Original Research Article

Application of Ziegler-Nata Catalysts in the Synthesis of Polyolefin

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ABSTRACT

Discovering Ziegler-Nata catalyst, Karl Ziegler had a great impact on the development of the chemical industry. Since then, important changes have been made in the method of production and use of this catalyst. More active and functional catalysts have been developed to produce different products. In 1950, while working on the synthesis of olefins using the catalytic reaction of triethyl aluminum, Karl Ziegler accidentally discovered that due to the presence of nickel in the reaction vessel, instead of the usual wax-like product, the reaction product was exclusively 1-butene, indicating that Nickel catalyzed the hydrogen removal reaction. After Ziegler's discovery, triethyl aluminum was used with a wide range of intermediate metals, and after many experiments, titanium tetrachloride became the most active compound. The discovery of Karl Ziegler and her colleagues in 1953 was one of the most important discoveries in the field of polymer synthesis at that time, leading to a remarkable scientific and industrial breakthrough in the production of polyolefin.

GRAPHICAL ABSTRACT
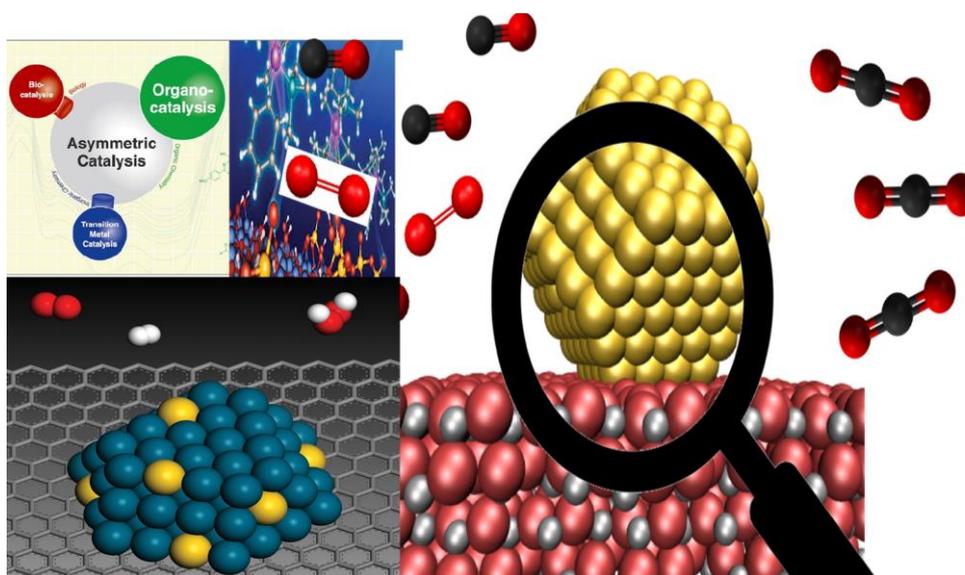
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Introduction

Basically, the catalyst is considered as a chemical compound able to exert an accelerating and directing effect on the progress of a reaction that is thermodynamically possible. When the catalyst is soluble in the reaction medium, it is called a "homogeneous catalyst" and when the phase catalyst forms a separate phase from the reaction phase, it is referred to a "heterogeneous catalyst". In most cases, a heterogeneous catalyst is a solid catalyst that causes gas or liquid reactors to evolve due to its contact with them, and as a result, the term "catalyst" is often used to refer to a heterogeneous catalyst. Catalysts are generally divided into three categories [1].

1. Metal catalysts, such as Fe, Co, Ni, Rh, Pt, etc;
2. Insulation catalysts, such as silica, alumina, zeolites and activated alumina; and,
3. Semiconductor catalysts, such as metal oxides and sulfides.

