CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Introduction of Z/N Catalyst

Ziegler and co-workers developed the first generation of Z/N catalysts, a combination of $TiCl_4$ and $Al(C_2H_5)_2Cl$, for ethylene polymerization in the early 1950s. Later, Natta developed a wide variety of other catalysts of the same general type, based on titanium and vanadium compounds and suitable for stereospecific olefin polymerization. Traditionally, all these catalyst are classified as Z/N catalysts. Although, every Z/N catalyst is capable of ethylene polymerization, some are specially designed for this purpose. Soluble catalysts are typically prepared from a transition metal compound and an organoaluminium compound such as bis(cyclopentadienyl) titanium dichloride-diethylaluminium chloride, titanium tetraalkoxides-alkylaluminiums, and vanadium acetylacetonate-trialkylaluminium. Interaction of these components in solution reduces the transition metal species, which remain soluble in hydrocarbons (aromatics or alkanes), producing classical homogeneous catalysts. These catalysts are capable of ethylene polymerization at -20 to 50 °C. They are, however, not used in commercial application because of the superiority of heterogeneous systems. Pseudo-homogeneous catalysts are soluble in inert solvents, but their reaction products are insoluble. The most important of these are $TiCl_4$-Al $(C_2H_5)_2Cl$, $TiCl_4$-$Al(C_2H_5)_3$, VCl_4-$Al(C_2H_5)_2Cl$ and $VOCl_3$- $Al(C_2H_5)_3$. The $TiCl_4$-Al $(C_2H_5)_2Cl$ catalyst found wide commercial application in HDPE synthesis in the late 1950s and 1960s, but was gradually replaced by more active heterogeneous catalyst.[7] In heterogeneous Z/N catalysts, they divided into non-supported and supported catalysts.

2.1.1 Heterogeneous Non-Supported Catalysts[8]

The discoveries by Ziegler were concerned with ethylene polymerization in the presence of an in situ prepared catalyst. They were obtained as a precipitate from the reaction of a soluble transition metal halide, especially $TiCl_4$, with a metal alkyl or alkyl metal halide, primarily $Al(C_2H_5)_3$ or $Al(C_2H_5)_2Cl$. The reaction was carried out at the activator to a procatalyst molar ratio not much greater than unity and in an inert hydrocarbon medium. Most non-supported catalysts used for alkene slurry polymerization process are obtained using the δ-$TiCl_3$.$1/3AlCl_3$ solid solution. Titanium was found that ball milling of the product obtained from the reduction of $TiCl_4$ by aluminium metal or aluminium alkyls led to a more active catalyst than pure α-$TiCl_3$. Furthermore, it was revealed that during the milling process both the α-and the γ-forms of $TiCl_3$ was converted to the δ-form, which displayed double-layer stacking. Catalysts of the above type are referred to as first-generation Z/N catalysts. Most first-generation commercial catalysts are based on a precursor of the δ-$TiCl_3$.$xAlCl_3$ solid solution type and have been dry milled and heat-treated. These catalysts have specific surface areas in the range 10-40 m^2/g. Their productivity is a few kilograms of polyethylene or polypropylene (with an isotactic index of 88-93 %) per gram Ti per hour. The production processes, involving slurry-type polymerization, were complicated and expensive and, because of their complexity, not very versatile. Although the catalyst productivity could be much higher for ethylene than for propylene, it was necessary to extract the catalyst residues in order to reduce the quantities of Ti and Cl in the product to acceptable levels.

2.1.2 Heterogeneous Supported Catalysts

The large-scale production of polyolefins has been enhanced by the development of very high-activity supported Z/N catalysts. Higher catalyst activities mean lower production cost owing to possibilities of eliminating some operations from the production technology. Since Natta *et al.* demonstrated that only a small percentage of the Ti atoms in the non-supported catalysts (typically less than 1% in the first-generation catalysts) were active for alkene polymerization. It was realized that much of the procatalyst mass acted simply as a support for the active sites fromed by activation. Equation 2.1 shows this relation.

$$(TiCl_3)_{x+y} + zAlR_3 \longrightarrow (TiCl_3)_y.(TiRCl_2)_z + zAlR_2Cl \qquad 2.1$$
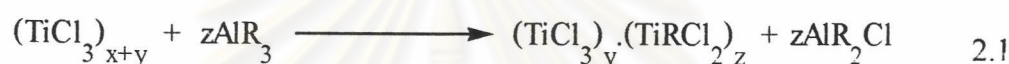
Depositing the active Ti species on a support could make significant improvement whose residues, unlike those to $TiCl_3$, would be inert and not detrimental to the properties of the polymer. Thus, it was evident that higher catalyst activities were likely to be achieved through the use of transition metal compounds supported on appropriate matrices. Early attempts to support $TiCl_4$ directly on silica, alumina or magnesia did not lead to a sufficient increase in catalyst productivity. The first useful high-yield catalyst involved Mg(OH)Cl as a support. Over the years, a wide range of support catalyst have been successfully developed and used for the industrial polymerization of ethylene, and more recently propylene. In the case of ethylene polymerization, supported catalysts have been implemented in to practice relatively easily. Various metal oxides, chloride, oxychlorides and alkoxides such as Al_2O_3, SiO_2, $Al_2O_3.SiO_2$, MgO, ZnO, TiO_2, ThO, Mg(OH)Cl, $Mg(OC_2H_5)_2$ and $MgCl_2$ have been applied as catalyst supported. Organic polymers may also play the function of the catalyst support. However, a variety of magnesium compounds have been used most successfully as supports; pre-eminent among these is $MgCl_2$ or reaction mixtures that can produce this compound, at least on the support surface. The massive increase in
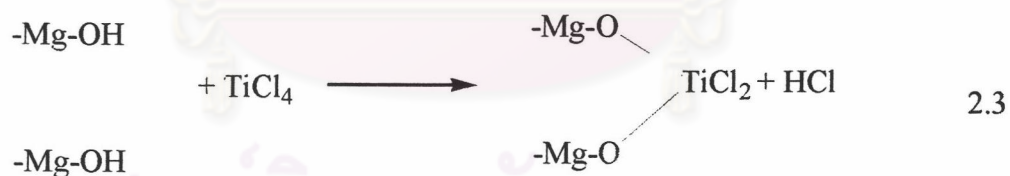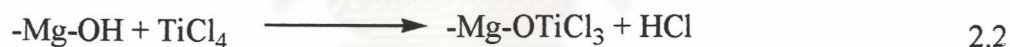
activity of $MgCl_2$-supported catalysts has been claimed to be due to an increase in the percentage of Ti atoms forming active sites (approaching nearly 100%) and not to a significant increase in reaction rate at the active site (intrinsic catalyst activity). This was the third-generation catalyst system, and the discovery of magnesium chloride in the active from, as an ideal support for the fixation of $TiCl_4$ and its derivatives, opened a new era in the field of Z/N catalysed polymerization, from both industrial and scientific points of view. During the 1980s, active $MgCl_2$-supported catalysts brought about revolutionary developments in the production of polyolefins compared with the first-and second-generation Z/N catalysts. The introduction of the catalyst support concept significantly increased the complexity of the catalyst construction but also reduced the complexity of industrial olefin polymerization processes. The active polymerization centres could now be dispersed throughout the support surface, making them all essentially accessible to the polymerized monomer. Since all the titanium chloride molecules were now available to take part in the polymerization, fewer were needed. Consequently, the yield of polymer per gram of titanium was so high that no extraction procedures were necessary in order to produce a viable commercial resin. Elimination of the de-ashing part of the industrial process had obvious economic and environmental advantages and resulted in the explosive growth of polyolefins in the global plastic marketplace.

