STUDY OF ETHYLENE POLYMERIZATION USING SUPPORTED METALLOCENE CATALYST SYSTEMS

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By

SENSARMA, S.

Polymer Chemistry Division
National Chemical Laboratory
Pune

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CONTENTS

CHAPTER-1

1. SUPPORTED METALLOCENE CATALYSTS SYSTEM FOR OLEFIN POLYMERIZATION : A REVIEW

CHAPTER - 2

2 SCOPE AND OBJECTIVE OF RESEARCH

CHAPTER-3

3 EXPERIMENTAL SECTION

CHAPTER-4

4 SYNTHESIS AND CHARACTERIZATION OF MAGNESIUM CHLORIDE SUPPORTED BIS(CYCLOPENTADIENYL) TITANIUM (IV) DICHLORIDE CATALYST AND POLYMERIZATION OF ETHYLENE USING THIS CATALYST IN CONJUNCTION WITH MAO

CHAPTER-5

5 SYNTHESIS AND CHARACTERIZATION OF MAGNESIUM CHLORIDE SUPPORTED BIS(CYCLOPENTADIENYL) ZIRCONIUM(IV) DICHLORIDE CATALYST AND POLYMERIZATION OF ETHYLENE USING THIS CATALYST SYSTEM

CHAPTER-6

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6 SYNTHESIS AND CHARACTERIZATION OF SILICA-MAGNESIUM CHLORIDE SUPPORTED BIS(CYCLOPENTADIENYL) TITANIUM (IV) DICHLORIDE CATALYST AND POLYMERIZATION OF ETHYLENE USING THIS CATALYSTS

CHAPTER-7

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7 SYNTHESIS AND CHARACTERIZATION OF SILICA-MAGNESIUM CHLORIDE SUPPORTED BIS(CYCLOPENTADIENYL) ZIRCONIUM(IV) DICHLORIDE CATALYST AND POLYMERIZATION OF ETHYLENE USING THIS CATALYST

CHAPTER-8

GLOSSARY

PE	Poly(ethylene)
PP	Poly(propylene)
MAO	Methylaluminoxane
TEAL	Triethylaluminum
TIBAL	Triisobutylaluminum
TMA	Trimethylaluminum
DEAC	Diethyaluminum chloride
EDTA	Ethylene diamine tetra acetate solution salt
bd	Bulk density
MI	Melt index
S.A.	Surface area
Cp	Cyclopentadienyl
Ind	Indenyl
Flu	Flurenyl
Et	Ethylene
k_p	Rate constant for propagation
k_{tr}	Rate constant for termination
[C*]	Active site concentration
M_n	Number average molecular weight
M_w	Weight average molecular weight
MWD	Molecular weight distribution
T_m	Melting point
$[\eta]$	Intrinsic viscosity

ABSTRACT

The thesis describes investigation of the role of magnesium chloride ($MgCl_2$) and silica (SiO_2) as a support for metallocenes and their homo- and copolymerization behavior towards ethylene as well as ethylene-hexene-1 in conjunction with methylaluminoxane (MAO). Several kinds of supported catalysts were synthesized utilizing the principles that both the metallocene as well as $MgCl_2$.tetrahydrofuran complexes are soluble in tetrahydrofuran (THF). These are $MgCl_2$-Cp_2TiCl_2 (Mg-Ti), $MgCl_2$-Cp_2ZrCl_2 (Mg-Zr), SiO_2-$MgCl_2$-Cp_2TiCl_2 (Si-Mg-Ti), SiO_2-$MgCl_2$-Cp_2ZrCl_2 (Si-Mg-Zr). Titanium, presumably on account of its lower ionic radius could be incorporated more efficiently than zirconium. The supported catalysts were used for the polymerization of ethylene using MAO as cocatalysts. All the catalysts showed an initial increase in catalyst activity followed by a steady decay. The Mg-Ti catalyst was active for ethylene polymerization even at 70°C. This is in contrast to unsupported Cp_2TiCl_2 catalysts which rapidly undergoes deactivation beyond 50°C. Mg-Zr was found to be active even at a temperature of 100°C for a period of more than one hour at a pressure of 5 bar. The molecular weight of the polyethylene obtained from both the Mg-Ti and Mg-Zr catalysts are found to be higher than unsupported catalysts. The molecular weight distributions were found to be in the range of 2.0-2.6.

Si-Mg-Ti and Si-Mg-Zr polymerize ethylene with higher activity as compared to silica supported titanium or zirconium based metallocene catalysts. The polymer molecular weight obtained from catalysts Si-Mg-Ti and Si-Mg-Zr are higher than silica supported catalysts. The molecular weight distribution was narrower than that generally observed for Si-Ti and Si-Zr catalysts. Both the Mg-Zr and Si-Mg-Zr catalysts were active for copolymerization of ethylene with hexene-1. The beneficial role of $MgCl_2$ in supported metallocene catalysts are discussed in terms of an active center model, wherein the "cation-like" Cp_2M^+ (M = Ti or Zr) derived additional stabilization from a weak lewis base like $MgCl_2$.

LIST OF TABLES

LIST OF FIGURES

LIST OF SCHEMES

1.1 INTRODUCTION

Since Ziegler's discovery of a catalyst for the polymerization of ethylene[1] followed by Natta's discovery of the stereoselective polymerization of propene[2], the polymers of ethylene and higher α-olefins has developed into a giant industry. Most of the commercial processes are based on titanium catalysts, predominantly supported on magnesium chloride, wherein, the chain growth occurs on dislocation and edges of $TiCl_3$ crystals[3]. Consequently, there are many different types of active sites, resulting in multiplicity of kinetic chains and hence a broad molecular weight distribution[4]. Nevertheless, the heterogeneous titanium based Ziegler catalysts are very versatile and, hence the workhorse polyolefin catalysts in industry today. They polymerize propene with a high degree of stereoselectivity and catalyze copolymerization of ethylene with higher α-olefins. However, with increasing maturity of markets there is continuous need for new products in the market place with properties superior to those produced by the heterogeneous catalysts. The advent of soluble metallocenes as catalysts for olefin polymerization, within the last ten years, has led to a whole new field of polyolefin catalysts capable of producing polyolefins, homo- and copolymers, with unique combination of properties.Metallocene catalyst technology is seen by many in the polymer industry as having a significant impact on the manufacture of polyolefins, similar to the excitement created at the time of the first introduction of the Ziegler-Natta catalyst almost forty years ago. It is estimated that investment in research into this technology has already exceeded US dollar 4.6 billion within the last decade of its discovery, a testament to the vigor of research, and the expectations that companies have on the rewards on this investment. Stanford Research International, Palo Alto, California, predicts that over 50 % of global PE and PP production will be based on metallocenes by the year 2005[5].

1.2 METALLOCENE CATALYSTS : POLYMERS BY DESIGN

The discovery of highly active and stereospecific metallocene-MAO catalysts have stimulated renewed commercial and scientific interest in homogeneous catalysts[6-8]. The uniform or single site catalysts, are based on a combination of group IV bent metallocene (a Ti, Zr, Hf complex with two cyclopentadienyl ligands and two halides or alkyl ligands) and a cocatalyst, and offer several advantages over traditional multi site Zeigler-Natta type catalyst (ligand tuning) allows a wide range of polymers to be formed when a prochiral olefin is polymerized, namely, propene : isotactic, syndiotactic, atactic, hemiisotactic, and stereoblock. The stereoselectivity has a relationship with the symmetry property of the metallocenes. The most interesting new catalysts together with the most important polymers obtained are shown in **Fig 1.1**. New products that have attracted the greatest commercial interest are random ethylene-α-olefins for LLDPE[9,10], as well as syndiotactic polypropylene[11-13], and syndiotactic polystyrene[11,12].

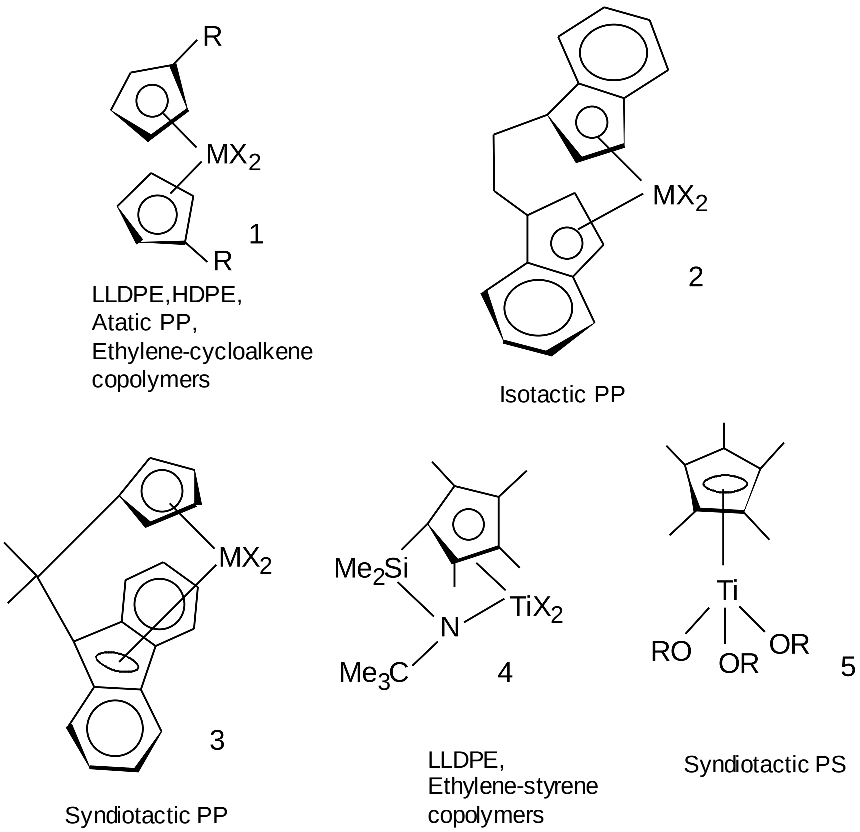


Fig 1.1 : New uniform site procatalysts for olefin polymerization (M = Zr, Hf, Ti; X = Cl or Me)

Over the past year, many companies such as Exxon Chemical, Dow Chemical Co., Hoechst AG., Mobil Chemical, BP Chemicals Ltd. and Mitsui Petrochemicals have retrofitted gas-phase, slurry, and high pressure reactors to produce linear low density polyethylene and polypropylene using metallocene based catalysts. **Table 1.1** shows commercial metallocene ventures and their current status.

TABLE 1.1 : METALLOCENE VENTURES TURN RIVALS INTO PARTNERS*

Company	Polymer	Status
BASF	i PP, PE	Has developed a proprietary catalyst, and completed plant-scale trials
Boreails A/S	PE	Its slurry-loop process has been combined with metallocene catalysts in a demonstration 130, 000 tpa
BP Chemicals	PE	A gas phase fluid bed 160, 000 tpa plant is being retrofitted in Grangemouth, U.K.
Dow-Dupont	EPDM	Will use Dow's Insite catalyst to produce and market elastomers and plastomers, such as EPDM. A 90, 900 tpa plant, now being converted at Plaquemine, la., is onstream.
Dow	PE	Has developed a slurry PE process, and has 250, 000 lb/yr of capacity, is converting a 56, 820 tpa plant in Tarragona, Spain. Has conducted pilot trials for cyclic olefins.
DSM-Exxon	PE-1-octene copolymers	A DSM-Exxon joint venture is retrofitting a 115, 000tpa PE plant.
Exxon	PE	Has converted a PE line to produce 100, 000tpa at Muont Belvieu, La., with a capacity for an additional 354, 500 tpa.
Fina Oil & Chemical	s PP	A joint development program with Mitsui Toatsu; has test produced pilot plant quantities of sPP
Hoechst AG	iPP	The firm has signed a joint venture agreement with Exxon. Plant scale(150, 000 tpa) Pilot plant trials have already been conducted.
	Cyclic olefin copolymers (COC)	A joint venture to develop COC has been formed with Mitsui. The company has a 3, 000 tpa plant in Japan for producing COC.
	Waxes	The company has produced test amounts of PE waxes.
Idemitsu Petrochemical	s PS	The company has a plant capacity of 10 million tpa, the result of joint program with Dow.
Mitsu Toatsu	i PP	The company is building a 75, 000 tpa plant
Mitsui Petrochemical	LLDPE	PE technology, developed jointly with Exxon
Mitsubishi	LLDPE	The company has a 100, 000 tpa plant.
Mobil	LLDPE	The company has run demonstration-scale tests

Company	Polymer	Status
Nippon Petrochemical	LLDPE	The company has a plant for producing 50, 000 tpa
UCC	LLDPE	The company plans to convert a 50, 000 tpa plant to LLDPE., using its gas-phase process and propriety metallocene catalysts; partnership with Exxon in catalyst development and process licensing..
Ube Industries	PE	The company is operating a 20 million tpa gas phase LLDPE plant based on Exxon-Mitsui technology.

PE : Polyethylene; PP : Polypropylene; iPP : Isotactic polypropylene; sPP : Syndiotactic polypropylene; sPS : Syndiotactic polystyrene; EPDM : Ethylene-propylene-diene monomer rubber; LLDPE : Linear low density polyethylene .tpa : Ton per annum

*data taken from Chemical Engineering, February 1996, p 35

1.3 RATIONALE FOR SUPPORTING HOMOGENEOUS METALLOCENE CATALYSTS

The principle disadvantages of the soluble homogeneous metallocene-methylaluminoxane catalyst system are the need for a large molar excess of MAO, (Al/Metal mol ratio > 10^5) for obtaining acceptable polymerization activities and poor control on polymer powder morphologies. Furthermore, when used in gas or slurry phase processes there is a tendency for reactor fouling by forming deposits on the surface of the walls of the reactor and stirrer. These deposits result in the agglomeration of the polymer particles when the either metallocene or aluminoxane or both exist in the suspension medium. Such deposits in the reactor system must be removed regularly. Otherwise, they prevent adequate heat removal from the reaction, adversely affecting the product quality. Practical application of metallocene catalysts requires their heterogenization on suitable supports. Instead of the polymer dust produced by homogeneous metallocene catalysts, the solid catalyst particles generate coherent polymer grains[14,15]. As with classical heterogeneous catalysts these grains appear to be enlarged replicas of the catalyst particle[14,16]. Catalyst heterogenization allows less MAO to be used, and offer improved polymer morphological control, whilst preserving the advantage of a uniform site catalysts. One of the challenges in metallocene research is to find stable methods for heterogenizing soluble metallocenes on a support, thus enabling its use in existing production facilities, for instance, in slurry or gas-phase

1.4 SUPPORTED METALLOCENE CATALYSTS FOR OLEFIN POLYMERIZATION

1.4.1 Introduction

Slotfeldt-Ellingsen and coworkers heterogenized Cp_2TiCl_2 on silica gel and used for the polymerization of ethylene using $AlEt_nCl_{3-n}$ as cocatalyst[18]. Subsequently, a large number of studies have been devoted to the transformation of solublemetallocene complexes into heterogeneous catalysts by supporting them onto inorganic and organic carriers. It is generally believed that the support plays an inert role during polymerization. The nature of the support and the technique used for supporting themetallocene influence the catalytic behavior. Inorganic oxides, finely divided polymers or other high surface area materials have been used as supports. Surface modification of the support is also reported to improve catalyst performances. This may include reactions with organometallic compounds such as Mg or Al-alkyls or other compounds like $SiCl_4$, $SiMe_2Cl_2$ etc as well as thermal treatments. The main inorganic supports used are silica, alumina, and magnesium compounds. Nevertheless, less common materials such as cyclodextrin[19], polystyrene[20,21], polysiloxanes[22] magnesium ethoxide[23], alumina, magnesium fluoride and calcium fluoride[24], zeolites[25-30] and polymer supported metallocene catalysts[31] have also been described. The field has been recently reviewed[32].

1.4.2 Magnesium chloride supported metallocene catalysts

1.4.2.1 Unique role of magnesium (II) cation as a support for metallocenes

It is observed that Mg^{+2} cation plays a unique role in high activity $MgCl_2$ supported Ziegler-Natta catalysts during olefin polymerization. This was attributed to the similarities in size, shape, co-ordination number, electronegativity and electronic structure of magnesium and titanium. These similarities probably permitted an easy substitution of magnesium ions in the titanium halide lattice[33]. Due to similarities in ionic radii, Ti^{+4} can easily sit in the interstetial position of the $MgCl_2$ crystallites and thus has a better surface interaction. However, zirconium on account of its larger atomic radii, cannot be easily accommodated. Thus, one would expect a poor interaction between Zr^{+4} and $MgCl_2$ crystal lattice. This makes $MgCl_2$ a superior support for titanium based metallocenes as compared to zirconium based metallocenes.

1.4.2.2 Synthesis of magnesium chloride supported metallocene catalysts

Based on available literature, three broad approaches to the preparation of $MgCl_2$ supported metallocene catalysts are evident. These are:

i) decomposition of a Grignard reagent in an electron donor solvent followed by supporting of metallocene

ii) decomposition of soluble bivalent salts of magnesium in presence of an electron donor followed by supporting of metallocene

iii) supporting of metallocene by physical and intimate mixing of the metallocene component with a slurry of anhydrous $MgCl_2$ in a diluent.

i) Decomposition of Grignard reagent in an electron donor solvent followed by immobilization of metallocene

Organomagnesium compounds are known to reduce titanium (IV) to titanium (III). This leads to the cocrystallization of a Mg-Ti complexes with disordered structure, as evidenced by X-ray diffractions. This catalyst shows a high polymerization activity in conjunction with aluminum alkyls.

$$TiCl_4 + RMgCl \rightarrow TiCl_3.MgCl_2 + \text{organic fragments}$$

Haward *et al.*[34] and Munoz-Escalona *et al.*[35] have extensively studied the effect of Grignard reagents on the reduction of $TiCl_4$ in polar and non-polar solvents.

A Japanese patent describes the preparation of $MgCl_2$ support by the reaction of BuMgCl and $SiCl_4$ in an electron donor solvent followed by supporting of metallocene[36]. Recently, Satyanarayana and Sivaram[37] reported a novel method for the preparation of $MgCl_2$ supported Cp_2TiCl_2 catalyst prepared via Grignard decomposition of an intermediate organomagnesium compound. The support was prepared by exploiting the solubility of both $MgCl_2$ and Cp_2TiCl_2 in THF.

ii) Decomposition of a soluble bivalent salts of magnesium in presence of an electron donor followed by immobilization of metallocene

Soluble bivalent magnesium compounds such as Bu_2Mg, $(RO)_2Mg$, Mg-stearate upon treatment with titanium compounds in presence or absence of electron donor in non-polar solvents yield high activity Ziegler-Natta catalysts[38-40]. It is observed that during the catalyst preparation steps, the original structure of the bivalent magnesium compounds is completely destroyed and new crystalline species are formed with large surface area. Modification of properties of catalysts is also possible by introduction of additional elements or donors in the catalytic complexes, or by carrying out the reaction in presence of an acid halide. Magnesium chloride can also be prepared by Grignard decomposition of a bivalent organic salt of magnesium with an alkyl halide compounds. Bailly *et al.* reported the reaction of dibutyl magnesium and t-BuCl in diisoamyl ether as electron donor[41]. The support thus prepared has a surface area of 45 m^2/g onto which Cp_2ZrCl_2 was supported. The supported catalyst was employed for the polymerization of ethylene in a gas-phase process. A Japanese patent also describes the treatment of magnesium ethoxide with $EtAlCl_2$ followed by direct impregnation of metallocene[42].

iii) Slurry method of preparing magnesium chloride supported metallocene

This method involves physical mixing of the metallocene and the support in a diluent in which the metallocene is soluble. In this method the dry support contacts first with the metallocene in a diluent such as toluene or first contacting the support with an organoborane compound followed by immobilization of metallocene. Soga and Kaminaka synthesized various supported stereorigid homogeneous metallocene catalysts on $MgCl_2$ and used them for the polymerization of propene, ethylene and ethylene with higher alpha olefins[24]. More recently, Soga *et al.* have reported synthesis of $MgCl_2$ supported $XTiCl_3$ (X = cyclopentadienyl, pentamethylcyclopentadienyl, indenyl, heptamethylindenyl)[43]. The supported catalysts were prepared by dissolving the metallocene in toluene and depositing it on $MgCl_2$. The supported catalysts thus prepared were used for the polymerization of ethylene.

A summary of various methods of preparation of $MgCl_2$ supported metallocene catalysts. is provided in **Table 1.2**.

1.4.2.3 : Comparison of performance of $MgCl_2$ supported metallocenes vs unsupported catalysts

Metallocene catalysts in a soluble form are unsuitable for the production of polyolefins in practical processes. In order to use them in existing technical processes they require heterogenization on suitable support. The molecular weight of the polymers obtained from metallocenes is low and it is affected by polymerization temperature, metallocene concentrations, and ethylene pressure. Most polyethylene grades used commercially have M_w of 20,000-300,000, and, to be broadly applicable to large volume polyethylene production, metallocene must yield polymers with similar molecular weights[44]. With zirconocenes at low concentration in toluene and 8 bar ethylene pressure the following molecular weights are obtained[45] : 800,000 at 20°C, 150,000 at 70°C, 10,000 at 100°C. This M_w vs. temperature relationship suits operation in commercial slurry and gas phase polymerization process which operates at 70-110°C. It is however, not, suitable for use in solution or high pressure processes which operate at temperatures above 150°C. Again to obtain reasonable activity from homogeneous metallocene catalysts a large Al/Metal mol ratio is required. Catalyst heterogenization allows lowering in Al/Metal mol ratio with desired polymer characteristics and good particle morphologies.

a) Ethylene polymerization using $MgCl_2$ supported metallocene catalysts

Anhydrous magnesium chloride has been widely used as an efficient support for ethylene and propylene polymerization using Ziegler-Natta catalysts and forms the basis of commercial polyolefin process[46-48]. So far less attention has been paid to the use of anhydrous magnesium chloride as a support for metallocenes. Bailly *et al.* prepared a $MgCl_2$ supported Cp_2ZrCl_2 and used it for the gas-phase polymerization of ethylene[41]. Polyethylene produced using $MgCl_2$-Cp_2ZrCl_2 catalyst had good particle morphology and narrow molecular weight distribution (2.3-2.6). Satyanarayana and Sivaram prepared a $MgCl_2$ supported Cp_2TiCl_2 catalyst exhibiting measurable activity for ethylene polymerization[37]. Unlike, homogeneous Cp_2TiCl_2, the supported Cp_2TiCl_2 can be activated with TIBAL. Although the catalyst activity was modest, the yield was quantitative. The supported catalyst exhibited a steady state kinetics with no loss of activity upto 1 h, at a low Al/Ti ratios. A number of examples in the patent literature describe MgCl supported metallocene catalysts for the polymerization of ethylene (**Table** metallocene are significantly reduced (generally in the range of 50 to 1000). However, the catalyst activity is found to be usually lower than homogeneous catalysts under identical polymerization conditions. Furthermore, polymerization using $MgCl_2$ supported metallocene catalysts can be carried out at a relatively higher temperature with reduced rate of catalyst deactivation. When a metallocene is supported on $MgCl_2$, polymers with narrow molecular weight distribution are obtained. This indicates that the catalytically active sites are uniform and the metal is in a similar electronic and steric environment on the support. The lowering of catalyst activity in case of $MgCl_2$ supported catalysts can be attributed to reduced accessability of the monomer to the catalytically active site, especially, when the site is buried in the crystalline lattice of $MgCl_2$. In general, the molecular weight of the polymers obtained from $MgCl_2$ supported metallocenes are found to be higher than those obtained by using homogeneous catalysts. This is presumably due to the reduced rate of chain migration, when the catalytically active site is anchored to a support. Thus the high ratio of Al/Zr required for homogeneous catalysts from 10000-100, 000 can be reduced to 100-1000[49].

b) Copolymerization of ethylene and α-olefin using $MgCl_2$ supported metallocene catalysts

Soga *et al.* reported copolymerization of ethylene with propene and 1-hexene using $MgCl_2$ supported $Et[IndH_4]_2ZrCl_2$ catalyst in combination with trialkylaluminum[50]. It was observed that when copolymerization was carried out in presence of TIBAL the resulting copolymer displayed a strong peak around 125°C in addition to the peak attributed to the copolymer. It was suggested that $Al(iC_4H_9)_nCl_{3-n}$ (n = 1 or 2) is produced by the reaction of TIBAL and $MgCl_2$. Therefore, an active species formed by the reaction of $Et[IndH_4]_2ZrCl_2/MgCl_2$ and $Al(iC_4H_9)_nCl_{3-n}$ might be responsible for the homopolymerization of ethylene leading to peak at 125°C. The monomer reactivity ratios were $r_e = 10.5$ and $r_p = 0.06$. An increase in comonomer content caused a gradual decrease in molecular weight. The molecular weight and MWD of the E-P (mol % of propene = 5.2 to 32.2) copolymers were 4-58 x 10^3 and 3.5-5.8 respectively.

c) Propylene polymerization using $MgCl_2$ supported metallocene catalysts

Polypropylene synthesized using homogeneous chiral ansa-metallocenes gives low and broad T_m (110°C). The low T_m observed (40 to 50°C lower than isotactic PP produced by heterogeneous titanium catalysts), results both from a low degree of isotacticity (70 to 95 %) and imperfect regiospecificity. Most of the polypropylenes produced with homogeneous metallocenes show in addition to the normal 1-2 addition some misinsertions resulting in the formation of 1,3- or 2,1- linkages. Kaminaka and Soga[24,51,52] examined several kinds of heterogeneous zirconium based metallocene catalysts for propylene polymerization. $Et[IndH_4]_2ZrCl_2$, $iPr(Flu)(Cp)ZrCl_2$ and Cp_2ZrCl_2 were supported on $MgCl_2$ and used for the polymerization of propylene in conjunction with common trialkylaluminums. Isotactic polypropylene was obtained when $Et[IndH_4]_2ZrCl_2$ was supported on $MgCl_2$. The supported catalyst in combination with AlR_3 (R = Me or Et) showed one hundredth the activity of the homogeneous $Et[IndH_4]_2ZrCl_2$/MAO catalyst[51]. $MgCl_2$ supported catalyst gave narrow molecular weight distribution and melting points (130-140°C). The molecular weight and the degree of isotacticity of the polypropylene obtained using $MgCl_2$ supported catalyst was found to be as higher as compared to unsupported metallocene.

