

CHAPTER II

LITERATURE REVIEW

2.1 History of Ziegler-Natta Catalyst

The discovery of the first examples of this catalyst was the culmination of many years of the basic research of organometallic chemistry by Professor Ziegler and his students(1). The experiment made at the end of 1953 when ethylene reacted with AlEt_3 and $\text{Zr}(\text{acac})_2$ (2,3). The white powder that filled the autoclave was high molecular weight linear polyethylene. During the period of 1900-1953, a number of research groups had actively investigated organometallic chemistry, particularly the reaction of dienes including ethylene and substituted ethylenes.

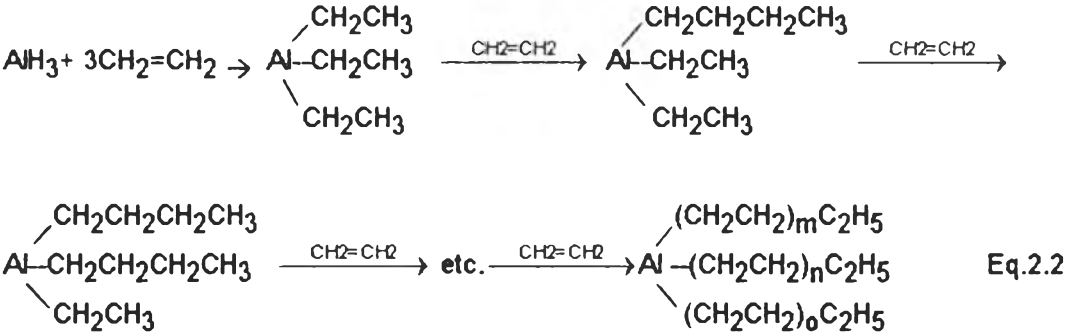
In 1930 Frederick and Marvel discovered that ethylene could be polymerized to low molecular weight products in the presence of lithium alkyls(4). Ziegler and his co-workers investigated the mechanism by which alkali metal alkyls initiated the polymerization of conjugated dienes(5). Until after 1945, DuPont workers reported that ethylene could polymerize by a lithium-copper powder catalyst (6) and by lithium alkyl and aryl compounds (7).

After World War II, Ziegler reinitiated a program on ethylene polymerization with lithium alkyls to synthesize higher molecular weight polymers. However, it proved to be an unsuitable catalyst because the growing alkyl polymer was prematurely eliminated (Eq.2.1, where n is a small number) with precipitation of LiH (8).



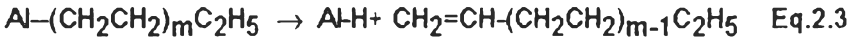
While attempting to improve this reaction, the ether promoted the reaction. Ziegler and co-workers, however, speculated that the ether soluble LiAlH_4 could also serve as a source of lithium alkyl, and this led them to the next advance(9). They demonstrated that LiAlH_4 reacted with ethylene to form LiAlEt_4 . At first they thought that ethylene could polymerize only on the LiEt portion and not polymerize on AlEt_3 ; this turned out to be wrong - AlEt_3 polymerized ethylene even more efficiently.

Ziegler and Gellert used $AlEt_3$ instead because of the experimental advantages. The equilibrium between metal alkyl and metal alkyl hydride plus olefins could now establish since all the metal alkyl and metal alkyl hydride components remained soluble. The organometallic synthesis of olefins by the following steps called the Aufbau reaction.



Where m, n, and o are small numbers.

Higher molecular weight polymers were not formed because a displacement reaction also took place at high temperatures, as in Eq.2.3



The Al-H bond reacted with the remaining ethylene to form polymer chains of comparable molecular weight. The termination step removed the growing alkyl from the aluminum before it has a chance to become very long.

Instead of polyethylene waxes, 1-butene was predominantly recovered from the reactor(10,11). They speculated that the displacement reaction had become catalyzed by a contaminant that shown to be colloidal nickel.

Cobalt and platinum salts behaved as nickel, but $Zr(acac)_2$ did not. Instead of 1-butene or waxes, they now synthesized high molecular weight polyethylene at low olefin pressure(2,3).

Transition metal salts(groups IV to VI) were also active, but the most active catalyst was made from $TiCl_4$ and $AlEt_3$, and this was developed for the large scale production of high density polyethylene plastics and designated by Ziegler as the Mülheim Atmospheric Polyethylene Process.