The Main Characteristics of catalysts

1. During the reaction, the catalyst remains unchanged and only increases the reaction rate [2].
2. Catalyst should be selective when there are several mechanisms for the reaction. In principle, the catalyst must increase the ratio of production of the desired substance to the unwanted substance.
3. The reaction rate is proportional to the concentration of the catalyst and the catalyst surface and active surfaces are very important in gas-solid reactions.
4. In a reversible reaction, the catalyst affects the rate of the return reaction as much as it increases the reaction rate. Therefore, the combination of equilibrium percentage of the system is the same with or without the presence of a catalyst.
5. In autocatalytic reactions, a small amount of product must be present first [3].

History of Ziegler-Nata Catalysts

Polymers play a major role in humans' life today. Polymerization is a process that usually does not progress without a catalyst. Today, complex catalysts are used in polymer production plants. Polypropylene is one of the most widely used polymers and is the source of catalysts used in the production of polypropylene today. Discovering the Ziegler-Nata catalyst, Karl Ziegler had a great impact on the development of the chemical industry. Since then, important changes have been made in the method of the production and use of this catalyst [4]. In 1950, when Karl Ziegler was working on the synthesis of olefins using the catalytic reaction of triethyl aluminum, he discovered that due to the presence of nickel in the reaction vessel, instead of the usual wax-like product, the reaction product was exclusively 1-butene, indicating that nickel catalyzed the hydrogen removal reaction. After Ziegler's discovery, triethyl aluminum was used with a wide range of intermediate metals, and after many experiments, titanium tetrachloride became known as the most active compound. These catalysts (titanium tetrachloride and triethyl aluminum) were first used to make high volumetric mass polyethylene [5-7]. The discovery of Professor Karl Ziegler and her colleagues in 1953 was one of the most important discoveries in the field of polymer synthesis at that time, which led to a remarkable scientific and industrial breakthrough in the production of polyolefin. One of Ziegler's students focused on the growth reaction in the preparation of ethylene oligomers at high temperatures (100-200 °C) using alkyl aluminum compounds. He accidentally found that the agglomeration reaction could be performed at lower temperatures and milder pressures with small amounts of Nickel catalyzed compounds and linear high molecular weight polymers. The extensive research by the Ziegler Research Group using other metals in this field made it possible to obtain a mixture of zirconium acetate steel and

catalyst triethyl aluminum, which is much more active than other compounds [8-10]. Further research and studies have documented that the compounds of metals of group's v and IV of intermediate elements show similar results when used with different compounds of alkyl aluminum. Of these, titanium and vanadium compounds are more active. Ziegler and colleagues focused mainly on the polymerization of ethylene and its copolymerization with alpha-olefins. Simultaneous with Ziegler's discovery, Giulio Nata and his colleagues conducted extensive research on this discovery. Nata et al. also polymerized propylene using a combination of titanium tetrachloride and triethyl aluminum. They also proved that with special types of halides of intermediate metals, crystalline salts of these metals such as $TiCl_3$ and VCl_3 and special space polymers can be produced from their styrene butene-1 and so on. In 1954, Nata Group in Italy succeeded in separating crystalline polypropylene for the first time using Ziegler catalyst. In their experiment, a mixture of amorphous and crystallized polypropylene was produced, and they extracted the crystalline material using a solvent [11].

Structure of $TiCl_4$ Catalyst

Titanium trichloride can be obtained from $TiCl_4$ in various ways such as reduction by hydrogen, irradiation and commercially by reduction with aluminum alkyls. Nata showed that this catalyst is obtained in four structures according to the unique method used to reduce $TiCl_4$. The shapes α, γ and δ have a bright purple color and their structure is layered [12]. In the α structure the arrangement of chloride ions is hexagonal stacking and in the γ structure the arrangement of chloride ions is cubic stacking. The δ shape has an interface between α and γ. The β structure is chain and brown, with this structure the yield of the isotactic polymer is low, but with purple $TiCl_3$ the yield of the isotactic polymer is high [13].