$i\text{-}Pr(Flu)(Cp)ZrCl_2$ and Cp_2ZrCl_2 supported $MgCl_2$ activated with AlR_3 gave highly syndiotactic PP and atactic PP[52] respectively. The polymers produced with the syndiospecific heterogeneous catalysts showed higher (T_m = 134-138°C) and higher [rrr] pentad fraction (81-86%) compared with those produced with homogeneous systems (T_m = 123°C and [rrr] pentad fraction 77%). The properties of PP obtained from $MgCl_2$ supported and unsupported metallocene catalysts are shown in **Table 1.3**.

More recently, Soga *et al.* have synthesized several kinds of $MgCl_2$ supported half titanocene ($XTiCl_3$; X= Cp, Me_5Cp, Indenyl, Me_7Indenyl) catalysts and used them for the polymerization of propylene[43]. It was observed that when polymerization was conducted without any external donor the catalyst predominately gave atactic polypropylene. However, addition of a suitable monofunctional lewis base such as ethylbenzoate caused to change the stereospecificity of polymer from aspecific into highly isospecific. On the contrary, the use of bifunctional donor like di-n-butylphthalate killed the catalyst activity

Table 1.3 : Comparison of the polypropylene properties using $MgCl_2$ supported and unsupported catalysts[a]

Catalyst	Al/Zr (mol)	Activity (Kg PP/g Zr.h)	M_n x 10^{-3}	T_m (°C)	Tacticity (%)
Et[IndH$_4$]$_2$ZrCl$_2$/MAO[b]	3000	23	3.3	111	71(mmmm)
Et[IndH$_4$]$_2$ZrCl$_2$/MgCl$_2$/AlR$_3$[c]	850	0.22	1.6-8.5	131-139	91(mmmm)
iPr(Flu)(Cp)ZrCl$_2$/MAO[b]	3250	8	39.3	123	77(rrr)
iPr(Flu)(Cp)ZrCl$_2$/MgCl$_2$/TMA[c]	480	0.1	10.7	134	81(rrr)
Cp$_2$ZrCl$_2$/MAO[b]	1000	1.44	0.33	-	Atactic
Cp$_2$ZrCl$_2$/MgCl$_2$/TMA[c]	-	0.1	0.37	-	"

[a] Polymerization were carried out at 40°C, in toluene; [b] time = 1 h; [c] time = 18 h.

Among the polymerization features which distinguish $MgCl_2$ supported metallocene from their homogeneous counterpart are the following:

- Smaller Al/M ratio is required to obtain acceptable polymerization activity with supported catalyst systems. Aluminoxane to metal ratio can be usually reduced from several thousands to the range 50-400.

- Some supported metallocene catalyst systems can be activated by common alkylaluminums in the absence of any MAO. This obviates the use of expensive MAO.

- A more limited dependence of polymerization activity on MAO and Al/Metal ratio is observed. This is due to the lesser extent of the catalyst deactivation by bimolecular processes due to the anchoring of active sites on the surface support.

- Supported metallocene catalysts are generally less active when compared to the homogeneous catalysts.

- Supported catalysts can be used in gas-phase or slurry phase polymerization processes and can be operated at a relatively higher temperature and pressure. They produce high molecular weight polymers with narrow molecular weight distribution.

- Better control on polymer morphology by regulating the morphology of the catalyst particles is possible with $MgCl_2$ supported metallocene catalysts.

- Supported catalysts show a greater degree oftacticity control.

- A more homogeneous comonomer composition distribution is found while using $MgCl_2$ supported catalysts in copolymerization.

In spite of the many advantages, $MgCl_2$ supported metallocene catalysts have some drawbacks.

- $MgCl_2$ is brittle in nature and hence susceptible to attrition. To some extent thermal shocks can be avoided by using the techniques of polymerization.

- $MgCl_2$ support contributes to higher degree of ash in the polymer.

- A higher level of chlorine content in the polymer, which may require neutralization to prevent the adverse effects of chloride ions in down stream processingequipments such as extruders.

Table 1.2 : Olefin polymerization using $MgCl_2$ supporte

Metallocene	Support	Polymerization conditions
A : Ethylene		
$Et[4,5,6,7\text{-}IndH_4]ZrCl_2$	$MgCl_2$-2-ethylhexanol	Solvent = toluene, P= 5 bar, T = 60°C, time=2 h, Cocat. = TEAL
Cp_2ZrCl_2	$BuMgCl\text{-}SiCl_4$	Cocat. = MAO
Cp_2TiCl_2	$MgCl_2$,2-ethylhexanol	Solvent = Isobutane, T=50°C, Cocat.= TIBAL
Cp_2TiCl_2	$MgCl_2$	Solvent =hexane, P=6 Bar, T=80 °C, time=1 h, Cocat.= $Al(CH_2CHMe_2)$
Cp_2ZrCl_2-	$MgCl_2$.ether.n-BuOH	Solvent =hexane, T=70 °C, cocat = MAO, ethylene(flow rate)= 60 g/h, H_2 = 50 mL, time=7 min

Cp_2ZrCl_2 + MAO	$Mg(OR)_2$	Solvent = heptane, P = 8 bar, T =8 0°C, time=4 h
Cp_2TiCl_2	$MgCl_2$	Solvent = xylene, Cocat. =TIBAL, Al/Ti = 100, P 1 bar, T = 40°C, Time = 1 h
B : Ethylene/propene		
$Et(IndH4)_2ZrCl_2$	$MgCl_2$	Solvent = toluene, 40°C, 1 atm, 1 h
D : EthyleneButene-1		
Cp_2TiCl_2	$MgCl_2$ + $At(OEt)_3$	Solvent = toluene, Cocat = MAO, time = 2 h, T = 60°C, P=9 bar
C : Ethylene/4-methylpentene		
$(Me\text{-}Cp)_2ZrCl_2$ + $TiCl_4$	$MgCl_2$- -EtOH	Solvent = cyclohexane, Cocat.= MAO (prepd. fro TMA+$Al_2(SO_4)_3.14H_2O$, T = 70-80°C
Cp_2ZrCl_2 + $TiCl_4$	$MgCl_2$.EtOH-Et_2AlH	T = 70-80°C, P= 8 bar
Ethylene/Hexene-1		
$Et(IndH4)_2ZrCl_2$	$MgCl_2$	Solvent = toluene, 40°C, 1 bar, 1 h

Propene		
(i-Pr)(Cp-1-fluorenyl)$ZrCl_2$	$MgCl_2$	Solvent = toluene, Cocat. = MAO, T = 20°C
(i-Pr)(Cp-1-fluorenyl)$ZrCl_2$	$MgCl_2.6H_2O$	Cocat. = TEAL
isopropylidene(Cp)(9-fluorenyl)$ZrCl_2$	$MgCl_2$	T = 40°C, time = 1 h, cocat. = TEAL, Catalyst = 2 mg
“	"	T = 40°C, time = 1 h, cocat. = TEAL (0.3 g), Catalyst = 0.5 g
i-Pr(Cp)(1-fluorenyl)$Zr(OMe)_2$	$MgCl_2$	Cat. = 300 mg, TEAL = 0.51 mL
i-Pr(Cp-1-fluorenyl)$ZrMe_2$	$MgCl_2$	Solvent =hexane, T=80 °C, time=2 h
$(MeCp)_2TiCl_2$	$MgCl_2$.ethylbenzoate	Cocat. =MAO
isopropylidene(Cp-1-fluorenyl)$ZrCl_2$	$MgCl_2.6H_2O$	T = 60°C, Cocat. =MAO, Time = 2 h
Cp_2ZrCl_2	$MgCl_2$	Solvent = toluene, Cocat. = TMA, T = 40°C, time 18 h

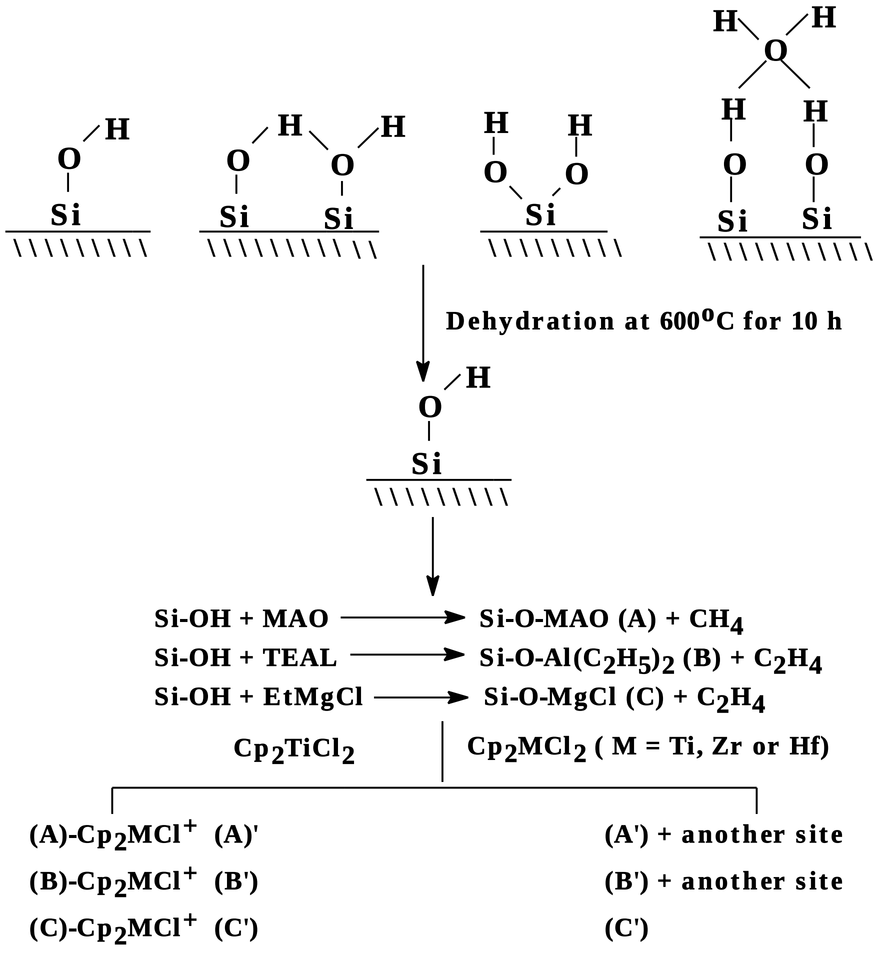
Et[IndH$_4$]ZrCl$_2$	MgCl$_2$	Solvent = toluene, T=40°C, time = 18 h, Cocat.= TMA, Al/Zr = 850 mol
iPr(Flu)(Cp)ZrCl$_2$	MgCl$_2$	Solvent = toluene, T = 40°C, time = 18 h, Cocat . TMA, Al/Zr = 480 mol
CpTiCl$_3$	MgCl$_2$	Solvent = toluene, 40°C, 2 h,Cocat. = MAO
“	“	Solvent = toluene, 40°C, 2 h,Cocat. = TIBAL
XTiCl$_3$- (X = Cp)	MgCl$_2$	Heptane, 40°C, 1 h, cocat. = TIBAL
“		Heptane, 40°C, 1 h, cocat. = TEAL
X = Me$_5$Cp		Heptane, 40°C, 1 h, cocat. = TIBAL
“		Heptane, 40°C, 1 h, cocat. = TEAL
X = Indenyl		Heptane, 40°C, 1 h, cocat. = TIBAL
“		Heptane, 40°C, 1 h, cocat. = TEAL

1.4.3 Silica supported metallocene catalyst systems

1.4.3.1 Silica as a support to metallocenes

Silica is the most widely used support for metallocene based catalysts. Silica is an inert support and has negligible interaction with the active metal center. Due to its large surface area (300-600 m^2/g) metallocene can easily be dispersed on silica.

Silica contains many different types of surface functionalities which actually govern the performance of the catalyst. These are free hydroxyl, hydrogen bonded hydroxyls, paired hydroxyls and adsorbed water. Upon calcining silica under nitrogen atmosphere, only free hydroxyl group remains and when calcined silica is treated with organoaluminum compounds the free hydroxyl groups also disappears. A possible model of active sites for SiO_2 supported metallocene catalysts is shown in **Fig. 1.2**.



1.4.3.2 Preparation of silica supported metallocene catalysts

Many methods of supporting metallocenes on silica have been reported in the literature. These are:

(i) Direct impregnation of metallocene on silica. This can be achieved either

a) under mild conditions or

b) at high temperature and prolonged time (refined route)

In this method the silica support is brought into direct contact with a solution of metallocene. The solid part is then recovered by filtration and washed with a hydrocarbon diluent. Mixing temperature and the contact time may influence both the catalytic performance and final properties of the polymers.

Soga and Kaminaka[24b,53] used method (a) to support stereorigid metallocene on silica. Kaminsky and Renner[54] reported a silica supported ethylenebis(indenyl)zirconium dichloride ansa-metallocene catalysts. This method involves direct impregnation of metallocene with silica at a temperature of 70°C, and for a period of 20 h (method i, b). The catalyst prepared in this way needs prolonged extraction to remove any homogeneous catalyst present on the surface. Catalysts prepared according to (i) are listed in **Table 1.4**. In some cases silica was modified by the addition of $Cl_2Si(CH_3)_2$ before impregnation by the metallocene derivative. The structure of the supported catalyst prepared according to (i) is shown in **Scheme 1.5**.

(ii) Treatment of silica with organoaluminum compounds followed by supporting metallocenes.

In this method silica is first pretreated with a small amount of organoaluminum compound such as MAO, at room temperature. The pretreated support is then filtered and washed with toluene followed by treatment with a solution of metallocene. The supported catalysts obtained in this way can then be reactivated by MAO[55-57] or by common alkylaluminums[24a,58-60].

Collins *et al.*[61] used partially hydroxylated silica pretreated with TMA and the catalyst slightly modified procedure to support Cp_2MCl_2 (M=Ti, Zr or Hf) on silica[62]. Silica was pretreated with $Al(C_2H_5)_3$ and $(C_2H_5)MgCl$ instead of MAO followed by reaction with metallocene. Ciardelli *et al.* also prepared supported metallocene (Ti or Zr) using SiO_2 modified with MeLi and treated with $AlMe_3$ and Me_3SiCl as carriers[27]. Chang has reported the direct synthesis of supported aluminoxanes. TMA was treated with water adsorbed on the support such as silica gel followed by contacting the aluminoxane coated support with a metallocene solution to form the final catalytic system[63-65]. Instead of contacting the support with aluminoxane, the latter was generated in situ and the supported catalyst thus prepared was used for the polymerization of ethylene in slurry or gas-phase reactor.

Lee *et al.*[66] applied the method developed by Chang to synthesize SiO_2 supported Cp_2ZrCl_2 catalysts. Hydrated silica was prepared by two methods. In the first case silica was fully hydrated in deionized water, filtered and fluidized in a column using nitrogen gas flow, yielding silica with 45 wt. % of water. In the second method, silica was fluidized with wet nitrogen. Silica with 16 wt. % of water was obtained. The silica thus produced, contacted with a solution of TMA in toluene. The supported catalyst was finally synthesized by addition of metallocene to the above support in toluene suspension.Sacchi *et al.*[67] reported preparation of highly isospecific catalyst by supporting zirconocene on MAO modified silica. Hlatky and Upton recently prepared a supported ionic metallocene catalyst[68]. Silica was treated with borane containing compounds followed by supporting of hafnium based metallocene. The catalyst thus prepared was used for the polymerization of ethylene (**Table 1.4**).

Roos *et al.* have described preparation of a silica gel supported $Me_2Si[Ind]_2ZrCl_2$ catalyst. Silica gel was pretreated with MAO followed by supporting of metallocene[69]. The supported catalyst thus prepared contained 1 wt. % of zirconium and Al/Zr mol ratio of 386 and was used for the gas phase polymerization of ethylene without further addition of any cocatalysts. A structural model of the supported catalysts prepared according to method (ii) is shown in **Scheme 1.6**.

(iii) Chemical attachment of metallocene on silica.

In this method, the ligands are attached chemically to the support. The method generally

Step-1 : Modification of the silica surface by addition of compounds such as $SiCl_4$, $C_2H_2Br_4$, $SOCl_2$ or Me_2SiCl_2. Typically silica is refluxed for a period in the range of 20 to 48 hours. Depending on the ligand the resultant products have structures as shown in **Fig. 1.3**.

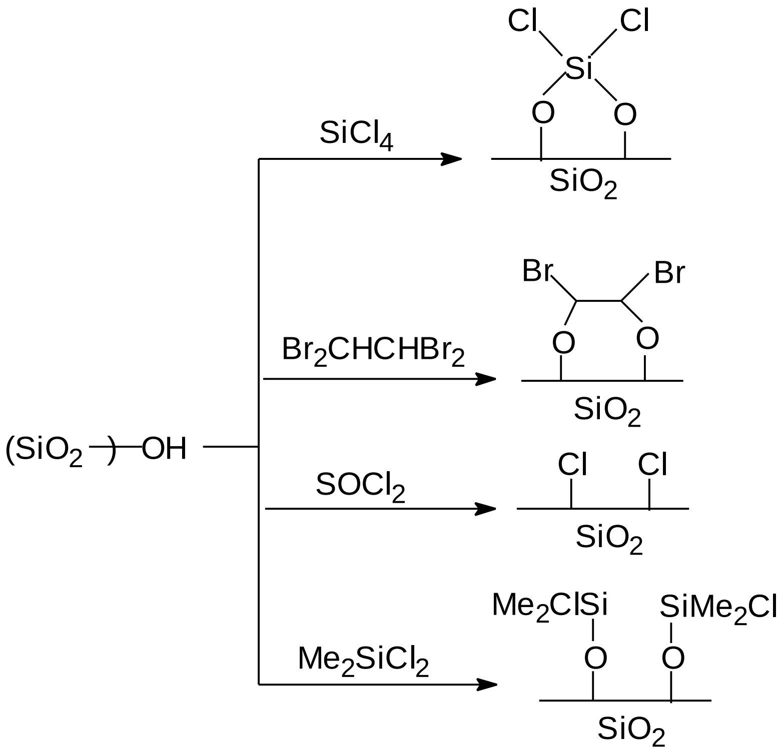


Fig. 1.3 : Modification of silica surface by addition of different compounds

Step-2 : Reaction of modified silica with the lithium salt of aryl derivatives to be supported (indenyllithium, cyclopentadienyllithium, fluorenyllithium, etc.). The reaction is generally carried out in tetrahydrofuran medium at a relatively low temperature.

Step-3 : Treatment of the resulted aryl grafted silica gel with a solution of butyllithium in hexane at room temperature to form a new aryllithiated derivative.

Step-4 : Reaction of the aryl lithiated derivative with neodymium[70] or zirconium or titanium[71-73] halides resulting in the supported metallocene catalysts.

Silica is filtered, washed with large quantities of tetrahydrofuran after each modification step. The silica supported stereorigid metallocene catalysts is finally dried to obtain the solid product. These supported systems can be used either with MAO or wit trialkylaluminums as cocatalyst for polymerization of ethylene, propylene and higher α-olefins.

A typical catalyst preparation, according to this procedure, as well as the structure of the species formed are shown in **Fig. 1.4**.

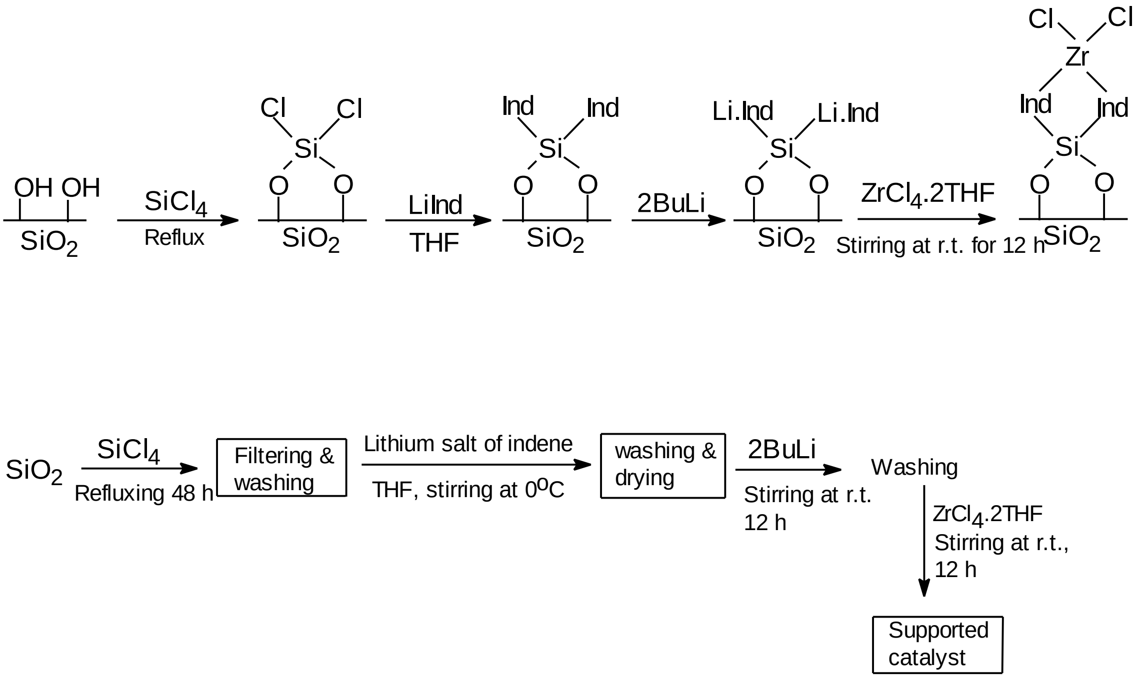


Fig 1.4 : Preparation of supported metallocene through ligands attachment on SiO $_2$ surface.