Supports used for obtaining Z/N catalysts can differ essentially from one another. Some of the supports may contain reactive surface groups (such as hydroxyl groups present in specially prepared metal oxides) while others do not contain such reactive functional groups (such as pure anhydrous metal chlorides). Therefore, the term 'supported catalyst' is used in a very wide sense. Supported catalysts comprise not only systems in which the transition metals compound are linked to the support by means of a chemical covalent bond. But also systems in which the transition metal atom may occupy a position in a lattice structure, or where complexation, absorption or even occlusion may take place. The transition metal may also be anchored to the
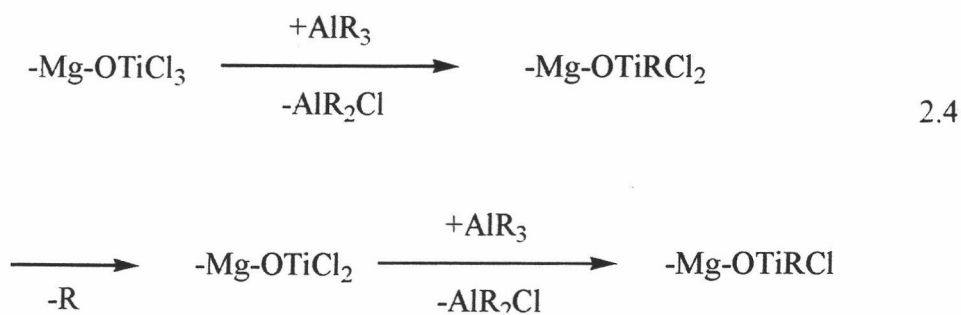
support via a Lewis base; in such a case the metal complexes the base, which is coordinatively fixed on the support surface. Supported precursors for Z/N catalysts may be obtained in two ways depending on the kind of support. By treatment of the support containing surface hydroxyl groups with a transition metal compound with chemical covalent bond formation. And by the treatment of a magnesium alkoxides or magnesium chloride support with a Lewis base and transition metal compound with coordination bond formation.

The use of supports containing hydroxyl groups such as alumina, silica, Mg (OH)Cl, etc., for chemical fixing of the transition metal compound has been widespread since the early 1960s. Heat treatment of such supports can control the number and type of surface hydroxyl groups and indirectly the amount and distribution of transition metal atoms anchored to the surface. The most commonly used Z/N catalyst of this type is obtained by application of the precursor yield from the reaction of $Mg(OH)Cl$ support and $TiCl_4$:

$$-Mg-OH + TiCl_4 \longrightarrow -Mg-OTiCl_3 + HCl \qquad\qquad 2.2$$

$$
\begin{array}{c}
-Mg-OH \\
\\
+ TiCl_4 \longrightarrow \\
\\
-Mg-OH
\end{array}
\qquad
\begin{array}{c}
-Mg-O \\
\diagdown \\
TiCl_2 + HCl \\
\diagup \\
-Mg-O
\end{array}
\qquad 2.3
$$

The obtained supported precursors are then subjected to activated by trialkylaluminium, which can be shown schematically for the $MgOTiCl_3$ species as follows:

$$-\text{Mg-OTiCl}_3 \xrightarrow[-\text{AlR}_2\text{Cl}]{+\text{AlR}_3} -\text{Mg-OTiRCl}_2$$

2.4

$$\xrightarrow{-\text{R}} -\text{Mg-OTiCl}_2 \xrightarrow[-\text{AlR}_2\text{Cl}]{+\text{AlR}_3} -\text{Mg-OTiRCl}$$

Supporting the titanium catalyst component has been claimed to lesson the tendency of titanium active site to be reduced by the activator. Many of the catalysts obtained from such precursors and trialkylaluminium as the activator exhibit high activity in the polymerization of ethylene, but are not, however, useful for the polymerization of propylene and higher α-olefins.

2.2 Factor to Determined Behavior of Polyolefin Catalysts[9]

Behavior of catalyst is meaning the catalyst activity, molecular weight of resulted polymer and others. The factors described are related to the chemical structure of the metal alkyl and the transition metal salt.

2.3 The Metal Alkyl

2.3.1 Group of Metal

Not every metal in-group I to III form an active metal alkyl as in claimed in many of the patent relating to Z/N catalysts. Active catalysts from the following metals have been established for ethylene and/or propylene.

