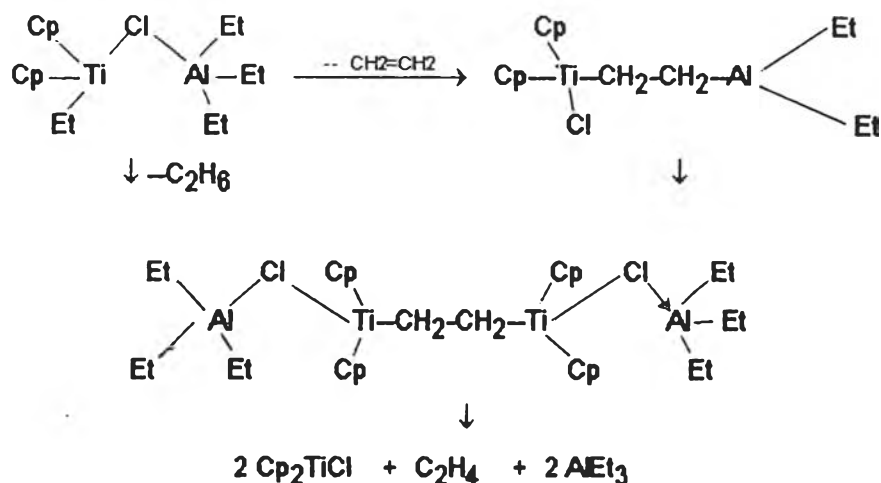


Figure 3.7 Mechanism of the reduction [55]

The activity of these catalysts is relatively low. However, activities in an order of higher magnitude are obtained when small amounts of water are added to the catalyst. This result is somewhat surprising since the presence of water is normally associated with a reduction of activity in Ziegler-Natta systems. The chlorine free TiMe_2Cp_2 , which shows no association with aluminium alkyls and little activity, when the AlR_3 has been pretreated with 50 mole% of water. The reaction between water and the aluminium alkyl is believed to produce cyclic aluminoxanes containing between 5 and 12 aluminium atoms (Figure 3.8). Peak activities are found using between 0.2 and 0.5 moles of water per mole of aluminium alkyl.

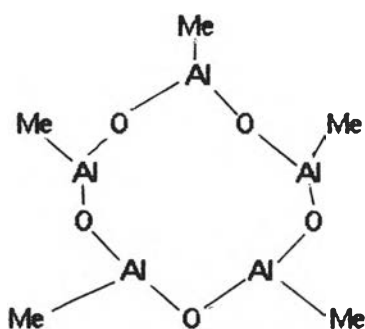


Figure 3.8 Cyclic aluminoxane from the reduction of TEA and water [55]

3.5 THE MECHANISM OF ZIEGLER-NATTA POLYMERIZATION

Since Ziegler's discoveries in 1952 [56], and the commercial importance of alkene polymerization, the mechanism involved in these catalytic reactions has still not been probably established. Where one remembers that the polymerization is occurring at a small percentage of sites on the surface of a solid, this fact becomes less surprising. Techniques for investigating surface structure, in particular of amorphous or polycrystalline are not numerous. It is generally accepted that the polymerization process involves the formation of a complex between the alkene and the active site, followed by a propagation step in which the alkene adds to a polymer chain. Until recently this has been envisaged as a simple insertion into a metal-alkyl bond. However, proposals involving the existence of metallocyclopentanes or metal carbenes as intermediates have added to the debate.

3.5.1 Nature of the active sites and mechanism of propagation

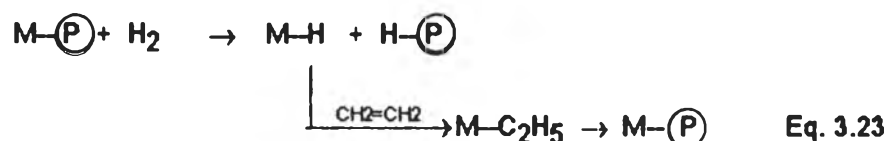
Numerous proposals have been put forward about the form of the polymerization and the nature of the active site. An early suggestion was on a radical mechanism. Various possible initiators were proposed: the transition metal center, the aluminium center, or alkyl radical resulting from the reduction of a titanium alkyl from an oxidation state of four to three, or from three to two.

However, true Ziegler-Natta polymerization of ethylene gives a very different product from the polyethylene produced by the high-pressure process. The Ziegler-Natta ethylene homopolymer has a higher density and crystallinity due to very few chain branchings associated with the radically produced polymer.

An anionic mechanism was proposed by Gilchrist [57]. The polymer chain ends in an anionic carbon is not bound to any metal center. Initiation is by transfer of an alkyl anion from the metal alkyl activator to an adsorbed alkene.

More likely mechanisms are the propagation at a metal-alkyl bond. This could be the transition metal alkyl, the activator alkyl, or an alkyl group which is bridging between this two. However, there are several pieces of experimental evidence which point to the active center being a metal-alkyl bond.

The use of aluminum alkyl labelled with ^{14}C had been showed to lead to the formation of polymer with the labelled carbon. Hydrogen is used as a chain transfer agent to the molecular weight without destroying the active center as in Eq. 3.23. The transfer reaction is consistent with a metal-alkyl bond. Use of deuterium ($^2\text{H}_2$) or tritium ($^3\text{H}_2$) has given polymers centering the appropriate label. A label is also found in the polymer if the polymerization is quenched by a labelled alcohol.



