CHAPTER III

THEORY

3.1 INTRODUCTION

Polymerization of α olefins with transition metal catalysts (Ziegler-Natta catalysts) is of tremendous industrial importance. Titanium-base transition metal catalyst known as Ziegler-Natta catalysts were discovered by Karl Ziegler in Germany and Giulio Natta in Italy in 1953 and 1954, respectively. Since then, there has been significant progress in industrial α-olefin polymerization process. In modern olefin polymerization process, high and low density olefin polymers are produced by liquid slurry, solution and gas-phase polymerization process using highly active and stereospecific catalysts that do not require catalyst dashing and atactic extraction steps after the polymerization. These new developments are a culmination of extensive and persistent research efforts in many industrial and academic laboratories. Along with the developments of high efficiency industrial polymerization catalysts and process, there has been an enormous accumulation of scientific and patent literature in this field during the past decade. However, many aspects of fundamental behavior in olefin polymerization remain poorly understood.

3.2 DEFINITION OF THE ZIEGLER-NATTA CATALYST

The broad definition of a Ziegler-Natta catalyst is a mixture of alkyl, aryl or hydride of the group I-IIIA metals and transition metal compound of group IV to VIIIB metals such as titanium, vanadium, chromium, zirconium; this definition is too broad since not all possible combination of the two component will from active and stereoregulating catalyst for the polymerization of ethylene and α-alkenes [35].

$$\text{Transition metal compound} + \text{Metal alkyl, aryl or hydride} \rightarrow \text{Active Ziegler - Natta catalyst} \qquad \text{Eq.3.1}$$

3.3 FACTORS DETERMINING CATALYTIC BEHAVIOR

The chemical nature of the catalyst, that is the choice of metal alkyls and transition metal compounds of difference chemical composition for the polymerization of olefins. Besides the choice of metal for each component, other factors such as the nature of ligand can be significant, and it is the sensitivity of the final catalyst to these factors that makes these catalyst so versatile, and yet so difficult to elucidate. It is not possible, however, to make broad generalizations and extensions in going from one type of catalyst to another or from one type of monomer to another.

3.3.1 The Metal Alkyl

3.3.1.1 Group of Metal

Not every metal in groups I to III forms an active metal as is claimed in many of the patents relating to Ziegler-Natta catalysts. Active catalysts from the following metals have been established of ethylene and propylene. Table 3.1 show selected [36] examples of typical catalysts for group I, Group II, group III metal alkyl. Of these, aluminum alkyls have been the most extensively used, and the reason for this partly scientific and partly economic. The most widely used aluminum alkyls have been $AlCl_3$, Al-i-Bu_3, $AlEt_2Cl$, $AlEtCl_2$ and $AlEt_2OR$.

Table 3.1 Group of Metal Alkyl

Group I	Group II	Group III
Li Na K	Be Mg Zn Cd	Al Ga

Of the group I metal, metal alkyls from lithium, sodium and potassium have received the most attention. Relative to group II and III metal alkyls, these are more ionic and, with the exception of some lithium alkyls, normally used in olefin polymerization. The activity of the n-BaLi-$TiCl_4$ catalyst for polymerization of ethylene was found very sensitive to Li/Ti ratio and presence of ethylene when the catalyst components were mixed [37]. This sensitivity was later found for many other combination of metal alkyl and transition metal compounds especially when the latter was added in its highest valence state.

Of the group II metal alkyl, those based on Zn have been most widely examined. Beryllium alkyls probably would have been more extensively investigated if it were not for their toxicity. in combination with α-, γ-, δ-$TiCl_3$ -$BeEt_2$ formed highly isotactic - specific catalyst.

Of the other metal of group III, only gallium is attractive, but its high cost has prevent it from further examination [38]. The activity of GaR_3- $TiCl_4$ catalysts in the low pressure polymerization of ethylene was lower compared analogous aluminum alkyls order, $GaPr_3$ > $GaMe_3$ >$GaEt_3$. There is very little data on metal alkyls of indium and thallium.

3.3.1.2 Ligands [39-41]

There are two type of ligands

i) An all-hydrocarbon alkyl or aryl, as ethyl or phenyl

ii) A heteroatom or radical containing a heteroatom, such as Cl or -OC_6H_5.

Both of these types of ligands have the potential of undergoing exchange reactions with the ligands of the transition metal. When the alkyl or aryl group is exchanged, a transition metal - carbon bond is formed. The active center is a transition metal - carbon bond. Should the heteroatom be exchange for a ligand of the transition metal, inactive center is not formed because the transition metal - heteroatom bond is not active. However, the electronic and steric environment of the metal atom is altered. If this metal atom later becomes alkylated, then this center will probably how a different stereoregulating ability relative to the other center not bearing the heteroatom. The chemical behavior of a metal alkyl is strongly influenced by the nature and number of these two type of ligands.

3.3.2 Transition Metal Compound

Transition metal are active center of catalyst. While individual factors such as choice of metal, ligand, valence, mode of reaction, etc., are very importance, it is ultimetely the combined effect of these factors that decides the contribution of the transition metal salt.

3.3.2.1 Choice of Metal

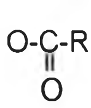
Transition metals have formed active metal salts for one or more monomers. The number of active metals in greatest for ethylene and diminishes for propylene and higher α-olefins. The Availability of $TiCl_4$ as an inexpensive materiel in the 1950's undoubtedly promoted considerable reaches aimed at industrial applications. It is not surprising that many paper and patents have appeared that use $TiCl_4$ or a derivative, especially $TiCl_3$'s and $TiCl_2$'s of verying compositions and crystal structures.

Other transition metal, such as Se, V, Cr, Nb, Zr, and W have been examined. Vanadium salts attracted much attention because they predominanly led to random alternating copolymer, in contrast to blocky polymers obtained with titanium salts.

3.3.2.2 Ligands [42,43]

Active catalysts for ethylene, propylene, and higher α-olefins have been made from transition metal salts bearing ligands of varied structures. These ligands include the groupings shown in table 3.2. From a practical point of view, not all of these are always attractive. One must select each transition metal salt on the basis of the monomer polymerized as well as such other constraints as yield, stereoregularity, copolymer composition, morphlogy, or a combination of these.

Table 3.2 ligands of Transition metal.

Ligands
-Cl
-OR (R = alkyl such as Bu, Me)
-SR (R = alkyl such as Bu, Me)
$-NR_2$ (R = alkyl such as Bu, Me)
acetylacetonate
nitroso
phosphate
chromate
π-C_5H_5
 $O-\underset{\underset{O}{\|}}{C}-R$ (R = CH_3)
oxide
sulfide (disulfide)
sulfate
carbon monoxide

3.3.2.3 Elemental Composition

The transition metal salt can have a neat composition if its synthesis did not use other metal or metal compounds.

$TiCl_4 + H_2 \rightarrow \alpha\text{-}TiCl_3$ Eq.3.2

$TiCl_4 + \text{radiation} \rightarrow \beta\text{-}TiCl_3$ Eq.3.3

$VCl_4 + \text{heat} \rightarrow VCl_3 + Cl_2$ Eq.3.4

However, a number of important titanium and vanadium transition metal salts have been prepared by reduction of $TiCl_4$ or VCl_4 with metal alkyl or with metals and mixture of metals and metal chlorides. Sometimes these catalyst were prepared in the polymerization reaction,often in the presence of the olefin being polymerized.

3.3.2.4. Crystalline Modification

Four crystalline modification have been identified for $TiCl_3$. $\chi AlCl_3$ salt, namely the α, β, γ and δ forms. As stated earlier, $TiCl_3$ exists in form crystalline modification, the α, β, γ and δ forms. These $TiCl_3$'s can have the simple composition (one Ti per three Cl) or more complex structure whereby a second metal is cocrystallized as an alloy in the $TiCl_3$ crystal. Literature of Ziegler-Natta catalyst is concerned with different crystalline modification. It is likely that $TiCl_3$'s are widely used. It is understandable then why so much effort has been made to develop $TiCl_3$'s of higher activity and stereoregulating ability and of a particular morphology. It is important to recognize that the actual performance of $TiCl_3$ modification can vary significantly according to the particular condition of synthesis. For example the initial and constant rate of polymerization will depend on the overage size of the $TiCl_3$ crystallites because the surface of the latter largely determines the number of active centers. The polymer particle shapes and sizes will depend on the sizes and reactants, mode of mixing, temperature of reaction, etc., will determin the characteristics of the particular catalyst [44-51].

The particular method of reduction determines both the composition and crystalline modification, as show in Table 3.3. Table 3.3 summarizes the synthesis of most important $TiCl_3$'s that have been report in the Ziegler-Natta literature. The α-$TiCl_3$ was synthesized by reduction of $TiCl_4$ with H_2 at elevated temperature (500-800 °C).$TiCl_4$ can be reduced with aluminum powder at lower temperature (about 250 °C); the formed $TiCl_3$ also has the α-crystal structure but, in addition, contain Al cations in the crystal lattice. In later polymerization studies, these α-$TiCl_3$ were replace by more active modification, namely γ and δ. The γ modification is formed by heating the β modification (at 100 to 200 °C) ; the higher the temperature, the shorter is the time required for the transformation. For a β modification containing one Al per three Ti, the transformation takes only seversal hours at about 140 °C. The β modification (free of Al) is synthesized by decomposition of CH_3TiCl_3, but this form does not form a highly active and highly stereoregulating catalyst for polymerization of propylene to isotactic polypropylene. The γ modification derived from it also has a low activity. The preferred composition contains Al cations, and they are synthesized by reducing one $TiCl_4$ with about 1/3 $AlEt_3$, one $AlEt_2Cl$, or 1-2 $Al_2Et_3Cl_3$.

Table 3.3 Preparation of the α, β, γ, and δ crystalline modification of $TiCl_3$ and $TiCl_3 \cdot AlCl_3$

Expt. no.	Preparation	Crystalline form	Composition
1a.	$TiCl_4 + H_2$ at high temp. (800 C)	α	$TiCl_3$
b.	$TiCl_4$ + Al at 100°-200°C in aromatic solvent	α	$TiCl_3 \cdot 0.33\ AlCl_3$
c.	$\beta TiCl_3$ heated to 300°-400°C	α	$TiCl_3$
d.	$3\ TiCl_4 + Al + 0.5\ AlCl_3 > 190°C$ (no solvent)	α	$TiCl_3 \cdot 0.5\ AlCl_3$
e.	$2\ TiCl_4 + Mg + 2\ AlCl_3 > 200°C$ (no solvent)	α	$2\ TiCl_3 \cdot 0.5\ MgCl_2 \cdot AlCl_3$
f.	$9\ TiCl_4 + Ti + 2\ Al > 200$ C (no solvent)	α	$10\ TiCl_3 \cdot 0.2\ AlCl_3$
2a.	CH_3TiCl_3 heated > 25 C ($AlMe_2Cl$ or $AlMe_3 + TiCl_4 \rightarrow CH_3TiCl_3$)	β	$TiCl_3$
b.	$TiCl_4 + H_2$ exposed to silent electric discharge at low temp. or to γ radiation	β	$TiCl_3$
c.	$TiCl_4 + AlR_3$ or AlR_2Cl or $AlEt_2Cl$ < 25 C	β	$TiCl_3 \cdot xAlCl_3$
d.	$TiCl_4$ + activated Al below 100°C (e.g. in benzene at 80 C)	β	$TiCl_3 \cdot 0.33\ AlCl_3$
e.	$TiCl_4$ + Al, $AlCl_3$: aromatic solvent and ether treatment	β	$TiCl_3$ (98%)
3a.	$\beta TiCl_3$, Δ120°-200°C, up to several hours	γ	$TiCl_3$
b.	$TiCl_3 \cdot xAlCl_3$, Δ120°-200°C, up to several hours	γ	$TiCl_3 \cdot AlCl_3$
c.	$TiCl_4$ + Al + $AlCl_3$, inert solvent	γ	$TiCl_3 \cdot xAlCl_3$
d.	$TiCl_4$ + Al at 160°C in 9:1 $C_{10}H_{22}$/xylene, solvent	γ	$TiCl_3 \cdot 0.33\ AlCl_3$
4a.	$\alpha TiCl_3$ mechanical grinding, 25°C	δ	$TiCl_3$
b.	$TiCl_3 \cdot xAlCl_3$, mechanical grinding, 25°C	δ	$TiCl_3 \cdot xAlCl_3$
c.	$\alpha TiCl_3 + AlCl_3$, mechanical grinding	δ	$TiCl_3 \cdot xAlCl_3$

The δ crystalline modification is synthesized by prolonged grinding of the α and γ forms. Because the γ $TiCl_3$ (containing $AlEt_3$) is already highly active, it is not practical to transform it to the δ form. On the other hand, the activity of α $TiCl_3$ form (containing $AlCl_3$) is much improved by transforming if to the δ form. Figure 3.1 summarizes the observed transformations of the various crystalline modification.