Table 2.1 Metal group I to III for Z/N catalyst preparation

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

Aluminum alkyls have been the most extensively used, and the reason for this is partly scientific and partly economic. They were much safer to use in solution because, once properly diluted, they were less pyrophoric and not flammable unless contacted with a combustible material. Simple syringing techniques, using N_2 or Ar as an inert atmosphere

2.3.2 Ligands of Metal

Two types of ligands are compared: (1) an all-hydrocarbon alkyl or an aryl, such as ethyl or phenyl; and (2) a heteroatom or a 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 as the active center. The heteroatom should be exchanged for a ligand of the transition metal, an active 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. The chemical behavior of a metal alkyl is strongly influenced by the nature and number of these two types of ligands.

2.4 Transition Metal Salts

2.4.1 Choice of Transition Metal

The availability of $TiCl_4$ as an inexpensive material in the 1950 ' s undoubtedly promoted considerable research aimed at industrial applications.   It is not surprising that many papers and patents have appeared that use $TiCl_4$ or a derivative, especially $TiCl_3$ and $TiCl_2$'s of varying compositions and crystal structures. As a result, many interaction and important findings developed with these $TiCl_3$ ' s, and this led to more research on elucidation of mechanism, etc. The same was true for aluminum alkyls.

2.4.2 Ligand of Transition Metal

Active catalysts for ethylene polymerization have been made from transition metal salts bearing ligands of varied structures. These ligands include the groupings as shown in table 2.2.

Table 2.2 Ligand of transition metal
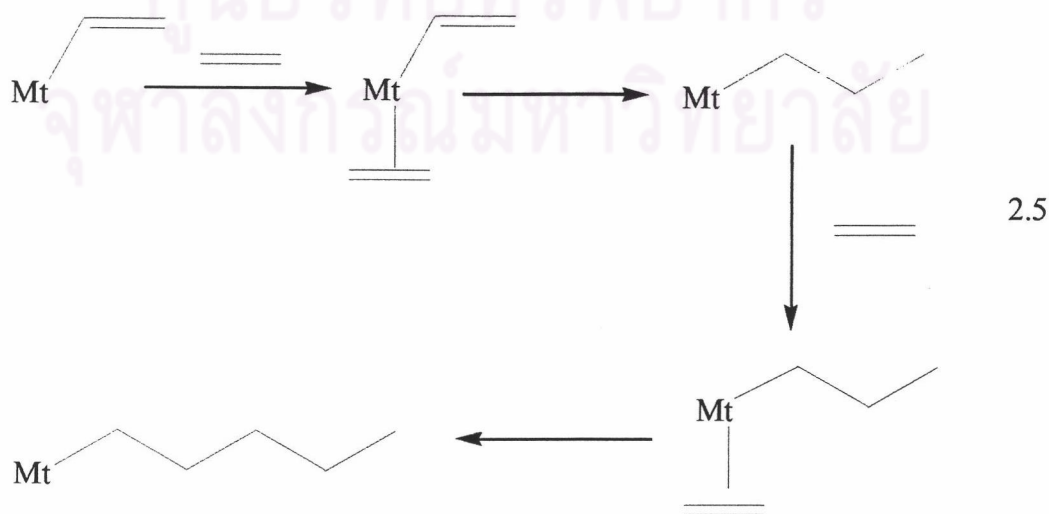
Ligands	
-Cl. Br, l or F	indenyl
-OR(R = alkyl such as Bu, Me)	arenes
-SR(R = alkyl such as Bu, Me)	O-CO-R(R = CH_3)
-NR$_2$ (R = alkyl such as Bu, Me)	oxide
acetylacetonate	sulfide (disulfide)
nitroso	sulfate
phosphate	carbon monoxide
π-C_5H_5 ,Cp	

Ethylene can be polymerized to highly linear products with catalysts containing the largest array of transition metal salts, that is, those having different ligand structures. Economics and the balance of properties shown by the polyethylene probably dictate the choice of the salt. The variation in ligand structure is great, including sulfides, oxides, oxychlorides dialkylamine, alkoxy, acetylacetonate, arene, cyclopentadienyl, halide (= Cl, Br, F, or I), phosphate, sulfate, and so on. Because in many of these catalysts the transition metal salt and the metal alkyl undergo exchange of ligands in varying degrees, the activity of the catalyst is sensitive to the molecular ratio of the two components. In addition, the ligand structure of the active center may be significantly different from that of the staring salt, and only little insight is gained by consideration of the structure of the parent salt. One should be wary about comparisons of activities of the transition metal salts bearing different ligands if the polymerizations are no done under similar conditions.

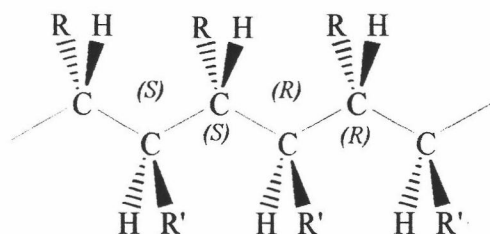## 2.5 Model of Active Sites and the Polymerization Mechanism.[8]

Although a two-step mechanism, involving monomer coordination and enchainment by the insertion of the coordinating monomer (Equation 2.5) is commonly accepted for olefin polymerization with coordination catalysts, there is no general uniform mechanism that might operate in all polymerization systems and under all polymerization conditions applied.
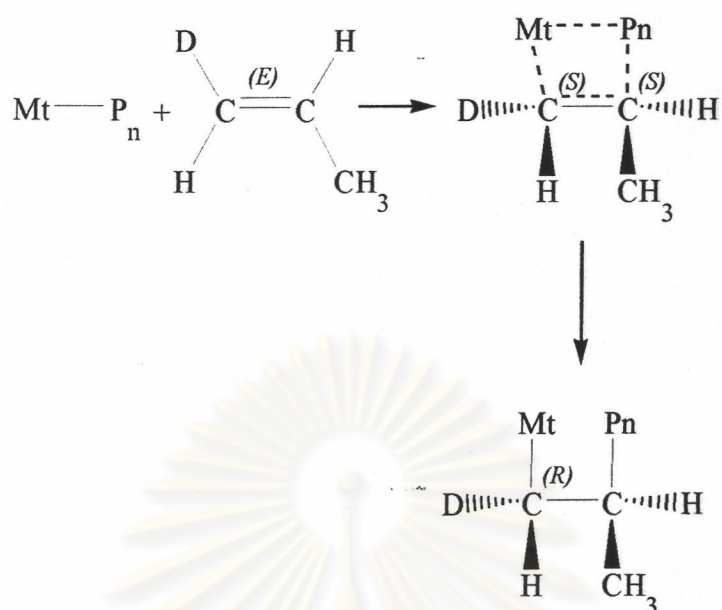

2.5

As already mentioned, even questions concerning the rate controlling steps have yet to be resolved. However, for most common polymerizations under common conditions, the insertion of the coordinated monomer is assumed to be the rate-determining step.