3.5.2 Propagation at the activator alkyl

The early mechanisms suggested the activator alkyl as the propagation site. These proposals were influenced by knowledge of Aufbau reaction. Ethylene is polymerized to low molecular weight polymer by Group I-III alkyls alone, without the aid of a transition metal component. The function of the transition metal is to complex with the alkene and, by polarizing it, activating it towards insertion into the activator alkyl bond. The simplest way is that in which the activator is considered to be adsorbed onto the TiCl_3 surface. This envisages the growing polymer chain as a bridging group between the transition metal and activator, for example, Ti and Al. An incoming alkene forms a π -bond with the titanium, cleaving the bridging bond. The polymer chain then migrates onto the alkene, which having been polarized by bonding to the transition metal and now forms a δ -bond with Ti. Finally, the bridge reforms as in Figure 3.9.

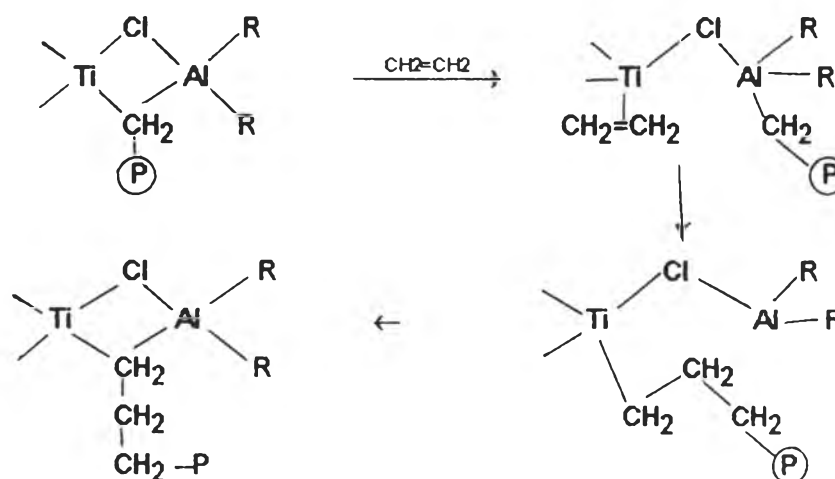
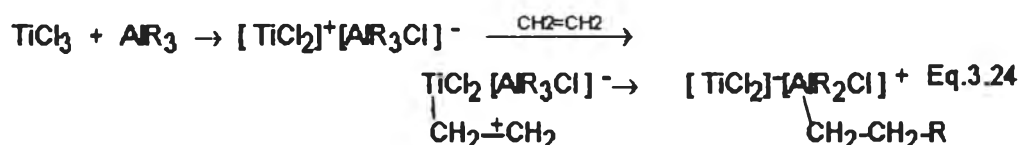
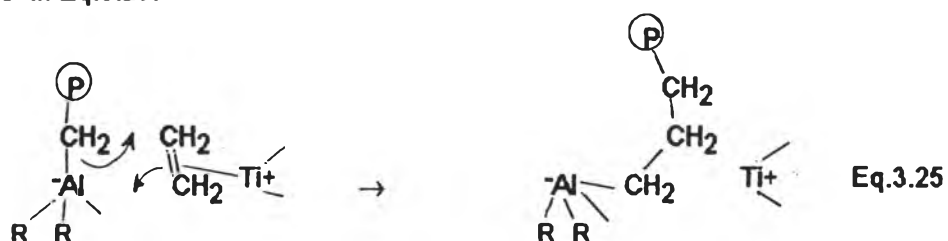


Figure 3.9 Growing polymer chain at Ti-Al complex [55]

A similar mechanism as in Eq.3.24 was proposed by Patat and Sinn[58] in 1958. Here again the alkene is polarized but this time by a $TiCl_3$ cation, before insertion into an Al-R bond.



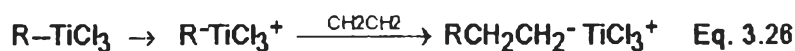
A mechanism suggested by Boor[59] saw the insertion as a concerted process in Eq.3.25.



Further mechanisms suggest that the $TiCl_3$ surface simply acts to activate adsorbed aluminum alkyl and the polymerization occurs when the polymer chain transfers from one aluminum to an alkene which is coordinated to another. Electroneutrality is maintained by electron transfer through the $TiCl_3$ surface.