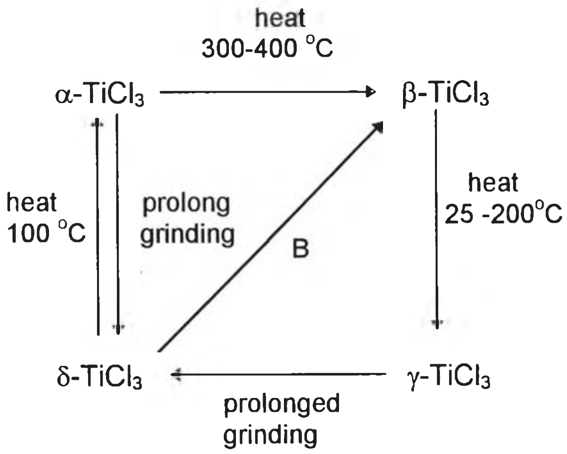


Figure 3.1 Crystal - crystal transformation

3.4 MECHANISMS OF ZIEGLER-NATTA POLYMERIZATION

Despite the many research activity that has focused on Ziegler-Natta catalyst systems since in the early 1950's. The mechanism involved in these catalytic reaction has still not been unequivocally established. One reason for this is the complexity of the systems employed. For instance, the catalyst it self may react as solid or may be soluble in the reaction medium; activation by an organometallic compound is usually required. The monomers that are homo-, or co-polymerization may be gases or liquids; electrons doners may be added to improve stereoregulating; and the whole process may be performed under slurry, solution or gas phase condition. When one remembers that the polymerization in occurring at a small percentage of sites on the surface of a solid, this fact becomes loss surprising.

It is generally accepted that the process of polymerization involves the formation of a complex between the alkene and active site, followed by 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. Various mechanisms have been proposed which differ according to whether the growth center is a bound radically a bound anion or a metal-alkyl bond. Of these the last is by far the most widely accepted group and can be subdivided according to whether the growth center is an activator-alkyl bond or a transition metal-alkyl bond. All of these mechanisms will be considered together with supporting and contradictory experimental evidence.

3.4.1 Early Mechanisms

A number of early mechanisms were based on a radical mode of polymerization propagation. Various possible initiators were proposed: the transition metal center, the aluminum center, or and alkyl from radical resulting from the reduction of a titanium alkyl from an oxidation state of four to three, or from three to two. Under appropriate condition some monomers, for example vinyl chloride, do polymerize by a radical mechanism in the presence of some or all of the components of a Ziegler-Natta catalyst. However, true Ziegler-Natta polymerization of ethylene give a very different product from the polyethylene produced by the high-pressure radical process. The Ziegler - Natta ethylene homopolymer has a higher density and crystallinity due to having very few of the side chain branches associated with be radically produced polymer. Nenitzescu and co-worker [52] suggest the posibility of a radical mechanism, shown in Eq. 3.5, 3.6, 3.7.

$$R_3Al + TiCl_4 \rightarrow R_2AlCl + RTiCl_3 \qquad \text{Eq.3.5}$$

$$RTiCl_3 \rightarrow R^{\cdot} + TiCl_3 \qquad \text{Eq.3.6}$$

$$R^{\cdot} + C_2H_4 \rightarrow RCH_2CH_2^{\cdot} \rightarrow \text{Polymer} \qquad \text{Eq.3.7}$$

In 1956, Friedlander and Oita [53] proposed a free radical mechanism in which initiation occurred when an electron was transferred from the metal to the olefins (Figure 3.2).

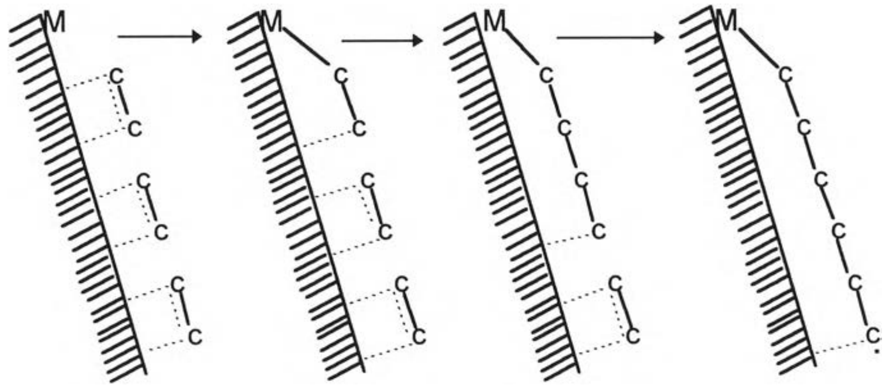
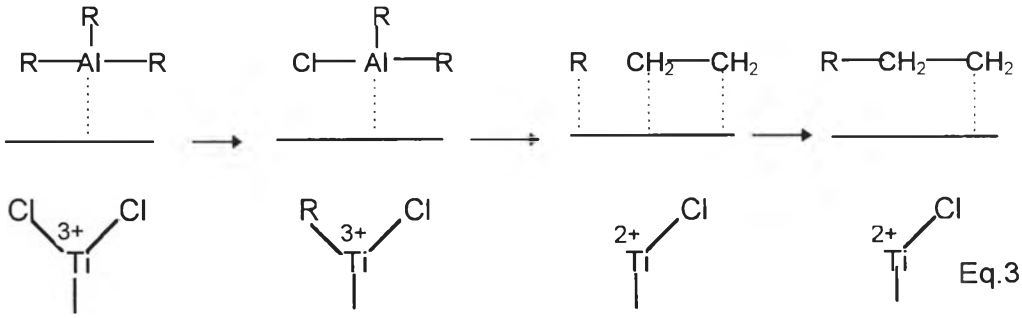


Figure 3.2 Friendlander and Oita's radical mechanism

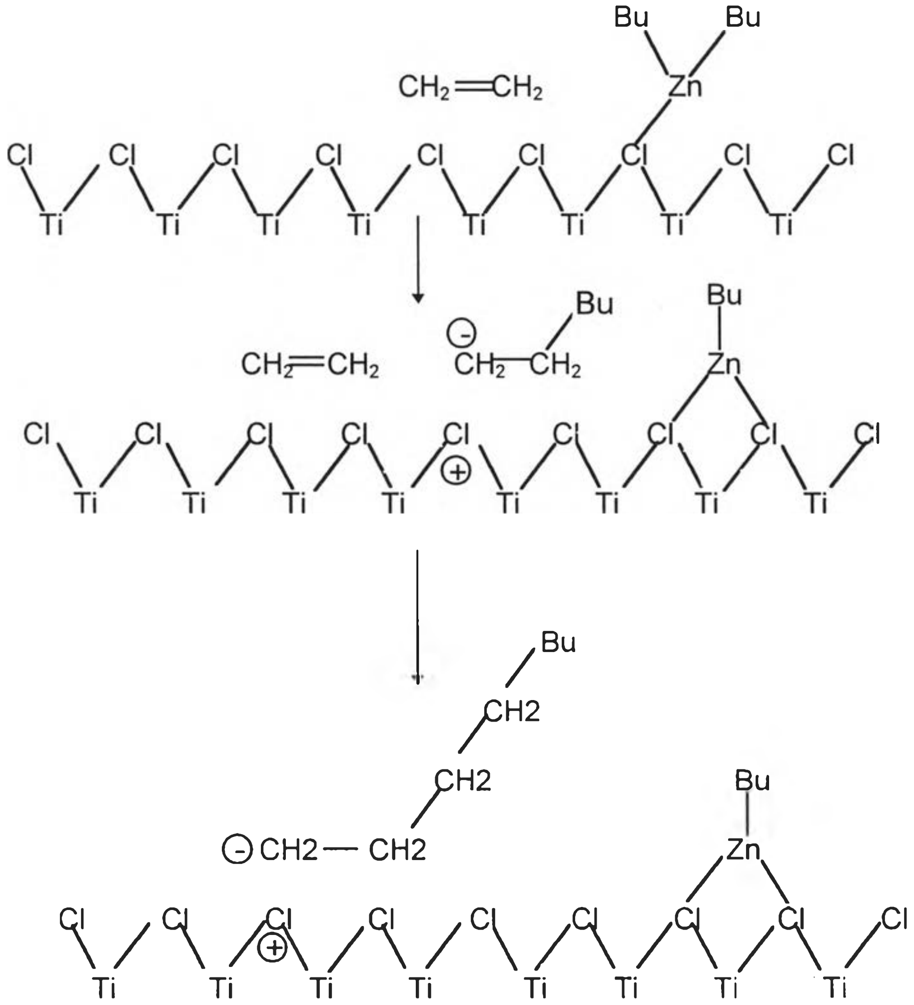
Topchiev, Krentsel, and co-worker [54] proposed that initiation occurred by radical, which is bound the surface of $TiCl_3$, as show in Eq.3.8. The mechanism is a chemisorption aluminum alkyl molecule alkylates a surface titanium atom, and the formed Ti-R decomposes to yield an R radical that adds to ethylene to form a new radical.



Eq.3.8

The new radical also remains bound to the surface and adds another chemisorbed ethylene molecule. This process is repeat with the radical being transferred to the last added monomer each time. Repetition of this step constitutes the polymerization; both the radical and the reacting ethylene molecules are bound to the $TiCl_3$ surface.

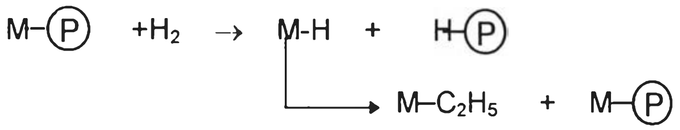
An anion mechanism was suggested by Gilchrist [55]. In this proposal the polymer chain ends in an anion carbon which is not bound to any metal center. Initiation is by transfer of an alkyl anion from the metal alkyl activation to an absorbed alkene (Eq.3.9).



Eq.3.9

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 these two. Despite the differences between radically produced polymers and those made using Ziegler-Natta catalyst, the radical and anionic mechanisms described briefly above are perhaps sufficiently different from conventional radical and anionic system for the normal tests not to be appropriate. However, there are several pieces of experimental evidence which point to the active center being a metal-alkyl bond.