Although conflicting conclusions have also been drawn from investigations using *ab initio* molecular orbital methods in combination with molecular mechanics methods, most studies agree that the insertion step is the rate controlling one. The insertion of coordinated olefin proceeds very fast; energetically favorable spatial arrangement of ligands, metal-carbon bond (Mt-C bond) and coordinated monomer determines high rates of insertion. The insertion involves the cleavage of the metal-carbon bond and the double bond in the monomer molecule, and the formation of a new Mt-C bond. It is characteristic that olefin polymerization with both heterogeneous and homogeneous catalysts involve *cis*-insertion of the C=C bond in the coordinated olefin into the Mt-C bond in all cases, irrespective of the monomer enchainment mode (1,2 or 2,1) and the tacticity of the poly (α - olefin) formed. A *cis*-opening of the olefin double bond has been proved conclusively by using deuterated propylene for the polymerization and determining the chain microstructure of the polymers formed. For example, poly (1-deuteropropylene) of *erythro*-diisotactic structure (Figure 2.1) is formed in the polymerization of *cis*-1- (^{2}H)-propene with heterogeneous Z/N catalysts. Such in Equation 2.6, a polymer structure results from the monomer *cis*-insertion.

2.6

Figure 2.1 *erythro*-diisotactic structure

If the polymerization of *cis*-1- (^{2}H)-propene occurred with monomer enchainment via another route (namely via the addition of the *trans* type), poly (1-deuteropropylene) of *threo*-diisotactic structure (Equation2.7) would be formed, but this is not the case.

2.7
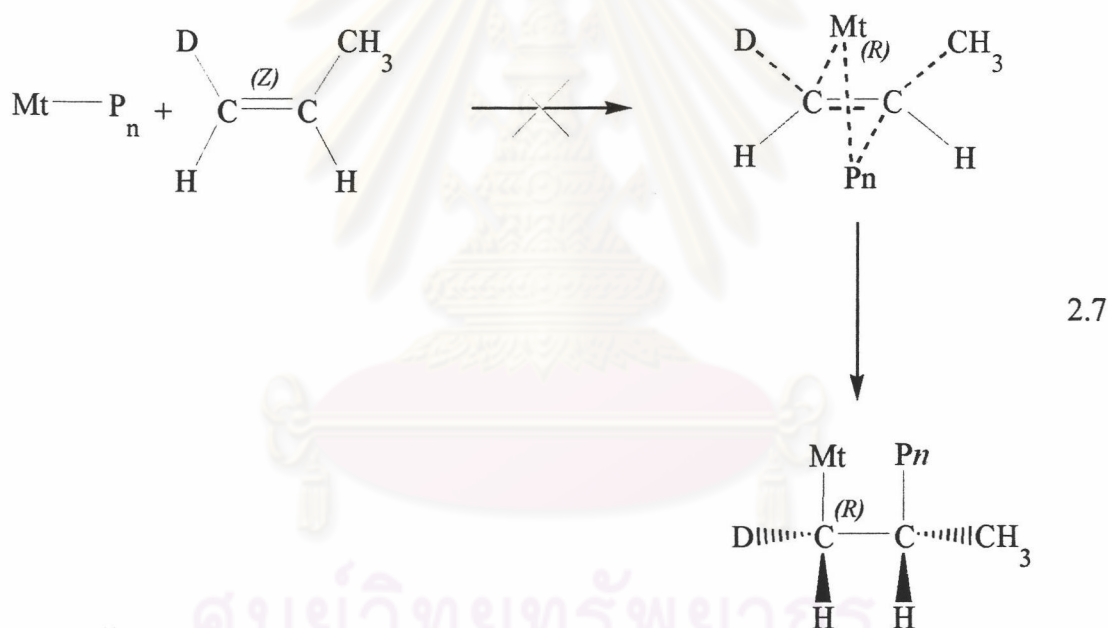
Similarly, in the polymerization of *cis* 1,2,3,3,3-penta-1- (^{2}H)-propene run with the homogeneous (IndC^{2}H)$_2$ZrCl$_2$-[Al(Me)O]$_x$ catalyst, the respective poly (pentadeutero-propylene) of *erythro*-diisotactic structure is formed, which confirms the insertion to be of the *cis* type.

On the other hand, the polymerization of *trans*-1-(^{2}H)-propene with heterogeneous Z/N catalysts leads to the formation of the respective polymer of *threo*-diisotactic structure [Equation 2.8], which proves the *cis*-insertion of the monomer.

$$Mt \text{---} P_n + \begin{array}{c} D \\ \\ \end{array} \begin{array}{c} H \\ (E) \\ C \text{==} C \\ \\ H \end{array} \begin{array}{c} H \\ \\ CH_3 \end{array} \longrightarrow \begin{array}{c} Mt \text{----} Pn \\ (S) \quad (S) \\ DI\text{ illll} C \text{---} C \text{·····lll} H \\ \\ H \quad CH_3 \end{array}$$

2.8

$$\begin{array}{c} Mt \quad Pn \\ | \quad (R) \quad | \\ DI\text{ illll} C \text{---} C \text{·····lll} H \\ \\ H \quad CH_3 \end{array}$$

Furthermore, studies of the microstructure of copolymers formed by the low temperature copolymerization of *cis*1-(^{2}H)-propene (or *trans* isomer) and perdeuteropropene in the presence of soluble vanadium-based Z/N catalysts showed syndiospecific propagation to involve a monomer insertion of the *cis* type.