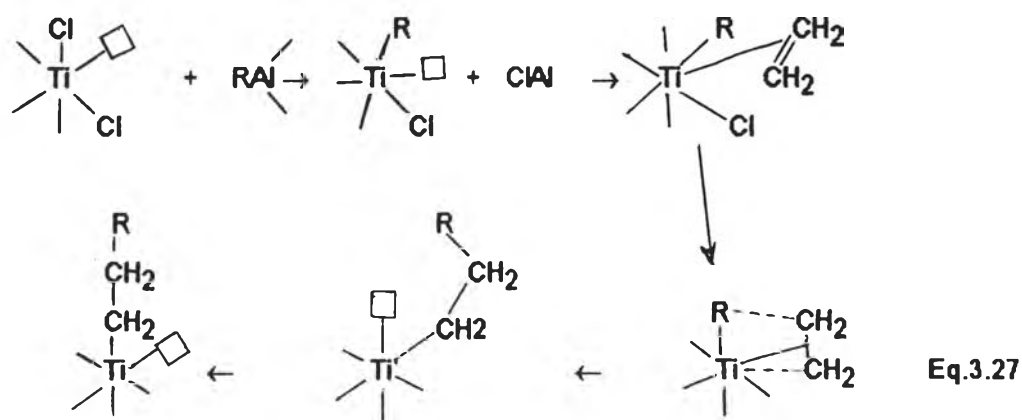
3.5.3 Propagation at the transition metal alkyl

The titanium had various valencies ranging from 4 to 2. An early suggestion was that polymerization occurred at a tetravalent alkyltitanium halides, as shown in Eq. 3.26[60].

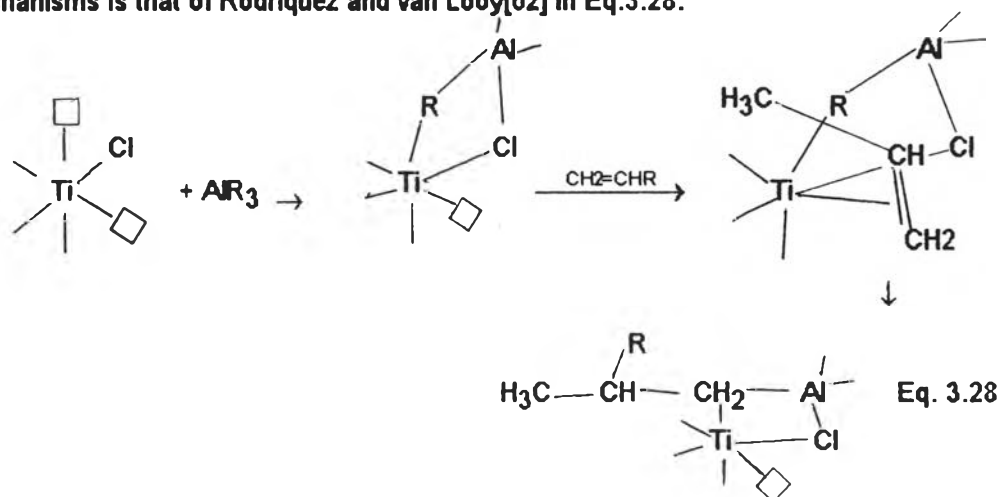


The proposal stated that a divalent alkyl titanium halide was involved, complexation of the alkene was followed by insertion into Ti-R bond. The suggestion would seem to be reasonable based on an observed maximum activity in catalysts produced by the reduction of $TiCl_3$ with aluminium alkyl, when the average titanium valency was two. Divalent titanium catalysts are known, many being extremely active in ethylene polymerization, although the activity for the propylene polymerization is generally low.

The most accepted and comprehensive mechanism for alkene polymerization is that of Cossee and Arman[61] as the mechanism shown in Eq. 3.27. It was suggested that polymerization occurs at surface Ti atoms which possessed a vacant coordination site. The activator's function is to alkylate one chloride ligand of the octahedrally coordinated Ti alone by an alkyl. The monomer complexes at the vacant site and then, via a four-membered cycle intermediate, the alkyl group is transferred to the bound alkene which now forms a δ -bond to the transition metal atom. The resultant structure is similar to that of the original active site, except the changed position of the alkyl ligand and vacant sites.

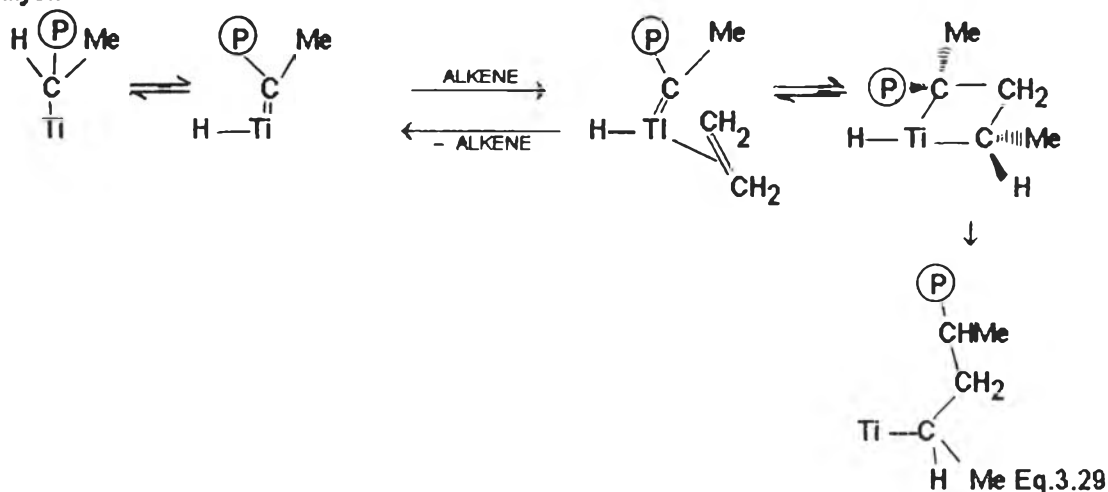


Other mechanisms have been proposed that more than the single transition metal atom is involved. The alkene coordinates at one Ti atom but then migration occurs from the M-R bond of a neighbouring Ti. Coordination of alkene then occurs at the second Ti and the alkyl ligand migrates back. The most important rival to the Cossee and Arman mechanisms is that of Rodriguez and van Looy[62] in Eq.3.28.