The use of aluminum alkyl labeled with C^{14} leads to the formation of polymer which contain labeled carbon [56]. Hydrogen is commonly used as a chain transfer agent. This additive controls the molecular weight of the polymer without destroying active center. The transfer reaction is consistent with the existence of a metal-alkyl bond. Use of deuterium ($^2H_2$) or tritium ($^3H_2$) has given polymer containing the appropriate label. A label [57,58] is also introduced into the polymer if the polymerization is quenched by a labeled alcohol, e.g. MeO^3H (Eq.3.10)



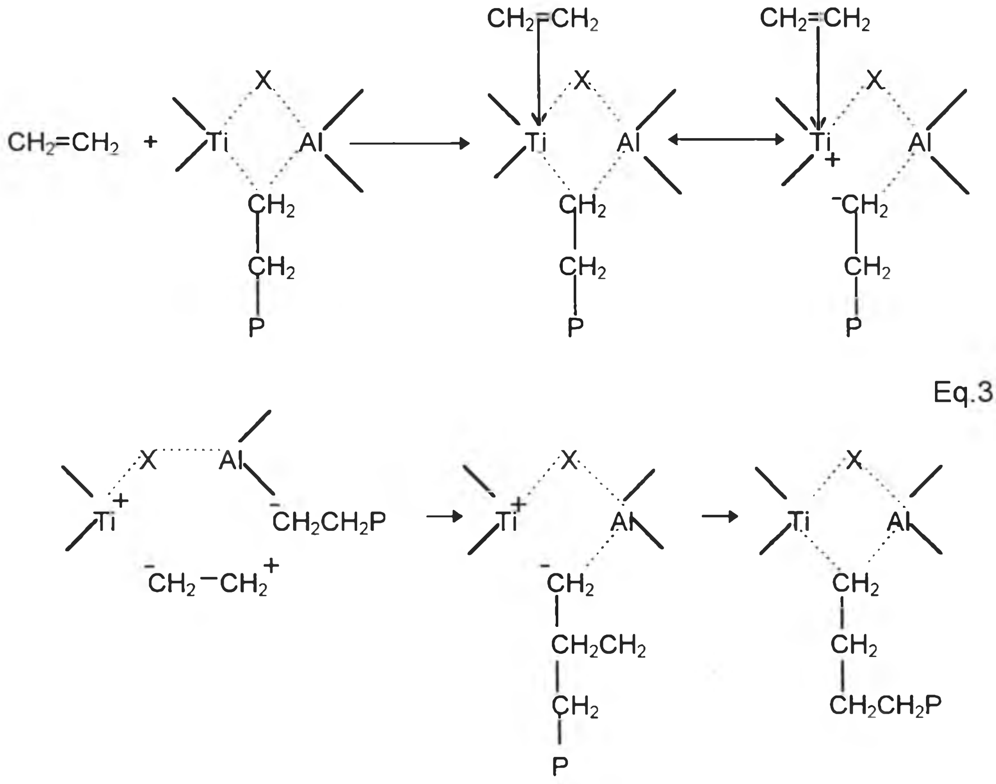
$$M\text{-}\textcircled{P} + H_2 \rightarrow M\text{-}H + H\text{-}\textcircled{P}$$
$$M\text{-}H \rightarrow M\text{-}C_2H_5 + M\text{-}\textcircled{P}$$

Eq. 3.10

3.4.2 Propagation at the Activator-Alkyl Bond.

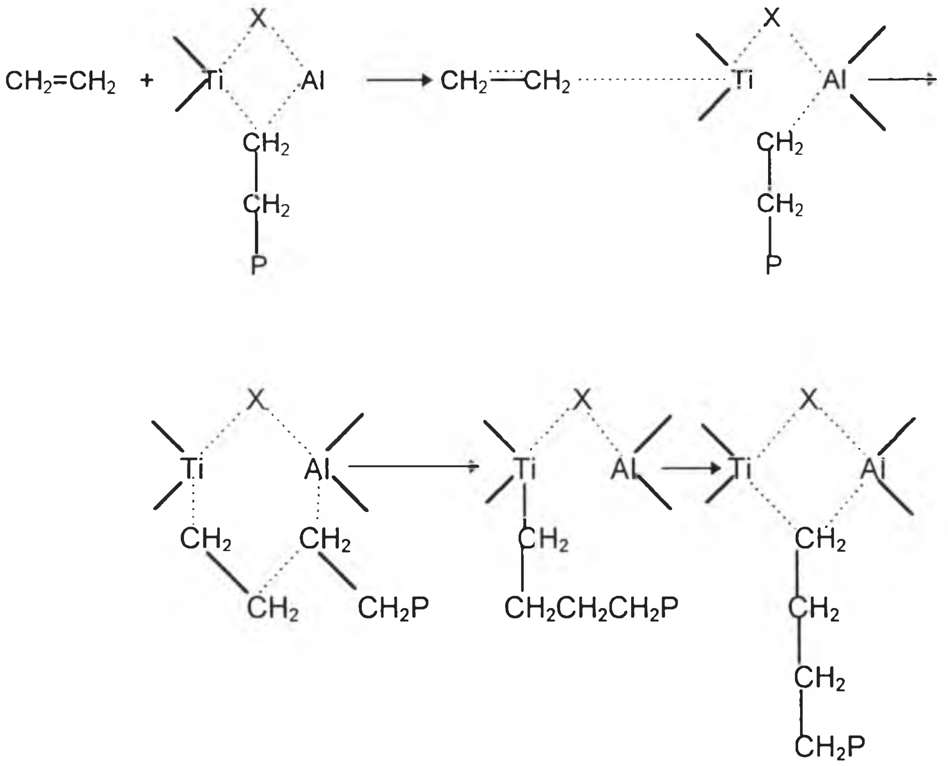
Many of the early mechanisms suggested the activator alkyl as propagation site. Clearly these proposals were influenced by knowledge of the Aufbau reaction. In this, ethylene is polymerized to low molecular weight polymer by group I-III alkyl alone, without the aid of a transition metal component. The role of the transition metal in this case could be to complex with the alkene and, by polarizing it, activate it towards inversion into activator-alkyl bond.

The mechanism of Natta [59] was an important early example of the type. Natta's previous work on the Aufban reaction suggested that polymer growth occurred via insertion of an alkene molecule into an Al-C bond. The incoming alkene molecule forms a π bond with the transition metal atom, simultaneously cleaving the bridging bond. The alkene molecule is polarized by bounding to the transition metal and then inserts into the aluminum-alkyl bond. Finally the bridging bond reforms (Eq.3.11).



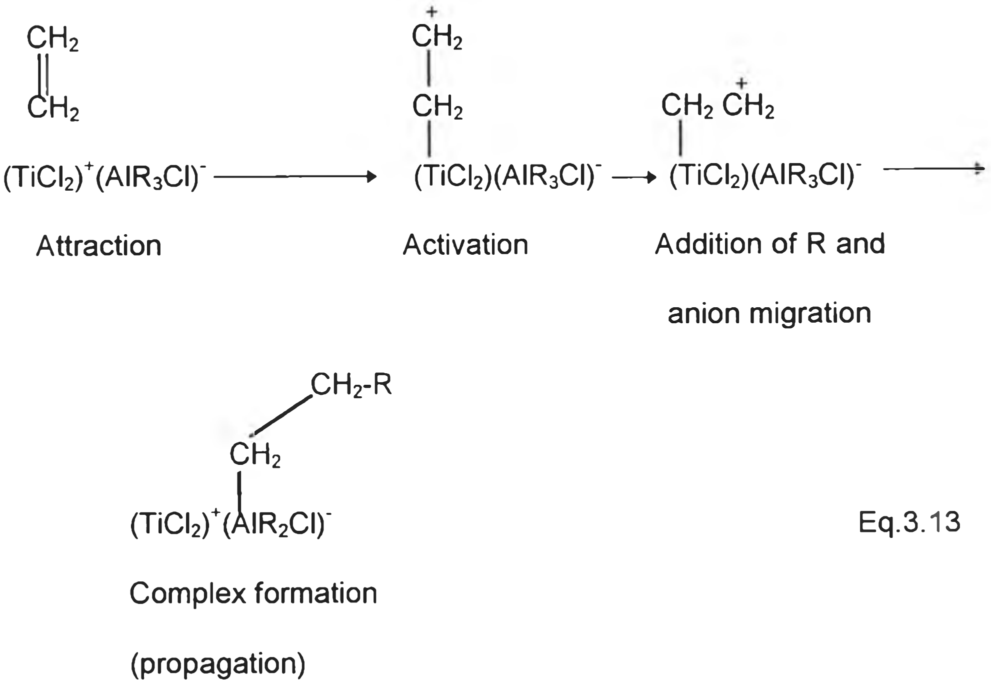
Eq.3.11

A mechanism essentially similar to Natta's was proposed by Patat and Sinn [60]; the olefin becomes partially bonded between the methylene of the last added monomer unit and the titanium atom. The latter is partially bonded via an alkyl bridge to the aluminum. When a σ bond forms between the olefin and the methylene, the methylene unit becomes detached from the aluminum and now the new methylene unit becomes partially bonded to both metal atoms (Eq.3.12).



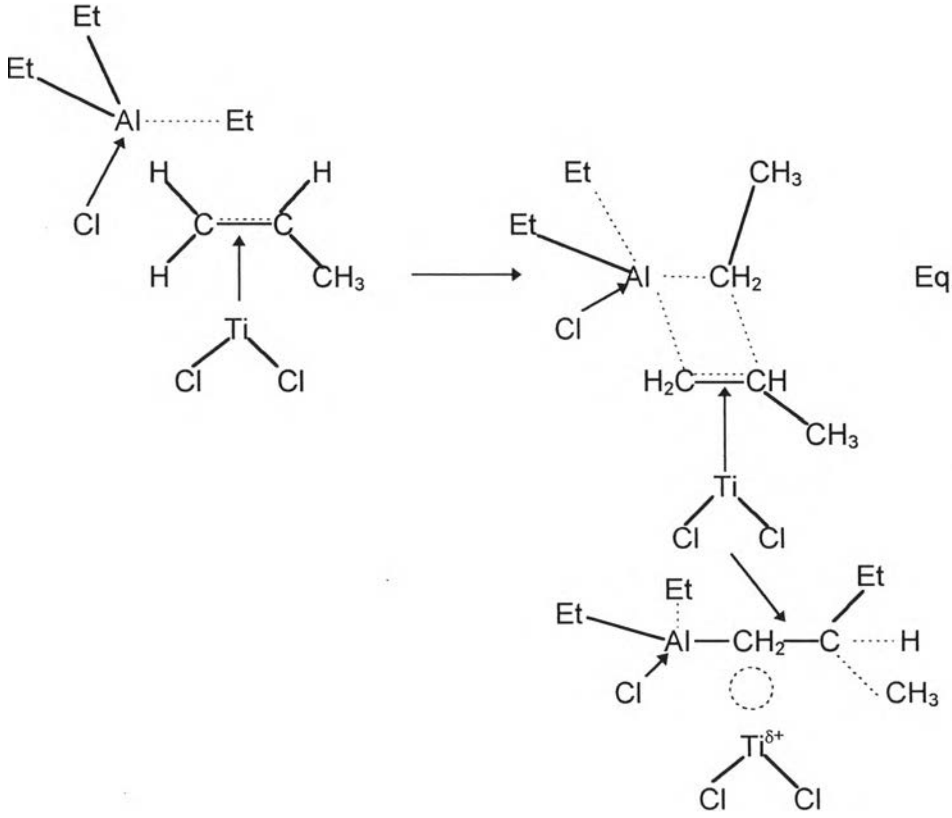
Eq.3.12

Uelzman [61] consolidated the essential features of the different proposed mechanisms and suggested the formation of an ion pair from the reaction between $TiCl_3$ and the activator. The cation produced $(TiCl_2)^+$ attracts and activates an alkene molecule which reoriontates and then inserts into an aluminum alkyl bond, $(AlR_3Cl)^-$ acting as the growth center (Eq.3.13).



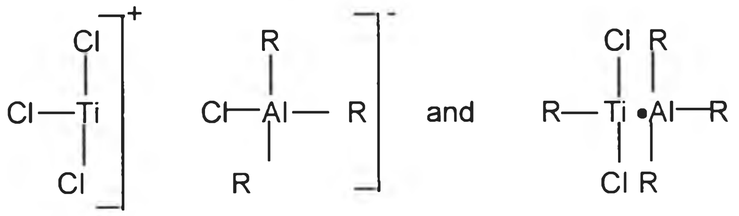
Eq.3.13

Boor [62] proposed a concerted mechannism (Eq.3.14) in which bond breaking and making occurred simultaneously.



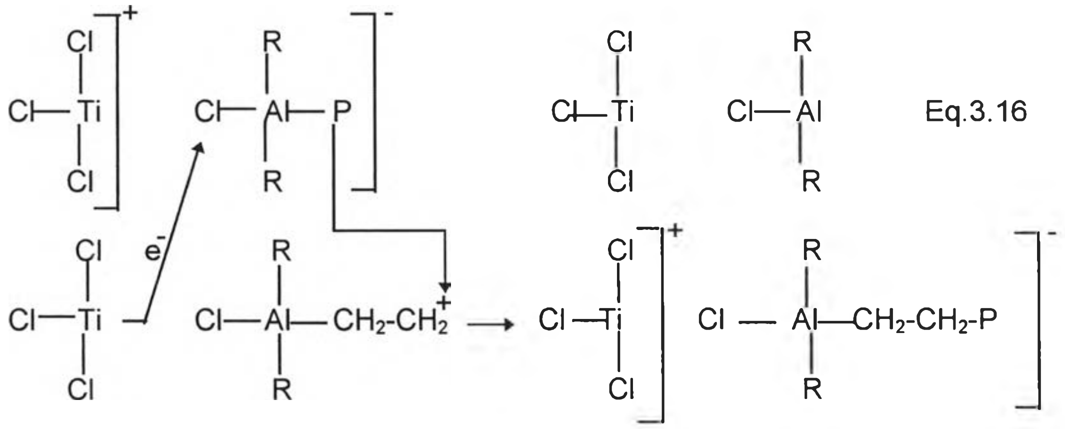
Eq.3.14

Bier , Gumboldt and Schemidt [63,64] proposed that aluminum alkyls are absorbed on the $TiCl_3$ surface in two ways, as show in Eq.3.15.