Catalytic Active Centers

Cossee-Arlman have shown that the active catalytic centers are the titanium ions with empty coordination sites. The first step in this catalytic process is the alkylation of the intermediate metal compound. Alkyl is a catalytically active intermediate metal. The alkene (olefin) then co-ordinates with the intermediate metal at the vacancy, and as the alkyl group migrates to the olefin, a new metal alkyl, a growing polymer chain is formed and a co-ordination site is vacated [14].

Production of Commercial Catalysts

To prepare the first commercial catalysts, $TiCl_4$ was reduced at sub-zero temperatures with triethyl aluminum in a hydrocarbon solvent, resulting in a β-structure that was not suitable for isotactic polymer polypropylene. Therefore, its slurry was gently heated to 160 to 200 °C to cause a phase change in the γ structure. To increase efficiency and selectivity with the ball mill, TiCl3 subcrystals with more catalytic active centers were prepared [15].

Selecting Catalyst Support

The most important role of the catalyst support is to alkylate the Ti atoms on the crystal surface. In most commercial catalysts, $TiCl_4$ is used with the help of diethyl aluminum chloride catalyst, which has a yield of isotactic polymer product by 90 to 95% and is more active than triethyl aluminum (70 to 85% yield). Another commercial catalyst is $TiCl_3$, $XAlCl_3$. However, the presence of $AlCl_3$ leads to the production of ethyl aluminum dichloride catalyst toxin, which reduces the rate of polymerization by forming a complex with active catalytic centers. To eliminate this effect, in the late 1960s, electron donors such as ether, ester and amine (Lewis base) were added to the catalyst as a third component to increase its activity [16].

The Second Type of Catalysts

In 1970, type II catalysts were developed. To produce them, $TiCl_4$ was produced at low temperatures with alkyl aluminum to obtain $TiCl_3$ and $XAlCl_3$. Aluminum trichloride is extracted by ether and the phase conversion is performed in the presence of additional $TiCl_4$ between 60 and 100 ° C. The working capacity of type II catalysts is four times than that of type 1 catalysts. Today, the catalyst is mounted on the $MgCl_2$ layer structure using a ball mill. Due to the fact that the stability of this catalyst against reduction is higher compared with the γ structure, here tri-alkyl aluminum can be used as a catalyst support. Stereochemistry in the polymer chain can be isotactic polymer, syndiotactic polymer or atactic polymer. Single-arrangement polymers exist when all chiral centers have the same stereochemistry. The polymer centers of all arrangements change with the spatial state of the polymer. Atactic polymer polymers do not have ordinary chiral centers. Due to their excellent performance Ziegler-Nata catalysts have a vital role in the preparation of isotactic polymers, where free radical polymerization results in the atactic of polymers. Catalytic systems, such as VCl_4, produce syndiotactic polymer and go through a different trajectory compared to $TiCl_4$ systems [17-19].

Preparation of Catalysts

Ziegler and Nata catalysts are produced by α-$TiCl_3$ crystals with $[AlCl_5]_2C_2H$. Titanium metal forms a crystalline structure in which all titanium ions with 6 chlorine ions crystallize in an octagonal structure. One of these empty sites can be filled by giving electrons from one of the $AlCl(CH_3$ in Et$)_2$ groups. The other empty sites are filled with a monitoring system such as Alken. Incoming alkene metal ligands are restricted due to the growth of the polymer chain, thus imposing a special spatial structure on it. During the stages involving electron transfer and migration, under Cossee-Arlman mechanism, polymer expansion is stereospecifically described. The entry of a new alkyl group into the polymer chain occurs in the intermediate metal, and the polymer grows and forms a bond with the alkyl ammonium catalyst as shown in the reaction below.

$$R_2Al\ (CH_2CH_2)_nH \rightarrow R_2AlC_2H_5 + (n-1)\ CH_2=CH_2$$

With the removal of a beta hydrogen, a final step occurs in which hydrogen is adsorbed by the metal to form a carbon terminal by forming a double bond. Through reaction we have:

$$R_2AlH + CH_2=CH_2R \rightarrow R_2AlCH_2CH_2R'$$

Another equivalent method for forming this catalyst is to use $TiCl_4$ and $AlEt_3$. Titanium chloride triethyl aluminum is placed in a solution that is sensitive to water and pyrophoric to air. Therefore, the catalyst must be prepared in a neutral atmosphere [20-22].