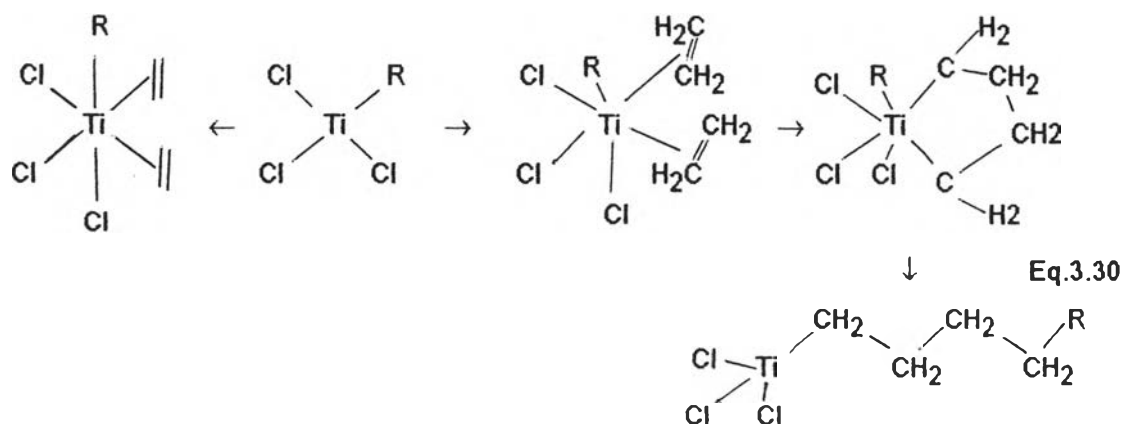


The recent mechanism of polymerizations are the ring-opening polymerization of cycloalkenes and alkene metathesis in which it has been asserted, metallocyclobutane and metal-alkene-carbene interconversion play a crucial part.

The mechanism was proposed by Ivin et al.[63] shown in Eq.3.29. The metal-alkyl(M-R) bond first undergoes α -elimination to produce a metal hydride and a carbene. Alkene coordinates at a vacant site and then involves with the carbene to form a metallocyclobutane. The hydride ligand migrates back to the tertiary carbon atom (the more sterically crowded of the two involved in M-R bonds). If the latter step is slow or the hydride can be removed from the metal center, then the catalyst becomes a metathesis catalyst.



Schrock and his coworkers[64] have proposed a mechanism for alkene polymerization based on a metallocyclopentane intermediate. The mechanism requires two vacant coordination sites on the transition metal atom as in Eq.3.30.

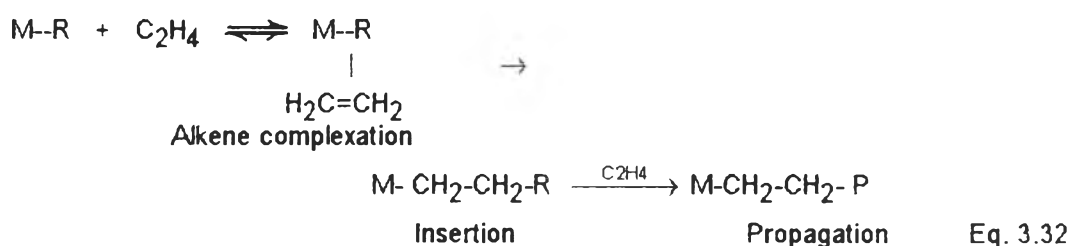


After the formation of the metallocycle, alkyl group migration then completes the polymerization process. Semi-empirical molecular orbital calculations on this model suggest that the intermediate in which the four carbon atoms of the two bonded alkenes are coplanar with the Ti is stable relative to the situation in which they are parallel in the case when the Ti is divalent but not when it is tetravalent. The mechanism is perhaps only likely when low Ti valencies are involved.

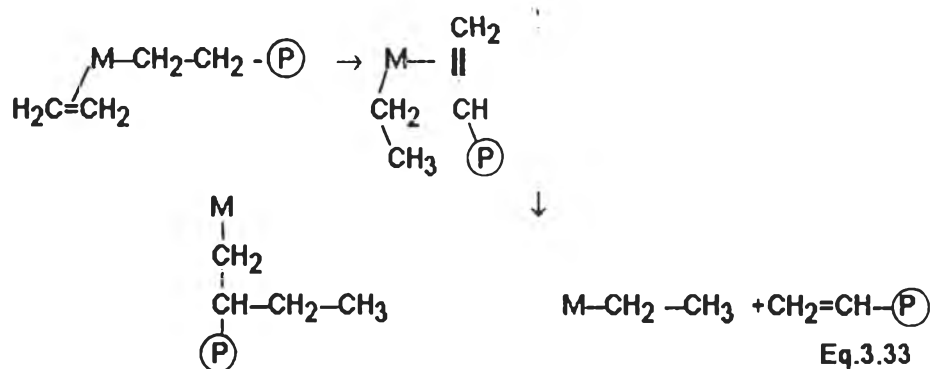
3.5.4 Reactions occurring during polymerization

It is not supposed to discuss here the details of the work carried out on the kinetics of Ziegler-Natta polymerization. There are several sources of further information available to the interested readers. It is perhaps useful, however, to describe a recent paper by Bohm for better understanding[65].