Table 1.4 : Preparation of different SiO_2 supported

Metallocene	Method	Support pretreatment	
$CpZrCl_3$	(i)	800°C, 3 h	
$CpTiCl_3$	“	200°C, 6 h	
$Et[IndH_4]_2ZrCl_2$	"	400°C, 6 h	
$iPr(Flu)(Cp)ZrCl_2$ or	“	400°C, 6 h	
Cp_2ZrCl_2	1 & 2	400°C, 6 h	Cl
$Et[Ind]_2ZrCl_2$ or	2	--	
$Et[IndH_4]_2ZrCl_2$	“		
$Et[Ind]_2ZrCl_2$	1	500°C, 3 h	
$Et[Ind]_2ZrCl_2$	“	500°C, 6 h	
$Et[Ind]_2ZrCl_2$ or	“	650°C, 5 h	
Cp_2ZrCl_2			
Cp_2ZrCl_2	2	“	

Et[$IndH_4$]$_2ZrCl_2$	“	400°C, 6 h	Pr
Et[Ind]$_2ZrCl_2$	“	350°C, 18 h, 200°C, 4 h	Pr
rac-MeSi[Ind]$_2ZrCl_2$	“	--	P
Cp_2MeCl_2	“	600°C, 10 h	P
Cp_2ZrCl_2	2	Hydrated in deionized water	Hy
$Me_2Si\{Ind\}_2ZrCl_2$	2	-	
Cp_2HfMe_2	2	800°C, 20 h	t

Table 1.5 : Patent literature on SiO_2 supported

Metallocene	Support	Method of preparation	Polymn. Condit
A : Ethylene			
Et[Ind]$_2$ZrCl$_2$	“	“	Firstly prepolymn. wer out then gas-phase pol 4 bar, T = 80°C, 30 min N,N-Me$_2$-anilinium(te pentafluorophenyl)
t-BuNSiMe$_2$RZrCl$_2$	SiO_2	SiO_2 pretreated MAO + metallocene	Heptane, cocat. =
Cp$_2$ZrCl$_2$ + [Ind]$_2$ZrCl$_2$	“	--	isobutane, cocat. =
(1,3-Me$_2$Cp)$_2$ZrCl$_2$	“	SiO_2 + Mtallocene + Mol. Seive 4 A°, r. t., 3 h, 60°C	Toluene, cocat. =
Me$_2$Si(Me$_4$Cp)(dodecylamido)TiMe$_2$	“	SiO_2 treated with TEAL	Cocat. = N,N-M anilinium(tetraks pentafluorophenyl)

(1,3-Me$_2$Cp)$_2$ZrCl$_2$	“	SiO$_2$ treated MAO + metallocene	Cocat. = TIBA
MeSi(2,4-Me$_2$Cp)$_2$ZrCl$_2$	“	SiO$_2$ + metallocene + [N, N-Me$_2$Ph][BC$_6$F$_5$]$_4$	T = 80°C, 30 m
(Bu-Cp)$_2$ZrCl$_2$	SiO$_2$ gel, contg. 12.5 wt % water	silica gel = Me$_3$Al + metallocene, T = 70°C, 30 min.	--
Cp$_2$TiCl$_2$	“	SiO$_2$ + BuEtMg + EtAlCl$_2$ + metallocene	Hexane, cocat. = T
(2-methoxyethyl Cp)$_2$ZrCl$_2$ or [(tetrahydro-3 furan methyl)Cp]$_2$ZrCl$_2$	“	SiO$_2$ + metallocene	Gas or slurry phase p
Zirconocene	Silica gel	silica gel + ClSiMeR^{1}R^2 + ZrCl$_4$ (R^1 = Cp-1-yl, R^2 = Flu-9-yl)	Cocat. = MA
Cp$_2$ZrCl$_2$	SiO$_2$	SiO$_2$ + metallocene at 280°C, 3h	Cocat. = MAO, T = 7

$(Ph_2CH_2Cp\text{-}Flu)ZrCl_2$	“	SiO_2 + MAO + metallocene	Cocat. = TIBAL, T = 8 bar, 1 h
$(MeCp)_2ZrCl_2$	$MgCl_2 + SiO_2$	$SiO_2 + MgCl_2$ (aq. soln.) + TMA + metallocene	T = 80°C, P = 8 ba
Cp_2ZrCl_2	“	$SiO_2 + MgCl_2$ + metallocene, reflux 50°C, 10 h + $Ph_3C^+B(C_6F_5)_4^-$ at 25°C, 20 h.	Solvent = butane, T = min, P = 10 ba
$(Me_5Cp)(2\text{-}MeCp)Cr$	SiO_2	SiO_2 + metallocene	Isobutane, T = 90°C, 1 bar
$(MeCp)_2ZrCl_2$	SiO_2	“	T = 65°C, P = 8 bar
Cp_2ZrCl_2	“	SiO_2 + metallocene	T = 20°C, 1 h
$t\text{-}BuNSiMe_2RZrCl_2$	“	SiO_2 + MAO + metallocene	Heptane, cocat. =
Cp_2ZrX_2	“	SiO_2 + MAO + TEAL metallocene	hexane, T = 90°C, 1 h,

Cp_2ZrCl_2	“	SiO_2 + TMA + H_2O reflux at 85°C, + metallocene	P = 3 bar, 5 h
“	Refractory oxide or $MgCl_2$	--	--
Cp_2ZrCl_2	“	“	Cocat. = TIBAL, T = 8 P = 8 bar
B : Ethylene/Butene-1			
$(iPr\text{-}Cp)_2ZrCl_2$	silica gel	Silica gel pretreated with MAO + Metallocene	65°C, P = 21 bar, cocat
$[\eta^5\text{-}n\text{-}Pr(Cp)]_2ZrCl_2$	Silica	SiO_2 + metallocene	Cocat. = MAC
Cp_2ZrCl_2	“	SiO_2 + MAO + metallocene	T = 85°C, 10 min, P =
C :Ethylene/hexene-1			
$(Ph_2CH_2Cp\text{-}Flu)ZrCl_2$	“	SiO_2 + TMA +CCl_4 + Bu_2Mg + metallocene	-

Cp_2ZrCl_2 + $TiCl_4$	“	SiO_2 + Bu_2Mg + $TiCl_4$ + metallocene	Cocat. = MAO, T = 8
$(n\text{-}BuCp)_2ZrCl_2$	SiO_2	SiO_2 calcined 600°C, + MAO + metallocene	Heptane, T = 70°C, P cocat. = TIBA
D : Ethylene/Hexadecene-1			
$CpTiCl_3$	SiO_2	SiO_2 + metallocene	Cocat. = MA
E : Propylene			
$Et[Ind]_2Zr(IV)$ bistrifluoromethane sulphonate	SiO_2	“	cocat. = TIBA
$iPr(Cp\text{-}1.Flu)ZrCl_2$	“	“	Hexane, cocat. = TIBA h
Isopropylidene(Cp)(2,7-di-t-Bu-9-Flu)$ZrCl_2$	SiO_2	Silica treated MAO + metallocene reacted with Me_3SiLi	T = 40°C, 1 h
$MeCpTiCl_3$	“	SiO_2 + metallocene + TMA	T = 40°C, 18 h, co $Ph_3CB(C_6F_5)_4$

$CpTiCl_3$	“	--	Cocat. = MA
1,4-cyclohexanediylidene(Cp-Flu)$ZrCl_2$	Silica gel	---	Cocat. = MAO, T = 6
$[Ph_2CH_2(Cp)Flu]ZrCl_2$	Silica gel	Silica gel + metallocene +TMA	Cocat. = TIBA
“	“	Silica gel + metallocene +TMA in toluene, reflux, 56 h	Cocat. = TIBAL, T =
$Et[Ind]_2ZrCl_2$	SiO_2	SiO_2 + metallocene + [N, N-Me_2Ph][BC_6F_5]$_4$	Hexane, cocat. = T
$(Ph_2CH_2Cp\text{-}Flu)ZrCl_2$	Silica gel	Silica gel + MAO + metallocene	Cocat TIBAL, T = 60
“	“	“	“
$Et[Ind]_2ZrCl_2$	“	SiO_2 + MAO + metallocene	Cocat. = TIBAL, T =

Et[Ind]$_2$Zr bis(trifluoromethane sulphonate	“	“	Cocat. = TIBA
Ph_2CH_2Cp(9-Flu)$ZrCl_2$ + Me_2Si(2,4-Me_2Cp)$ZrCl_2$	“	SiO_2 + MAO + metallocenes	Cocat. = TIBAL, T = 6
[Ind]$_2ZrCl_2$	SiO_2	SiO_2 + TMA + TIBAL + metallocene	Cocat. = [N, N-Me_2Ph]

1.4.3.3 Comparison of performance of silica supported metallocene

a) Ethylene polymerization

Silica supported catalysts have been extensively used in case of chromium based supported catalysts[74-76]. Silica supported bis(cyclopentadienyl), bis(indenyl) and bis(fluorenyl) chromium catalysts show good activity in ethylene polymerization[75]. The capability of cyclopentadienyl chromium-based active centers to produce lower molecular weight polyethylene in the presence of hydrogen was observed to decrease in the following series of ligands : cyclopentadienyl > indenyl > fluorenyl. The CrO_3/SiO_2 catalysts have very little, or any response to hydrogen as a chain transfer agent. As a result of high hydrogen response with the chromocene catalyst, a highly saturated polyethylene is produced. Polyethylene produced with CrO_3/SiO_2 catalyst usually have one double bond per molecule, indicating a different chain transfer process from the chromocene catalysts[77]. Thermal aging of the chromocene catalysts led to the removal of cyclopentadienyl ligand and loss of high hydrogen response of the catalysts[78]. Polyethylene produced with the chromocene catalysts usually gives narrow molecular weight distribution. Addition of ethers[79], ammonia[80] or siloxanes[81] to the silica supported metallocene prior to the polymerization led to modifiedcatalyst which produced polymers with a more narrow molecular weight distribution.

When metallocene is adsorbed on the silica support different adsorptions occur. A large amount of the metallocene is also destroyed by the acid centers present on the support. Differences in the nature of the bonding lead to different kinds of active sites and hence result in the broadening of molecular weight distribution of the polymers as compared to homogeneous systems[82].

Kaminsky and Renner[54] synthesized polyethylene with a molecular weight of one million using a $Et[Ind]_2ZrCl_2$ supported on silica followed by activating with MAO. It was suggested that supporting of the zirconocene on silica prevents deactivation by bimolecular processes and thus increases molecular weight (**Table 1.6**).

Soga *et al.*[59] reported silica gel modified with $Cl_2Si(CH_3)_2/NaHCO_3$ supported Cp_2ZrCl_2 catalyst. In one case metallocene was directly immobilized on the support and, in an other case, the modified support was pretreated with MAO followed by supporting the metallocene. The polymerization activity dramatically increases with the modified support and is strongly dependent on the nature of alkylaluminums (DEAC < TIBAL < TMA). Catalyst activity of around 60 kg PE/g Zr. h was obtained when the modified silica gel was treated with MAO. In addition, MAO-free catalysts composed of modified silica, Cp_2ZrCl_2, and TMA could be also activated by simple trialkylaluminums and produced catalyst exhibiting good activity (43 kg PE/g Zr.h).

Ihm *et al.*[62] immobilized Cp_2ZrCl_2, Cp_2TiCl_2 and Cp_2HfCl_2 on modified SiO_2. The silica was pretreated with small amounts of MAO, TEAL, and C_2H_5MgCl and the supported thus prepared was used for the polymerization of ethylene in conjunction with MAO or simple alkylaluminums. Titanocene based catalyst showed the lowest activity. This was attributed due to the bimolecular reductive disproportionation of titanium compounds. Bimodal MWD's were observed for titanocene supported on SiO_2/MAO (MWD = 11.8), $SiO_2/AlEt_3$ (MWD = 5.6) but not for SiO_2/C_2H_5MgCl (MWD = 4-5). It was speculated that the interaction of titanium and aluminum species (in case of MAO and $AlEt_3$) affects the molecular weight distribution. Cp_2ZrCl_2 supported on SiO_2 modified by MAO showed the highest activities among the various supported metallocene catalysts.

Sacchi *et al.*[67] reported a comparison of ethylene polymerization on silica supported Cp_2ZrCl_2 or silica pretreated with MAO. The pretreated SiO_2/MAO systems show good catalyst activities (3.6 kg PE/g Zr.h), which is, however, lower than homogeneous systems (23 kg PE/g Zr.h), whereas the polymer properties ($M_w = 267 \times 10^3$, MWD = 3.9) obtained with these systems remain nearly identical to those produced using homogeneous systems ($M_w = 263 \times 10^3$, MWD = 5.2). On the contrary, when the catalyst was prepared by direct treatment of silica with Cp_2ZrCl_2 catalyst activity of 2 kg PE/g Zr.h was found and the molecular weight was higher ($M_w = 309 \times 10^3$, MWD = 4.4). The same observation was also made by Chen *et al.*[57] who studied the performances in olefin polymerization of stereorigid metallocenes, supported directly on SiO_2 or on MAO modified SiO_2.

Lee *et al.*[66] reacted a partially hydrated silica (H-SiO_2) with trimethylaluminum (TMA) to produce aluminoxanes in situ. The resulting H-SiO_2/TMA/Cp_2ZrCl_2 systems are effective for ethylene polymerization even in the presence of simple trialkylaluminums as cocatalysts. The catalyst activity was found to be dependent on the amount of water content on silica, i.e. on the H_2O/TMA ratio, and on the nature of metallocene and cocatalyst. These systems are also compared with conventional MAO/SiO_2 or TMA/SiO_2 supported catalysts. While TMA treated silica shows low polymerization activity, modified MAO (MMAO) treated silica gives high productivity. In the case of H-SiO_2 supported catalysts, those obtained from H16-SiO_2 (16 wt. % of water) exhibit higher activity than H45-SiO_2 (45 wt. % water). This is explained on the basis of uncontrolled fast reaction between TMA and water in the case of H45-SiO_2. The effect of cyclopentadienyl (Cp) substituent in the supported zirconocenes was also investigated. Catalyst with monoalkyl substituted Cp (nBu-Cp, Me-Cp) shows higher activity than those with Cp or indenyl ligands. It was suggested that the alkyl Cp substituents increase electron density at metal and thus favoring ethylene co-ordination[66,83,84]. Determination of pore volume and surface area of H16-SiO_2/TMA catalyst precursor suggests that TMA react in the pores with water so that pores are filled with produced MAO compound. This type of reaction might occur even in the cracks of pores and even break them apart. In addition, ^{13}C NMR data lead to the conclusion that the organoaluminum compounds on H16-SiO_2/TMA are similar to those observed in case of SiO_2/MAO systems.

Hlatky and Upton reported polymerization of ethylene using silica supported ionic Cp_2HfMe_2 catalysts[68]. The ionic catalysts was prepared by the reaction of Cp_2HfMe_2 with $[NHMe_2Ph][B(C_6F_5)_4]$ (A) and $[Ph_3C][B(C_6F_5)_4]$ (B) and used for ethylene polymerization in conjunction with TEAL. The supported ionic catalyst when treated with A shows catalyst activity of 3 kg PE/g Hf. h. bar. However, when treated with B an activity of 5 kg PE/g Hf. h. atm was obtained. More recently, Roos *et al.* synthesized silica gel (pretreated with MAO) supported silicone bridged $Me_2Si[Ind]_2ZrCl_2$, catalyst which was used for the gas phase polymerization of ethylene[69]. The supported catalyst thus prepared gives an activity of 9.6 kg PE/g metallocene.h at 80°C without addition of further organoaluminum compounds.

Most of the research work that has been performed in academic and industrial laboratories is focused on supporting zirconocene, titanocene, and hafnocene catalysts. Very little attention has been paid to supporting lanthanocenes. Recently Jin *et al.*[70] described several SiO_2 supported neodomocene catalysts as efficient for ethylene polymerization, when combined with suitable cocatalysts like alkylaluminum, MAO, butyllithium(BuLi) or ethylbutylmagnesium(BuMgEt). BuMgEt and TIBAL as cocatalysts gave highest activity and the highest molecular weight. The life time of lanthanocene catalysts is substantially improved when compared to homogeneous catalysts.

b) Propylene polymerization

Silica has been extensively used to support metallocene and useful for the polymerization of propylene. Some of the results from the literature are shown in **Table 1.6**.

Kaminaka and Soga[24a,53,85] examined several kinds of supported zirconocene catalysts for propylene polymerization. $Et[IndH_4]_2ZrCl_2$, $iPr(Flu)CpZrCl_2$ and Cp_2ZrCl_2 were supported on SiO_2 by direct treatment of metallocene with SiO_2. Simple trialkyllaluminums were used in place of MAO. The SiO_2 supported catalysts did not show any activity for propylene polymerization in conjunction with simple trialkylaluminums. However, highly active SiO_2-supported metallocenes would be obtained, with simple alkylaluminums as cocatalysts, provided silica is pretreated with a small amount of MAO. Soga and kaminaka[24a,87] have shown that $Et[IndH_4]_2ZrCl_2$-(SiO_2/MAO) associated with AlR_3 as cocatalyst can induces isotactic polymerization of propylene. The catalyst activity is dependent upon the cocatalyst used and markedly increases in the order TEAL < TMA < TIBAL. By changing the sequence of addition of MAO and zirconocene on silica (i.e. SiO_2 is first treated with zirconocene and then by MAO), the resulting supported catalyst associated to alkylaluminum shows hardly any polymerization activity. It was also observed that in these conditions majority of the zirconium compound, physically adsorbed on the SiO_2 surface was removed from the support by MAO, into the liquid toluene phase. Soga and Kaminaka[86] showed that by supporting metallocenes it is possible to improve the stability and the morphology of the catalyst to a great extent. They synthesized a MAO modified silica support and immobilized rac-$(CH_3)_2Si(2,4\text{-}(CH_3)_2\text{-}C_5H_3)(3',5'\text{-}(CH_3)_2\text{-}C_5H_3)ZrCl_2$ and compared this system with homogeneous metallocene for propylene polymerization. The use of support markedly improves the molecular weight and bulk density of isotactic polypropylene. In addition the size distribution of the polymer particles can be controlled by conventional methods used with Ziegler-Natta catalysts (pre-polymerization). The life time of active species formed on the silica is also significantly higher.

Collins *et al.*[61] reported isotactic polymerization of propylene with high productivity using partially hydroxylated SiO_2 pretreated with TMA to support $Et[Ind]_2ZrCl_2$ and $Et[IndH_4]_2ZrCl_2$. Activities of such supported catalysts combined with MAO remain lower (about 9 times) than those obtained with homogeneous catalysts. Significantly, the ratio of Al/Zr can be substantially reduced. Nevertheless, polymer properties such as stereoregularity, MWD, degree of crystallinity are not much affected. It is also observed that metallocenes are decomposed during the supporting process, especially, when $AlMe_3$-free SiO_2 is used as carrier (**Fig. 1.5**).

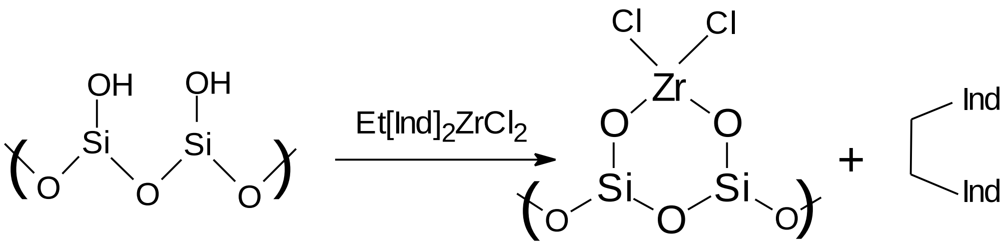


Fig. 1.5 : Reaction of metallocene compound with surface hydroxyl groups

Supported catalyst with monocyclopentadienyl titanium derivatives were also reported by Park *et al.*[87] and Soga *et al.*[24b]. $RCpTiCl_3$ was supported on silica and activated by trialkylaluminum and $Ph_3CB(C_6F_5)_4$ yielding high molecular weight (M_n = 106 x 10^3, at 40°C) atactic polypropylene. Random copolymers of ethylene and propylene with structure similar to that obtained with homogeneous vanadium catalysts would also be prepared with these supported catalyst systems. These catalysts in spite of their advantages, are not efficient for the improvement of stereoregularity. This is reflected by the low T_m.

Kaminsky *et al.*[54] synthesized SiO_2 supported $Et[Ind]_2ZrCl_2$ catalyst by direct impregnation of metallocene onto the support. The catalyst thus prepared gives highl isotactic polypropylene with $M_w = 6.10 \times 10^5$-8.10^5, [mm] = 93 to 96 % and T_m = 160-161°C. The activity is, however, low. The molecular weights and the melting temperatures of polypropylene also increase with temperature in contrast to homogeneous catalysts. Improvement of the polypropylene properties, by use of supported metallocene is best understood in terms of the direct interaction taking place between the support and the metallocene. It is proposed that supporting of metallocene prevents deactivation by bimolecular processes and, in turn, favors improved stereo and regiospecificity[54,88].

Other highly isospecific supported metallocenes were prepared by Chen *et al.*[57], Sacchi *et al.*[67] reported that aspecific $[Ind]_2ZrCl_2$ when supported on SiO_2 it gives rise to isospecific polymer, [mm = 71 % and $M_w = 2 \times 10^5$] while the homogeneous zirconocene or the zirconocene supported on MAO modified SiO_2 gave only atactic oligomers. This fact suggests that isospecific centers can be formed by anchoring metallocenes onto silica, independent of their stereochemical structure. This is in agreement with the data reported by Kaminsky[88] for a silica supported syndiospecific metallocene, $Me_2C[(Cp)(Flu)]ZrCl_2$. By supporting this syndiospecific metallocene on silica, the nature of the catalyst changed into an isospecific one (polypropylene isotactic pentad fraction ≈ 90 %). The exact structure of the metallocene on the surface after supporting is still unclear. Sacchi and co-workers[67], on the basis of chemical composition of the supported metallocene system, proposed that the Zr-Cl bond might be involved in the reaction between the metallocene and the silica.

Soga and co-workers reported another approach to obtain highly isospecific catalysts for propylene polymerization[22,60,71-73,89]. They synthesized a series of metallocenes with aromatic ligands chemically bound to the solid surface. These catalyst systems lead to great improvements of the polypropylene isotacticity and molecular weights when compared with analogous homogeneous systems. The proposed structures of some rigidly immobilized metallocenes are shown in **Fig. 1.6**.

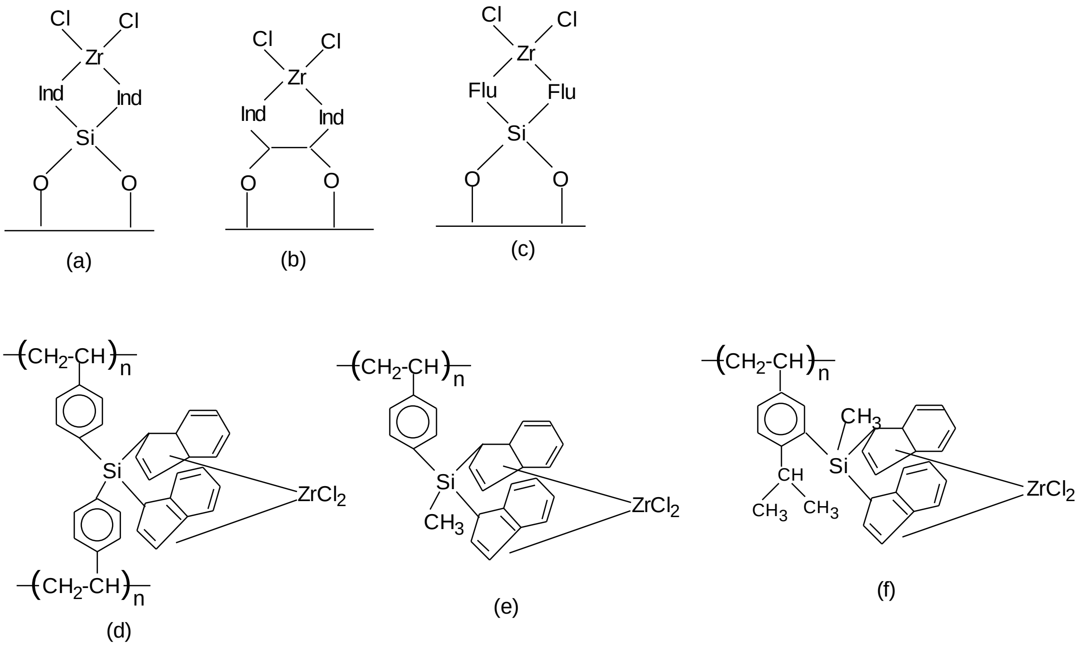
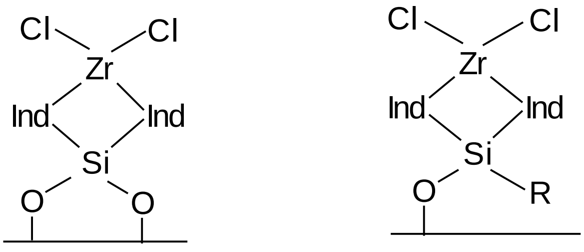


Fig. 1.6 : Proposed structure for rigidly immobilized zirconocenes; (a) $Si[Ind]_2ZrCl_2-SiO_2$; (b) $Et[Ind]_2ZrCl_2-SiO_2$; (c) $Si(Flu)_2ZrCl_2-SiO_2$; (d) $Si[Ind]_2ZrCl_2$-polystyrene; (e) $MeSi[Ind]_2ZrCl_2$-polystyrene; (f) $MeSi[Ind]_2ZrCl_2$-polystyrene alkaline

Soga *et al.*[72b] have shown that catalyst prepared according to the method (iii) lead to higher molecular weight isotactic polypropylene. However, it must be understood that chemically attaching ligands on SiO_2 followed by addition of zirconium halide may lead to catalysts containing a mixture of meso and racemic metallocene isomers, leading to both atactic and isotactic polypropylene. In some cases isotactic polypropylene produced with these supported catalysts displayed two melting temperatures, suggesting that two kind of ispspecific active centers are present. Soga *et al.*[83] proposed that zirconocene supported on SiO_2 calcined at lower temperatures (200-400°C) might be more rigidly bound on the SiO_2 surface, thus yielding isotactic polypropylene with higher stereoregularity, whereas, SiO_2 calcined at higher temperatures at 900°C, may have rigidly bound metallocene (**Fig. 1.7**).