Since Ziegler concentrated with ethylene at the Max Planck Institute for Coal Research, much of his initial effort with this new catalyst apparently devoted to polyethylene and copolymers of ethylene and propylene. The full potential of this new catalyst was not realized in Ziegler's laboratory.

Before he informed the scientific community of his discovery, Ziegler disclosed the catalyst to Montecatini Company (Italy) and Goodrich-Gulf Chemical Company (USA)(12). Professor Natta was a consultant to Montecatini and he brought Ziegler's discovery to his attention. He undertook the research investigations of this new catalyst under an agreement between Ziegler and Montecatini.

Natta and his school were in a very good position to explore the catalyst(13). Being active in studying the kinetics of ethylene addition to aluminum alkyls, they were experimentally ready to study the new catalyst(14). Natta had hoped that the new catalyst would produce stereospecific (crystalline) polymers from α -olefins.

Early in 1954, the Natta group succeeded in synthesizing crystalline polymers (15-19). Their first experiments were with the Mannheim catalyst ($\text{AlEt}_3 + \text{TiCl}_4$) which they found to produce a mixture of amorphous and crystalline fraction polypropylenes. The solvent extraction method could isolate the crystalline portion. When other titanium chlorides (especially $\alpha\text{-TiCl}_3$, made by reducing TiCl_4 with H_2 at high temperature) were used in place of TiCl_4 , the polymers obtained were much more crystalline. Under his direction, this group continued to lead and dominate the investigation of the Ziegler-Natta catalysts and to open new areas of research in polymerization chemistry.

As mentioned above, the Goodrich-Gulf Chemical Company had also informed by Ziegler of his discovery before it became public, and this company examined it for dienes polymerization. Once the Ziegler-Natta discoveries became public, worldwide investigations immediately undertook to elucidate the mechanisms of these catalysts and to develop them for commercial application(20).

In 1955 Vandenburg at Hercules(21) and Ettore and Luciano at Montecatini(22) applied for patents that disclosed that molecular hydrogen acted as a true chain transfer agent. This was very important discovery because many of Ziegler-Natta catalysts produce polymers with too high molecular weight to process. Therefore the desired

The other discoveries came from the Natta school and many contributions made in the synthesis of new stereospecific polymer(23). Three very important synthetic discoveries disclosed in 1962 that enhanced the versatility of this catalyst. Zambelli, Natta, and co-workers(24) announced that the synthesis of highly syndiotactic polypropylene at -78°C when $\text{AlEt}_2\text{Cl} + \text{VCl}_4$ was specifically used.

The Royal Academy of Science of Sweden awarded the 1963 Noble Prize for Chemistry to Professors Karl Ziegler and Giulio Natta. The polymer and catalysis fields of science became profoundly enriched through the achievements of these two giants and their co-workers.

2.2 Related papers

Hong Man Park and Wha Young Lee[25] investigated the reaction of the ethanol of $\text{MgCl}_2 \cdot 6\text{EtOH}$ completely forming a complex with TiCl_4 . The $\text{EtOH} \cdot \text{TiCl}_4$ complexes couldn't remove during the washing of catalyst and it contributed to the enhancement of Ti contents. TEA in the preparation catalyst step removed ethanol in MgCl_2 before the impregnation of TiCl_4 . Organoaluminium compounds could react with an internal alcohol in a crystal very well. From the SEM photographs, it found that the particles of MgCl_2 before the impregnation of TiCl_4 fragmented into small particles in this step. It supposed that the activity enhances because of the removal of ethanol through TEA treatment.

D.N.Taveira Magalhaes[26] had prepared a number of catalysts from $\text{MgCl}_2 \cdot (\text{ROH})_n$ and evaluated them in ethylene and propylene polymerization. To prepare highly active MgCl_2 was to precipitate it from solution. MgCl_2 had some solubility in electron donor solvents such as alcohols and ethers and their dissolution products used as supports for Ziegler-Natta catalysts. It found that the alcohol-adduct from both methanol and ethanol had porous and irregular surfaces. The catalysts obtained through single and double treatments with TiCl_4 . The titanium content from double treatment method has lower content than that from single treatment. These results indicated that, in the second treatment with TiCl_4 , the catalyst surface was "cleaned" by removing some titanium derivatives soluble in TiCl_4 . These titanium derivatives were inactive sites for ethylene and propylene polymerization.