Since olefin insertion into the Mt-C bond has been established to be of the *cis* type, it has been considered to proceed by a concerted mechanism involving the formation of a four-membered transition state. However, various models of active centres and of the insertion mechanism have been proposed for olefin polymerization systems with coordination catalysts.

2.6 Polymerization with Heterogeneous Z/N Catalysis[9]

A number of models of the active centres in Z/N catalysts have been postulated. The diversity of these models arises from the multitude of products found that to be formed or believed to be formed in the reaction of the catalyst precursor with the activator. The proposed active centres fall into either of two general categories: those containing monometallic species with the central transition metal atom (e.g. Ti),

and those containing bimetallic species with the central transition metal atom linked via bridges with the metal atom originating from the activator (e.g. Al).

The most widely accepted olefin polymerization mechanism that has been postulated to operate in systems with monometallic active centres is that proposed by Cossee. According to this proposal, concerning polymerization with catalysts based on layered violet titanium trichloride (α-TiCl$_3$), the active centres are located on lateral surfaces and formed by the replacement of the singly bonded non-bridging Cl atom protruding from the titanium trichloride surface by an alkyl group from the activator (Equation 2.1). Hence, the active centres contains the Ti atom surrounded by four Cl atoms from the crystal lattice bridged to two other Ti atoms), an alkyl group, which forms an active Ti-C bond, with the metal, and a coordination vacancy ($\square$). The Ti atom in such a site, Cl$_4$ Ti($\square$) R, attains an octahedral configuration when the coordination vacancy becomes occupied by the coordinating olefin molecule, namely Cl$_4$ Ti(olefin)R. The olefin is postulated to be coordinated at the vacant site with the double bond parallel to an octahedral axis. The polymerization of olefin according to the mechanism devised by Cossee is as Equation 2.9.

2.9
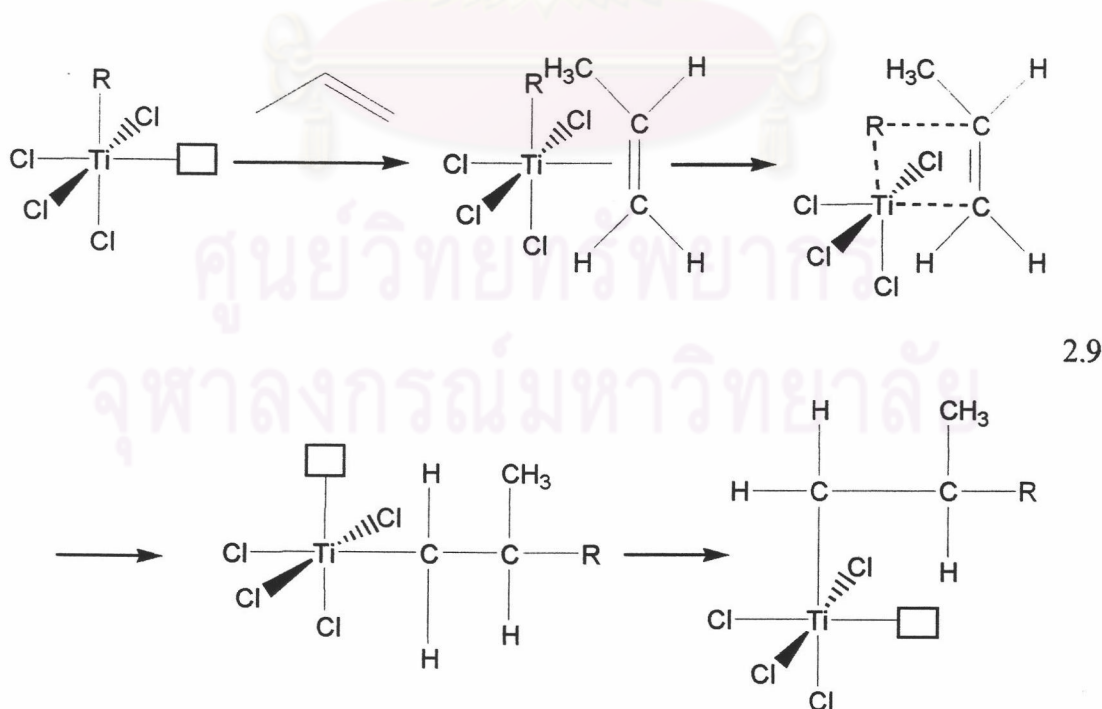
The metal-carbon (Ti-R) bond at the uncomplexed $Cl_4 Ti(\square) R$ active centre is relatively stable. The coordination of the olefin molecule at this centre, due to π bond formation (Figure 2.2), leads to lowering of the energy in the resultant π complex, $Cl_4 Ti(olefin)R$. The molecular orbital originating from the mixing of $3d_\pi$ orbitals from titanium with π^* orbitals from the olefin is sufficiently lower in energy with respect to the original $3d_\pi$ titanium orbitals for an electron easily to be transferred into it from the excited Ti-C active bond.
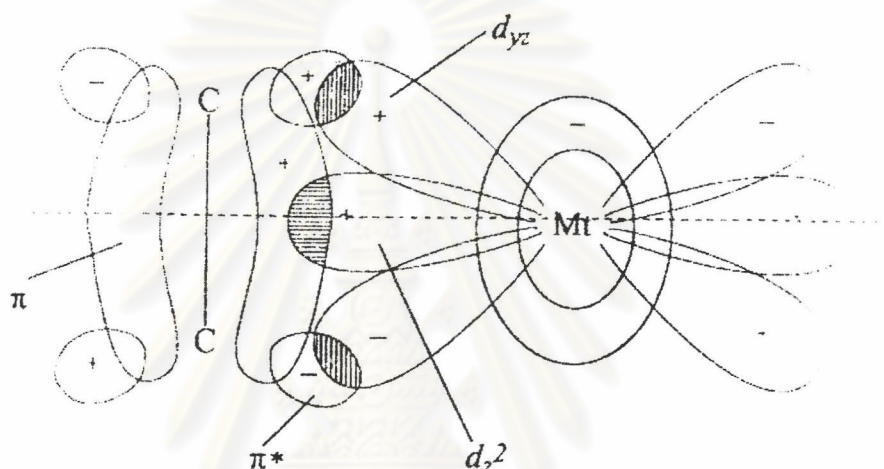
**Figure 2.2** Schematic presentation of the olefin coordination at the transition metal