To prepare this open catalyst, Lewis and magnesium chloride are ground together and mixed with a heptane solution containing $TiCl_4$. And the resulting solid is easily separated by sieving. The catalyst is then added to the heptane solution, which is saturated with the desired alkene, and when the $AlEt_3$ is added and the solution is slightly heated slowly, the polymerization reaction begins [23-25].

Mechanism and Origin of Space Selection

This orderly space resulting from the polymer expansion mechanism is known as the Cossee-Arlman mechanism, where it sits on the surface of titanium chlorine in unoccupied areas. Other organic-metallic compounds are able to form order space polymers, such as metallocene compounds. One of these compounds is Cp_2 $(TiCl_2)$, which does not have an unoccupied position like $TiCl_3$ crystals and therefore must be activated with alkyl ammonium compounds.
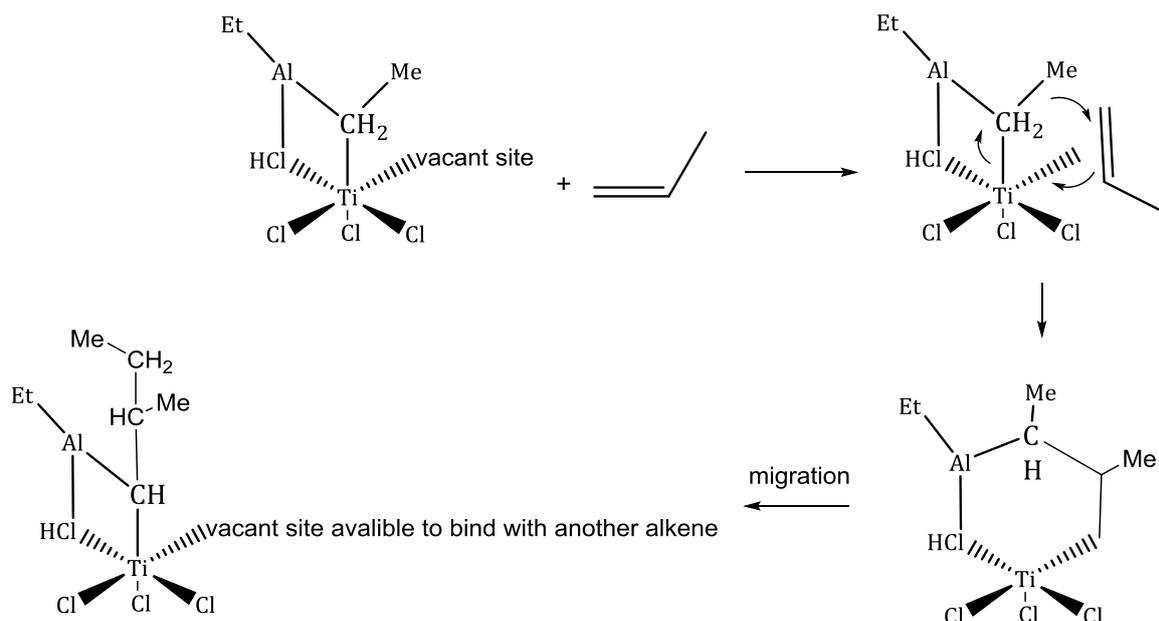
Figure 1. Mechanism and Origin of Space Selection

It is very common to use MAO compounds or methyl alumine oxane (CH_3 AlO)n as a catalyst support. Like $AlEt_3$, it activates the intermediate metal complex by behaving as a Lewis acid and adsorbing one of the halides, hence an unoccupied site in which an alkene is added to the complex [26-28].