D.N.Taveira Magalhaes and his coworkers[27] had also studied more active support for the catalysts prepared through the elimination of alcohol molecules by thermal desolvation. The ethylene polymerization carried out at A/Ti ratio of 100. The titanium content of the catalysts depended on type of support and on the number of treatments with TiCl_4 . It indicated that the double treatment of TiCl_4 facilitated the deposition of TiCl_4 on the supports. The catalysts from the single treatment with internal base, ethyl benzoate, had high Ti content than that without internal base. This difference can be explained by the possible complexation of TiCl_4 with ethyl benzoate, facilitating the deposition of TiCl_4 on the surface of support.

B.V. Kokta and R.G. Raj[28] had investigated the interaction between the catalytic components of a Ziegler-Natta stereospecific system formed by TiCl_4 and AlEt_3 in heptane by IR spectroscopy. The first step of reaction between $\alpha\text{-TiCl}_3$ with AlEt_3 was an alkylation or exchange of Cl for ethyl. They prepared TiCl_3 from the reduction of TiCl_4 with hydrogen on Tungsten spiral. It was ground under inert atmosphere. The extent of interaction

was determined quantitatively by the analysis of chlorine exchange in liquid phase. The IR spectroscopy was carried out to follow the AlEt_2Cl formation during the interaction of catalyst components in Ziegler-Natta catalytic system.

B.V.Kokta and R.G.Raj[29] had also tried to correlate the interaction between the catalytic components and the polymerization process. The interaction depended on the degree of conversion of the exchange and decomposition reactions. It related to the theoretical quantity of hydrocarbon (RH, ethane in the case of AlEt_3) formed by the exchange of all Cl in TiCl_3 and the decomposition of alkylated titanium. The conversion depended on the ratio of catalytic components. The addition of electron donor to the catalyst system formed by non-activated TiCl_3 and AlEt_3 could either increase or inhibit the rate of polymerization depending on the reaction conditions. The increase of polymerization rate was closely relevant to increase in RH formation. $\text{TiCl}_3\text{-AlEtCl}_2$ system was very low activity compared to the system with AlEt_3 because AlEtCl_2 was an inhibitor in stereospecific polymerization.

Sergeev and his coworkers[30] studied the interaction between highly dispersed MgCl_2 and ethyl benzoate(EB) at different molar ratios of EB/MgCl_2 . The effect of grinding induced the formation of a new compound between MgCl_2 and EB. With increasing EB/MgCl_2 , the crystallite size of MgCl_2 slightly decreased whereas those of the new compound attained constant values at $\text{EB/MgCl}_2 = 0.33$. The decrease of the catalyst activity and the increase of its stereospecific were apparently due to the blocking of that part of MgCl_2 which by way of interaction with TiCl_4 led to the formation of nonspecific centers. The destruction of the phase of the new compound was for obtaining a highly active catalyst. This achieved by grinding the new compound. It interacted with free MgCl_2 to provide a uniform distribution of EB in MgCl_2 .

Chien, Dickinson and Vizzini[31] had investigated the physical states of the organic modifier and their chemical interaction with MgCl_2 using the solid state magic-angle spinning cross-polarization $^{13}\text{C-NMR}$ (MAS-CP $^{13}\text{C-NMR}$) technique. All materials handled in Schleg tubes and stored in a pure Ar atmosphere. The broad line widths indicated dispersity in binding sites giving a range of chemical shifts. p-Creso(PC) also formed a rigid complex with MgCl_2 and had the effect of rendering the bound EB less rigid. Treatment with TiCl_4 removed most but not all the PC moieties by extraction and conversion of the aluminum compounds to AlCl_3 .

Chien and Wu[32] had studied a $MgCl_2$ -supported high mileage olefin polymerization catalyst by EPR. The catalyst was treated with HCl at elevated temperature, ethyl benzoate by milling, p-cresol, $AlEt_3$, and $TiCl_4$. It produced a catalyst with a singly EPR observable Ti^{3+} species strongly attached to the surface with D_{3h} symmetry. It had to be at two or even three surface sites. The weak ligand or solvent molecule occupied the vacant sites. Activation with preformed $AlEt_3$ /methyl p-toluate(MT) complexes produced a single Ti^{3+} species with rhombic symmetry. $MgCl_2$ -supported high mileage catalyst was known to have high initial rates for polymerization but the rate fell off rapidly. Apparently, MT could weaken the Ti-Cl-Mg bond. The role of MT was to complex with $AlEt_3$ so that the complex would have moderated alkylation power compared with uncomplexed TEA. Reaction of the catalyst first with MT apparently weakened the bonding between the titanium and the support. The subsequent activation with TEA produced Ti^{3+} species that apparently had significant freedom of motion.