Hence, the resultant alkyl radical attaches itself to the nearest carbon atom of the coordinated olefin a concerted way, involving a four-centered transition state. Therefore, Cossee's mechanism assumes that, in the insertion step, the growing polymer chain migrated to the position previously occupied by the coordinating olefin molecule. Such a mechanism is referred to as the chain migratory insertion mechanism. The *cis*-migration of the chain to the π-alkene ligand, with π-σ rearrangement, gives a new coordinatively unsaturated species that is able to coordinate another olefin molecule. However, in the last stage of the insertion, a back skip of the chain has been postulated by Cossee to take place in order to fulfil stereochemical requirements of α-olefin isospecific polymerization that the growing

chain always occupies the same position when a new monomer molecule is coordinated (Equation 2.9).

It should be emphasized that strong support has been provided for this mechanism of α-olefin polymerization, involving sites located on lateral α-TiCl$_3$ faces, from molecular orbital calculation. Analogous model sites, but located on layers in relief with respect to lateral faces of layered TiCl$_3$ structures, as well as for catalysts with the MgCl$_2$/TiCl$_4$ precursor, have also been considered in molecular mechanics studies.

Although it is apparent that for isospecific polymerization the polymer chain must skip back to the original position after each chain migratory *cis*-insertion in order to maintain sterically identical propagation steps, such a stage has been considered as a weakness of Cossee's mechanism. In connection with this, it has been hypothesized that the insertion of a π-complexed olefin molecule is initiated by another incoming monomer molecule; according to this hypothesis, a coordinated olefin is unable to undergo insertion without the aid of another incoming monomer molecule.

Monometallic centers as in the model proposed by Cossee have been widely accepted, though this model does not take into consideration the presence of an activator or products formed from it in Z/N polymerization systems. Bimetallic models give plausible answers concerning the role of activators and are in closer agreement with many experimental involving. The most commonly known olefin polymerization mechanism involving bimetallic active centres is that postulated by Rodriguez and Van Looy. According to this mechanism, which is based on Cossee' s mechanism. A molecule of the activator or the product origination from it (AlR$_2$Cl) is complexed to the transition metal (Ti) via the Cl bridge; the chain propagation, however, is monometallic. Equation 2.10 shows this mechanism.
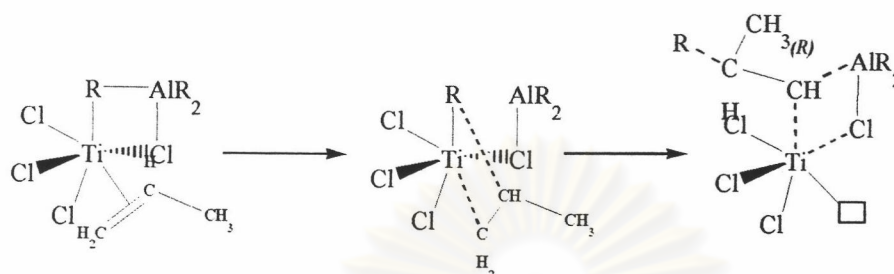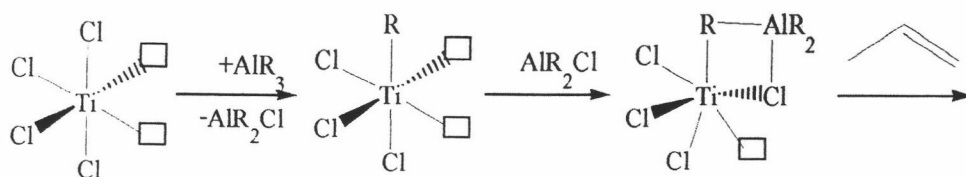
2.10

Variation in monometallic and bimetallic mechanisms has been proposed. The monometallic mechanisms seem to be inherently simpler than bimetallic mechanisms except for requiring a migration step. On the other hand, bimetallic mechanisms that consider the presence of the activator in the polymerization system can be more convincing in some instances.

2.7 Oxidation State of Catalysts and Active Centers [9]

The most extensive work, aimed at showing that both trivalent and tetravalent titanium centers are active in the $Al(C_2H_5)_3$-$TiCl_4$ and $Al(C_2H_5)_2Cl$-$TiCl_4$ catalysts when used for polymerizing ethylene, was reported by Schindler. He used deuterium gas (D_2) as a probe to differentiate types of centers in these catalysts. The polyethylene that was formed under these conditions had CH_2D, CHD, and CD_2 groups present according to infrared spectroscopic measurements. The CH_2D group was readily explained by a transfer reaction, as shown in Equation 2.11.

$$cat\text{-}CH_2CH_2CH_2R + D_2 \longrightarrow cat\text{-}D + DCH_2\text{-}CH_2CH_2R \qquad 2.11$$

$$cat\text{-}CH_2CH_2CH_2R + D_2 \longrightarrow cat\text{-}CH_2CHDCH_2R + HD \qquad 2.12$$

The CHD and CD_2 groups were explained by an exchange reaction involving D_2 and the labile β-hydrogen, as shown in Equation 2.12. Because he did not observe this exchange reaction with catalysts that were free of Ti(IV), such as $Al(C_2H_5)_2Cl$ + $TiCl_3$, he concluded that the active center produced these results contained Ti(IV). This assessment was based on the earlier findings of Bestain and Clauss that the β-hydrogen of a polyethylene chain which is attached to a Ti(IV) center is very labile. A double exchange would give CD_2. Using this diagnostic probe, Schindler examined in detail several catalysts prepared at different Al/Ti ratios for the relative contents of Ti (III) and Ti(IV) centers (Table 2.3). Also, he described a method by which the Mn and Mw values of two polyethylene polymers formed on Ti(III) and Ti(IV) centers were determined (Table 2.4). This method involved the evaluation of CH_3 or CHD group distributions in fractionated polymers prepared in the absence or presence of deuterium, respectively. In addition to Ti(III) and Ti(IV) centers, inactive Ti-H centers were proposed.