A B

Fig. 1.7 : Models of singly and doubly bounded metallocene species.

These two metallocene species A and B could be responsible for production of polypropylenes with a higher and lower melting temperature respectively. Another interesting observation was made in case of $Cl_2Zr[Ind]_2Si-SiO_2$ and $Cl_2Zr[Ind]_2Et-SiO_2$ catalysts by method (iii). The supported catalysts produces isospecific polypropylene while the homogeneous systems show increasing stereoregulating order : $Me[Ind]_2ZrCl_2 < Et[Ind]_2ZrCl_2 < Me_2Si[Ind]_2ZrCl_2$. In addition, the polypropylene obtained with $Cl_2Zr(Flu)(Cp)Si-SiO_2$ catalyst prepared by method (iii) show high isotactic triad fraction and a single T_m. The soluble heptane fraction (75 %) is also isotactic (and not syndiotactic one) but with less stereoregularity. Based on these observations and the results obtained with similar supported catalysts prepared by using the same ligand Fluorenyl or MeCp on both ligand frames, Soga and co-workers proposed that the formation of isospecific species might be due to the nature of SiO_2 surface. However, the number of ligands attached to zirconium and the structure of the isospecific centers remain unclear. More recently, Soga[71] used a different type of bridge (Sn bridge to connect metallocene ligands on the silica surface. Isotactic polypropylene with the tin bridged catalyst showed a single T_m at 162°C. It is thus predicted that higher reactivity of $SnCl_4$ toward the surface hydroxyl groups might be responsible for the formation of more uniform active species on SiO_2. Supported titanocenes yielding highly isotactic polypropylene with considerably high M_w but exhibiting low activity are also described.

Table 1.6 : Comparison of performance of SiO_2 su

Catalysts	Support	Cocatalyst	Polymn. conditions	
A: Ethylene				
Cp_2ZrCl_2	SiO_2/MAO	TIBAL	Toluene, 40°C, 1 h	
“	$SiO_2/Cl_2Si(CH_3)_2$/MAO	"	“	
“	“	TMA	Toluene, 40°C, 1 h,	
“	$SiO_2/Cl_2Si(CH_3)$	"	"	
Cp_2ZrCl_2	-	MAO	Toluene, 50°C, 1 h, Al/Zr = 500 mol	Cat. a
“	“	"	Toluene, 50°C, 1 h, Al/Zr = 200 mol	
“	SiO_2/MAO	"	Toluene, 50°C, 1 h, Al/Zr = 200 mol	Cat.
“	SiO_2	"	Toluene, 50°C, 1 h, Al/Zr = 200 mol	Cat. ac
“	SiO_2/MAO	TIBAL	Toluene, 50°C, 1 h, Al/Zr = 130 mol	
$Et[Ind]_2ZrCl_2$	SiO_2/MAO	MAO	Toluene, 50°C, 1 h, Al/Zr = 500 mol	Cat. a
“	SiO_2	"	Toluene, 50°C, 1 h, Al/Zr = 500 mol	Cat. a
Cp_2ZrCl_2	-	MAO	Toluene, 60°C, 1/2 h	
“	SiO_2/MAO	"	Toluene, 60°C, 1/2 h	
“	“	TIBAL	Toluene, 60°C, 1/2 h	

Cp_2HfCl_2	-	MAO	Toluene, 60°C, 1/2 h	
“	SiO_2/MAO	"	Toluene, 60°C, 1/2 h	
“	“	TIBAL	Toluene, 60°C, 1/2 h	
Cp_2TiCl_2	-	“	Toluene, 60°C, 1/2 h	
“	SiO_2/MAO	"	Toluene, 60°C, 1/2 h	Cat
“	“	TIBAL	Toluene, 60°C, 1/2 h	Cat
$Et[Ind]_2ZrCl_2$	SiO_2	MAO	Toluene, 50°C, 1 h, Al/Zr = 39 mol	Cat. ac
di(men)Sil-bis-[Ind]$ZrCl_2$	-	MAO	Heptane, 25°C, 15 min, Al/Zr = 2500 mol	
“	“	TIBAL/Ph_3C $B(C_6F_5)_4$	Heptane, 25°C, 30 sec, Al/Zr = 400 mol	Cat. ac
“	SiO_2/MAO	“		
“	SiO_2	"	Heptane, 25°C, 2 min, Al/Zr = 400 mol	Cat. a
“	“	TIBAL	Heptane, 25°C, 1 h, Al/Zr = 50 mol	Cat. a
			Heptane, 25°C, 1 h, Al/Zr = 50 mol	Cat. ac
$Et[Ind]_2ZrCl_2$	SiO_2	TIBAL	Heptane, 25°C, 1 h, Al/Zr = 50 mol	Cat. ac
“	“	"	Heptane, 25°C, 1 h, Al/Zr = 50 mol	Cat. ac

Cp_2ZrCl_2	-	MAO	Toluene,40°C, 2 h, Al/Zr =10 000 mol	Cat. ac
“	SiO_2/MAO	TMA	Toluene, 40°C, 2 h, Al/Zr = 1000 mol	
“	SiO_2/TMA	MAO	Toluene, 40°C, 2 h, Al/Zr = 1000 mol	
“	SiO_2	TMA	Toluene, 40°C, 2 h, Al/Zr = 1000 mol	
Si[Ind]$_2$NdMe	SiO_2	TIBAL	Toluene, 40°C, 6 h, Al/Zr = 300 mol	Cat. act.
“	"	MAO	Toluene, 40°C, 6 h, Al/Zr = 300 mol	Cat. act
“	"	BuMgEt	Toluene, 40°C, 6 h, Al/Zr = 49 mol	Cat. act
MeSi[Ind]ZrMe$_2$	"	BuLi	Toluene, 40°C, 6 h, Al/Zr = 46 mol	
Cp_2ZrCl_2	SiO_2/TMA	-	70°C, 1 h	
“	SiO_2/MAO	-	“	
“	H16-SiO_2/TMA	-	“	Cat. a
“	H45-SiO_2/TMA	-	“	Cat. ac
“	H16-SiO_2/TEAL	-	“	
(Me-Cp)$_2$ZrCl$_2$	H16-SiO_2/TMA	-	70°C, 1 h	Cat. a
(n-BuCp)$_2$ZrCl$_2$	“	-	70°C, 1 h	Cat. a

$[Ind]_2ZrCl_2$	“	-	70°C, 1 h	Cat. a
rac-$Me_2Si[Ind]_2ZrCl_2$	SiO_2	-	40°C, 200 min, 5 bar, Al/Zr = 386 mol	
“	“	-	80°C, 200 min, 5 bar, Al/Zr = 386 mol	
B : Propylene				
$Et[IndH_4]_2ZrCl_2$	-	MAO	Toluene, 40°C, 1 h, Al/Zr = 3000 mol	Cat. act
“	SiO_2/MAO	TMA	Toluene, 40°C, 1 h, Al/Zr = 121 mol	Cat. a
“	“	TMA	Toluene, 40°C, 1 h, Al/Zr = 610 mol	Cat. ac
“	“	TEAL	Toluene, 40°C, 1 h, Al/Zr = 121 mol	Cat. act
“	“	TEAL	Toluene, 40°C, 1 h, Al/Zr = 610 mol	Cat. act.
“	“	$AliPr_3$	Toluene, 40°C, 1 h, Al/Zr = 61 mol	Cat. act
“	“	$AliPr_3$	Toluene, 40°C, 1 h, Al/Zr = 365 mol	Cat.
$iPr(Flu)(Cp)ZrCl_2$	-	MAO	Toluene, 40°C, 1 h, Al/Zr = 3250 mol	Cat. act.
“	SiO_2/MAO	AliPr3	Toluene, 40°C, 1 h, Al/Zr = 270 mol	Cat. act.

Et[Ind]$_2$ZrCl$_2$	-	MAO	Toluene, 50°C, 2 h	
“	SiO$_2$	"	Toluene, 50°C, 2 h, Al/Zr = 150 mol	Cat. act.
“	SiO$_2$	-	Toluene, 50°C, 2 h, Al/Zr = 37 mol	Cat. act.
Me$_2$C[(Cp)(Flu)ZrCl$_2$	-	MAO	Toluene, 50°C, Al/Zr = 5900 mol	M_n = 4
	SiO$_2$	"	Toluene, 50°C, Al/Zr = 180 mol	M_n = 350
Et[IndH$_4$]$_2$ZrCl$_2$	-	MAO	Toluene, 30°C, 1.5 h,	Cat. act.
“	PDS-TMA	"	“	Cat. act.
“	DS	"	“	
“	PDS	"	“	
“	100 % OH-S	"	“	
Et[Ind]$_2$ZrCl$_2$	PDS-TMA	MAO	"	Cat. ac
Et[Ind]$_2$ZrCl$_2$	-	MAO	Toluene, 50°C, 1 h, Al/Zr = 300 mol	Cat. act.
“	SiO$_2$/MAO	"	“	Cat. act.
“	“	"	Toluene, 50°C, 1 h, Al/Zr = 110 mol	Cat. act.
“	SiO$_2$	"	Toluene, 50°C, 1 h, Al/Zr = 300 mol	Cat. act.

[Ind]$_2$ZrCl$_2$	-	MAO	Toluene, 50°C, 1 h, Al/Zr = 300 mol	Cat. ac
	SiO$_2$/MAO	“	“	Cat. a
	SiO$_2$	"	“	Cat. act.
Cp$_2$ZrCl$_2$	SiO$_2$	MAO	Toluene, 50°C, 1 h, Al/Zr = 300 mol	
rac-(CH$_3$)$_2$Si(Cp$_n$R$_n$)$_2$ ZrCl$_2$	-	MAO	Toluene, 30°C, 2 h, Al/Zr = 3000 mol	Cat. act.
	SiO$_2$/MAO	TIBAL	Toluene, 30°C, 2 h, Al/Zr = 312 mol	Cat. act.
di(men))Sil-bis[Ind]ZrCl$_2$	-	MAO	Heptane, 25°C, 20 min, Al/Zr = 2500 mol	
“	“	TIBAL/Ph$_3$C B(C$_6$F$_5$)$_4$	Heptane, 25°C, 8 min, Al/Zr = 200 mol	Cat. ac
“	SiO$_2$/MAO	"	Heptane, 25°C, 15 min, Al/Zr = 40 mol	Cat. a
Cp$_2$ZrCl$_2$	-	MAO	Toluene, 40°C, 1 h, Al/Zr = 1000 mol	
“	SiO$_2$/MAO	TIBAL	Toluene, 40°C, 1 h,	
CpTiCl$_3$	-	MAO	Toluene, 40°C, 2 h	
	SiO$_2$	"	Toluene, 40°C, 2 h	C

$Me_2Si[Ind]_2ZrCl_2$	-	MAO	Toluene, 40°C, 1 h	Cat. act.
$Si[Ind]_2ZrCl_2$	SiO_2	"	Toluene, 40°C, 20 h	Cat. act.
“	“	"	“	Cat. 153
“	“	TIBAL	Toluene, 40°C, 20 h	Cat. a &
$Et[IndH_4]_2ZrCl_2$	-	MAO	Toluene, 40°C, 1 h	Cat. a
$Et[Ind]_2ZrCl_2$	SiO_2	"	Toluene, 40°C, 20 h	T_{m}. = 1
“	“	TIBAL	Toluene, 40°C, 20 h	M_w = 4
“	“	TEAL	Toluene, 40°C, 20 h	
$iPr(Flu)(Cp)ZrCl_2$	-	MAO	Toluene, 40°C, 1 h	Cat. ac
$(Flu)(Cp)SiZrCl_2$	SiO_2	"	Toluene, 40°C, 20 h	M_w
$(Flu)_2SiZrCl_2$	“	“	Toluene, 40°C, 20 h	M_w
	“	TIBAL	Toluene, 40°C, 20 h	T
$(MeCp)_2SiZrCl_2$	“	MAO	Toluene, 40°C, 20 h	
“	“	TIBAL	Toluene, 40°C, 20 h	M_w = 27

Cat. act. = Catalyst activity expressed in Kg /g metal.h. [a] immobilization of the metallocene on the supp
MAO. [b] heptane insoluble part.

1.4.4 Other supports used with metallocene catalysts

Although silica has been extensively used in case of metallocene catalysts, use of other organic materials and inorganic materials as supports are also reported. HY-zeolite was selected as a carrier by Ciardelli and co-workers for the preparation of supported metallocenes with controlled structure[27]. When Cp_2ZrCl_2 was directly supported on thermally treated HY-zeolite, the catalyst displayed rather modest activity towards ethylene polymerization in conjunction with trialkylaluminums as cocatalysts. However, the activity substantially improved by using MAO as cocatalyst. When HY-zeolite was treated with TMA, considerably high activities (31 kg/g Zr.h) were obtained in presence of MAO. Cp_2ZrMe_2 supported on dealuminated HY pretreated with TMA (HY*-zeolite) used in conjunction with MAO, gives comparable activity to the homogeneous metallocene. Results from ^{13}C NMR (MAS) analysis of the supported zirconocene and of the zeolite pretreated with TMA suggest that the zirconocene on the supports maintain its original structure. However, kinetic analysis shows interesting differences between soluble and zeolite supported metallocene species. The ethylene polymerization rate of Cp_2ZrMe_2 immobilized on HY*-TMA remains constant, for a longer period of time, in contrast with the typical decay profile observed with soluble systems. Entrapment of active species in the zeolites channel might therefore prevent deactivation reactions of the catalyst and thus modifing catalytic activity. A similar observation was also made by Woo *et al.* in the case of Cp_2ZrCl_2 supported on NaY zeolite modified with MAO. It was suggested that steric hindrance in the supercage might decrease the chain transfer rate. The molecular weight and MWD of the polyethylene are higher and relatively broader than those obtained from homogeneous analogues. Recently, Woo *et al.* synthesized MCM-41 and VPI-5 supported $Et[Ind]_2ZrCl_2$ catalyst and used for the polymerization of propylene[28,29]. It was observed that stereoregularity, melting point and molecular weight of the polypropylene increase compared to unsupported catalyst. It was speculated that small, regular, cylindrical pores of MCM-41 and VPI-5 suppress the formation of inactive bimolecular species formed between metallocene molecules, or between metallocene and MAO, resulting in stable active sites.

Tudor and O'Hare have reported MCM-41 supported metallocene catalyst, produced by modifying mesoporous MCM-41 by grafting the chiral alkene polymerization catalyst Et[Ind]$_2$ZrCl$_2$ onto the surfaces of the mesopore[30]. The catalyst was active for polymerization of propylene to isotactic PP. The activity of this catalyst was compared with soluble catalyst and a clay supported catalyst. The clay supported catalyst was more active than the metallocene supported on MCM-41 by about three fold. It was suggested that the low activity could be due to a diffusion limiting effect; whereby, active centers located in the center of the mesoporous channel are effectively screened from monomers units by active centers closer to channel ends which hinder polymer chains. The clay supported catalyst produces the highest M_n value, with the values for the MCM-41 support is slightly lower, but both of these supported catalysts produces very high molecular weight (a five fold increase in molecular weight compared to homogeneous analogue). Among the three catalysts, MCM-41 supported catalyst produces polypropylene with higher T_m (141°C) whereas the homogeneous catalyst produces isotactic PP which exhibited T_m of 128°C and clay supported catalyst 135°C. ^{13}C NMR analysis shows that isotacticity is nearly the same in case of both the supported catalyst and is much lower in case of the soluble catalyst.

Collins *et al.*[61] reported isotactic polymerization of propylene with catalyst prepared by pretreating partially hydroxylated alumina with TMA followed by supporting Et[Ind]$_2$ZrCl$_2$. The activity of the supported catalyst was about nine times lower than the homogeneous catalyst. Significantly, the Al/Zr ratio would be substantially reduced. The molecular weight of the polypropylene obtained from supported catalyst was found to be similar (M_n = 19,500) to the homogeneous catalyst (M_n = 18, 000). It was further observed that polymer properties such as, stereoregularity, melting point, degree of crystallinity are not much affected upon heterogenization.

Kaminaka and Soga[24,43,51,52] examined several heterogeneous zirconium based metallocene catalysts for propylene polymerization. Et[IndH$_4$]$_2$ZrCl$_2$, iPr(Flu)(Cp)ZrCl$_2$ and Cp$_2$ZrCl$_2$ were supported on different inorganic materials by direct impregnation method and used in polymerization in conjunction with simple trialkylaluminums instead of MAO. When Al$_2$O$_3$, MgF$_2$, CaF$_2$ and AlF$_3$ are used as supports, the resulting supported metallocene catalysts can be easily activated by common alkylaluminum. Isotactic polypropylene was obtained when Et[IndH$_4$]$_2$ZrCl$_2$ was supported either on Al_2O_3. The supported catalysts in combination with AlR$_3$ (R = Me or Et) show lower activities than homogeneous Et[IndH$_4$]$_2$ZrCl$_2$/MAO catalyst[24,51]. Al_2O_3 supported catalyst gives broad molecular weight distribution and high melting polypropylene (131-137°C). The molecular weight and the isotacticity of the polypropylene obtained by using Al_2O_3 supported catalyst was found to be high as compared to unsupported or MgF_2, CaF_2 and AlF_3 supported metallocenes.

i-Pr(Flu)(Cp)ZrCl$_2$ and Cp$_2$ZrCl$_2$ supported on Al_2O_3 activated with AlR$_3$ gave respectively highly syndiotactic PP and atactic polypropylene respectively[52]. The polymers produced with the syndiospecific heterogeneous catalysts showed higher (T_m = 138°C) and higher [rrr] pentad fraction (86 %) compared with those produced with homogeneous systems (T_m = 123°C and [rrr] pentad fraction 77 %.

Several organic materials have been examined as supports for metallocene. Lee *et al.* performed ethylene polymerization in the presence of Cp$_2$ZrCl$_2$ supported on cyclodextrin (CD) or MAO modified CD[19]. Both MAO and TMA were used as cocatalysts. When Cp$_2$ZrCl$_2$ was supported on CD/MAO or CD/TMA the polymerization could be initiated by ordinary trialkylaluminums. The molecular weight of the polyethylene obtained with CD supported catalyst was about 30 times higher than unsupported catalyst and the MWD of polyethylene obtained was narrow (2.3-2.5). Nishida *et al.*[20] reported the synthesis of polymer supported metallocene catalysts. The main preparative steps are identical, except they used lithiated polystyrene as the starting material.

Janiak *et al.*[90] studied the use of “polymeric MAO” with a high surface area as support for metallocene catalysts. Polymeric MAO is produced as a three dimensional lattice by reaction of MAO and 1,10-dodecadiol or 1,6-dodecadiol.

Soga *et al.*[22] reported a new method of supportingpolysiloxanes with electron donating substituents like indenyl, fluorenyl, etc. and used them as a ligands to immobilize metallocene on the polysiloxanes support. Several types of catalysts were prepared according to this approach: (i) [IndMeSiO)$_n$ZrCl$_2$, (ii) (FluMeSiO)$_n$ZrCl$_2$ and (iii) [Ind$_2$SiO]$_n$ZrCl$_2$ and considered as models of SiO$_2$-supported metallocene systems. The procedure involves three steps. (i) synthesis of organosilanes with aryl substituents, (ii) condensation reaction between equivalent amounts of water and the above prepared compounds to form polysiloxanes precursor; and (iii) anchoring metallocene on the precursor using identical procedure to the one previously referred. The corresponding synthetic procedure is summarized in **Fig. 1.8**. These catalysts show high activities for ethylene polymerization (between those of homogeneous and SiO_2 supported catalysts). The fluorenyl based catalysts show highest activity. The molecular weight and molecular weight distribution of polyethylene found to be markedly dependent upon the catalyst employed, whereas the melting point of the polyethylene was almost constant.**Table 1.7** shows different inorganic and organic supports (other than $MgCl_2$ and SiO_2) which are used to support metallocenes.

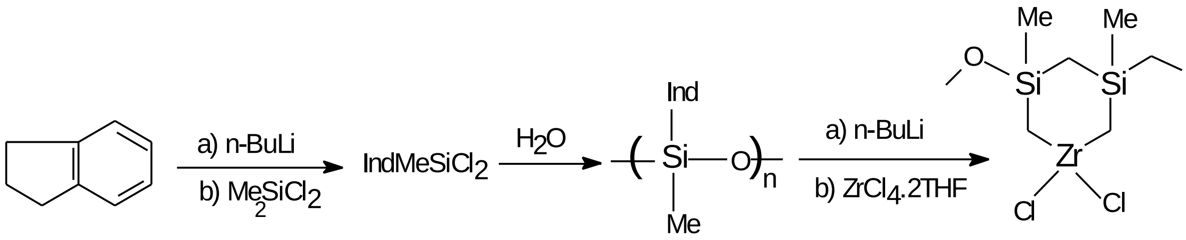


Fig. 1.8 : Synthetic scheme of the [IndMeSiO]$_n$ZrCl$_2$

Table 1.7 : Different organic and inorganic supports u

Metallocene	Support	Cocatalyst	Polymn. Conditions	Activity (Kg/g. M.h)	Tacticity (%
A : Ethylene					
Cp_2ZrCl_2	α-CD	TMA	Toluene, 40°C, 2 h, Al/Zr = 1000 mol	0.6	-
“	α-CD	MAO	"	8.5	-
“	α-CD/MAO	TMA	"	9	-
“	α-CD/MAO	MAO	"	10.5	-
“	α-CD/TMA	TMA	"	7	-
$MeSi(Ind)_2ZrCl_2$	PSLi	MAO	Toluene, 75°C, 0.3 h	35	-
$(CH_3)_2Si(Ind)_2ZrCl_2$	-	MAO	Toluene, 40°C, 1 h, Al/Zr = 4000 mol	211	-

(Ind)$_2$ZrCl$_2$	(MeSiO)$_n$	MAO	Toluene, 40°C, 1 h, Al/Zr = 10000 mol	24	-
(Flu)$_2$Zrcl$_2$	“	“	"	49	-
Cp$_2$ZrCl$_2$	-	MAO	Toluene, 25°C, Al/M = 1500 mol	4	-
“	HY	AlEt$_3$	toluene, 25°C, Al/M = 12 mol	0.03	-
“	“	MAO	toluene, 25°C, Al/M = 1500 mol	2	-
“	HY-AlMe$_3$	“	toluene, 25°C, Al/M = 1500 mol	31	-
Cp$_2$ZrMe$_2$	HY**-AlMe$_3$	AlMe$_3$	toluene, 25°C, Al/M = 100 mol	0.3	-
“	“	MAO	toluene, 25°C, Al/M = 3000 mol	6.5	-
Cp$_2$ZrCl$_2$	-	MAO	toluene, 50°C, 2 h, Al/M = 17500 mol	137	-
Cp$_2$ZrCl$_2$	NaY-MAO	MAO	toluene, 70°C, 1 h, Al/M = 560 mol	37	-

Cp_2ZrCl_2	$Mg(OEt)_2$	MAO	heptane, 80°C, 4h, P = 8 bar	Yield = 23g	-
B : Propylene					
$MeSi(Ind)_2ZrCl_2$	PS	MAO	Toluene, 40°C, 6 h	1.6	-
"	PS-Alkaline	"	"	0.8	
$Si[Ind]_2ZrCl_2$	PS	"	Toluene, 40°C, 6 h	5.4	-
$(Ind)_2ZrCl_2$	"	"	Toluene, 40°C, 24 h	26	-
$(Flu)_2Zrcl_2$	"	"	"	0.9	-
$Et(IndH_4)_2ZrCl_2$	-	MAO	toluene, 40°C, 1 h, Al/Zr =3000 mol	23	iso PP71%
“	Al_2O_3	AlR_3	18h, Al/Zr = 225-677 mol	0.1-0.15	Iso 90%
“	MgF_2	$AlMe_3$	18h, Al/Zr = 450 mol	0.16	Iso 90%
“	CaF_2	“	"	0.1	-
“	AlF_3	“	18 h, Al/Zr = 1300 mol	0.007	-
iPr(Flu)(Cp)$ZrCl_2$	-	MAO	toluene, 40°C, 1 h, Al/M = 3250 mol	8.3	Syn. 77%

iPr(Flu)(Cp)$ZrCl_2$	Al_2O_3	$AlMe_3$	toluene, 40°C, 18 h, Al/M = 110 mol	0.1	Syn. 86%
“	MgF_2	“	toluene, 40°C, 18 h, Al/M = 240 mol	0.03	-
$CpTiCl_3$	-	MAO	Toluene, 40°C, 1 h	0.05	Atactic
“	Al_2O_3	MAO	"	0.23	Atactic
“	“	TIBAL	"	0.1	Atactic
Zr based metallocene	Polymer support	MAO	Toluene, 24 h, Al/Zr = 17,000 mol, 40°C	44	Iso. 86
			Toluene, 24 h, Al/Zr = 17,000 mol, 70°C	40	Iso. 75
Et(Ind)$_2$ZrCl$_2$	MCM-41/MAO	MAO	Toluene, 60 min, 50°C, P = 8 bar Al/Zr = 800	15	Iso. 83.5 %
	“	TMA	Toluene, 60 min, 50°C, Al/Zr = 800 mol, P = 8 bar	0.15	Iso. 81 %
	VPI-5/MAO		Toluene, 120 min, 50°C, Al/Zr = 2000 mol, P = 8 bar	16	Iso. 84 %

Et(Ind)$_2$ZrCl$_2$	-	MAO	Al/Zr = 1000 mol	54	-
	MCM-41	"	"	13	-
	Clay	"	"	33	-
(CH$_3$)$_2$Si[Ind]$_2$ZrCl$_2$	-	MAO	Toluene, 1 h, 40°C, Al/Zr = 4000 mol	211	-
[Ind]$_2$ZrCl$_2$	(MeSiO)$_n$	"	Toluene, 1 h, 40°C, Al/Zr = 10000 mol	24	-
[Flu]$_2$ZrCl$_2$	"	"	"	49	-
Et[Ind]$_2$ZrCl$_2$	-	"	Toluene, 30°C, 1.5 h	16	89.9 [mmmm
"	PDA-TMA	"	"	2	89.7 [mmmm
"	PDA	"	"	1.5	-
"	DA	"	"	0.16	-
"	100 % OHA	"	"	nil	-

$[Ind]_2ZrCl_2$	$(MeSiO)_n$	MAO	Toluene, 40°C, 2 h	26	-
$(Flu)_2ZrCl_2$	"	"	"	1	-

1.5 MECHANISM OF OLEFIN POLYMERIZATION ON SUPPORTED METALLOCENE CATALYSTS

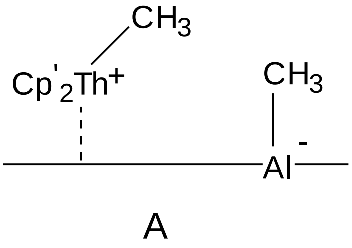
Many key transformations in heterogeneous catalysis involve the creation or modification of surface metal hydrocarbyl (alkyl, aryl, etc.) functionalities. One attractive approach to characterizing such highly reactive species is to create them by adsorption of well-defined molecular precursors onto carefully prepared inorganic surfaces[91,92]. For several classes of early transition metal hydrocarbyls, it has been known since the 1960s that adsorption on high surface area metal oxides is accompanied by dramatic enhancements in activity for olefin transformations such as hydrogenation, polymerization and metathesis[91,93,94]. The study of such materials is of both fundamental scientific significance in terms of defining surface coordination environment which give rise to such enhancements in chemical reactivity and technological interests.