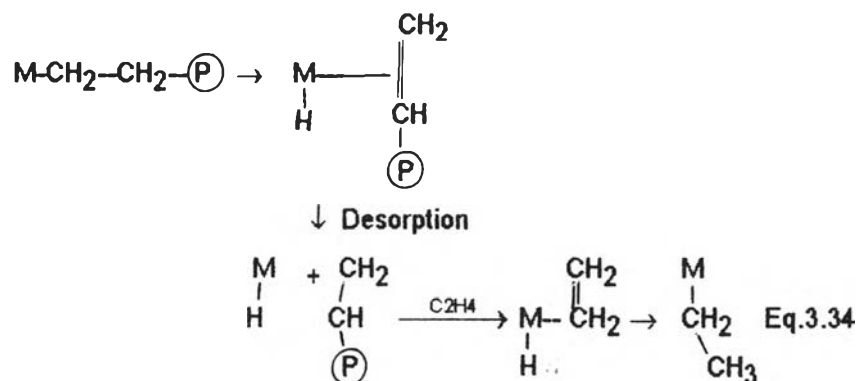
After the formation of the active center(Eq. 3.31) which is assumed to be a transition metal-alkyl bond. The complexation of alkene can occur and ethylene is an example in this case as in Eq.3.32. This is followed by insertion of the alkene in to the metal-alkyl bond. Propagation of the polymer chain occurs via repetition of the complexation-insertion cycle.



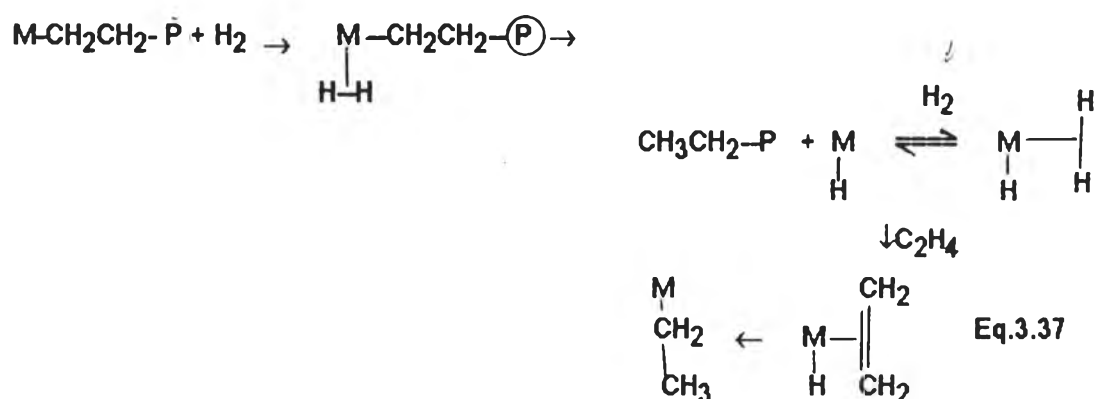
Various side reactions can occur. A β -elimination of hydrogen followed by addition to a complexed ethylene molecule can generate a vinyl group at the end of the polymer chain. Terminal vinyl unsaturation can thus be produced in some polymer chains by desorption of this group. Alternatively it can insert into the metal-ethyl bond to generate an ethyl branch as in Eq. 3.33 in ref.[65].



The hydride elimination can also occur in the absence of coordinated monomer to give an unsaturated polymer chain and a metal hydride. Desorption, followed by complexation of ethylene and insertion, leads to the formation of a M-R bond Eq.3.34. The hydride could also exchange with an alkyl group on the cocatalyst. Similarly, a chain transfer reaction is possible between the bound polymer chain and aluminium alkyl cocatalyst (Eqs 3.35 - 3.36).



Hydrogen can add to a polymerization as a means of reducing and thus controlling the average molecular weight of the polymer. Complexation of hydrogen is followed by the formation of a metal-hydride bond and elimination of a saturated polymer chain. Polymerization can be inhibited by complexation of hydrogen to the metal hydride as in Eq.3.37 which otherwise can complex and insert ethylene as before to regenerate the metal-alkyl bond. Other additives, such as zinc alkyls used to regulate molecular weight, act as chain transfer agents in a similar fashion to aluminium alkyls. They limit molecular weight since alkene insertion into a Zn-R bond does not occur.