Table 2.3 The effect of catalyst ratio on the distribution of titanium valence states in different catalyst systems

Al/Ti ratio	Catalyst system			
	$(C_2H_5)_3Al/TiCl_4$	$(C_2H_5)_3Al/TiCl_3$	$(C_2H_5)_2AlCl/TiCl_4$	$(C_2H_5)_2AlCl/TiCl_3$
Low	IV + III	III	IV + III	III
Medium	III	-	-	-
High	III + II	III + II	III	III

Table 2.4 Molecular weight calculated from the evaluation of fractionation data from polymer growth on Ti(III) and Ti(IV) sites, Molecular weight in unit of 1,000

Polymer number	Wt% polymer derived from Ti(IV) sites	Total polymer		Polymer from Ti(III) sites		Polymer from Ti(IV) sites	
		Mw	Mn	Mw	Mn	Mw	Mn
1	40.1	137.3	14.1	210.7	41.8	29.4	6.9
2	38.9	144.6	13.3	207.2	39.3	45.6	6.5
3	45.4	112.8	9.8	173.9	32.3	39.1	5.3
4	39.9	79.6	10.8	90.5	17.7	63.4	6.7
5	38.4	54.3	9.0	64.2	17.3	39.1	5.1
6	40.9	33.5	5.9	37.2	8.7	27.7	4.0
7	16.0	239.9	18.2	281.1	45.3	22.2	4.4
8	60.1	82.1	8.8	130.3	30.7	50.6	6.0
9	81.8	182.8	18.6	323.7	96.6	150.1	15.6
10	79.0	127.2	11.2	259.0	57.3	92.0	9.2

2.8 Kinetic-Mechanistic Aspects of Polymerization with Z/N Catalysts[9]

Chemical kinetics deal with the reaction rate, including all factors influencing this rate, and with the explanation of the rate value in terms of the reaction mechanism. Kinetic studies of olefin polymerization with Z/N catalysts have been especially useful in the industrial development of olefin polymerization processes but have contributed relatively little to the understanding of the polymerization mechanism. Such a situation arises from the very complex mature of Z/N catalysts, especially those heterogeneous catalysts in which active species display widely different activities and geometric location. Changes in the number and structure of active sites can take place with changing polymerization temperature and time. Therefore, the time dependence of the

catalyst intrinsic activity, of the overall polymerization and of the operating diffusion processes complicates the kinetic behavior of such polymerization systems. Moreover, monomer adsorption (coordination) as well as adsorption of the activator (complexation), byproducts formed during procatalyst alkylation and the Lewis base (Internal and external) in the case of heterogeneous Z/N catalysts often make the polymerization kinetics too complicated.

No precise information about the olefin polymerization mechanism has been obtained of kinetic measurements in systems with heterogeneous catalyst; analysis of kinetic data has not yet afforded consistent indications either concerning monomer adsorption on the catalyst surface or concerning the existence of two stops, i.e. monomer coordination and insertion of the coordinated monomer, in the polymerization process. Indirect indications, however, may favour particular steps. Actually, no general olefin polymerization mechanism that may be operating in the presence of Z/N catalysts exists, but rather the reaction pathway depends on the type of catalyst, the kind of monomer and the polymerization conditions.

A comparison of kinetic data concerning olefin polymerization with Z/N catalyst of various kinds permits the classification of typical kinetic significant in Z/N olefin polymerization in that their particular shape may be characteristic of a particular catalyst or catalyst-monomer system. A number of different type of kinetic rate-time profiles are encountered in studies of Z/N catalysts, and some typical examples are presented in Figure 2.3 (heterogeneous non-supported catalyst) and Figure 2.4 (heterogeneous supported catalysts).

Figure 2.3 Variation in the rate of propylene polymerization with time: A, $TiCl_3$-$Al(C_2H_5)_3$ catalyst; B, $TiCl_3$-$Al(C_2H_5)_2Cl$ catalyst

Figure 2.4 Variation in the rate of olefin polymerization in the presence of the $MgCl_2/TiCl_4$-$Al(I$-$Bu)_3$ catalyst with time: A, ethylene; B, propylene

It can be seen from Figure 2.3 that the use of the AlR_3 activator produces a more active but less stable catalyst than that with the AlR_2Cl activator. Polymerizations in the presence of these catalysts show an acceleration (or settling) period, the rate of which increase to reach maximum ($TiCl_3$-AlR_3 catalyst) or to reach a more or less steady value ($TiCl_3$-AlR_2Cl catalyst). The nature of this acceleration period is connected with an increase in the catalyst surface area. Spaces between loosely linked primary crystallites of $TiCl_3$ (of 0.03-0.07 μm size in the case of δ-$TiCl_3$), which form agglomerates (of 20-40 μm size in the case of δ-$TiCl_3$), are quickly

filled with the polymer formed during the initial polymerization period. Under the mechanical forces exerted by the growing polymer chains, the agglomerates undergo disintegration into the primary crystallites, which results in an increasing number of active sites and thus in a higher polymerization rate.

Curves presented in Figure 2.4 testify to the large specificity of supported Z/N catalysts regarding the kind of monomer. Some centers can polymerize ethylene do not polymerize propylene (or higher α-olefins, which may also be differentiated by particular catalyst centres, depending on the structure of the α-olefins, e.g. branched as in 3-methyl-1-butene or not branched). Therefore no hints about the monomer reactivity can be obtained by simple comparison of polymerization rates without simultaneous estimation of the concentration of active sites.