Supporting metallocenes on inorganic surfaces changes the catalytic performances towards olefin polymerization in terms of catalyst activity, catalyst life times, reactivity, and stereoregularity. Unfortunately, the structure and the chemistry of the resultingadsorbates are frequently unknown. A major problem is that very few analytical probes are available that can provide an understanding at the molecular level of such adsorbates. In addition, the possibility to form on the surface various types of active sites with different structures and reactivities must be taken into consideration. Nevertheless many efforts have been made to postulate the nature and the interactions betweenmetallocene and the supports.

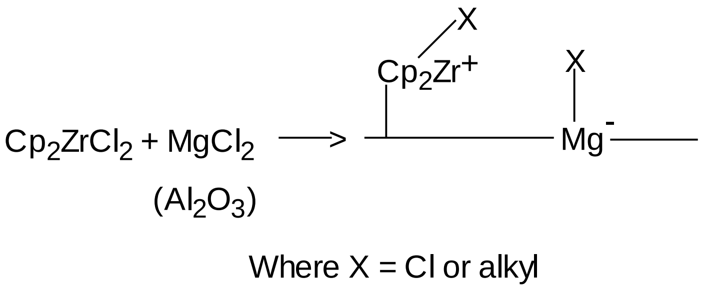
Group IV metallocenes polymerizing olefins through the intermediacy of a cationic active species $Cp_2M\text{-}R^+$. Over the years considerable evidence have accumulated in favor of this mechanism[95].

Marks and co-workers used an integrated chemical/spectroscopic approach which provided a detailed picture of surface organometallic chemistry[96-98]. They used a series a organoactinides, $Cp'AnR_2$ ($Cp' = \eta^5\text{-}(CH_3)_5\text{-}C_5$; An = Th, U; R = alkyl) as model adsorbates and studied their adsorption on a range of supports (Al_2O_3, $MgCl_2$, SiO_2-MgO, MgO) as well as their reactivity with respect to olefins. For supports with a strong lewis acid character such as $MgCl_2$ a transfer of a alkyl groups from the organoactinide to an accepter site on the surface was observed (**Scheme 1.1**) yielding to a “cation-like” Th^+-R

^{13}C CPMAS-NMR spectroscopic studies provided conclusive evidence for the existence of a “cation-like” initiating species, $Cp_2Zr^+CH_3$, in the reaction of a metallocene dialkyl and MAO[100,101]. Recently, Soga and co-workers have studied propylene polymerization using metallocene catalysts based on $Et[IndH_4]_2ZrCl_2$, $iPr(Flu)(Cp)ZrCl_2$ or Cp_2ZrCl_2 supported on $MgCl_2$, Al_2O_3 or SiO_2 in conjunction with trialkylaluminum[24,51,52]. These authors also invoked a similar surface species (**Scheme 1.2)** to explain the results. The species shown in **scheme 1.1 and 1.2**, the support acts as a weak acceptor for the halide or the methide anion. Furthermore, the cationic metallocene species is adsorbed on the support surface, whereby the active sites are isolated, thus preventing reductive disproportionation[102].



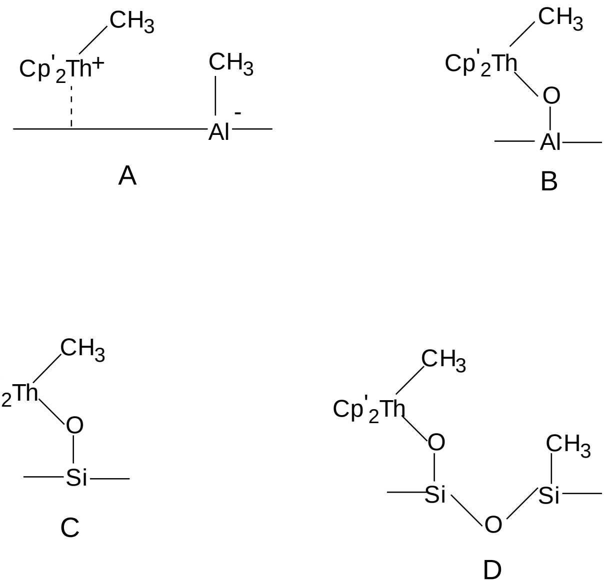
Scheme 1.1 : Surface species on various inorganic supports as shown by Finch *et al.*[98]



Scheme 1.2 : Surface species on $MgCl_2$ or Al_2O_3 supports as shown by Soga *et al.*[51,52]

In case of supports such as partially dehydroxylated alumina-(PDA), partially dehydroxylated silica-(PDS), a “μ-oxo like” structure is suggested. No evidence for alkyl transfer to surface (**Scheme 1.3 B and C**) exists in these cases.

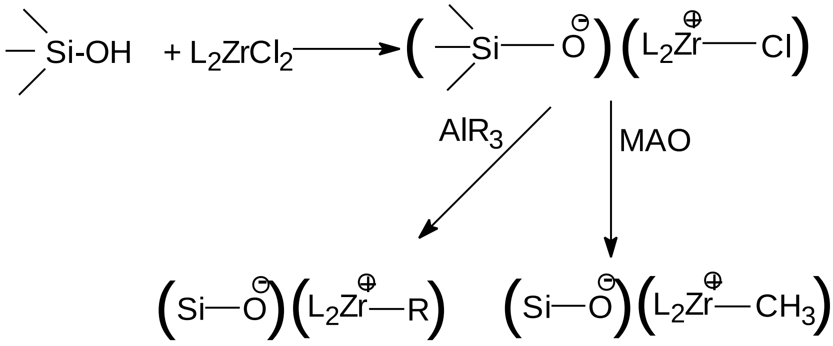
The third type of surface species is observed for dehydroxylated supports with weak lewis acid character and having relatively weak surface metal-oxygen bond [dehydroxylated silica-(DS), dehydroxylated silica/MgO-(DSM), where also a “μ-oxo like” structure and a surface transfer of alkyl are observed (**Scheme 1.4 D**). Significant catalytic activity is activity is observed in case of catalysts system having “μ-oxo like character “ [$Cp'_2Th(CH_3)O$-].



Scheme 1.3 : Surface species on various inorganic supports.

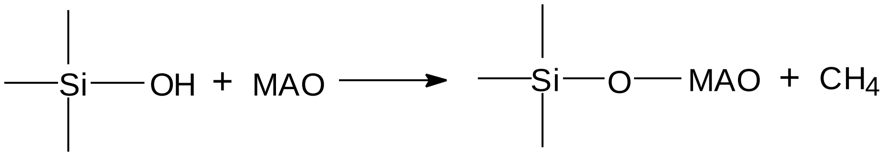
In case of metallocene capable of producing stereospecific polyolefins, the adsorbed metallocene does not always maintain its original stereoregulating capability. It is reported that syndiospecific metallocene $Me_2[(Cp)(Flu)]ZrCl_2$ is transformed to a highly isospecific catalyst when supported on SiO_2[103].

By analogy with homogeneous metallocene/MAO systems Kaminsky *et al.*[54], Chien *et al.*[56], Chen *et al.*[57] suggest a cation like active species, (Cp_2MMe^+. SiO^-) is formed (shown in **Scheme 1.4**) on silica supported catalysts. Recently Sacchi *et al.*[67] prepared isospecific $Et[Ind]_2ZrCl_2$ and aspecific $(Ind)_2ZrCl_2$ catalysts supported on SiO_2. The authors suggested that the nature of active species on silica is different depending upon the manner of supporting the metallocene. The reason could be that the formation and stabilization of cationic Zr^+ species is more difficult in case of supports without a strong lewis acid character (such as SiO_2). Nevertheless cationic species can only be formed if the cocatalyst is acidic enough to remove the alkylligand.



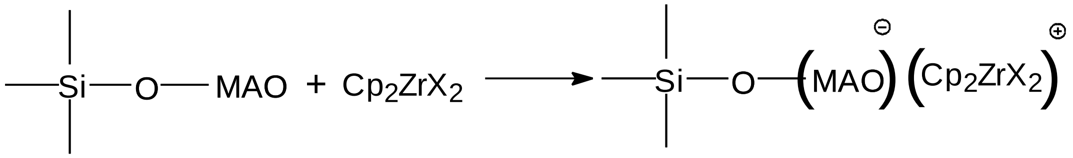
Scheme 1.4 : Formation mechanism of ($SiO^-.Zr^+$) species

In case of supports, such as silica, pretreated with MAO or trialkylaluminum before immobilization with metallocene Soga and co-workers[24a,52,58] proposed that MAO reacts chemically with the silica surface through the -OH groups (**Equation 1.1**) whereby CH_4 is evolved. In the latter stages the metallocene reacts with MAO fixed on SiO_2 surface to form the supported metallocene which can then be activated either with AlR_3 or with MAO (**Equation 1.2**).



$$-\text{Si}-\text{OH} + \text{MAO} \longrightarrow -\text{Si}-\text{O}-\text{MAO} + CH_4$$

Eq. 1 1

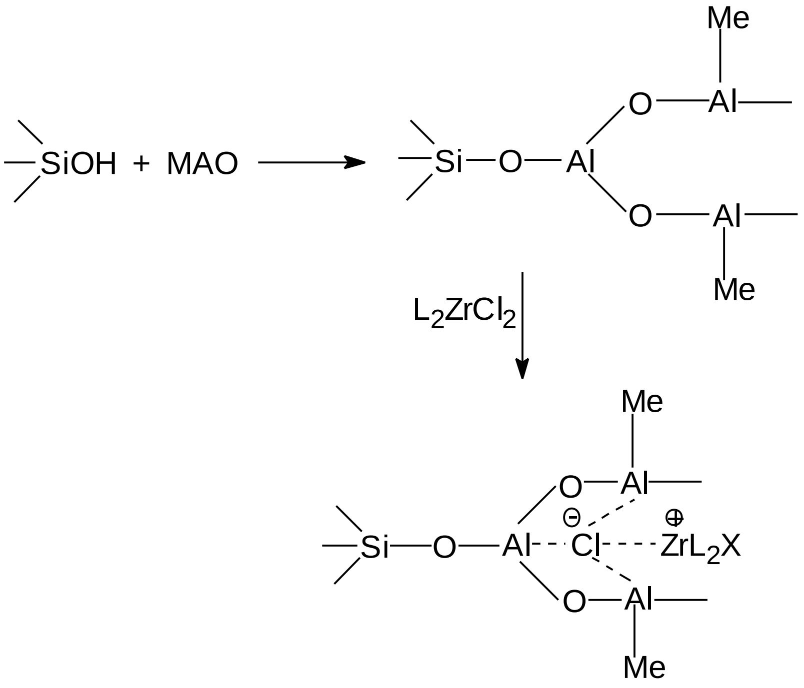


$$-\text{Si}-\text{O}-\text{MAO} + Cp_2ZrX_2 \longrightarrow -\text{Si}-\text{O}-(\text{MAO})^{\ominus}(Cp_2ZrX_2)^{\oplus}$$

Eq. 1.2

$X = CH_3$ or Cl

A slightly more detailed picture has been provided by Chien *et al.*[56] and Chen *et al.*[57]. They assumed the ionic species are trapped and stabilized by multicoordinating "Crown" aluminoxane complexes. It is speculated that the cationic zirconocene species may float over the SiO_2 surface, much like in solution as the latter is essentially covered by MAO (**Scheme 1.5**).



X = CH_3, Cl; L = ligand framework

Scheme 1.5 : Formation mechanism of zirconocenium species for MAO mediated catalysts

The structures as shown in scheme 1.5 are obviously highly simplified. Several types of surface groups may be present on the surface and depending on the nature of interaction of these groups with the surface different active species may be formed. In this context chemical and thermal treatment of the support may play a critical role on the nature of the surface groups of the support and thus the nature of the active species formed upon supporting of metallocene.

Ihm *et al.*[62] observed by IR spectroscopy, the presence of different types of surface groups on commercial silica: single hydroxyl, hydrogen bonded hydroxyl, paired hydroxyl and adsorbed water. Thermal treatment of the support at 600°C under N_2 atmosphere leaves only the single hydroxyl group on the surface. Thus by appropriate treatment it is possible to control the proportion of each type of hydroxyl surface group. Collins *et al.*[61] have studied well characterized supports presenting different proportions of surface hydroxyl groups: hydroxylated, partially dehydroxylated and fully dehydroxylated SiO_2 and Al_2O_3. With silica supports very low activities are observed. It was speculated that metallocene compounds react with surface hydroxyls of silica during adsorption step yielding inactive support by organoaluminum compounds, MeLi, or silane compounds prevent the deactivation of metallocene by reaction with silanol functionalities.

1.6 CONCLUSIONS AND FUTURE PERSPECTIVES

The versatility of metallocene and other single site catalysts will likely result in their utilization in a wide range of olefin polymerization processes in industry. The facile control of polymer properties by ligand, cocatalyst, monomer feed or process variation potentially allows a broad variety of different polymers with defined structure, to be produced in a single highly flexible plant. The most remarkable aspect of metallocene based catalysts appears to be that they can produce an unprecedented variety of structural variations in polyolefins. The range of stereo and regioregularities, molecular weights and polydispersities of copolymers and cyclopolymers available with these catalysts exceeds that accessible with classical heterogeneous Ziegler-Natta catalysts and open up new possibilities for producing tailored polyolefin materials.

The evolution of advanced catalysts and catalytic processes based on a rational understanding of the catalyst structure is now beginning to increasingly influence the design of new polyolefin catalysts. Practical application of metallocene catalysts requires their heterogenization on solid supports such as silica and alumina. Metallocene catalysts that are heterogenized on suitable supports can thus be used in existing Ziegler-Natta production facilities such as gas phase or slurry phase polymerization processes[15,16].

Among the feature that distinguish supported-metallocenes from their homogeneous counterpart are the following :

⇒ low Al/Metal mole ratio to obtain high activity;

⇒ ability to be activated by simple alkylaluminums such as TMA, TIBAL, TEAL without the use of MAO.

⇒ a more limited dependence of polymerization activity on MAO and Al/metal mole ratio. This can be related to slower catalyst deactivation by bimolecular processes due to the immobilization of active sites on the surface support.

⇒ supported metallocene systems are generally less active polymerization catalysts than

Enough understanding has developed which enables the selection of supports with optimal composition, particle size, pore size distributions and surface hydroxyl group density as well as their treatment with various alkylaluminums and aluminoxanes activators[15,16] prior or subsequent to adsorption of the metallocene complex. The more advanced of these protocols require only limited excess ratios of alkylaluminum activators per metallocene unit; Al/Metal ratios of roughly 100 to 400 : 1 appear to give entirely satisfactory performance for these surface supported metallocene catalysts[16]. In contrast to $MgCl_2$ supported heterogeneous Ziegler-Natta catalyst, silica supported metallocene catalysts are practically free of chlorine. This could be an advantage from an ecological standpoint when the chemical or thermal recycling of polymer products reaches a larger scale[104].

Supports pretreated with MAO exhibit high catalyst activities but lead to polymers with only slightly improved properties (T_m, isotacticity and M_w). These type of catalysts are found to be sensitive to the nature of the cocatalysts, to the Al/metal ratio and also to other experimental conditions resembling homogeneous metallocene catalysts[24a,57,67].

Catalysts prepared by direct impregnation of metallocene with the support lead to much more efficient catalysts for the synthesis of polypropylene with characteristics similar to those observed with traditional Ziegler-Natta catalysts. It is thus proposed that the interaction between the support and the metallocene may affect the metallocene structure and form a more stabilized and rigid species on the support surface[54,57]. These catalysts, however, possess very low catalyst activity, in view of the low concentration of the active species and due to deactivation occurring during the prolonged and high temperature impregnation process as well as a low rate of propagation[57]. Rigidly immobilized metallocenes seems to be a promising alternative for the synthesis of highly stereospecific catalysts, but their preparation is still very complex, and may result in mixtures of meso and racemic active site isomers, with the subsequent formation of isotactic and atactic polymer. Their activities are still very low and different isospecific sites may be formed in these catalytic systems.

The greatest challenges involved in utilizing the supported catalyst technology in an economically feasible process are (a) reduction of high cost of the cocatalyst, (b) control of polymer morphology and adaptation of the catalysts for use in existing polymerization plants. Although the exact approaches undertaken to overcome these hurdles ar catalysts will play a very important role for the production of polyethylenes and polypropylenes.

It is clear that the potential of supported metallocenes and related catalysts for olefin polymerization are yet to be fully exploited. The polymerization of functionalized olefins and internal cyclic olefins may need design of supported catalysts[105]. Copolymers constitute one of the area of greatest interest, partly because of the variety of new materials that are potentially accessible. Development of new catalyst, based both on empirical and theoretical predictions of catalyst structure-performance relationships, is expected to meet this and other challenges in the future, leading to a wide range of new polymeric materials.

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2.1 OBJECTIVES IN UNDERTAKING THE PRESENT INVENTION

Metallocenes such as Cp_2MCl_2 (M = Ti, Zr, Hf) in the presence of aluminum alkyls constitute a group of homogeneous catalysts for olefin polymerization[1]. Catalyst systems based on bis(cyclopentadienyl)titanium (IV) dichloride and dialkylaluminum chlorides were first shown by Breslow and Newburg to polymerize ethylene[2]. However, these catalysts show rapid rate decay and loss of catalyst activity within minutes of start of polymerization, especially, at temperature higher than 30°C[3]. The discovery of homogeneous, highly active and stereospecific matallocene-MAO catalysts stimulated renewed commercial and scientific interest in this area[4, 5, 6]. These catalysts based on group IV bent metallocenes and a cocatalyst generally contain a single kind of active site and offer potential advantages over traditional multisite Ziegler-Natta polymerization catalysts.

Homogeneous metallocene-MAO catalyst system for olefin polymerization is characterized by high catalyst activities, good copolymerization activities, narrow polydispersities, and excellent control on stereoregularity[7-9]. However, from the point of practical catalysis, it possesses some drawbacks. These are, the need for a large excess of MAO (Al/Metal > 10^5) for obtaining reasonable polymerization activities, inability to use the catalyst in the gas-phase or slurry processes, tendency to cause reactor fouling and poor control on polymer morphology. Three different strategies are evident in the literature to overcome these problems.

In the first approach, a single two component catalyst based on group IV metallocene dialkyls with a stoichiometric or near stoichiometric amount of an activator such as $[C_6H_5(CH_3)_2NH^+][B(C_6F_5)_4^-]$[10], $[(C_6H_5)_3C^+][B(C_6F_5)_4^-]$[11] or $[B(C_6F_5)_3^-]$[12] was developed to generate a single site cationic species. Jordan and co-workers found that ethylene polymerization proceeds effectively in presence of dicyclopentadienyl zirconium alkyl complexes in the absence of a cocatalyst[13]. Ewen *et al.* showed that cationic zirconium complex such as $Et[IndH_4]_2ZrMe^+$, $iPr[Flu(Cp)_2]ZrMe^+$ show very high activity for propylene polymerization[14]. These single site cationic species of d^0, 14 e^- metallocenes show low to medium polymerization activities without any cocatalyst. However, they are, generally, unstable at higher temperatures and very sensitive to light.

The second approach involves, supporting a metallocene on an inert carrier such as silica, alumina and magnesium chloride with or without aluminum alkyls or aluminoxanes such as MAO. One of the early attempts in this direction was made by Slotfeldt-Ellingsen and co-workers. Cp_2TiCl_2 was supported on silica gel and used to polymerize ethylene using Et_nAlCl_{3-n} as cocatalyst[15]. Soga and co-workers reported supported ethylenebis (tetrahydroindenyl)zirconium(IV)dichloride for the isospecific polymerization of propylene[16]. SiO_2, Al_2O_3 and $MgCl_2$ pretreated with MAO were used as supports and trialkylaluminums as cocatalyst. Al_2O_3 and $MgCl_2$ gave low molecular weight polymers with broad polydispersities. On the contrary, SiO_2 gave narrow poldispersities and low catalyst activity. Recently, Collins *et al.* and Chien *et al.* have shown that the isospecific polymerization of propylene can be performed with supported chiral ansa-metallocene in conjunction with MAO[17, 18]. The most active supports were those derived from partially dehydroxylated SiO_2 or Al_2O_3 that has been pretreated with excess of trialkylaluminums. Kaminsky *et al.* have disclosed a refined route for the preparation of silica supported ansa-metallocene catalyst which yields high molecular weight and high melting polypropylene with a performance similar to heterogeneous catalysts[19]. Recently, Ihm *et al.* employed a slightly modified procedure in order to support Cp_2MCl_2 (M = Ti, Zr, Hf) catalysts on silica. They replaced MAO by $Al(C_2H_5)_3$ and by C_2H_5MgCl during the SiO_2 pretreatment[20]. Lee *et al.*[21] developed another method to synthesize Cp_2ZrCl_2 supported on SiO_2. Hydrated silica was prepared by two procedures. In the first one silica was fully hydrated in deionized water, filtered and fluidized in a column under N_2 gas flow, yielding silica with 45 wt. % of water. In the second method, SiO_2 was fluidized with wet N_2. Silica with 16 wt. % of water was obtained. The catalyst support was then prepared by contacting the hydrated silica (H-SiO_2) with a solution of TMA in toluene. The supported catalysts were then synthesized by addition of metallocenes onto the support by direct impregnation method and used for the polymerization of ethylene. More recently, Jin *et al.* showed SiO_2 supported neodymocene catalyst used for the polymerization of ethylene[22].