3.5.5 Growth and replication

Polymerization catalysis is unusual in that, except under unusual circumstances, the products of the catalytic reaction are not separable from the catalyst during the actual polymerization. That very high conversions can be achieved is due to the physical state of the catalyst changing as a solid polymer is produced

3.6 Polymerization Process

The technologies available for HDPE manufacture are solution, slurry, or suspension, and gas-phase polymerizations. Each process has its own advantages and disadvantages.

The solution viscosity increases quickly with molecular weight and it is employed primarily for low molecular weight PE. Slurry(suspension) polymerization is the oldest and most widely used method because of process-engineering maturity and flexibility. This technology is the only one capable of producing the full range of HDPE grades, from low molecular weight waxes to ultra-high molecular weight HDPE. Gas-phase polymerization, the newest technology, is increasingly utilized since its low investment requirements and operating costs.

Solution Polymerization

At polymerization temperatures at above 120-130 °C, the polyethylene formed becomes soluble in the hydrocarbon medium. Several processes utilize the concept of solution polymerization; the DuPont process scheme is shown in Figure 3.10.

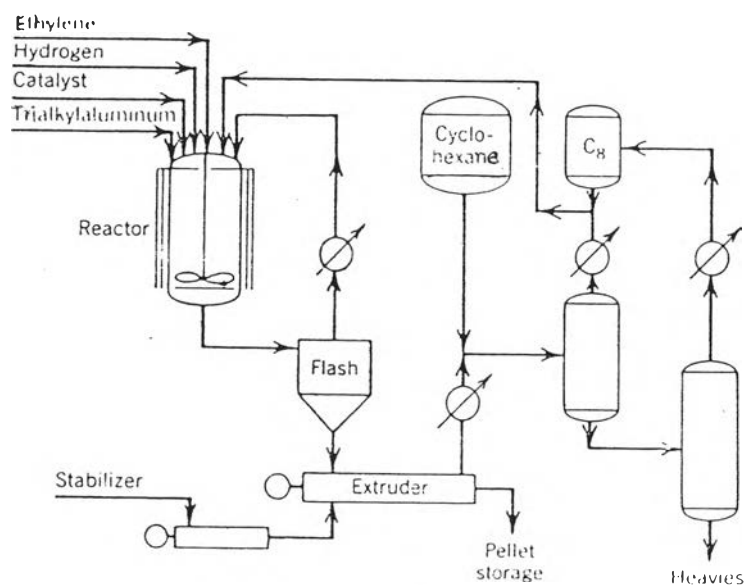


Figure 3.10 DuPont solution polymerization [66]

Ethylene, cyclohexane as the media, catalyst components, and hydrogen are continuously fed to a reactor at a total pressure of ca.8 MPa(1175 psig). The reaction occurs at 150 °C for 5-10 min. (residence time). The crucial parameter determining the performance of the unit is the viscosity of the polymer solution, since highly viscous systems cause stirring and homogeneity difficulties. If low molecular weight polyethylene is made, polymer concentration can reach 30-35%. Hot polymer solution is discharged from the reactor into a flash tank where most of the solvent is vaporized for further recycle. The remaining solvent (5% of the total) is removed during pelletization in a devolatilizing extruder. The solvent is combined with makeup cyclohexane and possibly a comonomer and then it returned to the reactor.

The DuPont process employs a three-component catalyst consisting of $TiCl_4$, $VOCl_3$, and $AlBu_3$. Other suitable catalyst systems include chromium-based catalysts and supported and unsupported Ziegler-Natta catalysts. Chromium(III) acetylacetonate and $Al(i-Bu)_3$ with a silica support is an effective system. Dow applies a titanium catalyst prepared from $TiCl_4$ and $Al(i-Bu)_3$ modified with NH_3 , and has also reported the $\delta-TiCl_3 \cdot 0.33AlCl_3$ -tridecylaluminum as catalyst.

The advantages of solution polymerization are a relatively small reactor(short residence times) and easy control of polymer properties. Solution polymerization is used primarily for low molecular weight HDPE and LDPE.

Slurry(Suspension) Polymerization

Polymerization in which catalyst and polymer particles are suspended in an inert solvent (light or heavy hydrocarbon) is termed as slurry or suspension polymerization. Historically, this was the first method used for commercial ethylene polymerization with the original Ziegler catalyst. At present, this method utilizes highly active catalysts (titanium or chromium based), which eliminates the deashing process.

Slurry ethylene polymerization in light hydrocarbons was firstly commercialized by Phillips Petroleum Co.in 1961 (Figure 3.11); a loop reactor was used in a liquid-phase process. The reactor consists of a folded loop containing four long (ca. 50 m) runs of pipe 1 m in diameter, connected by short horizontal lengths of ca. 5 m. It is jacketed for cooling. A slurry of HDPE and catalyst particles in a light solvent (isopentane or isobutane) circulates at a velocity of 5-12 m/s. Rapid circulation is needed for efficient

removal of the heat of polymerization and prevention of polymer deposition on the reactor walls causing fouling. The concentration of the polymer particles in the slurry is about 25% by weight.

Ethylene, alpha olefin comonomer (if used), solvent, and catalyst components are continuously charged to the reactor. The polymer is concentrated in settling legs and the solvent is separated from the hot polymer by flashing and recycled. Afterwards, the polymer is dried and pelletized. The process conversion is very high, omitting ethylene recovery. Heavier solvents can also be used in loop reactors.