Eq.3.15

During the growth step, the growing polymer chain migrates from one aluminum atom and becomes attached to the olefin that is coordinated to an adjacent aluminum alkyl. A simultaneous electron transfer occurs between adjacent titanium atoms. The $TiCl_3$ surface acts to activate and stabilize the metal alkyl growth centers but does not coordinate the olefin itself. In a way, this mechanism can be regarded as an Aufbau reaction, which is enhanced by the $TiCl_3$ surface, as shown in Eq.3.16



Eq.3.16

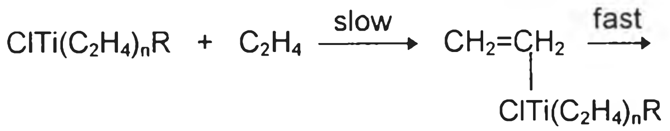
3.4.3 Propagation at the Transition Metal-Alkyl Bond

There are numerous mechanisms, this time proposing that polymerization occurs at the transition metal alkyl. Various valencies have been suggested for the titanium, ranging from four to two. An early suggestion was that polymerization occurred at a tetravalent alkyltitanium halide [52], as show in Eq.3.17

$$R\text{-}TiCl_3 \rightarrow R^{-}TiCl_3^{+} \xrightarrow{CH_2CH_2} RCH_2CH_2{}^{-}TiCl3^{+} \qquad \text{Eq.3.17}$$

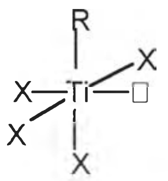
Another proposal, that a divalent alkyltitanium halide was involved, suggested complexation of the alkene followed by insertion into the titanium-alkyl bond [65]. Other similar proposals also involved complexation and insertion at a divalent transition metal, this time stabilized by complexing with an aluminum alkyl or halide. The suggestion of a valency of two for the titanium would seem to be based on an observed maximum of activity, in catalysts produced by reduction of $TiCl_4$ with aluminum alkyl, when the average titanium valence was two. Divalent titanium catalyst are know, many being extremely active in ethylene polymerization, although their activity for the polymerization of α-alkene such as propylene is generally low. Propylene polymerization catalysts have been obtained from tetravalent and trivalent titanium ions on zeolites and metal oxides ; however, divalent titanium shown no activity [66].

The rate of polymerization of ethylene using the system AlR_3-$TiCl_4$ (R = Et or Bu^i) is maximum when the average valency state of titanium is two. It has been interpreted as evidence for a divalent alkyltitanium halide being the active site[65]. A mechanism was proposed which envisaged that an ethylene molecule becomes complexed with the transition metal and is then inserted into the titanium-alkyl bond (Eq.3.18).



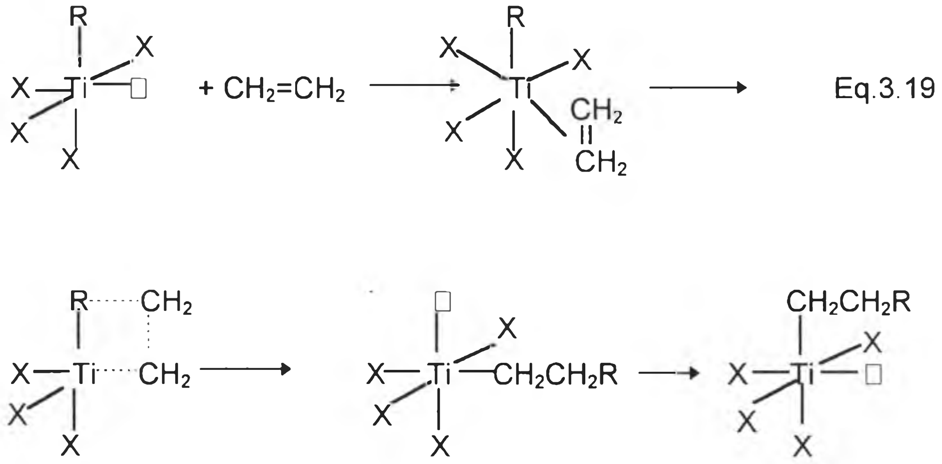
$$ClTi(C_2H_4)_nR + C_2H_4 \xrightarrow{slow} \underset{ClTi(C_2H_4)_nR}{CH_2{=}CH_2} \xrightarrow{fast} ClTi(C_2H_4)_{n+1}R \quad \text{Eq.3.18}$$

The most widely accepted of the mechanisms involving growth at the transition metal alkyl is that devised by Cossee and Alrman [67,68]. They supported by molecular orbital calculations. They proposed that active site was a transition metal atom in an octahedral configuration and that one position was vacant, □, due to a missing ligand, the remaining position being occupied by one alkyl and four ligands. In structure 1, M is the transition metal ion, R is the alkylderived from metal alkyl or growing polymer chain, x is the ligands of crystal (Cl in $TiCl_3$), and □ is the vacant octahedral position.



Structure 1

Polymerization occurs via complaxation of an alkene molecule at the coordination vacancy followed by transfer of the alkyl group to the bound alkene. A new σ bond is formed between the growing polymer chain and the transition metal atom. The new structure formed is equivalent to the original except that the position of the alkyl group and vacancy have exchanged. A final reexchange of the alkyl and vacancy position is required in order to explain the stereoregulating ability of heterogeneous catalysts in α-olefins polymerization (Eq.3.19).



Eq.3.19

Cossee [69] suggested a driving force for the polymerization on the basis of molecular orbital calculation. Figure 3.3 shows the overlap of the molecular orbital which are involved in the formation of a π bond between the alkene and the transition metal.

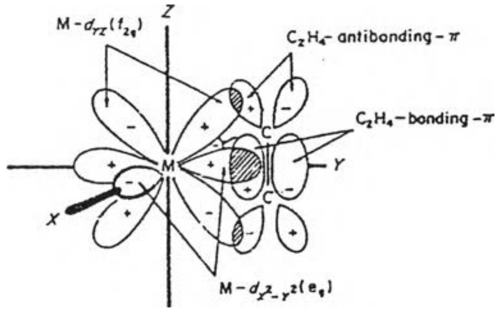
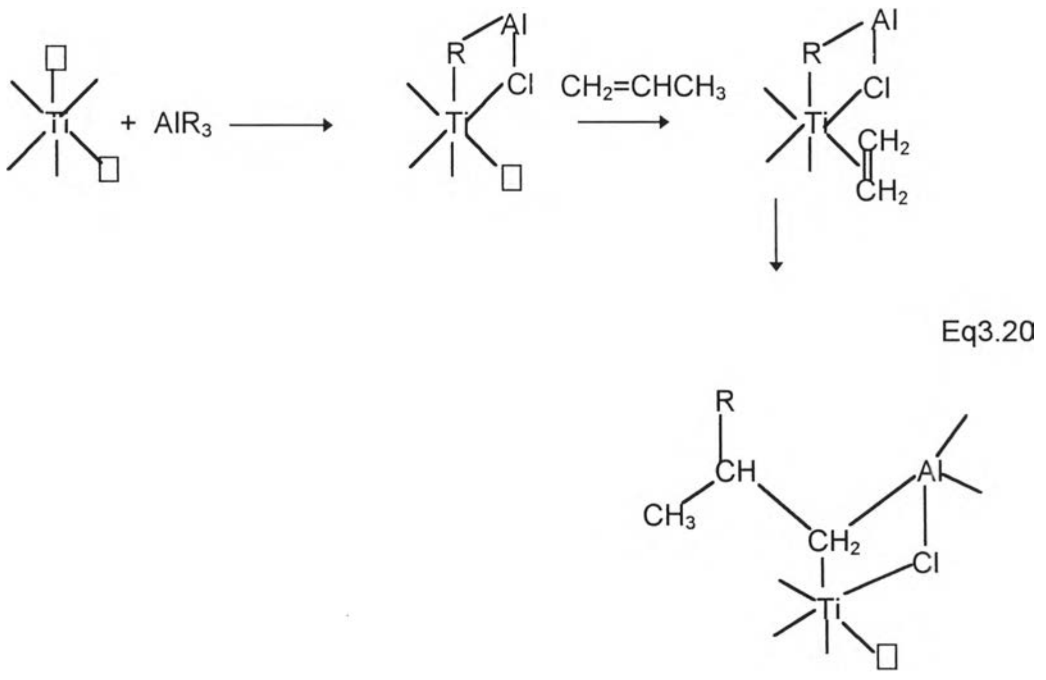


Figure 3.3 Molecular orbital overlap in the Cossee mechanism

Figure 3.3 described the π complex in terns of a molecular orbital diagram where M is titanium in the heterogeneous catalyst containing $TiCl_3$. Φ_{RM} is the energy level of the alkyl titanium bond. this bond is apparently stable when $RTiCl_4$□ is not complexed with an olefin because the catalyst can be stored for a long time. ΔE represents the energy that an electron in the Ti-R bond must be excited to in order to weaken the bond.

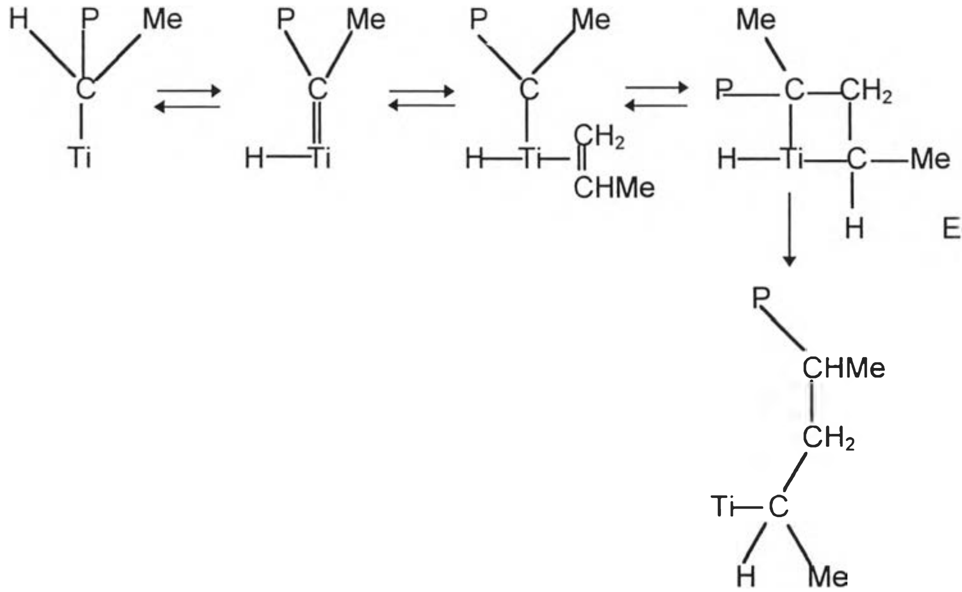
ΔE is large enough an energy barrier to maintain the Ti-R bond intact in the absence of olefins.