The objective of this present work is therefore to examine new methods for supporting homogeneous metallocene catalysts on different supports such as SiO_2, $MgCl_2$ and SiO_2-$MgCl_2$. Further, it is proposed to study the polymerization efficiency of these catalysts in conjunction with different aluminum alkyls or aluminoxane compounds under various polymerization processes using these solid catalysts capable of exhibiting high catalyst activities, especially at high temperatures.

2.2 APPROACHES: Synthesis And Charcterization Of Supported Catalysts And Ethylene Polymerization Using This Catalysts

2.2.1 $MgCl_2$ supported Cp_2TiCl_2 catalyst

2.2.1.1 Preparation of a bis(cyclopentadienyl)titanium (IV) dichloride supported on $MgCl_2$ *(prepared via Grignard decomposition) by exploiting the solubility of* $MgCl_2$ *in tetrahydrofuran(THF).* $MgCl_2$ *thus prepared has been shown to exist in dactive form.*

$$ClCH_2CH_2Cl + Mg \xrightarrow{THF} MgCl_2.2THF + C_2H_4\uparrow$$

$$MgCl_2.2THF + Cp_2TiCl_2 \longrightarrow Cp_2TiCl_2\text{-}MgCl_2.2THF$$

2.2.1.2 Characterization of the solid catalyst by means of FT-IR, XRD, TGA, surface area analyzer, ^{13}C *NMR.*

2.2.1.3 Polymerization of ethylene using this catalyst in conjunction with MAO as cocatalyst, in xylene or n-hexane as diluents at one bar ethylene pressure will be investigated.

2.2.1.4 Mechanism of ethylene polymerization using the solid catalyst and catalyst structure will be studied.

2.2.2 $MgCl_2$ supported Cp_2ZrCl_2 catalyst

2.2.2.1 Preparation of a bis(cyclopentadienyl) zirconium (IV) dichloride supported on $MgCl_2$ *by exploiting the solubility of* $MgCl_2$ *in THF.*

2.2.2.2 Characterization of the solid catalyst by means of FT-IR, XRD, surface area analyzer, TGA.

2.2.2.3 Polymerization of ethylene and higher α*-olefins using this solid catalyst in conjunction with MAO as cocatalyst, in xylene or n-heptane as diluents at 1 bar as well as 5 bar ethylene pressure will be investigated.*

2.2.2.4 Mechanism of ethylene polymerization, active site concentration and catalyst structure will also be studied.

2.2.3 SiO_2-$MgCl_2$ supported Cp_2TiCl_2 catalysts

2.2.3.1 Preparation of bis(cyclopentadienyl) titanium(IV) dichloride supported on SiO_2*-*$MgCl_2$ *will be studied.*

2.2.3.2 Characterization of the catalysts by means of FT-IR and surface area analyzer measurements.

2.2.3.3 Polymerization of ethylene using these solid catalysts in conjunction with alkyl aluminums and aluminoxanes as cocatalyst, in xylene as diluent at 1 bar and at 5 bar ethylene pressure will be investigated.

2.2.3.4 The mechanism of ethylene polymerization as well as catalyst structure will be studied.

2.2.4 SiO_2-$MgCl_2$ supported Cp_2ZrCl_2 catalysts

2.2.4.1 Preparation of a bis(cyclopentadienyl) zirconium(IV) dichloride supported on SiO_2*-*$MgCl_2$ *will be studied.*

2.2.4.2 Characterization of the catalysts by means of FT-IR and surface area analyzer measurements.

2.2.4.3 Polymerization of ethylene using these solid catalysts in conjunction with aluminum alkyls or aluminoxanes as cocatalysts, in xylene as diluent at 1 bar and 5 bar ethylene pressure will be investigated.

2.2.4.4 The mechanism of ethylene polymerization, active site concentration, and catalyst structure will be studied.

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3.1 INTRODUCTION

Metallocenes catalysts are sensitive to moisture and the active centers in the case of Ziegler-Natta polymerization are susceptible to termination by protic sources. Therefore, all reagents and solvents should be carefully purified and dried prior to use.

In this chapter, materials used, purification of the reagents, methods of polymerization and analytical techniques in the present study are discussed.

3.2 MATERIALS

Cp_2TiCl_2, Cp_2ZrCl_2 (Aldrich, USA) and methylaluminoxane (MAO, Schering A-G, Germany), diethylaluminum chloride (DEAC, Schering A-G, Germany), triisobutylaluminum (TIBAL, Schering A-G, Germany) trimethylaluminum (TMA, Schering A G, Germany) were used as received. The MAO as obtained had a Me/Al ratio of 1.7, free trimethylaluminum 31 wt. % and Al content 10.9 wt. % in toluene. SiO_2 (grade 952) was obtained from W. R. Grace & Co., USA. It had a surface area of about 280 m^2/g, pore volume 1.65 g/cc, free hydroxyl (-OH) group content 2.8 mmol/g. Anhydrous magnesium chloride was obtained from Toho Chemical, Japan. Xylene, tetrahydrofuran (THF), n-hexane and n-heptane were purified by refluxing over sodium and freshly distilled under nitrogen before use. 1-hexene (Aldrich, USA) and 1,2-dichloroethane were purified by refluxing over CaH_2 and freshly distilled before use. Polymer-grade ethylene was obtained from the gas cracker complex of Indian Petrochemical Corporation Ltd., Nagothane, India. It had a moisture content of < 4 ppm (Shaw Model SHA-TR moisture analyzer) and an oxygen content of < 3 ppm (Braun oxygen analyzer). All manipulations involving air-sensitive compounds were performed inside a Labconco Model 50004 inert atmosphere glovebox continuously purged with high purity N_2 from a generator (Spantech Model NG 300-1, England) or under a positive pressure of high purity N_2 using standard bench top inert atmosphere techniques.

3.3 ANALYSIS:

Titanium was estimated by UV-Visible spectroscopy using a Hewlett Packard 8452A Diode array spectrophotometer. Zirconium was estimated by Inductively Coupled Plasma Model No. Jobin Yvon JY 38, taking standard solution of zirconium salt (Aldrich, USA).

were determined using an Ubbelohde viscometer in decalin as solvent at 135°C. Polydispersities and molecular weight of polyethylene samples were measured by GPC (Waters 150-C ALC/GPC) at 135°C in trichlorobenzene solvent. μ-Styragel columns (10^5, 10^4, 10^3, 500 A) were used and the peaks were calibrated using standard polystyrene. A 0.3-0.4 % w/v solution was used at a flow rate of 1.0 mL/min. FT-IR of catalysts were recorded by Perkin Elmer 16PC series in Nujol. Powder XRD was recorded on a Phillips PW 1730 Spectrometer using Nickel filtered CuK_α radiation at a frequency of 1000 Cps. Thermogravimetric analysis of the catalysts were recorded on a Perkin Elmer TGA 7 at a heating rate of 10°C /min. Surface area of the catalysts were taken on a Coulter, Omnisorp 100 CX. The specific area of the catalysts were obtained from isothermic adsorption of nitrogen at liquid nitrogen temperature. ^{13}C CPMAS NMR of the solid catalysts were recorded at room temperature on a Bruker MSL 300 Model Spectrometer operating at 75.5 MHz for ^{13}C nuclei. DSC of the polymers and copolymers were measured on a Perkin Elmer DSC 7, at the heating rate of 10°C/min. Copolymer compositions were determined by ^{13}C NMR. The ^{13}C NMR of the copolymers were recorded at 120°C on a Bruker MSL 300 Model Spectrometer operating at 75.5 MHz for ^{13}C nuclei. The solution for analysis were prepared by dissolving 150 mg of the copolymer in 2 mL of 1, 2, 4-trichlorobenzene containing about 15 % by volume of deuterated benzene for internal lock. The spectra were obtained under conditions permitting quantitative analysis by allowing pulse delay of 8 seconds. In all polymerization experiments MAO was used as 5 wt. % (as Al) solution in xylene.

The conditions used for the ^{13}C NMR analysis, flip angle 45 °, pulse delay = 8 sec. The crystallinity of the copolymers was calculated from the heat of fusion using the following equation

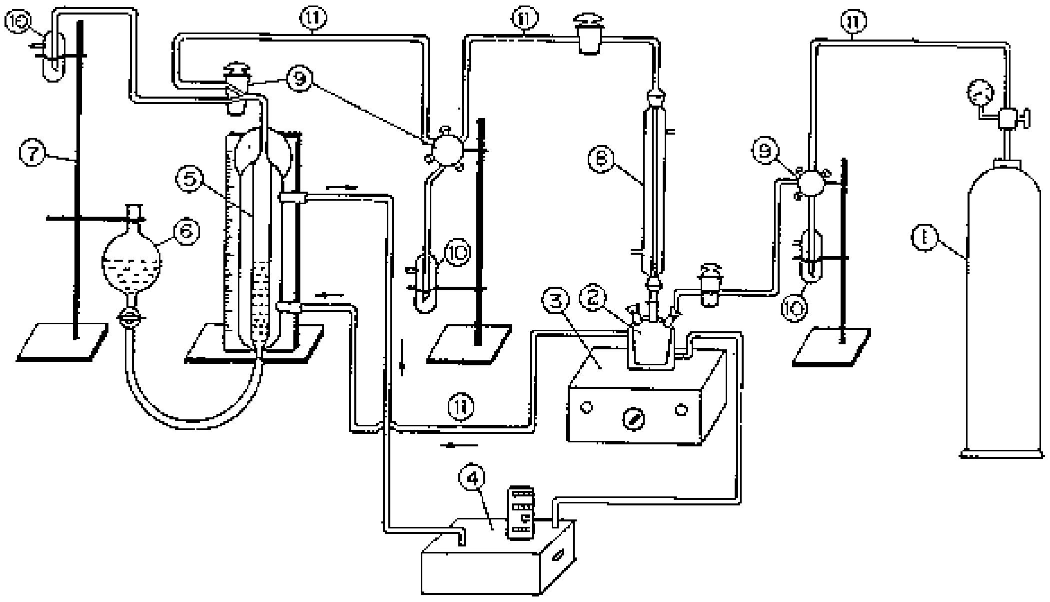
$$\text{Crystallinity (\%)} = \Delta H_f / \Delta H_f^{\circ} \times 100$$

where ΔH_f is the heat of fusion of the samples as determined from the DSC curve and ΔH_f° is the fusion of the folded-chain polyethylene crystals (290 J/g).

3.4 POLYMERIZATION TECHNIQUES

3.4.1 Description of apparatus used for ethylene polymerization under 1 bar pressure

A glass tube of capacity 3000 mL with a glass jacket, a three way stop cock and a supporting parallel glass tube was fabricated. The fabricated unit was mounted on a wooden platform. Graph sheets were pasted on the wooden frame neatly to calibrate the fabricated glass apparatus. Upon calibration, it was found that one unit on graph sheet corresponds to 30 mL of ethylene. The calibrated glass tube was used as a gas burette for measuring the differences in displacement of volume of ethylene during the polymerization. A three neck flat bottomed jacketed glass vessel of capacity 100-150 mL was used as the polymerization cell.



1 - Ethylene gas cylinder
2 - Glass reactor
3 - Magnetic stirrer
4 - Haake water bath
5 - Calibrated gas burrette on wooden platform
6 - Separating funnel with silicone oil
7 - Iron stand
8 - Glass condenser
9 - Three way stop cocks
10 - Silicone oil bubbler
11 - Polyethylene pressure tubing

Fig 3.1 : Ethylene polymerization set up at one atmosphere pressure

A separating funnel of capacity 4000 mL filled with silicone oil was connected through a PVC tubing to the gas burette. The reaction cell was mounted on a magnetic stirrer, which was connected to the gas burette via a T-shaped stopcock using pressure tubing. Two gas burette as shown in the diagram. The reaction cell was dried at 155°C, overnight and throughly checked for leaks by running a blank experiment under one atmosphere pressure for 2-3 hours. The silicone oil was saturated with ethylene gas before the start of experiment.

3.4.2 Polymerization of Ethylene

Polymerization was performed with the assembly described previously at one bar pressure in xylene and n-hexane. A gas burette with a reservoir containing silicone oil was used to feed ethylene continuously to the cell. The reaction cell was dried at 155°C overnight and cooled under ethylene. Required amount of catalyst was transferred into the cell inside the glove-box. Solvent was introduced into the cell using a hypodermic syringe. The solvent was saturated with ethylene. Polymerization was initiated by the addition of cocatalyst (MAO). The reaction temperature was maintained by circulating water from a thermostat through the jacket of the cell and the gas burette. Ethylene uptake was measured as a function of time. The reaction was terminated by addition of acidified methanol. The polymer was filtered, washed with methanol and dried at 40°C under vacuum.

3.4.3 Polymerization of ethylene at 5 bar pressure

50 mL of xylene (previously treated with trimethylaluminum in order to remove impurities) and MAO (required amount) were introduced under N_2 atmosphere into a stainless steel Sotelem reactor with a capacity of 500 mL, equipped with a stirrer rotating at 1800 rpm and with a heating and cooling system. The reactor was heated to 200°C and cooled under N_2 to the desired polymerization temperature. A stainless steel reservoir was used to feed ethylene continuously. Prescribed amount of previously prepared catalyst along with 20 mL xylene was transferred into the reactor by means of a separating funnel. Another 30 mL of xylene was added to the reactor through the separating funnel. The solvent was saturated with ethylene. Polymerization was initiated by stirring keeping ethylene pressure of 5 bar. The reaction was terminated by adding acidified methanol. The polymer was filtered, washed and dried at 40-50°C under vacuum.

3.4.4 Copolymerization of ethylene and 1-hexene

Copolymerization of ethylene and 1-hexene were carried out usingxylene as diluent at one feed ethylene continuously to the cell. The reaction cell was dried at 155°C overnight and cooled under ethylene. Required amount of catalyst was transferred into the cell inside the glove-box. Solvent (50 mL, previously treated with very low amount of TMA in order to remove impurities) was introduced into the cell using a hypodermic syringe. The solvent was saturated with ethylene. Prescribed amount of 1-hexene was added into the system by means of a syringe. Copolymerization was initiated by the addition of cocatalyst (MAO). The reaction temperature was maintained by circulating water from a thermostat through the jacket of the cell and the gas burette. Ethylene uptake was measured as a function of time. The reaction was terminated by addition of acidified methanol. The polymer was filtered, washed with methanol and dried at 40°C under vacuum.

4.1 INTRODUCTION

Catalyst systems based on bis(cyclopentadienyl) titanium (IV) dichloride in conjunction with dialkylaluminum chlorides were first shown by Breslow and Newburg to polymerize ethylene[1]. However, these catalysts show rapid rate decay and loss of activity within minutes of start of polymerization and at temperature, higher than 30°C[2]. The discovery that other group IV metallocenes (Cp_2MX_2, M = Zr, Hf; X = Cl, Me) in conjunction with methylaluminoxane (MAO) give extremely high rates of polymerization and acceptable catalyst life times has led to significant scientific and industrial interest in this area[3-5]. Metallocene based catalysts allow unprecedented control on polyolefin structures through catalyst design and have enabled the synthesis of entirely new families of homo and copolymers of ethylene and α-olefins.

Amongst the metallocenes, zirconium based catalyst systems have attracted the most attention. Fewer studies have been reported on the titanium based metallocene, presumably, on account of its poor catalyst properties. Cp_2TiCl_2/MAO polymerize ethylene at 20°C with a catalyst activity of 900 kg polyethylene/g-Ti. h. Mpa[6]. However, at temperatures higher than 50°C the catalyst loses its activity rapidly. On the contrary, the titanium based catalysts have assumed commercial significance in case of the mono-Cp catalyst systems[7].

It has been recently shown that supporting Cp_2TiCl_2 on magnesium chloride results in interesting modification of the catalyst behavior towards polymerization of ethylene[8]. Unlike Cp_2TiCl_2, the supported Cp_2TiCl_2 polymerizes ethylene in conjunction with triisobutylaluminum (TIBAL). Although the catalyst activity was modest, conversions were quantitative and high polymer molecular weights were obtained. Significantly, the catalyst system showed a steady state kinetic behavior and absence of rate decay upto one hour at 40°C. These observations are indicative of a catalytically active titanium center of unusual stability, presumably, as a result of interaction of the active center with the $MgCl_2$ support. Significant modulation of the activity of titanium based catalysts on $MgCl_2$ support are well documented in the heterogeneous catalyst systems[9].

Titanocenes in presence of MAO, produces stable cationic species at -20°C which is active for olefin polymerization[10]. Therefore, the study of $MgCl_2$ supported Cp_2TiCl_2 was extended to ethylene polymerization using MAO as cocatalyst. The objective was to explore the effect of the support on catalyst activity and stability of the active centers.

4.2 EXPERIMENTAL PART

4.2.1 Synthesis of the catalyst

In a three neck r.b. flask equipped with magnetic needle, reflux condenser, addition funnel, N_2 inlet and outlet which was flame dried and cooled under N_2. Magnesium turnings (0.4g, corresponding to 0.164 mol) activated by a pinch of iodine was placed followed by addition of 40 mL THF and the slurry was stirred at a temperature of 25-30^{0}C for 1/2 h. A mixture of 1,2-dichloroethane and THF (1:1) was added to the slurry by means of a syringe over a period of 1/2 h. It was observed that all the Mg turnings were slowly dissolved in THF with the formation of a clear solution. Steady evolution of ethylene gas indicates the decomposition of the intermediate chloroethyl magnesium complex with the subsequent formation of $MgCl_2$.THF complex and its dissolution into THF. Cp_2TiCl_2 (0.75 g) dissolved separately in 20 mL of THF and was added to the previous solution of $MgCl_2$ over a period of 15 min, at a temperature of 25-30°C. The whole solution was then added into a flask containing 300 mL of n-hexane when a white precipitates seperated out. Finally the whole precipitates was washed 3-4 times by n-hexane (using 50 mL each time) and dried under vacuum and kept for further studies.

The solid catalyst thus prepared contain Ti = 3.02 wt. %; Mg = 10.3 wt. %. This was designated as catalyst A in further discussion.

4.2.2 Extraction of the catalyst

Approximately 1 g of the Mg-Ti catalyst was placed in a three neck jacketted flask under N_2 atmosphere. Xylene (100 mL) was added to the flask and heated to 70^{0}C for 30 min. The flask was cooled to room temperature and the solid catalyst was allowed to settle down. The top xylene layer was decanted using a cannula. The solid catalyst was washed repeatedly with fresh xylene. The solid was dried in vacuum at 40^{o}C and transferred to vials for storage.

4.2.3 Aging of catalyst

Catalyst aging experiments were carried out in a stirred glass cell at 70°C. The reactor was assembled while still hot and after being purged with dry N_2 catalyst was transferred into the reactor inside the glove box. Dry xylene (50 mL) was introduced into the reactor by means of a hypodermic syringe. Once the temperature of the reactor was stabilized, the cocatalyst MAO was added into the reactor, under N_2 atmosphere. After an elapsed aging time, the reactor was connected to the ethylene gas burrette.

4.3 RESULTS AND DISCUSSION

4.3.1 Characterization of catalyst

The solid Cp_2TiCl_2-$MgCl_2$ catalyst analyzed for 3 % by wt. titanium and 9.8 % by wt. magnesium and which corresponds to an empirical formula $MgTi_{0.15}Cp_{0.30}Cl_{1.8}THF_{1.7}$. The catalyst had a surface area of 24 m^2/g. The presence of cyclopentadienyl ligand[11] and THF[12] in the solid catalyst was evidenced by the presence of peaks at 1462 and 810 cm^{-1} and 1038 and 892 cm^{-1} respectively in the IR spectrum (**Fig. 4.1**). A comparison of the ^{13}CP-MAS NMR of the solid supported catalyst with the homogeneous Cp_2TiCl_2 is shown in **Fig. 4.2**. The spectra show a signal at 120.96 ppm corresponding to the cyclopentadienyl ligand attached to titanium and a signal at 25.77 and 68.96 ppm which correspond to the THF moiety present on the solid catalyst (**Fig. 4.3**). Powder XRD of the Mg-Ti catalyst showed sharp peaks, indicating that the complex is highly crystalline (**Fig 4.4**). The spectrum showed the absence of strong reflection at $2\theta = 34.2^o$ and a reduction at $2\theta = 20^o$. Furthermore, a new reflection appeared at $2\theta = 32.1^o$ corresponding to that of $MgCl_2.2THF$ complex. Thermogravimetric analysis (TGA) of the catalyst complex was different from that of $MgCl_2.2THF$ and Cp_2TiCl_2. The complete decomposition of the catalyst occurred in three stages as shown in **Fig 4.5**. Since the weight loss is attributed to loss of THF, the results imply that all the THF is not complexed in an identical manner.

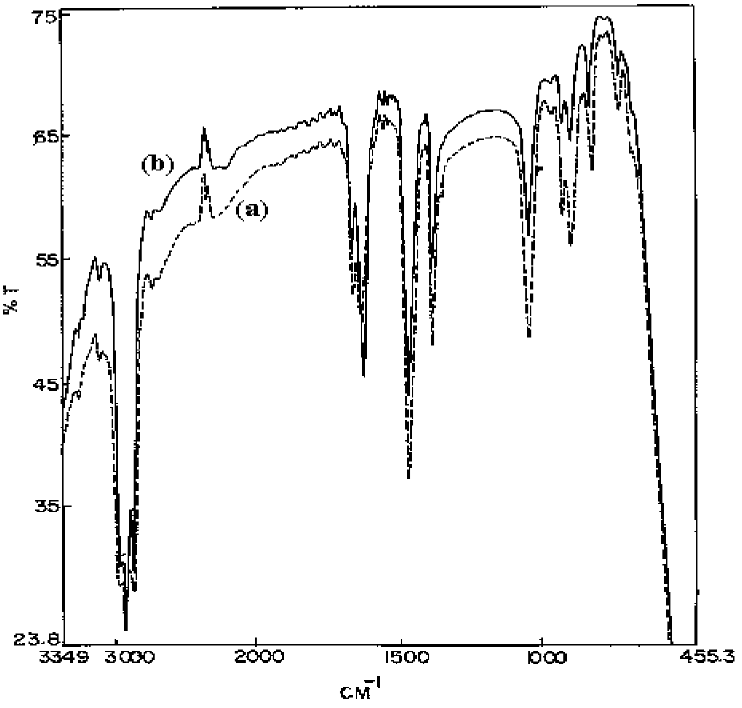


Fig. 4.1 : FT-IR spectra of $MgCl_2$ supported Cp_2TiCl_2 catalysts. (a) catalyst A, (b) catalyst B.