Activity and the End of the Chain
Activity depends on the nature of matter. Based on periodic Table for titanium column, titanium is the most active as a catalyst and hafnium and zirconium are highly volatile. Of course, titanium is a very good catalyst in its oxidation state because its d orbital is free of electrons, so without d electrons the bond of titanium and alkene with the reverse bond will not be stable, thus reducing the energy barrier for reaction and polymer chain growth [29].
This means increased catalyst activity. The length of the polymer is usually determined by the rate constant of two competing reactions; one is chain growth and the other is the final stage. The reaction usually ends with the removal of beta hydrogen [30].

These two reactions determine the effectiveness of the catalyst in creating long-chain polymers. Since the discovery of the Ziegler-Nata catalysts, researchers have worked on these two rate constants to design the adjustability of high- or low-molecular-weight systems [31-33].
For example, the use of zirconium species in the form of half-sandwich metallocenes is known as the species that form polymers with low molecular weight, the reason for the low activity of zirconium and also the increase in beta removal by the formation of a C-Zr bond. High molecular weight polymers are formed when bulky ligands which are used around the intermediate metal [34].

Ziegler-Nata Homogeneous Catalysts
Many efforts have been made to develop catalysts that can effectively deliver branched alkenes. Efforts have also been made to produce Ziegler-Nata homogeneous catalysts that do not require the help of aluminum catalysts. These species are cationic and lose themselves in the active ligand solution. One of these catalysts is $Cp_2Zr(CH_3)$ $CH_3B(C_6F_5)_3$. The borate anion is separated and empty active site is vacated to

form a bond with the alkene. Advances in creating of advanced coordinate anions will be continued [35].

The Main Components of the Ziegler-Nata Catalyst

Catalyst: Compositions of metals such as titanium, vanadium, zirconium, chromium, hafnium, tungsten, nickel and neodymium are among the most important compounds that have been introduced as catalysts.
$TiCl_3$-$TiCl_4$-$TiBr_3$-VCL_3-$ZrCl_4$-$NaCl_5$-$NiCl_3$-YCl_3 are some of these catalysts. In general, for the production of Isotactic polypropylene on an industrial scale, titanium compounds are used more than other compounds and vanadium compounds are mostly used for the production of syndiotactic products. The order of activity of the

major compounds of titanium and vanadium, which are used in industry for the polymerization of olefins, especially ethylene and propylene, is as follows and other compounds are not considered:
$TiCl_4$> VCl_4> VCl_3> $TiCl_3$
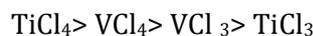
Co-catalyst or Activators: Alkyl aluminum and alkyl aluminum halides compounds are the most important activators for Ziegler-Nata catalysts. Except for a few catalysts, including Cp_2 $TiCl_2$, almost all catalysts require an activator for polymerization. Alkyl aluminum compounds are often used more due to their higher activity than other compounds. The type and amount of alkyl aluminum has a significant effect on the speed, activity and space selection of the catalyst [36].

Table 1. Effect of activator amount on polymerization of propylene using $MgCl_2$/DIOP/$TiCl_4$/TEA/ED catalyst

DPDMS			DIDMS			
$[\eta]$ (dl/gr)	Conversion Percentage	Catalysis Activity (kgPP/mol Ti)	$[\eta]$ (dl/gr)	Conversion Percentage	Catalysis Activity (kgPP/mol Ti)	AL/Ti
2.9	95.7	1.03	4.1	96.1	0.96	50
2.6	96.7	1.04	-----	96.4	1.09	85
2.3	96.8	0.94	3.5	97.5	0.85	340

Table 2. Effect of activator amount on propylene polymerization using CpTi $(OBz)_3$/ MAO catalyst