Other mechanisms have been proposed in which more than single transition metal atom is involved. One such suggested that the alkene coordinates at one titanium atom but then migration occurs from the metal - alkyl bond of a neighbouring titanium. Coordination of alkene then occurs at this second titanium and the alkyl ligand migrates back. However, probably the most important rival to Cossee and Arlman mechanism is that of Rodriguez and van Looy [70]. This mechanism has many similarities to that of Cossee and Arlman, but the growing polymer chain is considered to bridge between the transition metal and activator (Eq. 3.20)



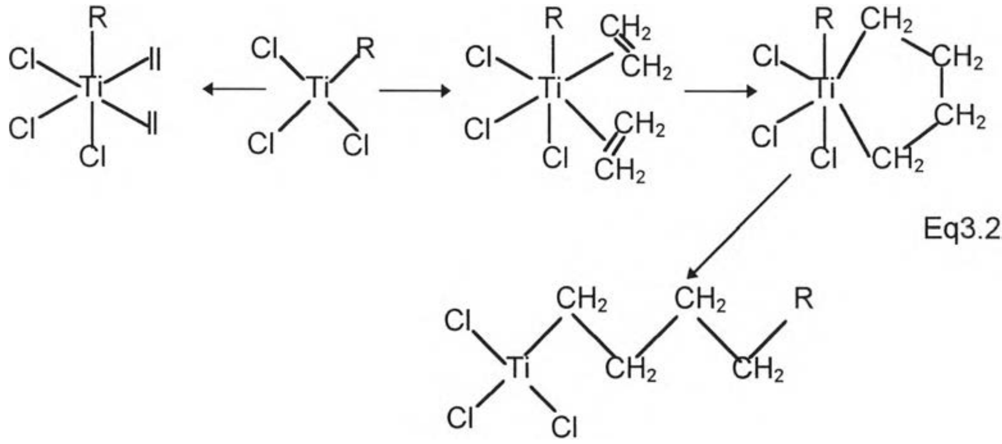
Eq3.20

A new proposals have been made about the mechanism of polymerization. These have originated from work on ring opening polymerization of cyclocalkenes and alkene metathesis in which, it has been asserted, metllocyclobutane and metal - alkene - carbene interconversions play a crucial part. The mechanism as proposed by Ivin et al. [71] is shown in Eq3.21. The metal - alkyl bond first undergoes an α-elimination to produce a metal hydride and carbene. Alkene coordinates at a vacant site and then is involved with the carbene to form a metallocyclobutane. The hydride ligand then migrates back to the tertiary carbon atom. If the latter step is slow or the hydride can be removed from the metal center, then the catalyst becomes a metathesis catalyst



Eq3.21

Schrock and co-workers [72] have proposed a mechanism for alkene polymerization base on a metallocyclopentane intermediate. The mechanism requires two vacant coordination sites on the transition metal atom (Eq3.22). After formation of the metallocyclo, alkyl group migration then completes the polymerization process. Semi - empirical molecular orbital calculations on this model [73] suggest that the intermediate in which the four carbon atoms of two bonded alkene are copolanar with the titanium is stable relative to the situation in which they are parallel in the case when the titanium is divalent but not when it is tetravalent. The mechanism is perhaps only likely when low titanium valences are involved. The calculations also suggest that in the case of propylene, equatorial 2, 4 substitution of the metallocyclopentene is the most stable form. This would lead to head - to - tail isotactic propagation.



Eq3.22

3.5 CHAIN TERMINATION [74]

3.5.1. Chain Termination by Organic and Inorganic Compound

Many works attempted to control molecular weight by terminating the growth of the polymer chain at the metal centers by the addition of reactive organic and inorganic compounds. Typical compounds included alcohol, alkyl halides, alkane thiols, H_2S, $SnCl_4$, $SiCl_4$, CCl_4, NaCl, NaBr, and BCl_3.

3.5.2 Chain Termination by Metal Alkyl

Metal alkyls can act as terminators of chain growth and under suitable condition, they function as true transfer agents. Natta and Pasquon

[75] first recognized that in a polymerization of propylene with $AlEt_3$ - α-$TiCl_3$ catalyst the molecular weight decreased at higher concentration of $AlEt_3$. Natta and co-worker later demonstrated that $ZnEt_2$ was a considerably more effective transfer agent when added to the $AlEt_3$ - $TiCl_3$ catalyst and used for polymerization of propylene. They could easily lower molecular weight from about $6*10^5$ to$2*10^5$ without lowering overall polymerization rate or the isotactacity of the polymer. At higher $ZnEt_2$ concentration, a decrease in rate of polymerization and increase in percent solubilities accompanied the decrease on polymer molecular weight.

The process by which aluminum and zinc alkyls terminate chain growth was shown by Natta and co-workers to involve alkyl exchange between ethyl groups of the $ZnEt_2$ and the growing polymer chains on the active centers. Using natation, [cat] = the catalyst complex on which the polymer chain Pn is growing, the reaction may be represented as follows

$$[cat] - Pn + ZnEt_2 \rightarrow [cat] - Et + PnZnEt \qquad \text{Eq3.23}$$

Its used left the equation of the metal open in the active metal-carbon bond, that is, Al-C or Ti-C in the $AlEt_3$-$TiCl_3$ catalyst. The rate of this exchange reaction was first order with respect to the $ZnEt_2$ concentration and was independent of the partial pressure of propylene.

3.5.3 Chain Termination by Hydrogen

Since the hydrogen as a chain transfer agent was first described by Vandenberg, Ettore, Luciano and Natta[76,77], it has been widely used to lower molecular weight of polymer synthesized with Ziegler-Natta catalyst. Natta proposed that chain termination involves hydrogenolysis of live metal - carbon bond centers, as shown in Eq.3.24

$$[cat] - Pn + H_2 \rightarrow [cat] - H + PnH \qquad \text{Eq.3.24}$$

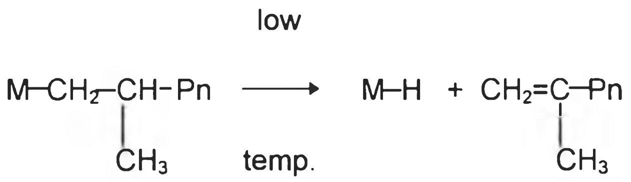
By infrared spectroscopy, they showed the presence of isopropyl end groups in the polymer when propylene polymerized. The active center is regenerated (Eq. 3.25) when an olefin molecule add to the M-H bond.

$$[cat] - H + CH_3CH{=}CH_2 \rightarrow [cat] - CH_2CH_2CH_3 \qquad \text{Eq. 3.25}$$

The patent literature strongly suggests that hydrogen is the preferred transfer agent for decreasing molecular weights of polyolefins. Without hydrogen, most catalyst process would produce polyolefins that have too high a molecular weight for most practical applications. The hydrogen method is inexpensive, easy to use and does not leave a residue in the polymer.

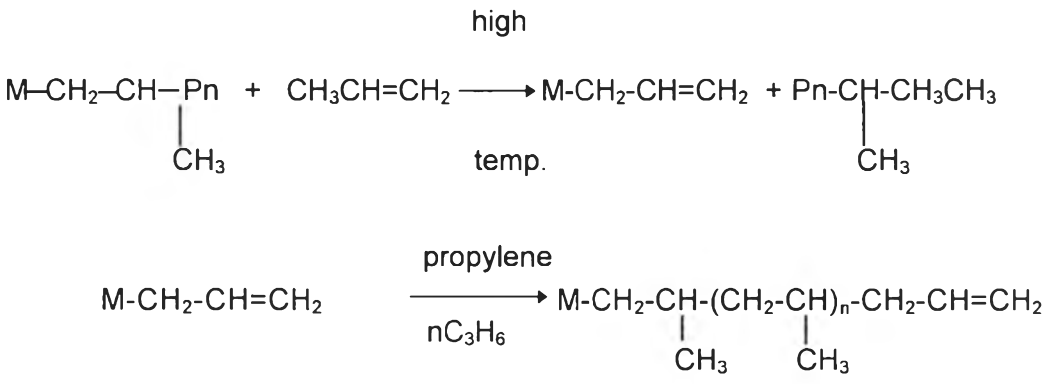
3.5.4 Chain Termination by Thermal Cleavage

Two chain termination reaction have been postulated to explain the formation of vinylidene and vinyl end group. as show in Eq. 3.26. Longi nd Co-workers [78] showed that the ratio between vinyl and vinylidene end groups increased from 1.0 at 100 to 2.0 at 200 °C. Spontaneous dissociation type of chain cleavage apparently is insignificantly for Ti-baseed catalyst at low polymerization, that is, below 60° to 80 °C.



$$M\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{CH}\text{-}Pn \xrightarrow[\text{temp.}]{\text{low}} M\text{-}H + CH_2{=}\underset{\displaystyle CH_3}{C}\text{-}Pn$$

Eq.3.26



$$M\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{CH}\text{-}Pn + CH_3CH{=}CH_2 \xrightarrow[\text{temp.}]{\text{high}} M\text{-}CH_2\text{-}CH{=}CH_2 + Pn\text{-}\underset{\displaystyle CH_3}{CH}\text{-}CH_3CH_3$$

$$M\text{-}CH_2\text{-}CH{=}CH_2 \xrightarrow[nC_3H_6]{\text{propylene}} M\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{CH}\text{-}(CH_2\text{-}\underset{\displaystyle CH_3}{CH})_n\text{-}CH_2\text{-}CH{=}CH_2$$

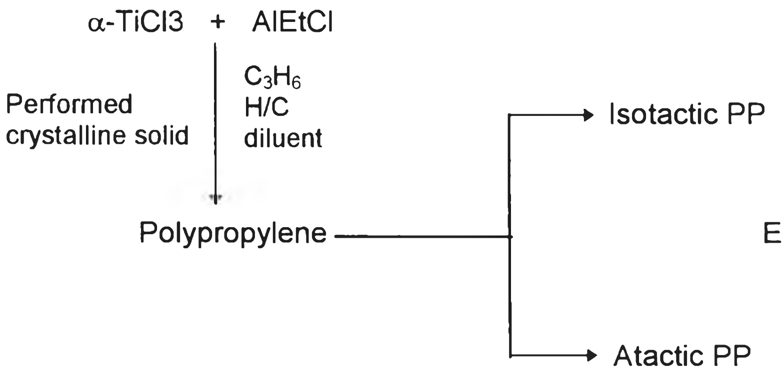
3.6 POLYMERIZATION CATALYST

The history of the development of high activity catalyst for ethylene nd α-alkene polymerization falls conveniently into three periods. During the early period, from 1955 and onwards, developments were concerned with solid $TiCl_3$-bases catalysts and the so-called first generation of industrial catalyst was produced. During a subsequent period higher activity catalysts were formulated. These catalyst were base on the use of appropriate additives and used with considerable success for the polymerization of propylene. Finally, during a third period, catalyst for the polymerization of propylene spectacular activity, base on the use of titanium tetrachloride, magnesium dichloride and electron donors, have been discovered. As will be appreciated these three periods overlap each other considerably.

3.6.1 Heterogeneous Catalysts

3.6.1.1 Non-Supported Heterogeneous Catalyst

The catalyst was produced as a precipitate by reaction of soluble transition metal halide with a soluble metal alkyl, the reaction being carried out in an inert dilution. Natta [79], however found it to be advantageous to use performed solid transition metal halides, usually in lower valence state(Eq. 3.27). Performed solid catalyst of this type were found to produce higher yields of isotactic propylene. The establishment by Natta et al that titanium trichloride could exist in four crystalline modifications had a significant effect on the course of catalyst development since the interconversion procedures had been used frequently in subsequent catalyst preparation.



Eq. 3.27

The α-form can be prepared by reduction of $TiCl_4$ with H_2 at temperature above 400 °C, usually at 800 °C [79]. Reduction with Al in hydrocarbon edium at 250 °C produced α-$TiCl_3 \cdot 0.33AlCl_3$ in which $AlCl_3$ is cocrystallized with the α-$TiCl_3$. β -$TiCl_3$ is obtain by reducing, $TiCl_4$ with Al or aluminium alkyl compound at low temperature or by reduction with H_2 γ-$TiCl_3$ is obtain by heating the β-form above 150 °C or reducing $TiCl_4$ at temperature 150-200 °C, reduction of $TiCl_4$ with Al yields a product having the $TiCl_3.0.33AlCl_3$ composition. The δ-$TiCl_3$ is obtain by prolonged grinding of α- or γ-$TiCl_3$. The α- and γ-forms have lower activities than δ-form which the β- form produces polymer which is essentially amorphous [82].

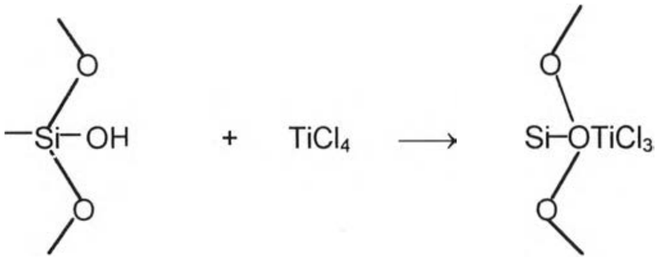
The morphology of δ-$TiCl_3$ has important effects on the catalyst activity and kinetic behaviors. The primary particles of δ-$TiCl_3$ are 0.03-0.7 μm in diameter and agglomerate to form secondary particles of 20-40 μm. These secondary particles are loosely constructed with voids between the primary particles. During the initial stages of polymerization these voids are rapidly filled with polymer leading to disintegration into primary particles [81]. The rate at which polymer is formed in the initial period determines whether the separate primary particles either disperse in the slurry or remain loosely bound into aggregates having the shape of the secondary particles but greatly increase in size.