Chien and Ang[33] had verified that the large polydispersity of the polymer and the rapid decrease of polymerization rate. Some researchers attributed the decreasing rate of propagation to the effect of encapsulation of the heterogeneous catalyst. It was semicrystalline polymers that retarded the diffusion of monomer to the catalytic sites. The most likely model for the catalyst system was the competitive adsorption of monomer and aluminum alkyls in propagation and chain transfer process.

Chien, Wu and Kuo[34] had clarified that the vast improvement in Ti use of the $MgCl_2$ -supported catalysts over the $TiCl_3 \cdot 1/3AlCl_3$ catalyst. It must be attributed in the large increase in the number of accessible active sites. The physical state of the catalyst must be an important point of the new system. Ball milling with EB significantly reduced its crystallite size and held together by complexation with EB. EB did not enter into the lattice of the $MgCl_2$ crystallites. Then the support would treat with PC, PC incorporated and that EB remained in the $MgCl_2$. It found that $MgCl_2$ crystallites had a surface layer highly coordinated with PC. The surface area increased after the reaction between the support and TEA. Final treatment with $TiCl_4$ produced a catalyst and the PC component had largely removed from the support in the process.

Chien and Hu[35] had found that only a very small fraction of the Ti in the classical catalysts, (Z-N catalysts), actually initiated propylene polymerization. With each improvement of active sites, $[Ti^*]$, increased in the order of hydrogen reduced $\alpha-TiCl_3 <$ chemically reduced $\alpha-TiCl_3 \cdot AlCl_3 <$ $\delta-TiCl_3 \cdot AlCl_3 <$ Solvay catalyst $<$ $MgCl_2$ supported

catalysts. High activity Z-N catalysts was prepared by impregnating Ti ions on the support's surface. Nearly all the Ti ions were active for ethylene polymerization. $TiCl_2$, $TiCl_3$, and $TiCl_4$ were all known to polymerize ethylene. The decline of the $[Ti^{3+}(EPR)]$ proceeded with time of aging because of the deactivation during aging. The main reaction of H_2O was the oxidation of Ti^{2+} ions to Ti^{3+} ions.

Gaponik[36] studied the catalytic system based on higher aluminum alkyls. It exhibited rather high polymerization activity which was due to a long lifetime of the active sites. Complexation of TEA with certain electron-donor compounds is able to increase its alkylating and reducing properties.

Sacchi[37] has used ^{13}C NMR to study the effect of the Lewis base on high yield supported Ziegler-Natta catalysts for isotactic propylene polymerization. They found that the role of the internal base as follows:

(i) The base, $MgCl_2$ and $TiCl_4$ formed a three-component complex, which was the real active center; thus the base had a direct function to catalyze.

(ii) The two-component complex $MgCl_2-TiCl_4$ was the true polymerization center; thus, the base had an indirect function, for instance, of controlling the titanium fixation on $MgCl_2$.

Yoon and Jeung[38] had examined the reduction of $Ti(III)$ to $Ti(II)$ by aluminum alkyls that had considered as a reason for the catalytic activity decay in propylene polymerization. The rate decay had explained with the increase of monomer diffusion path owing to the accumulation of polymer around the catalyst particles. The activity decay was attributed to an over-reduction of $Ti(III)$ to $Ti(II)$ by aluminum alkyls. The aging of the catalyst with TEA gave rise to a significant rate decay.

Chien, Youliang and Vizzini[39] studied two catalyst systems called as CH- and CW-catalysts. The CH-catalyst was from a soluble $MgCl_2$ -alcoholate and phthalic anhydride. The support reacted with $TiCl_4$ in the presence of another diester to give a CH-catalyst activated by TEA with $Ph_3(OEt)Si$. The Ti loading in a CH-catalyst was also very sensitive to the alcohol used to prepare the $s-MgCl_2.ROH$ adducts. All polymerizations showed the large decay of activity. It became to one-fifth or one-fourth of the polymerization rate with 0.5 hour. This behavior was generally observed for $MgCl_2$ supported high activity catalysts in Eq. 2.4-2.5,



Yano and Inoue[40] had indicated that ethyl benzoate would coordinate on the surface without interaction with TiCl_4 . It had found that the amount of titanium halides immobilized on MgCl_2 related to that of EB used in ball-milling with MgCl_2 . Titanium halides immobilized on a 110 or 101 plane of a MgCl_2 crystal by Cl bridges, and that EB, which coordinated to both the titanium halides and MgCl_2 , ensured that the titanium halides were supported on MgCl_2 . MgCl_2 played the role of an electron acceptor to ligands and an electron donor to TiCl_4 .