Mw $*10^{-4}$	Catalysis Activity (kgPP/molTi)	AL/Ti
6.44	50.3	85
4.05	100.2	150
3.82	31.2	240
1.82	22.1	480

Table 3. Effect of activator on polymerization of propylene using $MgCl_2$ / DIOP / $TiCl_4$ / TEA / ED catalyst

MWD	Mn ($*10^{-3}$)	Mw ($*10^{-3}$)	AL/ED (DIDMS)	MWD	Mn ($*10^{-3}$)	Mw ($*10^{-3}$)	AL/ED (DPMS)
9.2	104	955	1	10	36	359	1
7.7	67	518	10	11.6	37	432	10
9.4	40	376	20	7.8	38	296	50
11.2	42	475	50	-----	------	-----	-----

Tables 1 and 2 show that with increasing AL / Ti, the catalyst activity first increases and then decreases while the molecular weight decreases continuously due to the reduction of more amounts of Ti^{4+} to Ti^{2+} which is not active compared with propylene polymerization; Ti^{3+} activates the polymerization of propylene. Also, the type of activator has a great effect on the molecular weight and its distribution. Table 3 shows the effect of the type of the catalyst on the distribution of broad molecular weight and its strong dependence on the amount of activator [37].

Table 4. The effect of external electron donors on the polymerization of propylene using a Mg (OEt) 2 / DNBP / TiCl4 / ED / TEA catalyst

MWD	MW ($*10^{-4}$)	Conversion Percentage (٪)	Catalysis activity (KgPP/grTi)	External electron donor type
5.9	26.2	95.3	30.2	TMDMDP
5.9	26.8	95.2	29.9	TMMHDP
6.3	25	93.1	40	TMDHDP
5.5	27.9	97.2	34.3	TMMCDP
5.5	27.5	97	30.2	TMDCDP
5.6	38.5	97.2	42.2	TMDCDO
6.5	23	92.1	42.1	TMDMDS
5	32	98.6	62.2	IPTDM
5.3	28.7	98.2	51.7	BTDM
6.2	22.2	91.2	44.1	DMDM
5	31.3	98.5	60.1	CMDM

Table 5. The effect of external electron donors on the polymerization of propylene using a MgCl2 / DIBP / TiCl4 / ED / TEA catalyst

MWD	Mn ($*10^{-3}$)	Mw ($*10^{-4}$)	External electron donor type
6.22	65.1	40.5	DIDMS
3.67	55.1	20.2	DPDMS
5.92	76.6	45.3	DcPDMS
5.46	67.4	36.8	cHMDMS

The highest and lowest molecular weights with Mg (OEt)$_2$ based catalyst are obtained using TMDCDO and DMDM external electron donors (rows 6 and 10), respectively. For MgCl$_2$ base, DcPDMS electron donor has the greatest effect on molecular weight and DIDMS electron donor has the greatest effect on MWD [38].

Table 6. Effect of external electron donor amount on polymerization of butane-1 using MgCl$_2$ / TiCl$_4$ / TEA / EB catalyst

MWD	Mn $*10^{-5}$	Mw $*10^{-5}$	ED/Ti
5.01	1.1	5.61	0
4.98	1.53	7.62	0.25
5.32	1.11	5.89	0.5
4.45	1.1	4.91	0.75
4.91	1.13	5.56	1
4.74	1.62	7.69	2.5
4.39	1.59	6.99	5
4.05	2.05	8.29	7.5
4.87	1.95	9.51	10
5.23	1.79	9.35	15
4.17	2.8	11.66	20
4.47	3.2	14.31	25

Table 7. Effect of external electron donor on the polymerization of butane-1 using MgCl2 / TiCl4 / TEA / tetramethylpiperidine catalyst

MWD	Mn$*10^{-5}$	Mw$*10^{-5}$	ED/Ti
5.1	1.1	5.61	0
5.4	1.1	5.94	0.25
6.16	0.8	5.05	0.5
6.48	.95	6.17	0.75
5.52	1.19	6.56	1
5.83	1.17	6.8	2.5
6.39	0.9	5.75	5
5.87	1.1	6.48	7.5
5.71	1.32	7.56	10
6.47	1.17	7.95	15
6.06	1.65	10	20

Molecular weight and its distribution increase with the amount of external electron donor, the amount of which depends on the type of catalyst.