3.6.1.2 Supported Ziegler-Natta Catalysts

The 1958, Hogen and Banks [82] was discovery a highly active chromium trioxide catalysts supported on silica which could polymerize ethylene under mild condition of temperature and pressure to produce predominantly linear, high density polyethylene.

3.6.1.2.1 Catalysts base on reaction product of hydroxyl-containing compounds with transition metal compounds

The use of SiO_2, Al_2O_3 etc. to chemically anchor transition metal compound has been widespread since the early 1960's. Heat treatment of SiO_2 can control the number and type of surface hydroxyl groups and indirectly the amount and distribution of transition metal atom which are anchored to the surface[83] (Eq.3.28)



Eq.3.28

Chemically anchored transition metal catalysts have been used industrially for the preparation of high density linear polyethylene and ethylene - α-alkene copolymer.

3.6.1.2.2 Catalyst based on reaction of magnesium alkoxides with transition metal compounds.

Superactive catalyst for ethylene polymerization have been prepared by reaction titanium tetrachloride with magnesium alkoxides. The original structure of the alkoxides is usually destroyed during reaction and new species of increased surface area produced.

3.6.1.2.3 Catalysts based on reaction products of magnesium alkyl and titanium compounds.

The reactions between magnesium alkyls and titanium compounds have been used as a means of preparing higher active catalyst. Stamicarbon [82] have prepared highly active catalyst using $AlEt_2Cl$, Bu_2Mg and $TiCl_4$. Shell International Research have used the reduction $TiCl_4$ with organomagnesium compounds to prepare highly active catalysts for ethylene polymerization . These catalyst systems have been extensively investigated by Haward and co-worker, [84] as well as by Radenkov et al characterization studies have revealed that the catalysts contain appreciable amounts of magnesium chloride and that they have nodular structures. The size of the primary particles is believed to less than 0.05 μm.

3.6.1.2.4 Catalyst based on reaction product of magnesium chloride with transition metal compounds.

Extremely active catalyst can be prepared simply by milling together $MgCl_2$ and $TiCl_4$ [85]. Polymerization is carried out with trialkylaluminium as activator. More complex catalyst base on $MgCl_2$ have been development. Catalyst analogous to developed for polypropylene can be made by milling $MgCl_2$ with a Lewis base and then treating with liquid $TiCl_4$. The bases used, however, tend to be alcohols rather than esters. These catalyst can have even higher activities base on transition metal component, although total ash levels are not necessarily improved.

3.6.2 Homogeneous Catalyst

Homogeneous Ziegler-Natta catalyst are formed when a transition metal and a metal alkyl interact to produced a soluble catalyst. Usually the transition metal halide is itself soluble in the solvent used. However, the polymer is very often precipitated as it is formed.

Commercial use soluble catalysts has been limited so far to the field of diene polymerization and ethylene-propylene copolymerization. Nevertheless many of these catalyst and polymerization system have received considerable academic attention in the hope that they might provide models for heterogeneous systems since it was believed that problems associated with surface properties and particle size could be avoided. The behaviors of many soluble polymerization system is very complicated. Complex formation reactions often occur with much of the transition metal being locked up in inactive complex. In addition, systems may only be colloidally dispersed, which in others precipitation of the catalyst as well as the polymer may occur.

3.6.2.1 Homogeneous Vanadium Catalyst

$VCl_4.AlEt_3$, VCl_4-$AlEt_2Cl$, VCl_4-$AlEt_2Cl$ catalyst and its modification have been used exclusively for the polymerization of propylene to highly syndiotactic polypropylene[86] below -40 °C, preferable at -78 °C. For catalyst compound must contain at least one halogen atom. Furthermore syndiotactic polymer can only be prepared if the Al:V ratio are within certain ranges, e.g. Al:V = 3-10 : for VCl_4.

3.6.2.2 Soluble Metallocene Catalysts

One of the most fascinating developments in the field of transition metal polymerization during recent years has been the discovery by Sinn, Kaminsky and co-worker [87] that homogenous catalysts such as Cp_2ZrCl_2, or Cp_2ZrMe_2 in toluene solution, when activated with methylaluminoxane, can polymerize ethylene with activitys in excess of $25*10^6$ $gPE(gZr)^{-1}h^{-1}$. A large excess of aluminoxane is required for high activity. Molecular weight distribution, M_w/M_n = 1.6 to 2.4 are reported. These catalysts, in contrast to those in with water is added direct to the aluminum alkyl compound, are able to polymerize propylene and to copolymerization ethylene with propylene, hexane-1, etc. Only atactic polypropylene is formed the use of non-chiral compounds such as Cp_2TiCl_2. Aluminoxane are usually prepared from the hydrolysis of aluminum trimethyl with $CuSO_4 \cdot 5H_2O$ or $Al_2SO_4 \cdot 16H_2O$ in toluene.

3.7 POLYMERIZATION GROWTH SITES AND ACTIVE CENTER MODELS

Numerous proporsals have been made for the structure of the transition metal centres responsible for polymerization. Some of the more important models will be described here.

3.7.1 The Active Centre in $TiCl_3$ - Based Catalysts

A determinant factor in the formulation of such structures is the actual locus if polymerization on the $TiCl_3$ surface. For example, in the mechanism of Cossee and Arlman [68] polymerization is suggested to occur at exposed titanium atoms present on the lateral faces of $TiCl_3$ crystals formed by the edges of the close-packed anion planes. Evidence for such a hypothesis comes from electron microscopy studies which have clearly demonstrated polymer growth occurring along spiral dislocations and on surface defects of the ∝-$TiCl_3$ crystal. The geometry of the Cossee-Arlman active site is shown in Figure 3.4; the alkyl ligand and three of the cholrines around the titanium atom are square coplanar, the plane through them forming an angle of 55° to the close-packed anion planes. The environments of the alkyl ligand and coordination vacancy are not equivalent, necessitation the ' back-jump' step of the Cossee-Arlman mechanism.

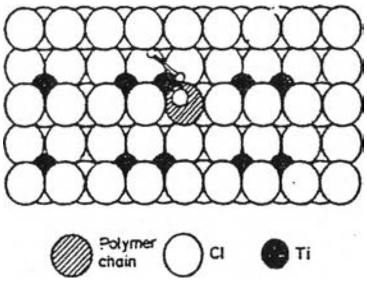


Figure 3.4 Geometry of the active center in the Cossee-Alrman

Theoretical calculations have also supported polymerization occourring at edge sites. Layer edges are present in all of the layer forms of $TiCl_3$, and apprecable amount of titanium atoms are located at edge sites in high surface area catalysts.

Kissin et al [88] have proposed a monomatallic active centre present in heterogeneous catalysts having two vacant coordination positions and which is located on the planes of the lattice crystals. The centres are produced by removal of chlorine atoms from the basal surfaces of the transtion metal halide by alkylation reactions, and thus contain metal-carbon bonds. The active site model is shown in Figure 3.5. Evidence for the Kissin model was provided by active centre concentration determination using a methanol inhibition technique. The value obtained for the polymerization of propylene by α-$TiCl_3$ - $AlEt_3$ was 3×10^{18} sites m^{-2} and suggested that the active sitespractically cover the whole surface of the catalyst. Since the basal planes account for some 95% of the total surface area then the majority of catalytic must be located on these planes. It should be noted that the Kissin theory relies on the validity of hte mathanol inhibition method and furthermore takes no account of catalyst modification and disintegraton during polymerization.

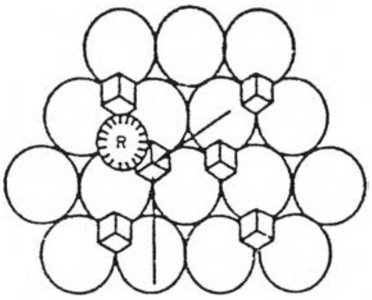


Figure 3.5 Model of active center according Kissin and Chirkov. R = alkyl

Fuji [89] has studied three different catalyst systems for the polymerization of ethylene: (i) $TiCl_4$ reduced by $AlEt_2Cl$; (ii) $TiCl_4$ reduced by $AlEt_2Cl$ and $TiCl_4$ added as cocatalyst; and (iii) $TiCl_4$ reduced by $AlEt_4Cl$ and $AlEt_4Cl$ added as cocatalyst. The titanium present in all three catalysts was in the T^{iii} state. However, differences in polymerization rates and the numbers of branches and double bonds in the polymer formes were attributed to the physical state around the titanium atoms. Investigations of concentrations of alkyl groups unstable to heat treatment at 140 °C, assumed to be Ti--R linkages, and those that were thermally stable, assumed to be either bonded Al--R or Ti---R---Al, led Fuji to propose the structures shown in Figure 3.6 for the active centres present in catalysts (i), (ii) and (iii).

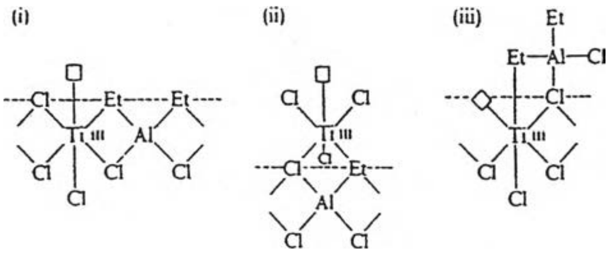
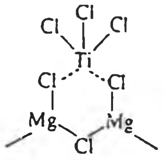


Figure 3.6 Active center described by Fuji

3.7.2 Modals for Active Centres in Magnesium Chloride Supported Catalysts

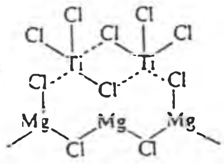
Commercially important catalysts for the polymerization of propylene have been developed which are based on the use of magnesium chloride as a suppport. In a typical preparation anhydrous magnesium chloride is ball-milled in the presence of an electron donor and then reacted with a titanium compound such as $TiCl_4$. Although many studies have been made concerning such parameters as the effect of ball-milled on the support, interactions with the electron donor, etc., few models have been proposed for the active centres present in these complex systems.

Chien et al[90] have made an extensive study of a 'high mileage' catalyst prepared by ball-milling magnesium chloride, pre-treated with HCl, in the presence of ethyl benzoate and then treating with p-cresol, $AlEt_3$ and $TiCl_4$. The oxidation states of the titanium atoms present were reported as Ti^{II} (8%), Ti^{III} (38%) and Ti^{IV}(54%). Electron paramagneric studies on the final catalyst revealed a single observable Ti^{III} species which was strongly attached to the catalyst surface (structure 2). This Ti^{III} species is coordinatively unsaturated; the vacant coordination position may be occupied by a weak ligand or solvent molecule.



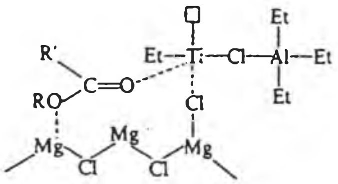
Struture 2

Only approximately 20% of the Ti^{III} present was attributed to the EPR observable species. It was concluded that the remainder of the Ti^{III} had adjacent sites occupied by one or more Ti^{III} ions. Chlorine bridge structures such as that shown in structure 3 were suggested as being responsible for the EPR silence.



Structure 3

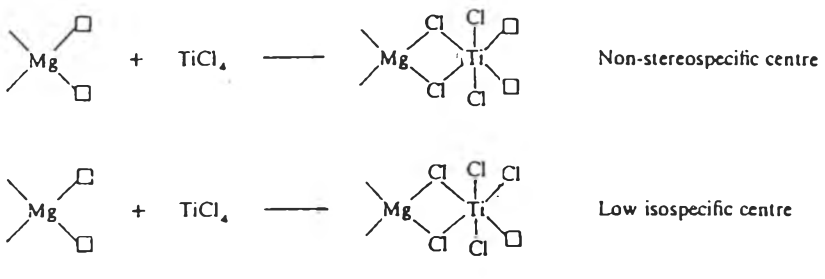
Activation of the catalyst with a mixture of $AlEt_3$ and methyl *p*-toluate (3:1) leads to a reduction of 90% of the Ti^{IV} to lower oxidation states. Furthermore, a single Ti^{III} species with rhombic symmetry is produced with a structure believed to be that shown in structure 4. The species was found to be unstable, and on ageing was converted to a Ti^{III} species with axial symmetry.