Kar[41] had found that heterogeneous olefin polymerization catalysts could replicate their morphology into the polymer particles. The catalysts' particles acted as a template for growth of the polymer particles. For high activity catalysts in olefin polymerization, the average particle size of the polymer was about 15-20 times larger than the size of the catalyst particle. Although the polymer particle replicated the morphology of the catalyst particle, the catalyst particle broke down or shattered during the polymerization process and the fragments became dispersed throughout the polymer particle.

Kashiwa[42] had produced polypropylene by a high active MgCl_2 supported TiCl_4 in conjunction with AlEt_3 and ethyl benzoate(EB). The effect of EB concentration on yield and stereoregularity of the polymer examined the reasons to the function of EB. A suitable amount of EB to increase yield and the polymer's stereospecificity, while, in contrast, decreased the yields rapidly. Of course, a large excess amount of EB would deactivate the catalyst activity, perhaps, due to the saturation of the vacant coordination sites in the active centers. The interaction between $\text{MgCl}_2/\text{TiCl}_4$ catalyst, AlEt_3 and EB investigated to inform the EB influence. EB introduced into the catalyst system fixed on the solid catalyst.

Lesna[43] had used $\text{TiCl}_3/\text{AlEt}_2\text{Cl}$, $\text{TiCl}_2/\text{AlEt}_2\text{Cl}$ and $\text{TiCl}_3/\text{AlEt}_3$ systems to study the retardation effect of CO_2 and CO on ethylene polymerization. It found that the adsorption of CO_2 on the active sites didn't significantly influence by the monomer type. CO was much more powerful retardation agent compared with CO_2 . The retarding effect of CO_2 on ethylene polymerization was probably not due to insertion of CO_2 into the growing bond but it was rather the result of reversible sorption on active centers of polymerization. However, it seemed quite plausible that carbon oxides could coordinate into the vacancy on the active centers that restricted the coordination of monomer.

Sun[44] had copolymerized ethylene and butadiene by supported titanium catalysts. It clarified that the increase of temperature would increase the termination process and could decrease molecular weight. AlEt_3 played the role of chain transfer agent. The increase of AlEt_3 concentration increased rate of chain transfer as well as caused a decrease of molecular weight of polymer.

Tait[45] had encountered the advent of second and third generation high activity supported catalysts. The overall kinetic behavior recognized to be more complicated with the added complication of the third component participation and related reactions. He also mentioned the breakdown of the TiCl_3 -matrix took place during the polymerization and this behavior both provided a simplification and a complication in kinetic studies of Ziegler-Natta catalysts. A simplification in that steady state rates could readily observe but a complication in that the actual surface area of the polymerization catalyst could not measure directly.

It was evident that the complex behavior controlled by both chemical and physical factors and these may including the following :-

- (a) catalyst particle size and morphology,
- (b) catalyst center forming and catalyst destroying reaction,
- (c) complexation reaction between the active centers and alkylaluminium species, between active centers and donor molecules, and between alkylaluminium species and donor molecules. These reactions will control the relative numbers of potential and actual active centers,
- (d) diffusion phenomena.

Escalona[46] had verified on how carriers influenced on the polymerization activity and stabilized the active sites, and also how the catalyst morphology influenced the kinetic behavior and the morphology of the resulting polymer. These catalysts exhibited higher activities than the conventional ones and also better ability in controlling the nascent polymer morphology. The support was intensively ball-milled to introduce sufficient Ti in its crystal lattice. The improvement of the catalyst morphology could achieve by treatment with high Al/Ti ratio. The catalyst particles formed by more or less loosely bound agglomeration of subparticles; at the same time consisted of primary particles, leaving cracks and pores inside. The polymerization took place at the active centers located on the surface of the primary particles. The pores and cracks filled by the growing polymer leading to the fissuring, rupture and expansion of the aggregate and of the whole particle, exposing new active centers to

polymerize. Therefore, the size, shape and texture of the catalyst particles controlled not only the resulting polymer morphology, but also the kinetic. When the catalyst particles became encapsulated with polymer and as a result, its activity tended to be lower. A good catalyst must have very high activity and excellent control of polymer morphology.