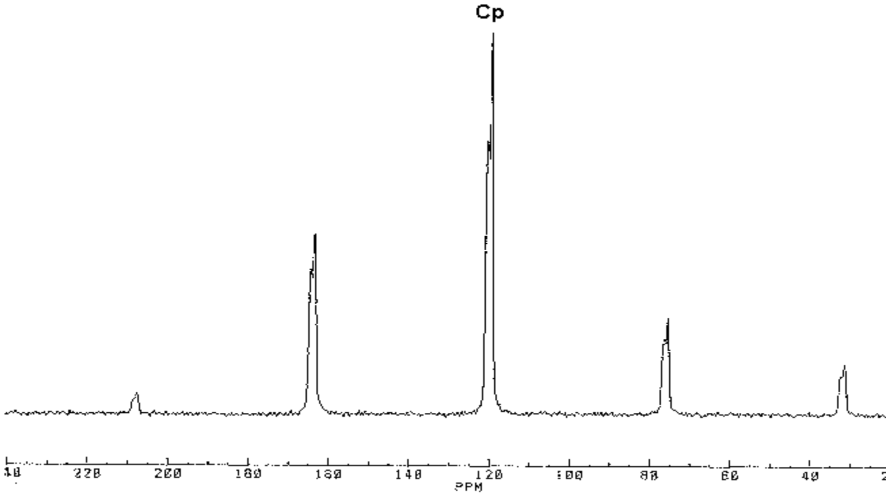


Fig. 4.2 : ^{13}C CP MAS NMR of homogeneous Cp_2TiCl_2

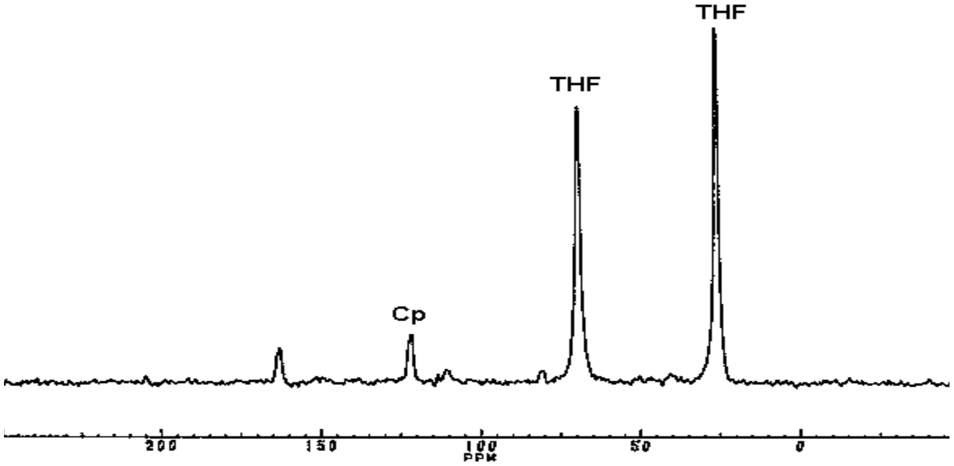


Fig 4.3 : ^{13}C CP MAS NMR of catalyst A

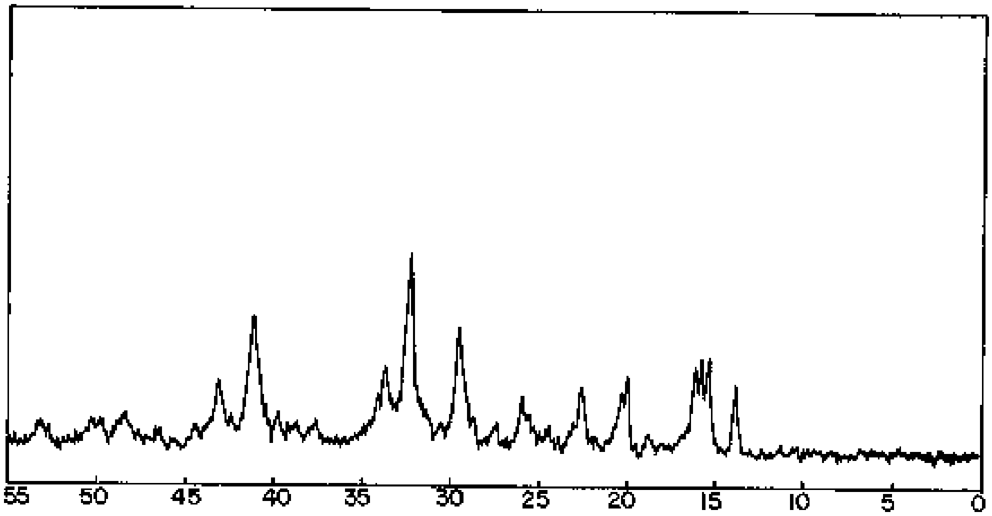


Fig. 4.4 : XRD of the unextracted $MgCl_2$-Cp_2TiCl_2 catalyst

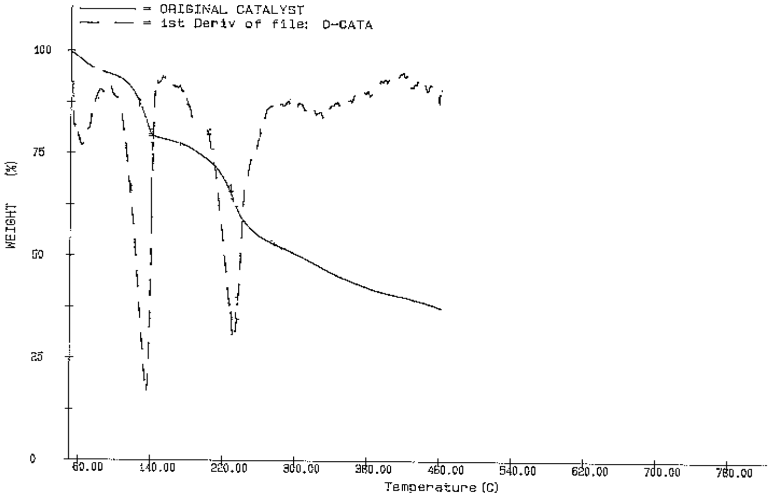


Fig. 4.5 : Thermogravimetric analysis of catalyst A

Catalyst A was subjected to extraction in hot xylene to remove any soluble titanocene. Catalyst A after extraction gave a material (designated as catalyst B) with a Ti content of 1.44 % and Mg content of 13.8 wt. % which correspond to an empirical formula $MgTi_{0.052}Cp_{0.104}Cl_{1.5}THF_{1.2}$. This indicates that approximately 50 % by wt. of the titanocene was extracted by hot xylene. The FT-IR and XRD spectra and ^{13}C CPMAS NMR were identical to that of catalyst A (**Fig 4.1, 4.6, and 4.7** respectively). TGA spectrum of the catalyst B (**Fig 3.8**) also shows a three-stage decomposition.

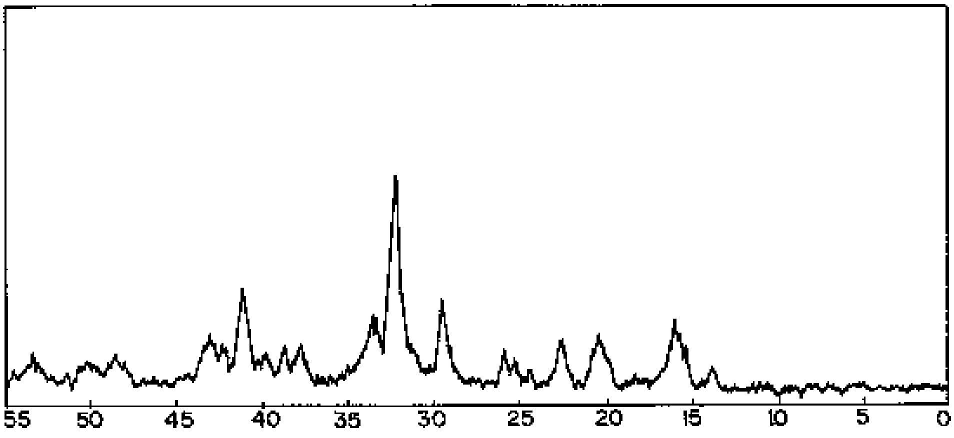


Fig. 4.6 : XRD of extracted catalyst B

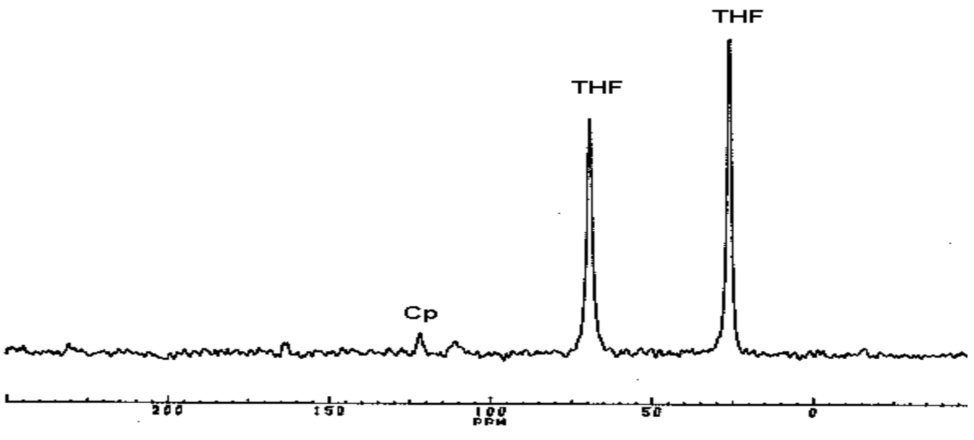


Fig 4.7 : ^{13}C CP MAS NMR catalyst B

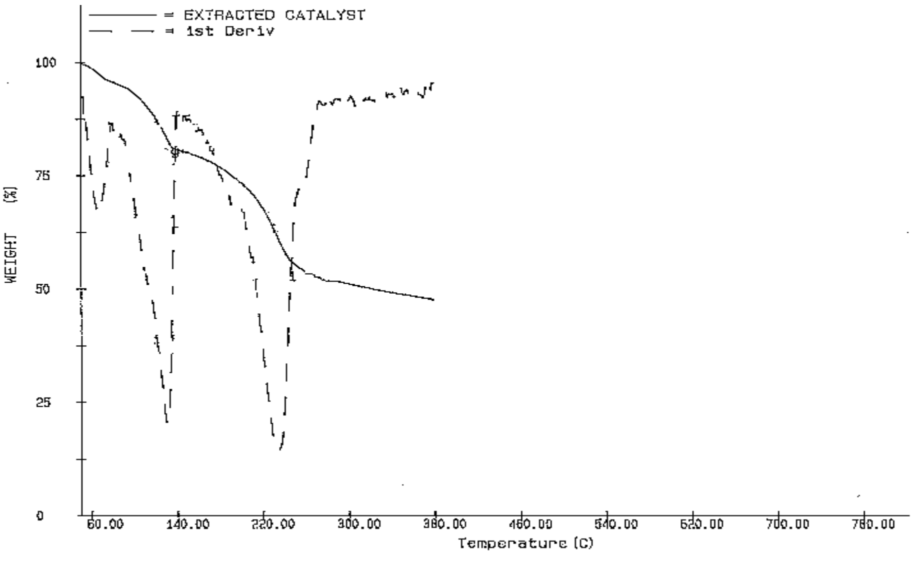


Fig 4.8 : Thermogravimetric analyisis of catalyst B

4.3.2 Polymerization of ethylene

Ethylene was polymerized using the two heterogeneous MgTi catalysts (A & B). The study was aimed to provide an understanding of the effect of heterogenization of homogeneous metallocene catalysts on polymerization of ethylene.

4.3.2.1 In xylene

a) Effect of cocatalyst

It is well known that the homogeneous titanocene catalyst in conjunction with trialkylaluminum is inactive for ethylene polymerization. However, with dialkylaluminum halides ethylene can be polymerized using titanocene. The active species, however is short lived and ethylene absorption ceases within ten minutes of mixing of catalyst and cocatalyst components followed by a rapid rate decay. On the contrary, MAO activated Cp_2TiCl_2 showed high polymerization activity and longer catalyst life times. In contrast to homogeneous Cp_2TiCl_2, the supported $MgCl_2$-Cp_2TiCl_2 catalyst showed significant activity even with TIBAL[13].

Catalyst A and B were used for polymerization of ethylene in xylene as diluent at 40°C using MAO as cocatalyst (**Table 4.1**).

Under identical conditions, the catalyst containing $MgCl_2$ as support show increased catalyst activity. All these catalysts in combination with MAO show similar kinetic curves, with an initial increase in rate followed by a steady decay (**Fig. 4.9**). The peak rate attained by supported catalyst is higher than unsupported catalyst. These results clearly demonstrate the beneficial role of $MgCl_2$ as support for titanium based metallocene catalysts.

Table 4.1 : Polymerization of ethylene using unsupported and supported Cp_2TiCl_2/MAO catalyst[a]

Entry No.	Catalyst	mol Ti x 10^6	mol Al x 10^3	Convn (%)	Activity (kg PE/g Ti.h)	[η] (dL/g)
1	Cp_2TiCl_2	6.4	6.4	100	1.6	1.24
2	Cat. A	4.0	4.0	100	3.2	1.73
3	Cat. B	2.9	2.9	100	4.2	1.40

[a] Polymerization conditions : xylene = 50 mL; temperature 40°C; P = 1 bar; Al/Ti = 1000; time 1 h.

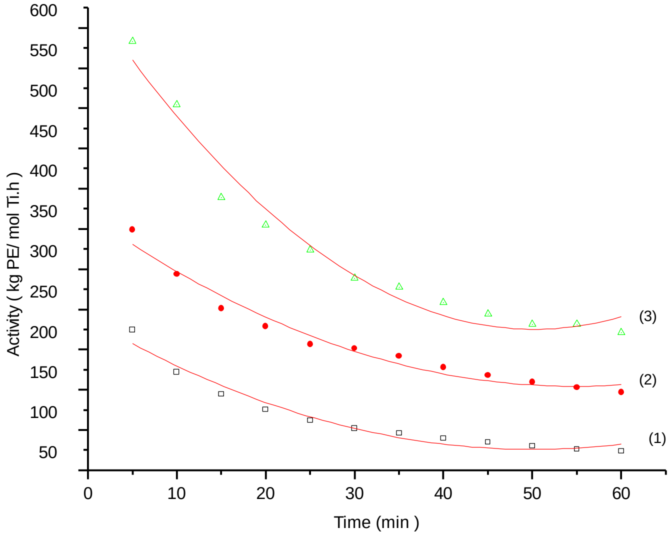


Fig 4.9 : Kinetic profile of ethylene polymerization using supported and unsupported Cp_2TiCl_2/MAO catalyst in xylene (50 mL), T= 40 °C, P = 1 bar, Al/Zr = 500, time = 1 h. (1) unsupported Cp_2TiCl_2; (2) cat. A; (3) cat. B.

b) Effect of Al/Ti ratio

Effect of Al/Ti ratio at constant temperature on ethylene polymerization was studied using the heterogeneous magnesium chloride supported catalysts (A & B) in conjunction with MAO. The results are shown in **Table 4.2**.

For catalyst A, catalyst activity was observed even at Al/Ti mol ratio of 50. However, catalyst B did not show any activity below Al/Ti ratio of 500 (**Fig. 4.10**). Both Catalyst A and B showed a progressive decrease in molecular weight and increasing rate of polymerization with increasing Al/Ti ratio. The catalyst activity increases with increase in Al/Ti ratio.

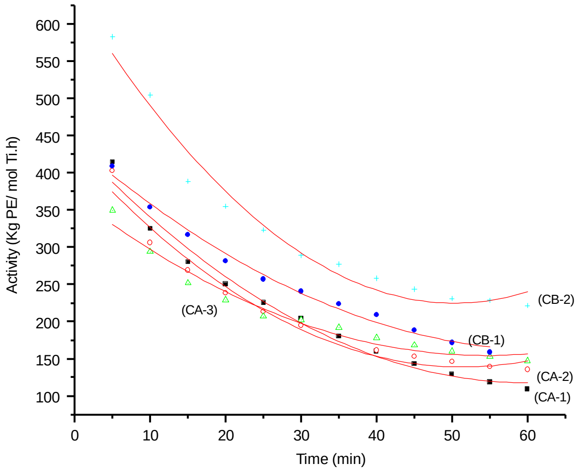


Fig 4.10 : Kinetic profile of ethylene polymerization using $MgCl_2$ supported Cp_2TiCl_2 catalyst at different Al/Ti mol ratio in xylene; (CA-1) : Cat. A at Al/Ti = 100; (CA-2) : Cat. A at Al/Ti = 500; (CA-3) : Cat. A at Al/Ti = 1000; (CB-1) : Cat. B at Al/Ti = 500; (CB-2) : Cat. B at Al/Ti = 1000.

Table 4.2 : Effect of Al/Ti ratio on ethylene polymerization with $MgCl_2$ supported Cp_2TiCl_2/MAO catalyst[a]

Entry No	Al/Ti (mol ratio)	Convn (%)	Activity (kg PE/g Ti.)	[η] (dL/g)
Cat. A				
1	50	100	1.6	2.94
2	100	95	2	2.73
3	250	97	2.2	-
4	500	100	3	1.84
5	1000	100	3.2	1.73
Cat. B				
6	100	-	-	-
7	500	100	3.1	2.26
8	1000	100	4.2	1.40

[a] Polymerization conditions : xylene (50 mL); temperature 40°C; P = 1 bar; amount of Cat. A 5-7 mg; amount of Cat. B 11-14 mg; time 1 h

c) Effect of temperature

Both catalysts A and B showed an increasing rate of polymerization as well as catalyst that of the homogeneous Cp_2TiCl_2 catalyst, which rapidly lose their activity at higher temperature.

Table 4.3 : Effect of temperature on ethylene polymerization with supported Cp_2TiCl_2/MAO catalyst[a]

Entry No	Temp (°C)	Convn (%)	Activity (kg PE/g Ti)	[η] (dL/g)
Cat. A				
1	40	100	1.7	1.84
2	50	99	2.1	2.15
3	60	100	3.4	1.76
4	70	100	3.7	1.01
Cat. B				
5	40	100	2	2.26
6	50	96	2.4	2.43
7	60	99	2.7	1.92
8	70	100	3	1.44

[a] Polymerization conditions : xylene = 50 mL; P = 1 bar; Al/Ti mol ratio = 500; amount of cat. A. 5-7 mg; amount of cat. B 11-14 mg; time 20 min.

In addition, both the catalysts A and B, showed significantly lesser rate decay with increasing temperatures (**Fig. 4.11**) and at temperature of 70°C the decay type kinetic profile changes to steady state. Polymer molecular weights decreased with increase in temperature. In general cat. B showed a higher activity compared to cat.A.

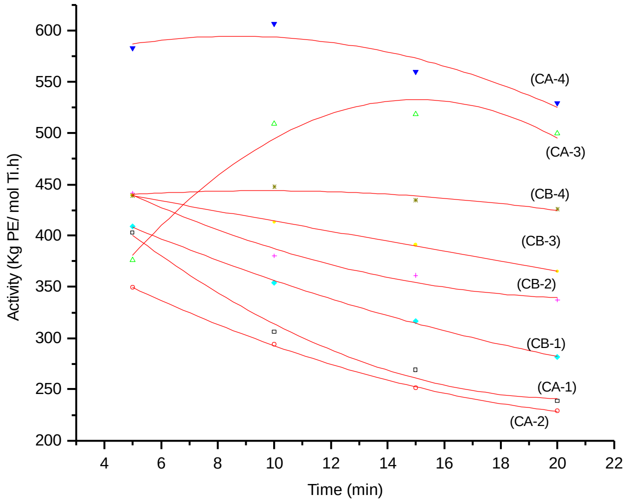


Fig. 4.11: Kinetic profile of ethylene polymerization uisng $MgCl_2$ supported Cp_2TiCl_2/MAO catalyst at different temperature in xylene; (CA-1) : Cat. A at 40 °C; (CA-2) : Cat. A at 50 °C; (CA-3) : Cat. A at 60 °C; (CA-4) : Cat. A at 70 °C; (CB-1) : Cat. B at 40 °C; (CB-2) : Cat. B at 50 °C; (CB-3) : Cat. B at 60 °C; (CB-4) : Cat. B at 70 °C.

d) Effect of Mg/Ti ratio

In order to understand the effect of Mg/Ti ratio on polymerization activity Mg-Ti catalyst with a varying contents of titanium were prepared. Catalyst with high titanium content showed stepper drop in activity and rate of polymerization when compared to catalyst with lower titanium content (**Table 4.4**).

Table 4.4 : Effect of Mg/Ti ratio on the polymerization of ethylene using $MgCl_2$-Cp_2TiCl_2/MAO catalyst system[a]

Entry no.	Mg : Ti	Convn (%)	Wt of polymer (g)	Activity (kg PE/g Ti.h)	[η] (dL/g)
1	10 : 3	100	0.80	11	1.01
2	13.5 : 1.28	98	0.50	9	1.44
3	9.2 : 4.96	99	0.32	6	1.53

[a] Polymerization conditions : xylene (50 mL); P = 1 bar; Al/Ti mol ratio of 500; time 30 min; temperature 70°C.

e) Effect of catalyst aging

As described in the experimental part, catalyst aging was conducted under a N_2 atmosphere at 70°C. No polymerization activity was found subsequent to one minute of premixing of catalyst and cocatalyst. This may be due to the over reduction of Ti^{+4} to Ti^{+2} and the consequent deactivation of catalyst[14-16].

f) Effect of catalyst amount

The catalyst activity and the rate of polymerization were found to increase with increase in Al/Ti ratio and decrease with increasing Cp_2TiCl_2 concentration. It has been reported that the number of active sites [C^*], lie between 75 to 100 % for Zr based catalysts[17]. Therefore, activity should be independent of [Zr][17]. But in reality, activity is found to increase with decrease in catalyst concentration (**Table 4.5**). This may be due to the increase of k_p (rate constant for propagation). The catalyst activity was found to be proportional to $[Cp_2ZrCl_2]^{-0.77}$. This indicates faster propagation at low [Cp_2TiCl_2 -$MgCl_2$] concentration.

Table 4.5 : Effect of catalyst amount on ethylene polymerization using $MgCl_2$-Cp_2TiCl_2/MAO catalyst system[a]

Entry no.	Catalyst amount (g)	Convn. (%)	Activity (kg PE/g Ti.h)
1	0.0044	100	7
2	0.0062	100	4
3	0.0093	100	2.4

[a] Polymerization conditions : xylene (50 mL); temperature 40°C; Al/Ti mol ratio of 500; P = 1 bar; time 30 min.

Chien and Wang[17] as well as Kaminsky[18] *et al.* showed that zirconocene/MAO catalyst exist in two active forms. These active species will differ by the number of MAO molecules complexed to them[17]. Based on the number of MAO molecules complexed to the active species, k_p, the rate constant for propagation, will vary. Chien and Wang have experimentally shown that the high activity can be achieved only at low [Zr] and large [MAO] which implies a higher k for species having larger content of complexed MAO i.e.

4.3.2.2 In n-hexane

a) Effect of Al/Ti ratio and temperature

Cp_2TiCl_2 is soluble in xylene but has no solubility in hexane. Hence, in hexane, no extraction of the soluble part is possible like in xylene. Therefore, the activity of cat. A towards ethylene polymerization was examined in hexane. In these experiments, MAO was added as a 5.4 wt. % (as Al) solution in toluene. The results are shown in **Table 4.6 and 4.7**.

Under comparable conditions, polymerization in hexane results in an increase in catalyst activity for supported catalyst A, when compared to the performance of the same catalyst in xylene. Also, the polymer molecular weights produced by the catalyst in hexane is significantly higher. More interestingly, molecular weights increases with Al/Ti ratio, unlike in xylene, where it decreased. The catalyst activity also increased with increase in Al/Ti ratio (**Fig. 4.12**).

Table 4.6 : Effect of Al/Ti ratio on ethylene polymerization with supported Cp_2TiCl_2 (cat A)/MAO in n-hexane[a]

Entry no	Al/Ti (mol)	Polymn. Time (min)	Wt. of polymer (g)	Convn (%)	Activity (kg PE/g Ti)	[η] (dL/g)
1	100	35	0.5	100	1.6	3.62
2	500	25	0.8	99	4.6	3.09
3	1000	25	1.0	100	5.6	2.67
4[b]	500	25	0.6	100	3.3	3.27

[a] Polymerization conditions : n-hexane (50 mL); temperature 30°C; P = 1 bar; amount of catalyst used 6-8 mg. [b] Unsupported Cp_2TiCl_2 was used.

Table 4.7 : Effect of temperature on ethylene polymerization using supported Cp_2TiCl_2 (cat A)/MAO in n-hexane[a]

Entry No.	Temp (°C)	Polymn. time (min)	Wt. of polymer (g)	Convn. (%)	Activity (kg PE /gTi)	[η] (dL/g)
1	20	25	0.8	99	4.4	3.92
2	30	25	0.8	98	4.6	3.09
3	40	25	0.6	100	4	2.33
4	50	30	0.1	100	0.35	1.54
5	60	No polymerization activity				

[a] Polymerization conditions : n-hexane (50 mL); Al/Ti mol ratio 500; P = 1 bar; amount of solid catalyst used 6-9 mg.

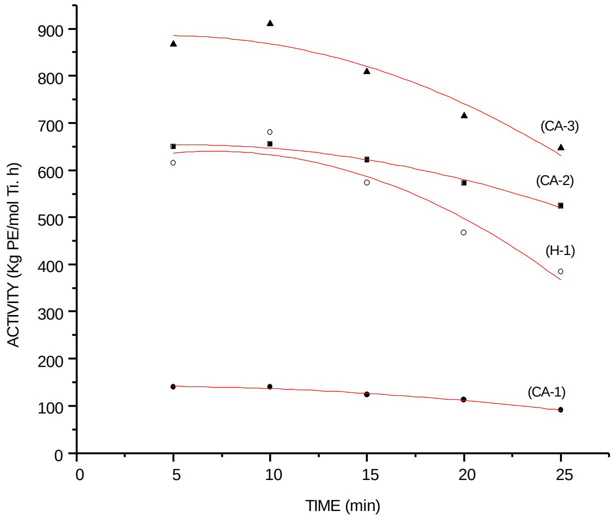


Fig 4.12 : Kinetic profile of ethylene polymerization using $MgCl_2$ supported Cp_2TiCl_2/MAO catalyst in n-hexane at different Al/Ti mol ratio; T = 30 °C; (CA-1) : Cat. A at Al/Ti = 100; (CA-2) : Cat. A at Al/Ti = 500; (CA-3) : Cat. A at Al/Ti = 1000; (H-1) : Unsupported Cp_2TiCl_2/MAO at Al/Ti = 500.