Structure 4

Structure (4) is coordinatively unsaturated and contains a Ti^{III} atom with a vacant site and an asymmetric field and thus fulfills the requirements of a site capable of stereospecific polymerization.

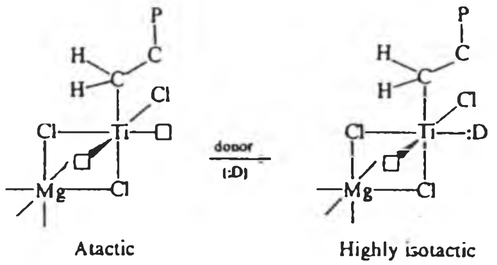
Kakugo et al. have studied the micrestructure of polypropylenes produced by $TiCl_3$-based and $MgCl_2$-supported catalyst using ^{13}CNMR spectroscopy. Two types of isospecific centres were identified in the catalysts studied wntch produced polymer with high and low stereospecificities. By analogy with $TiCl_3$-based systems, Eq3.29, 3.30 was proposed for the formation of active centres in $MgCl_2$-supported catalysts. He proposed that the addition of electron donors converts the non-stereospecific centres to ones of high isospecificity, whereas the low isospecific centres are rendered inactive as shown in Eq3.31, 3.32.



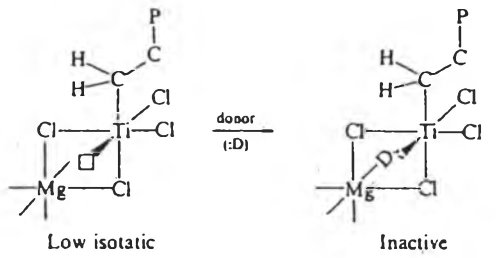
Eq.3.29

Eq.3.30

Scheme 17



Eq.3.31



Eq.3.32

Doi et al.[92] have carried out similar^{13}CNMR studies on the structures of polypropylenes produced by various catalyst systems, including $TiCl_4/AlEt_3$, δ-$TiCl_3$ /$AlEt_3$, $MgCl_2$ /$TiCl_4$/ethylbenzoate-$AlEt_3$ and $TiCl_4/MnCl_2$/ethyl benzoate-$AlEt_3$. Two types of active centre were proposed, one producing highly isotactic polypropylene and the other producing atactic polymer composed of isotactic and syndiotactic stereoblocks of short sequence length. The structures of the centres are shown in Figure 3.7. In site A the surface metal (Mg, Mn or Ti) is coordinatively saturated, whereas in site B it has a chlorine vacancy. Reversible migration of the alkylaluminum compound in site B was suggested as the cause of the frequent changes in polymer structure.

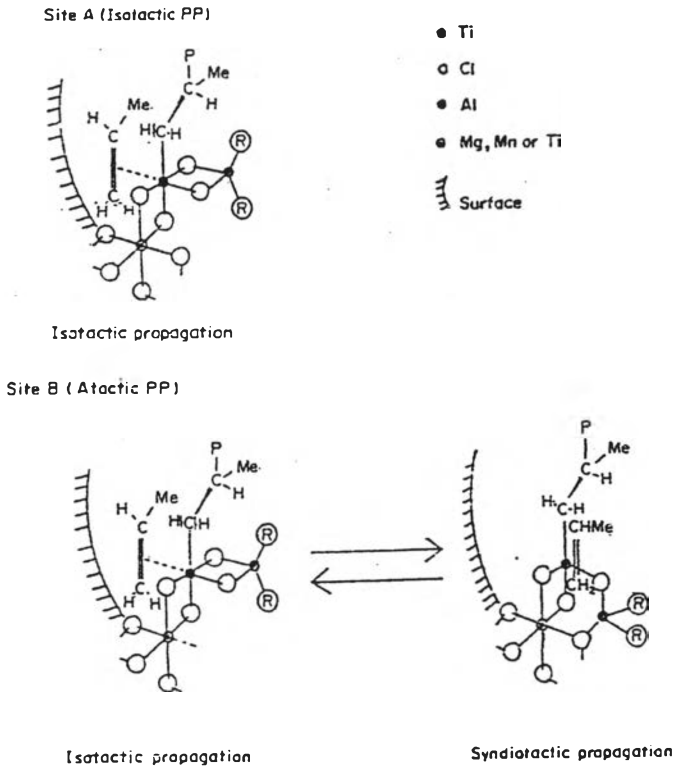
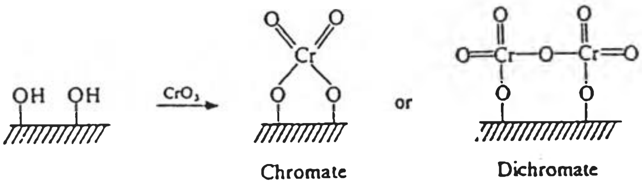


Figure 3.7 Structure Active centers proposed by Doi

3.7.3 Models for Active Centres in the Phillips Catalyst

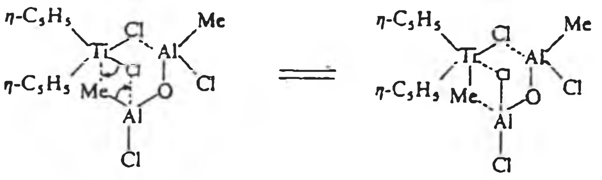
An importane catalyst for the commercial polymerization of HDPE is the Phillips Cr/silica catalyst. The Phillips system comprises an oxide support, usually silica or alumina-silica, impregnated with chromium(VI) oxide to a loading of 0.5-0.5% chromium, typically1%. Supports are often modified by compounds such as titania. The catalysts produce high polymerization rates and in contrust to true Ziegler-Natta systems do not required to activate the catalyst and to remove any moisture from the surface. Heating of unsupported CrO_3 in the range 473-703 K leads to decomposition to Cr^{III} with the evolution of oxygen. However, the use of a support such as silica stabilizes the Cr^{VI} and prevents reduction to Cr^{III} during the heat treatment. The stabilization of Cr is believed to be due to the interaction of CrO_3 with hydroxyl groups on the support surface. Hogan [93] showed that a CrO_3/SiO_2-Al_2O_3 catalyst containing 2.49 wt% Cr contains 96% as Cr^{VI} after calcination at 813 K in dry air,and he concluded that the stabilization was due to the formation of surface chromate and dichromate species (Eq.3.33). The valence state between Cr during polymerization has been the subject of considerable dispute; every valence state between Cr^{II} and Cr^{VI} has in fact been proposed that Cr^{V} was responsible for the polymerization of ethylene, few workers now believe that higher oxdation states are the active species. Most researchers at the present time believe that the active species i s Cr^{II} or Cr^{III}, or perhaps a combination of both. However, it is also possible that the coordinative unsaturation of the Cr is as improtant as its valency.



Eq.3.33

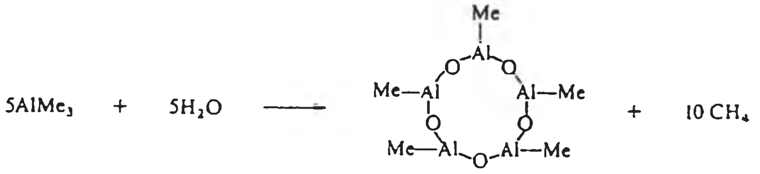
3.7.4 Active Centres in Soluble Catalyst Systems

Much work has been performed using homogeneous Ziegler-Natta catalyst systems with the aim of establishing a general mechanistic scheme; such systems are easier to study than heterogeneous systems in that each metal atom is supposed to form an active centre. More recently a fascinating discovery has been made whereby a very highly active catalyst for the polymerization of ethylene can be prepared by pre-treating $AlEt_3$ with water and adding to dialkylbis(cyclopentadienyl)titanium(IV) catalysts [94]. Earlier work had shown that the addition of water to homogeneous chloride-containing systems based on bis(cyclopentadienyl)titanium(IV) catalysts increased the activity. Cihlar et al [95] proposed the stabilized complexes shown in Eq.3.34 from similar studies.



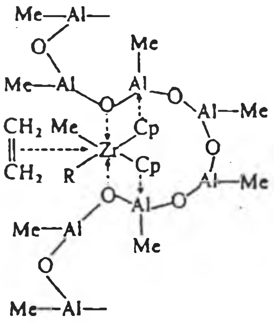
Eq 3.34

The addition of water to $AlMe_3$ leads to the formation of an oligomeric aluminoxanes with the structure $[-OAl(Me)-]_n$. Further condensation with elimination of $AlMe_3$ is believed to give rise to cyclic structures of the type suggested by Kaminsky and Sinn, shown in Eq.3.35



Eq.3.35

Kaminsky et al [97] have shown that cyclopentadienyl derivatives of zirconium (e.g. bis(cyclopentadieny) dimethylzirconium) in conjunction with alkylaluminoxanes produce exceptionally active catalysts for ethylene polymerization, >10^8 gPE/gZr. A large excess of aluminoxane was required and the rate was found to be proportional to the Zr concentration and to depend quadratically on that of the aluminoxane. The polymerization rate increased after an induction period to a maximun value and thereafter remain constant, indicating 'living' polymerization system. The complex shown in structure 5 was proposed. The system could also polymerization propylene to atactic polymer and copolymer ethylene and propylene.



Structure 5

3.8 POLYMERIZATION PROCESS [98]

Three types of polymerization processes are used today for low pressure polymerization: i)liquid slurry polymerization, ii) solution polymerization, iii) gas-phase polymerization.

3.8.1 Liquid Slurry Polymerization

The liquid slurry polymerization process encompasses by far the largest group of HDPE technologies. In most cases this process utilizes a catalyst of activity such that catalyst deashing is not required. Excellent temperature control is major attraction of the liquid slurry process. Currently, long jacketed loop reactors and continuous stirred tank reactors (CSTR) are most widely used in slurry polymerization.

The loop reactors, which are recycle tubular reactors, are used by the the Phillips Petroleum Co. and the Solvay et Cie. The Philips process is characterized by used of a light hydrocarbon diluent such as isopentane or isobutane in loop reactors which consist of four jacketed vertical pipes. Figure 3.8 shows the schematic flow diagram for the Philips loop reactor polyethylene process. The use of high activity supported chromium oxide catalyst eliminates the need to deash the product. This reactor is operated at about 35 atm. and 85 - 110 ^{o}C with an average polymer residence time of 1.5 hr. The Philips process relies on polymerization temperature for average molecular weight control, while the MWD is controlled by the type of catalyst empoyed and certain proprietary operational adjustment which alter MWD.

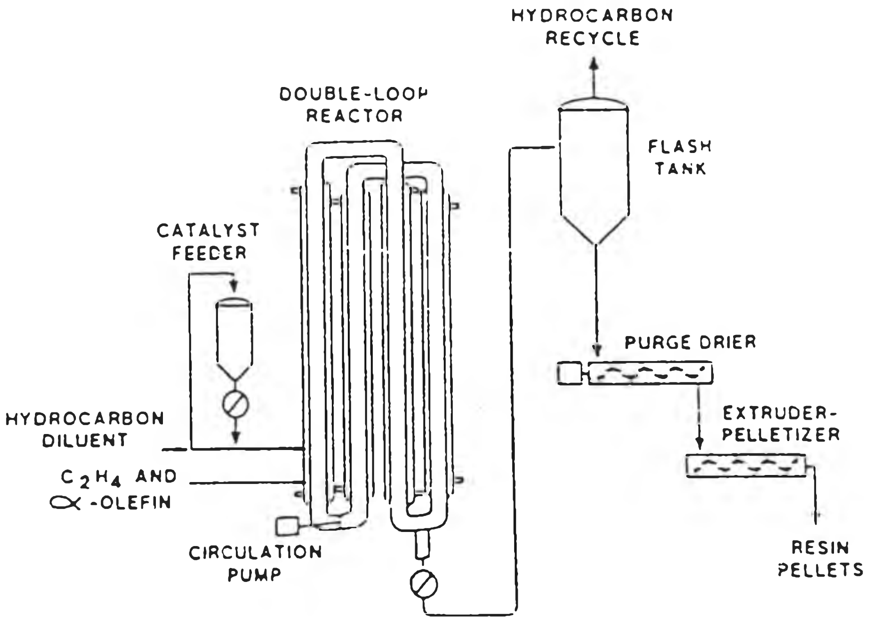


Figure 3.8 Philips loop reactor

Continuous stirred tank reactors are also widely used for hexane slurry ethylene polymerization by many manufactures. In the Hoechst process, the reaction is carried out in four CSTRs arranged in series such that the slurry phase and the vapor phase move in concurrent flow. polymerization occurs at 100 psig and 85 ^{O}C with 98% conversion of ethylene. The residence time in the reactor is about 2.7 hr. The product slurry is pumped into centrifuges, which separated the bulk of the hydrocarbon diluent liquid from the polymer fluff.