Ziegler-Nata catalysts classification
Ziegler-Nata catalysts can be divided into two types:
A- Based on the type of their combination, they are divided into four groups:
1. Heterogeneous Ziegler-Nata catalysts:
   A- without base and B- with base;
2. Homogeneous Ziegler-Nata Catalysts;
3. Modified catalysts; and,
4. Alkyl-metal mediated catalysts.

Ziegler-Nata based on magnesium alkoxides
These catalysts are generally made by Boehm and are about 20 times more active than the classic Ziegler-Nata catalysts. These catalysts are composed of $TiCl_4$ and $Mg(OEt)_2$ and alkyl aluminum compounds which are amorphous and have a surface area of about $60 m^2/gcat$ and a diameter of less than 0.0005mm in which the main structure of alkoxides is usually destroyed during the reaction, ending in producing particles with high surface [39].

Ziegler-Nata catalysts based on magnesium alkyl
These catalysts have been investigated. The most important magnesium alkyls as bases are $Bu_2 Mg$, $Et_2 Mg$, BuMgEt and grignard compounds such as BuMgCl.

Ziegler-Nata catalysts with magnesium chloride base
The most important magnesium used is $MgCl_2$, and $MgBr_2$ can also be mentioned, which will be discussed further. The above catalyst can be produced by mechanical method (milling) or chemical method or a combination of the two. The most important factors in the preparation of catalysts by chemical methods are the following: a) Purity of reactants, b) ratio of reactants and mixing method, c) reaction time and temperature, and d) stirrer speed.

The temperature and time of the base reaction with $TiCl_4$ must be carefully controlled to prevent the production of by-products such as benzoyl or phthalic anhydride, etc. The cocatalyst nature and the crystal structure of $TiCl_3$ are two important factors influencing the efficiency of the catalyst. Along with the above catalysts, cocatalysts such as aluminum alkyls or aluminum halide alkyls were used. The resulting isotacticity of polypropylene is shown below [40].

Conclusion

Among the first generation catalysts, we can mention $TiCl_3 / Et_2 AlCl$, which were used in the first industrial processes of polypropylene production. These catalysts are heterogeneous without base. These catalysts had low spatial selection and low activity (1 KgPP / gTi, II = 90%). There are several methods for synthesizing different $TiCl_3$ structures. The most important method for the industrial production of this catalyst is the reduction of $TiCl_4$ with Al metal or its alkyls. Table 8 shows a number of methods for preparing various types of $TiCl_3$ structures. The most important difference between the second generation of Ziegler-Nata catalysts and their first generation can be mentioned in the use of a third compound such as ether, ester, Ceylon. Other features of the second-generation catalyst can be summarized as:

- Catalyst composition: $TiCl_3 + AlEt_2 Cl$ + thid com (ether);
- Catalyst level: 150-200 m^2 / gCat (AA-$TiCl_3$);
- Activity: 1900 Gpp / $gTiCl_3$ (Approximately five times the activity of the first generation catalyst); and,
- Polymer istactivity: above 95%.

The most important feature of this generation was the use of the $MgCl_2$ base (late 1960s). The resultant catalyst could polymerize both ethylene and propylene under mild conditions. But base catalysts previously developed by Benex and Hogane (silica-based CrO_3), polymerized only

ethylene under mild conditions and were not suitable for propylene. $MgCl_2$ -based catalysts initially had low activity and space selection. However, with the use of external Lewis base electron donors, this defect was eliminated. $MgBr_2$ base was also used, but catalysts prepared on this basis had less activity and space selection.

Acknowledgements

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