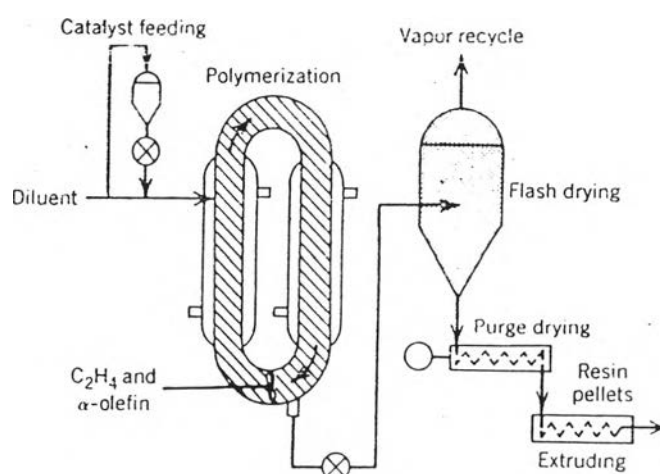


Figure 3.11 Phillips loop reactor process [66]

Phillips Petroleum Co. has developed catalysts compatible with this process, starting with a Cr₂O₃ on silica catalyst. The melt index of HDPE can be improved by Cr₂O₃ supported catalysts containing titanium compounds. They typically operate at 85-110 °C. Molecular weight is controlled by temperature; hydrogen is normally not required.

Such processes are used by Hoechst, Montedison, Mitsui, and Solway. In Hoechst process (Figure 3.12), hexane, ethylene, catalyst components, and hydrogen are repeatedly fed into a stirred reactor. The slurry of polymerization system is transferred into a postreactor for postpolymerization, after which the total charge is separated by a centrifuge into a diluent recycle to return to the initial reactor. Whereas the wet polymer is steam-stripped for the solvent recovery and removal, dried, and pelletized. The process utilizes a high activity supported Ti-based catalyst without deashing.

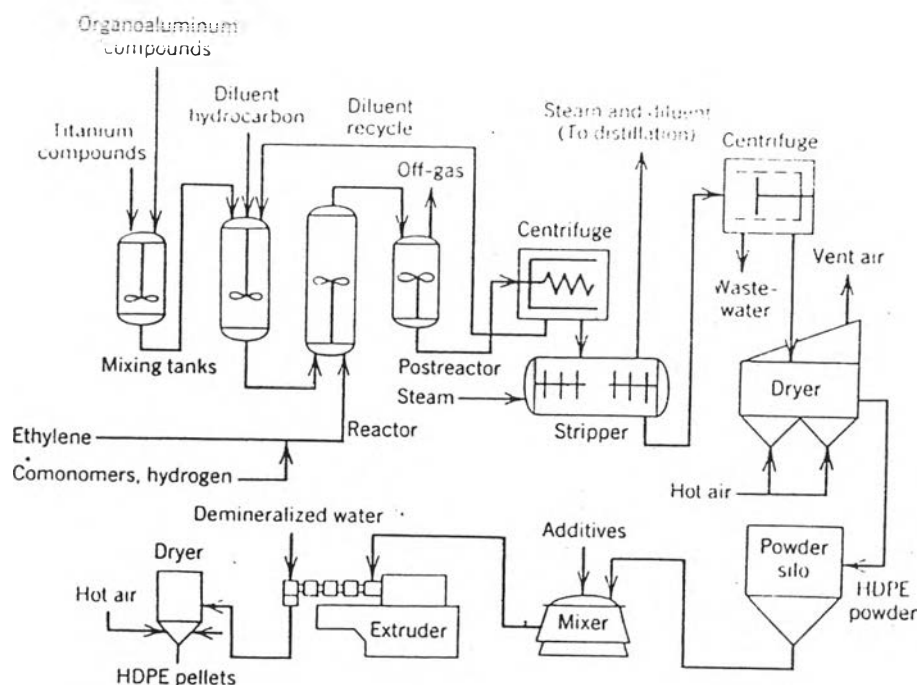


Figure 3.12 Hoechst slurry process [66]

Gas-phase Polymerization

Gas-phase polymerization, the most recent and advanced technology for HDPE production, was introduced by Union Carbide in 1968. Gas-phase technology is flexible, employing different catalyst systems capable of ethylene polymerization at relatively low pressure. Solid catalysts are used for ethylene polymerization or its copolymerization with light comonomers in gas phase. The system is agitated by mechanical devices, such as horizontal paddles or screws, or by a gas stream of ethylene which fluidizes the polyethylene particles bed.

The Union Carbide gas-phase process is suitable for the production of both HDPE and LLDPE shown in Figure 3.13. The reactor is a typical fluidized bed with a length-diameter ratio of ca. 7 and a disengagement zone at the top. Uniform fluidization is achieved by ethylene flow through a distribution plate at the reactor bottom, and rapid circulation ensures removal of heat of polymerization. Both fluidization and heat removal require rapid recycling of ethylene. Unreacted ethylene enters the disengagement zone, separates from the entrained polymer particles, is filtered, cooled, compressed and recycled. A catalyst is continuously fed to the reactor without the diluent, and polymer particles are continuously removed from the bed through a system valve. The reactor is maintained below 100 °C. Low ethylene conversion is used for precise temperature control, which is critical since elevated temperatures result in a sticky polymer detrimental to fluidization.