3.8.2 Solution Polymerization

Solution process have some unique adventages over slurry process in that the MWD can be controoed better, and process variables are also more easily controlled because the polymerization occurs in homogenous phase. The high polymerization temperature (130-150^{O}C) also leads to high reaction rates and high polymer throughput from the reactor. However, very high molecular weight polymer cannot be produced easily at these high temperature, and since the solid content is relative low compared with the slurry process, greater diluent recovery may be required. Figure 3.9 show the Dupont solution polymerization process. The catalyst components, cyclohexane, ethylene, octene-1, and hydrogen, are charged continuously to a CSTR operating at a temperature in excess of 150 ^{O}C and a pressure about 80 atm. Because of the short residence time (5-10 min) and high polymer concentration (~35%), relatively small reactors maybe used either in series or parallel to alter the MWD of the product.

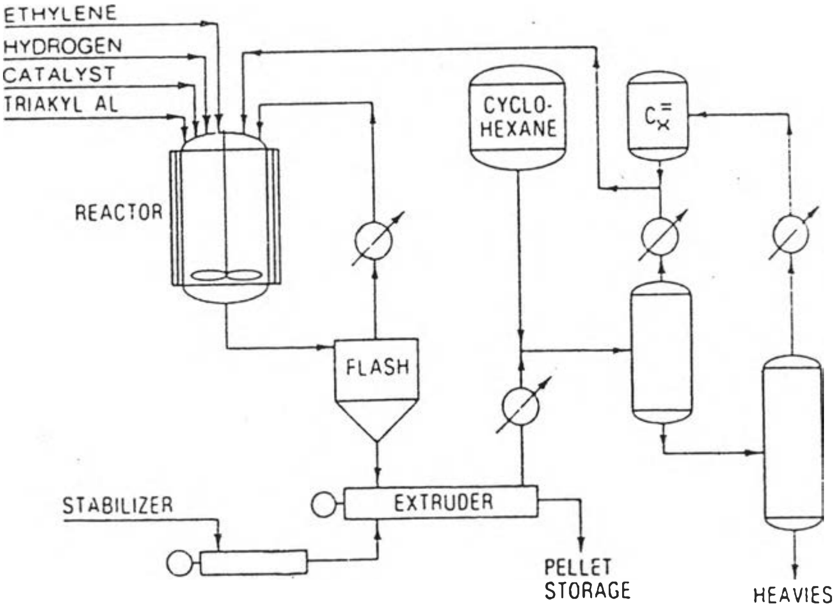


Figure 3.9 DuPont solution process

3.8.3 Gas Phase Polymerization

The successful development of such process represents one greast technological successes in this field. A gas phase, fluidized bed process(Unipol) was developed during 1960s by the Union Carbide Co. for the production of HDPE and first commercialized in 1968, as shown in Figure 3.10. The process was based initiallt on the use of chromium-type silica supported catalysts but may also be used with other types of high activity supported catalyst including those of a $SiO_2/MgCl_2/TiCl_4$/donor type. The process operates at a nominal reaction pressure of 18 atm and at temperature between 85 and 100 °C. A full range of HDPE polymers can be prepared. A versatility of the original process led to a new gas phase fluidized bed process for the commercial production of LLDPE in 1975 by copolymerizing ethylene with α-alkene such as butene-1. The essential key to this new process is the development of new high activity catalyst that operate at low temperature and at pressure of only 7-20 atm. Molecular weight is controlied by polymerization temperature and the use of hydrogen.

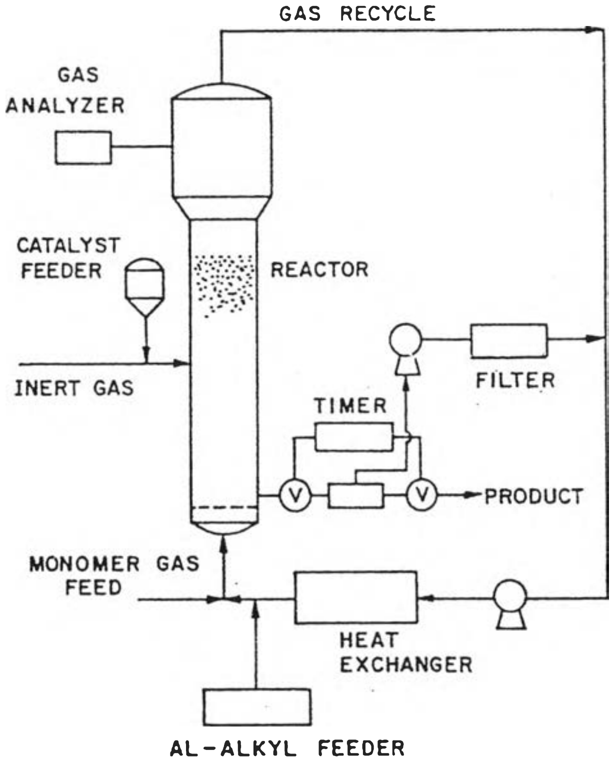


Figure 3.10 Union Carbide gas phase process

In the BP Chemicals gas phase process polymerization is carried out under mild conditions of temperature and pressure, typically at temperature of between 60 and 100 ^{O}C and pressure between 15 and 30 bar, in a fluid bed reactor. The growing polymer particles are maintained in a fluidized condition by mean of a gas stream containing ethylene, the α-alkene (in copolymerization) and hydrogen (for molecular weight control). The gas stream from the top of the reactor is cooled in a heat exchange and then recycle through a compressor. Polyethylene granules leave the reactor as a free-flowing power. Homogeneity in the fluid bed and temperature control are ensured by the use of high activity titanium and magnesium catalysts. The process has a high degree of flexibility and can produce a broad range of products, using the same catalyst. A diagrammatic representation of the process is shown in Figure 3.11[35].

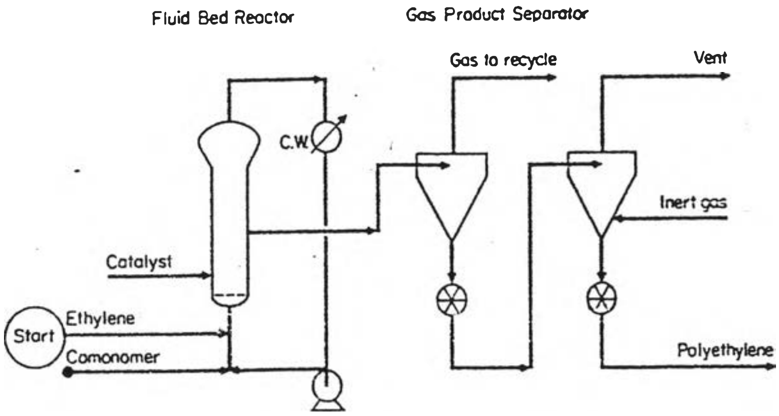


Figure 3.11 BP gas phase process

BASF uses a continuous stirred-bed reactor (CSBR) for gas phase ethylene polymerization as shown in Figure 3.12. The reactor is operated at a higher pressure and temperature (500 psig,100-110 °C) than employed in Union Carbide's fluidized-bed process. A fairly uniform temperature of about 110 °C is maintained in the bed, and the unreact ethylene gas leaves the top of the reactor at 105 °C. About 9% of the ethylene recycle leaves the reactor with effluent polyethylene power and is separated from the polymer at 40 psig. The recycle ethylene is compress to 1500 psig and cooled to 32 °C before being reintroduced to the reactor.

In the Amoco (Standard Oil of Indiana) process, a compartmented horizontal reactor depicted in Figure 3.13 is used. The compartments permit ariation in temperature and hydrogen pressure in the reactor as a means of controlling polymerization rate and molecular weight distribution.

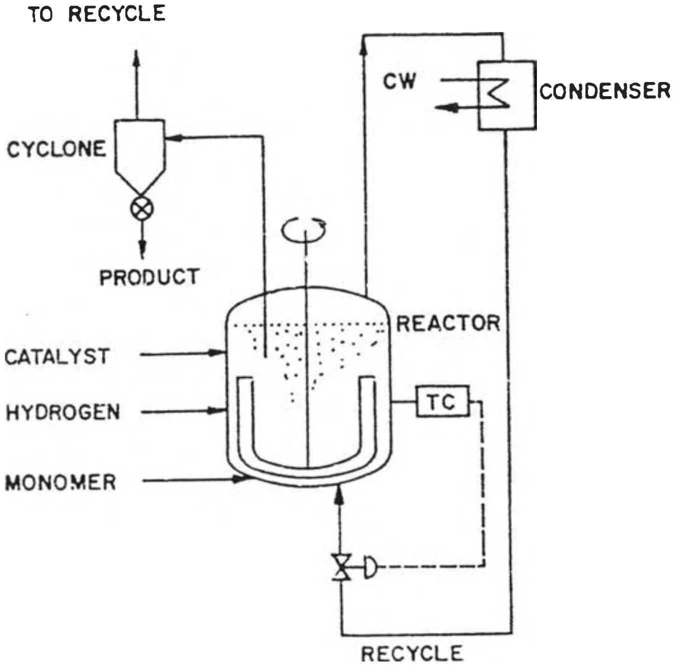


Figure 3.12 BASF gas phase process

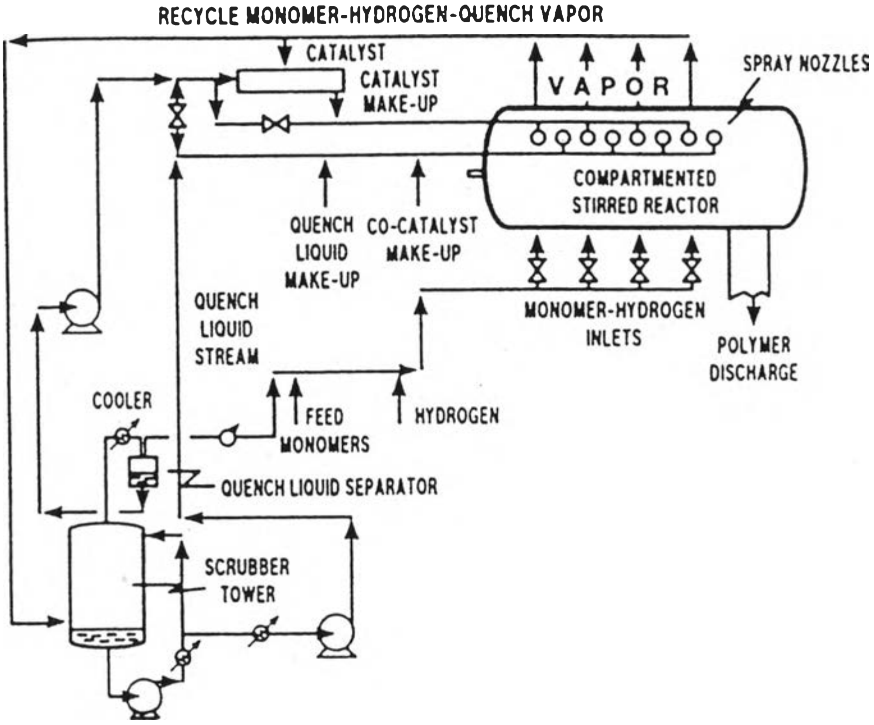


Figure 3.13 Amoco gas phase process