Many supported highly active catalysts show behavior similar to case B in Figure 2.4; the polymerization rate may also start at a maximum value and then decrease more or less rapidly with time. Such kinetic behavior is also characteristic of some homogeneous catalysts. Other polymerization systems show no acceleration period but have a polymerization rate that remains almost constant with time; this is a rare case and relates, for instance, to 4-methyl-1-pentene polymerization with $MgCl_2$-supported catalysts containing phthalate esters as well as to ethylene polymerization with the Cp_2TiCl_2-$[Al(CH_3)O]_x$ catalyst (apart from a short settling period in the latter case).

Ethylene and Propylene polymers yielded by heterogeneous Z/N catalyst are characterized by a rather large distribution of molecular weights. The Mw/Mn ratio is usually equal to 5-10 for polyethylene. Polymers obtained in polymerization with homogeneous metallocene catalyst display a much lower polydispersity; the Mw/Mn ratio usually does not significantly exceed a value of 2. Using of soluble vanadium-base Z/N catalysts at low temperature polymerized propylene. Very narrow MWD of the polypropylene has been found (the Mw/Mn ratio usually reaches valves of 1.15-

1.25) and a linear increase in its Mn with time has been observed, indicating a noticeable living character of the polymerization.

The change in polyolefin molecular weight with time in polymerizations run with heterogeneous Z/N catalysts may be, in principle, of two types: the molecular weight increases for an initial period of time and then reaches a constant (e.g. the α-TiCl$_3$-Al(C$_2$H$_5$)$_3$ catalyst) or the molecular weight continues to increase throughout the duration of polymerization although the rate of this increase diminishes with time (e.g. the δ-TiCl$_3$-Al(C$_2$H$_5$)$_2$Cl catalyst). The latter behavior can be explained in terms of the failure to reach a steady state in the polymerization system. Although the polymerization rate increases with increasing temperature, ethylene and α-olefin polymerizations in the presence of most Z/N catalysts are carried out at moderately elevated temperature, usually not exceeding 100 $^\circ$C. This is due to destabilization of system, which occurs when temperature is raised beyond a certain critical value. There are, however, few catalysts that operate in industrial polymerization processes at temperatures above 200 $^\circ$C.

2.9 Literature Reviews

Katzen, S. and *et al.*[2] studied mixing of chromium catalysts. The mixed chromium catalyst in this invention consists different silica-supported chromium catalyst component. The silica supports of catalyst differ in pore volume by at least 0.3 ml/g. The pore volume of the silica support of the first catalyst component is greater than 1.0 or 1.7 to 3.1 ml/g. In second catalyst, the pore volume of the silica support used for the second catalyst component is from 1.0 to 2.0 ml/g. The first and second catalyst components present at a weight ratio from 5:1 to 1:5 and each containing from 0.1 to 2.0 weight percent chromium. The most useful experiment is mixing of chromium catalyst supported on silica with 2.3 and 1.6 ml/g pore volume, which was modified by zirconium. After polymerization of ethylene, the resulting polymer shows MFR around 375.

Benham, E.A., and Mcdaniel, M.P. [3] studied processing of making bimodal polyolefins using two independent particulate catalysts. Chromium and titanium composed in catalyst mixture. They found that 1:1 of Ti:Cr catalyst can be used for ethylene polymerization and the resulting polymer shows MFR around 165.

Ahn, T.O., and *et al*. [6] investigated 2 steps polymerization by two types of catalyst. They used titanium-vanadium catalyst with TEA (Ti-V/TEA) for first step and dichlorodinitropentadienylzirconium with methylaluminoxane (CpZ/MAO) for second step. The resulting HDPE shows broader MWD than HDPE from each catalyst. Table 2.5 shows this result. This accomplish comes from different hydrogen sensitivity of catalyst.

Table 2.5 Results of ethylene polymerization by sequential addition of CpZ/MAO and Ti-V/TEA catalyst system with various polymerization times

Catalyst	Polymerization time (min)		Mw/Mn
	CpZ	Ti-V	
CpZ	60	0	2.9
CpZ -> Ti-V	50	10	7.3
CpZ -> Ti-V	30	30	7.5
CpZ -> Ti-V	20	40	5.0
Ti-V	0	60	5.1

Hsieh, J.T.T [10] studied mixed catalyst comprising a chromium catalyst and Z/N catalyst and it gives significantly broader MWD polymers when used in the polymerization of ethylene, to particularly HDPE homopolymer and HDPE copolymers of ethylene and higher olefins. The chromium catalyst comprises a chromium compound on an inert support as silica and Z/N catalyst comprises an aluminium component and a titanium component on a magnesium oxide support in

which the weight ratio of chromium catalyst to Z/N catalyst is from 3:1 to 15:1 for maximum compatibility. Table 2.6 shows result of this study.

Table 2.6 HDPE MFI_5 and melt flow index ratio (MFR) with chromium and Z/N catalyst ratio

(Cr) / (Z/N) weight ratio	MFI_2 $(g \times 10\ min^{-1})$	MFI_{21} $(g \times 10\ min^{-1})$	MFR	Density $(g \times ml^{-1})$
-	0.219	24.5	112	0.952
3.13	1.880	226	120	0.970
10.5	0.260	47.1	183	0.958
10.3	0.031	5.0	161	0.952
10.6	0.082	14.5	178	0.955

Fereres, M.G., and *et al*.[11] studied synthesis and olefin polymerization using supported and non-supported geometry constrained titanium complexes. This investigation found that the formation of higher molecular weight polymers was found in the heterogeneous system as compared to the homogeneous parent for polyethylene and polypropylene. But this trend does not appear on styrene monomer.

Bosowska, K., and Nowakowska, M.,[12] studied effect of catalyst composition on polyethylene properties. They reported that catalyst activity and polyethylene properties depended on Mg:Ti molar ratio. For Ti:Mg = 0.1, titanium catalyst shows higher activity than Ti:Mg = 0.5 but gives lower melting temperature of polyethylene. Table 2.7 shows the results from this investigation.

Table 2.7 The influence of the catalyst composition on its activity and properties of obtained PE

Ti:Mg (mol/mol)	Catalyst activity (kg PE$\times$ g^{-1} Ti $\times$ h^{-1})	Tm (^{o}C)
0.1	70.0	138.8
0.5	66.2	141.0