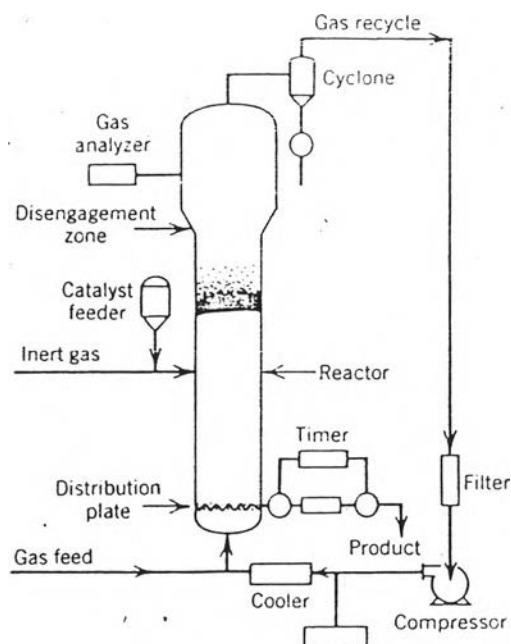


Figure 3.13 Union Carbide gas-phase process [66]

1-Butene is a frequent comonomer to control polymer density. The catalyst is sensitive to hydrogen, which is used to control molecular weight. Any variation in the amount of catalyst is accompanied by a change in heat regeneration. For this reason, the ethylene temperature in the disengagement is monitored. Nitrogen is charged to the bottom of the reactor along with ethylene, hydrogen, and 1-butene for precise control of polymerization and reactor parameters.

The product is periodically removed from the reactor through a discharge valve, where residual pressurized gases are separated and recycled; a filter removes trace particle fines. The polymer, with an average particle diameter of ca. 500 μm , is transferred to a finishing section where stabilizers are added. The stabilized polymer flakes are stored as such as pelletized.

The Amoco process utilizes an original compartmentalized horizontal stirred-bed reactor, shown in Figure 3.14. In each cylindrical compartment, polymer particles are agitated by internal mixing blades turning at low speed. The individual compartments contain a subfluidized bed maintained by the introduction of gases ($\text{CH}_2=\text{CH}_2$, H_2 , and comonomer) into the bottom inlets of each section. Similarly, catalyst components are sprayed into the bed from inlets to the top of the reactor. A distinctive feature of the Amoco process is the removal of heat by the vaporization of light liquid hydrocarbons, e.g., butane or isopentane, which are sprayed into the reactor from top inlet

ports. This process scheme gives a much higher ethylene conversion per pass, but hydrocarbon recovery and recycling are more complicated.

The reactor is operated at 70-80 °C and 2 MPa(304 psig). A comonomer such as propylene or 1-butene controls molecular weight and polymer density. The polymer is finally discharged at the end of the reactor through valves. Vapors are separated into a recycle-gas stream (ethylene, hydrogen, and comonomer) and recycle-solvent stream.

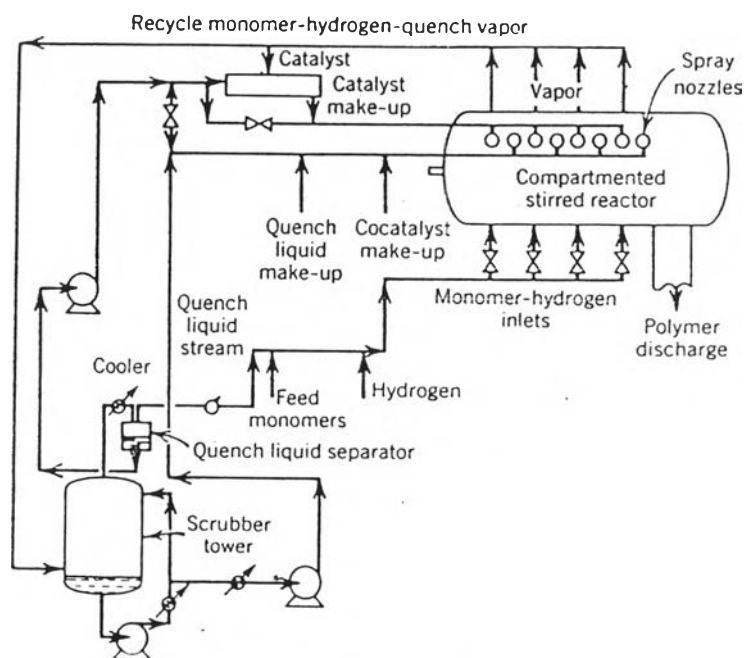


Figure 3.14 AMOCO gas-phase

A catalyst system patented by Amoco for its gas-phase process is derived from a titanium or vanadium alkoxide, hydrated magnesium stannate, and alkylaluminum dichloride. Specific aging techniques have been developed in order to control particle size distribution. Polymer particle size is substantially increased by utilizing a catalyst system comprising $\text{Mg}(\text{OEt})_2$, $\text{Ti}(\text{OBu})_4$, EtAlCl_2 , and AlEt_3 .