However, unlike in xylene, the catalyst activity rapidly decreases upon increasing temperature (**Fig. 4.13**). The catalyst shows no measurable activity at 60°C. Nevertheless, the catalyst shows considerably less decay in rate with temperature.

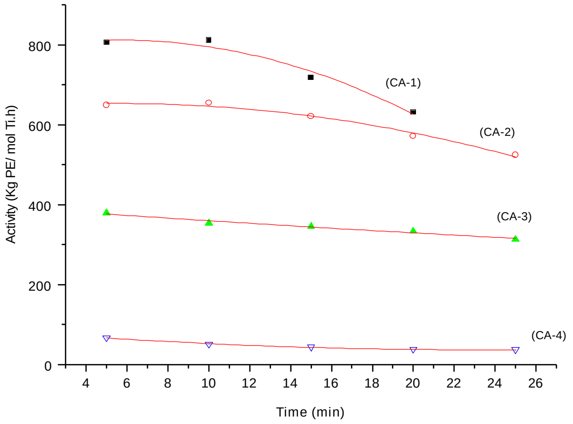


Fig. 4.13 : Kinetic profile of ethylene polymerization using $MgCl_2$ supported Cp_2TiCl_2/MAO at different temperature in n-hexane; (CA-1) : Cat. A at 20 °C; (CA-2) : Cat. A at 30 °C; (CA-3) : Cat. A at 40 °C; (CA-4) : Cat. A at 50 °C.

The effect of solvents on metallocene catalyzed olefin polymerization is not well understood. Dyachkovskii *et al.* observed a higher activity in CH_2Cl_2 compared to toluene using Cp_2TiCl_2-$AlMe_2Cl$[19]. This was explained by an increase in ionic dissociation which is favorable in a solvent of higher dielectric constant. Eskelinen and Seppala observed a lower catalyst activity in heptane compared to toluene with Cp_2ZrCl_2/MAO catalyst system[20]. The difference in behavior of the catalyst system between xylene and n-hexane is due to the transition metal catalysts itself and not the support since both supported and unsupported Cp_2TiCl_2 exhibited the same behavior, namely, increased in catalyst activity and higher molecular weight in n-hexane. Aromatic solvents such as xylene have strong π donor characteristics by virtue of which they can compete with the olefin in occupying the coordinatively unsaturated site on the transition metal. This would be expected to reduce the activity of the catalyst towards polymerization as well as contribute to displacement of growing chain (chain transfer to solvent). On the contrary, presence of a strong π donor in the coordination sphere with the monomer may confer additional stability to the active center, thus preventing it from deactivation at higher temperatures.

4.3.3 Molecular weight and molecular weight distribution of polyethylene

The polymer molecular weights obtained with cat. B were higher than those obtained with cat A. However, with both catalyst, molecular weights showed an initial increase, upto 50^{o}C, followed by a decrease. The polydispersities of the polymers obtained from cat A and B were compared (**Table 4.8**). It is observed that cat. A shows a slightly broader distribution of molecular weights compared to cat. B (**Fig. 4.14**)

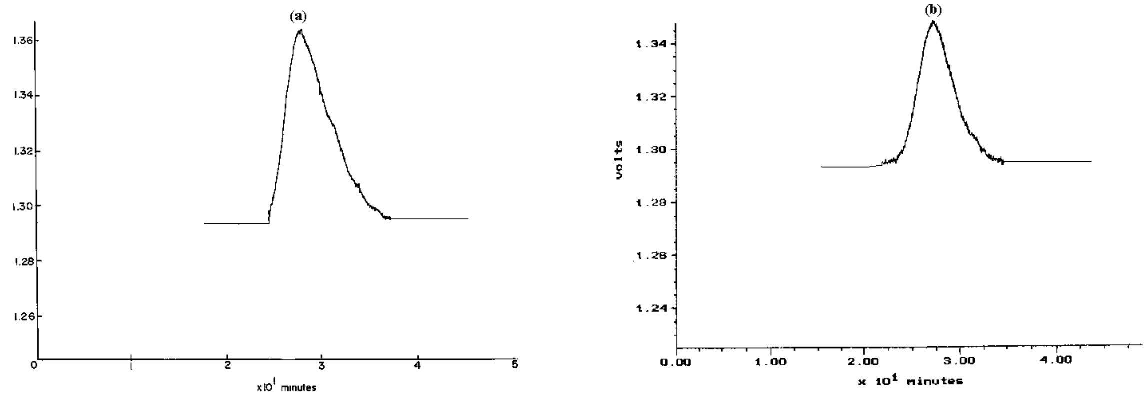


Fig. 4.14 : GPC chromatogram of poly(ethylene)s obtained by using $MgCl_2$ supported Cp_2TiCl_2/MAO catalysts in xylene, T = 70°C, Al/Ti = 500, P = 1 bar; (a) catalyst A; (b) catalyst B.

Table 4.8 : Molecular weight distribution of poly(ethylene)s obtained using supported Cp_2TiCl_2/MAO catalyst[a]

Entry No.	[η] (dL/g)	M_w x 10^{-5}	M_n x 10^{-5}	M_w/M_n
1	1.01	4.83	1.74	2.77
2	1.44	10.00	5.08	1.97

[a] Polymerization conditions : xylene (50 mL); temperature 70°C; Al/Ti mol ratio 500; P = 1 bar; time 20 min.

4.3.4 Mechanism of ethylene polymerization on magnesium chloride supported titanocene catalyst

a) Nature of Active species

Over the years the substantial evidences have accumulated in the literature in favor of the cationic species as the active center in the case of olefin polymerization using homogeneou surface metal hydrocarbyls functionalities to produce highly reactive species by immobilization of the transition metal onto suitable inorganic surfaces resulting in dramatic enhancement in activity for olefin polymerization[22-25].

Cp_2TiCl_2 supported on $MgCl_2$ shows higher activity as well as higher rate of polymerization when compared to unsupported Cp_2TiCl_2. The supported catalyst is active for more than one hour with significantly lesser rate decay. This is attributed to increased stabilization of the active center derived from Cp_2TiCl_2 when anchored on $MgCl_2$. Similar stabilization was previously observed by Marks and co-workers while supporting on organoactinide complexes on $MgCl_2$ [26-29]. This was understood by proposing that a cation-like Th-R^+ species on the surface of the supported catalysts. It was proposed that a transfer ofa alkyl group from the organoactinide to the surface of $MgCl_2$ occurs, yielding a cation like active species which is responsible for olefin polymerization and hydrogenation. ^{13}CPMAS-NMR spectroscopic studies provided conclusive evidences for the existence of a “cation-like” initiating species, $Cp_2Zr^+CH_3$, in the reaction of a metallocene dialkyl and MAO[30,31]. Soga and co-workers also suggested a similar active Zr-R^+ species in case of $MgCl_2$ supported zirconium metallocene catalysts[32]. Satyanarayana and Sivaram[8] also proposed a similar active species in case of Cp_2TiCl_2 supported on $MgCl_2$. A similar structure for the active center can also be envisaged for the $MgCl_2$-Cp_2TiCl_2/MAO catalysts system. A plausible mechanism for ethylene polymerization is shown in **Scheme 4.1**.

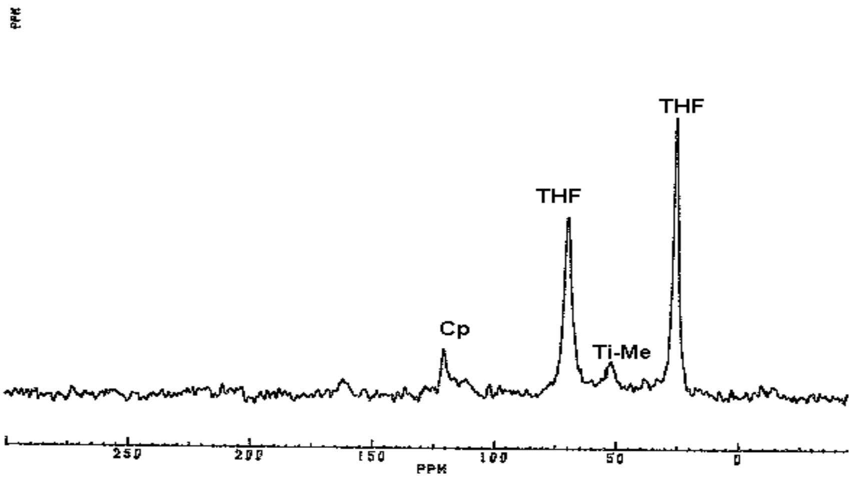
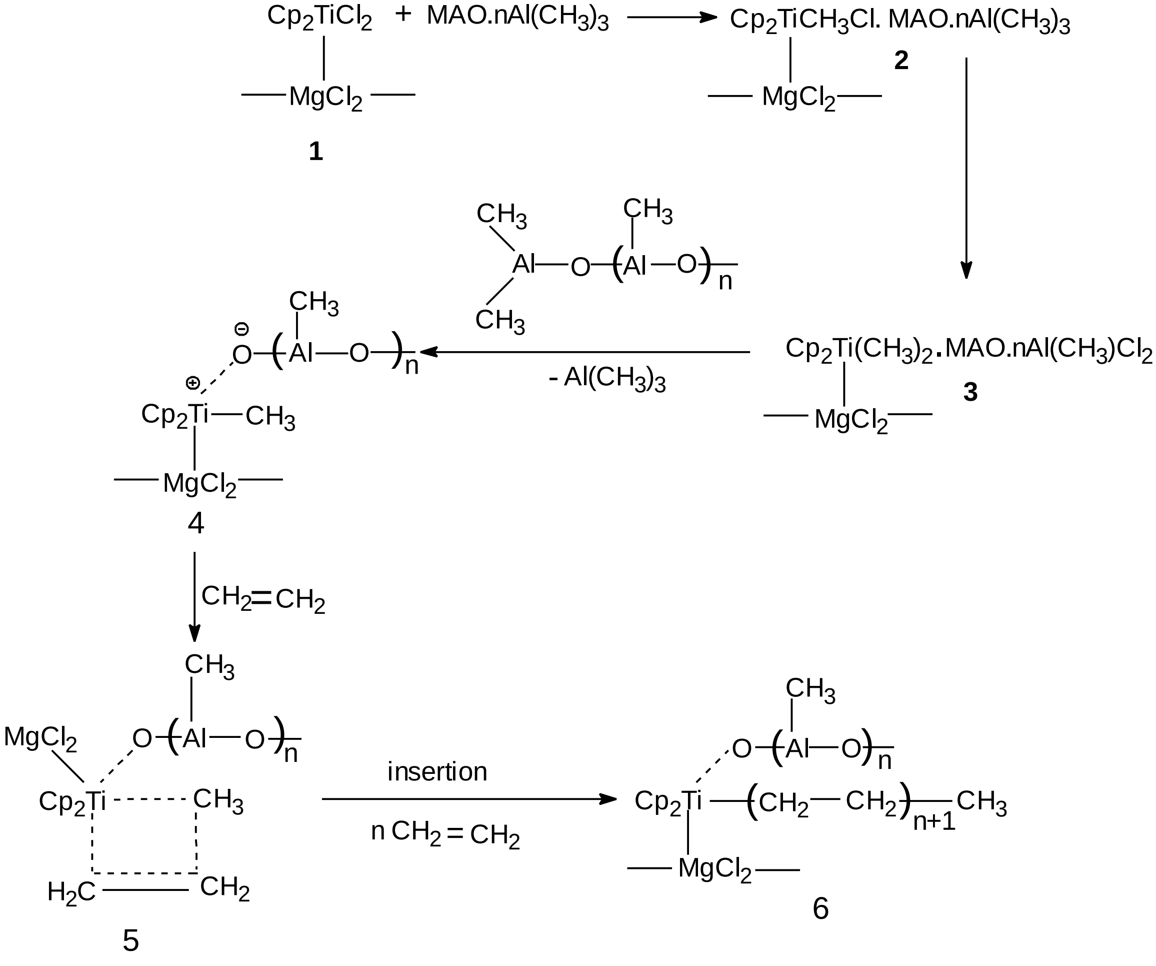


Fig 4.15 : ^{13}C CP MAS NMR of the catalyst pretreated with TMA.

The primary step for the formation of the active center is the methylation of the transition metal compound by residual trimethylaluminum (TMA) present in the MAO. The ^{13}C CPMAS spectra of the catalyst when treated with TMA shows the presence ofpeak Ti-Me at 51 ppm (**Fig 4.15**).

The active species shown in **Scheme 4.1** is obviously an over simplification. The role of MAO is not just limited to alkylation and coordination of metallocene. Polymerization is initiated by the insertion of ethylene into the metal-C bond, metal bearing aδ^+ charge.



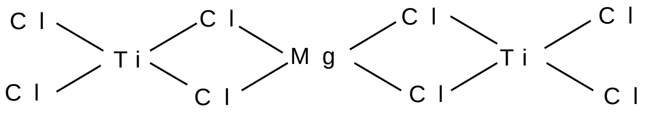
Scheme 4.1 : Mechanism of ethylene polymerization using $MgCl_2$ supported Cp_2TiCl_2 catalyst

b) Catalyst structure

A fundamental breakthrough in the field of high-activity catalysts was the realization, at the G. Natta Research center of Himont at Ferrara, that $MgCl_2$ is an ideal support for titanium halides[33]. This was attributed to the similarities in size, shape, co-ordination number, probably permitted an easy substitution between ions of magnesium and titanium catalyst frame work. The structure of the unusual crystalline modification of $MgCl_2$ is actually quite similar to that of γ-$TiCl_3$ corresponding to a close, cubic packed stacking of double chlorine layers. Within each layer, the magnesium atoms occupy all the octahedral positions. A thermodynamically less stable crystalline form of $MgCl_2$, characterized by hexagonal close-packed structure, similar to that off the α-$TiCl_3$ was also synthesized[34].

Active titanium catalysts supported on anhydrous magnesium chloride are characterized by higher rates of polymerization possibly due to the substitution of Mg^{+2} ions by Ti^{+4} in the crystal lattice of the Mg-Ti catalyst. As a consequence of the disordered structure and reduced size of the $MgCl_2$ crystallites, coordinatively unsaturated magnesium ions become available on the corners according to morphological studies, have been recognized as (110) and (100) planes.

Experimental evidences shows that polymerization of ethylene on $MgCl_2$ crystals, made to react with $TiCl_4$, occurs essentially at the corners, edges, and surfaces corresponding to lateral cuts of layers, but does not occur on the basal planes of the crystallites. Hence it can be supposed that, during the reaction with titanium halides, individual $TiCl_4$ molecules or bridged dimers, Ti_2Cl_8 are epitactically located on the corners, edges, and lateral surfaces on the $MgCl_2$ crystallites, thus giving rise to relief which are crystallographically co-herent with the matrix. According to the proposed catalyst microstructure, all titanium atoms are located on the catalyst surface and are available for activation for the cocatalyst. A typical picture of $TiCl_4$-$MgCl_2$ has been shown in **Fig. 4.16**. A similar structure can be proposed in case of Cp_2TiCl_2 supported on $MgCl_2$.2THF



(a)

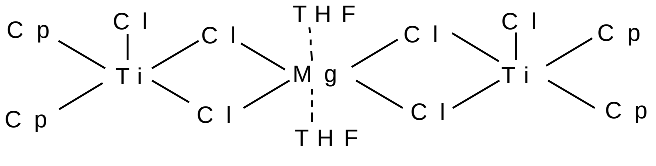


Fig 4.16 : Catalyst structure; (a) Structure of $TiCl_4$-$MgCl_2$; (b) Structure of Cp_2TiCl_2-$MgCl_2$.2THF

4.4 CONCLUSION

Cp_2TiCl_2 supported on $MgCl_2$ shows significant catalyst activity with reduced rate decay at temperatures as high as 70°C in xylene. This is in contrast to unsupported Cp_2TiCl_2 which shows practically no activity at temperatures higher than 50°C in conjunction with MAO. The active cationic titanium centers anchored on the surface of magnesium chloride are highly stabilized by immobilization and hence do not undergo deactivation by bimolecular reductive disproportionation even at higher temperatures. Such mechanism of stabilization have been invoked in case of cationic rare earth complexes supported on magnesium chloride[31]. The supported catalyst produce narrow polydispersity polyethylenes. Surprisingly, the supported catalysts show a higher catalyst activity in n-hexane as the polymerization medium at 30°C. This is contrary to the observation in case of Cp_2ZrCl_2/MAO catalyst system, where in n-heptane the catalyst activity was found to be lower than toluene[20]. Furthermore, the tendency for β-hydrogen transfer is lower in n-hexane compared to xylene, as evidenced by the higher polymer molecular weights in n-hexane. Since these observations are true for both supported and unsupported Cp_2TiCl_2, the intriguing behavior of the catalyst must be due to the nature of the transition metal and not the support.

4.5 REFERENCES

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5.1 INTRODUCTION

The discovery of new generation of homogeneous metallocene catalysts (Cp_2MX_2, M = Ti, Zr, Hf; X = Cl, Me) in conjunction with methylaluminoxane (MAO) give extremely high rates of polymerization and acceptable catalyst life times has led to the significant scientific and industrial interest in this area [1-3]. Metallocene based catalysts allow unique possibility of tailoring the stereoregularity of polyolefins structures by proper tuning of ligands around the transition metal centers and also enabled the synthesis of entirely new families of homo- and copolymers of ethylene and α-olefins as compare to conventional Ziegler-Natta catalysts. Homogeneous catalyst bis(cyclopentadienyl) titanium (IV) dichloride in combination with dialkylaluminum halide polymerize ethylene were first shown by Breslow and Newburg[4]. However, these catalysts show rapid rate decay and loss of catalyst activity within minutes of start of polymerization and at temperatures higher than 30°C[5]. Amongst the metallocene, zirconium based metallocene systems have attracted the most attention because of its high catalyst activity. However, homogeneous metallocene catalysts have certain drawbacks. A heterogeneous catalyst is more preferred for use in gas phase and slurry phase polymerization processes.

Use of anhydrous magnesium chloride as support for zirconium metallocene is not widely reported in the literature. Kaminaka and Soga have examined several kinds of heterogeneous zirconium based metallocene catalysts for the polymerization of propylene[6-8]. $Et[IndH_4]_2ZrCl_2$, $iPr(Flu)(Cp)ZrCl_2$ an Cp_2ZrCl_2 were supported on $MgCl_2$ by direct impregnation method and used for polymerization of propylene in conjunction with trialkylaluminums. Although catalyst activity was reduced, tacticity of polypropylene increased. Bailly *et al.* reported a novel method for the preparation of $MgCl_2$ supported Cp_2ZrCl_2 useful for the gas-phase polymerization of ethylene[9]. Polyethylene produced with these catalysts showed narrow molecular weight distribution with well defined particle morphology. Soga *et al.* have reported a $MgCl_2$ supported $XTiCl_3$ (X = Cp,) catalyst which was used for the polymerization of propylene[10].

This **chapter** describes the synthesis of a magnesium chloride supported Cp_2ZrCl_2 catalyst by exploiting the solubility of both Cp_2ZrCl_2 and $MgCl_2$ in tetrahydrofuran. All the by directly impregnating the soluble metallocene onto a solid support. An objective of the present work is to explore the possibility of preparing an olefin polymerization and copolymerization catalyst capable of producing polymers with high polymerization activity, especially, at a relatively high temperature and low aluminum to metal ratio.

5.2 EXPERIMENTAL SECTION

5.2.1 Synthesis of Mg-Zr supported catalyst

A three neck r.b. flask equipped with magnetic needle, reflux condenser, addition funnel, N_2 inlet and outlet which was flame dried and cooled under N_2. Magnesium turnings (0.4 g) corresponding to 0.164 mol of magnesium activated by a pinch of iodine was placed followed by addition of 40 mL THF, and the slurry was stirred at a temperature of 25-30^{0}C for 1/2 h. A mixture of 1,2-dichloroethane and THF(1:1) was added to the slurry by means of a syringe over a period of 1/2 h. It was observed that all the Mg turnings were slowly dissolved in THF with the formation of a clear solution. Steady evolution of ethylene gas indicates the decomposition of the intermediatechloroethyl magnesium complex with the subsequent formation of $MgCl_2$.nTHF complex and its dissolution into THF. Cp_2ZrCl_2 (0.31 g) corresponding to 1.06 x 10^3 mol as Zr was dissolved separately in 20 mL of THF and added to the solution of $MgCl_2$ over a period of 15 min at a temperature of 25-30^{0}C. The whole solution was then added into a flask containing 300 mL of n-hexane when a white precipitate separated out. Finally the whole precipitate was washed 3-4 times by n-hexane (using 50 mL each time) and dried under vacuum.

The solid catalyst thus prepared contains Zr = 0.65 wt. %; Mg = 10 wt. %.

5.3 RESULTS AND DISCUSSION

5.3.1 Characterization of the catalyst

The solid catalyst was analyzed for 0.65 % by wt. of Zr and 10 % by wt. of Mg and has the general empirical formula $MgCl_{2.1}THF_{2.01}Zr_{0.017}Cp_{0.034}$ with a surface area of 18 m^2/g. The presence of cyclopentadienyl ligand and THF in the solid catalyst was evidenced by the presence of peaks at 1460 and 812 cm^{-1} and 1038 and 892 cm^{-1} (**Fig. 5.1**). The XRD of the

Further a new reflection appeared at 2θ = 32.1^0. This reflection corresponds to that of THF complex of $MgCl_2$ (**Fig. 5.2**). Thermogravimetric analysis (TGA) of the complex showed that the complete decomposition of the structure occurred in three stages as shown in **Fig. 5.3**.

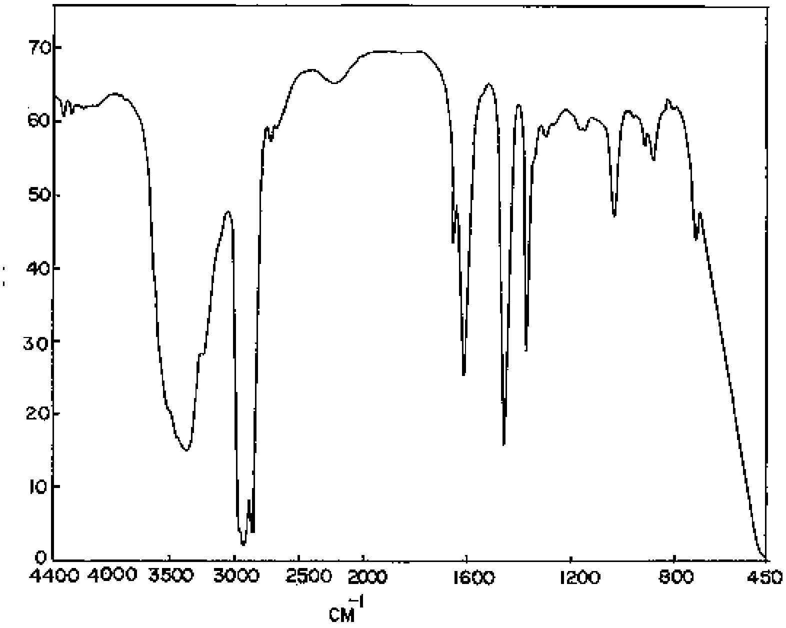


Fig. 5.1 : IR spectra of $MgCl_2$ supported Cp_2ZrCl_2 catalyst.

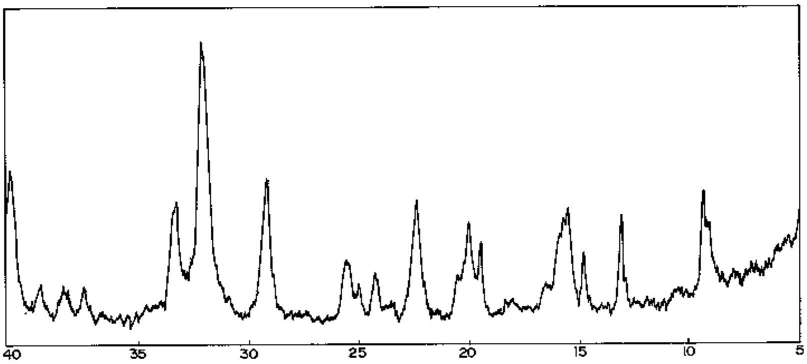


Fig. 5.2 : XRD of $MgCl_2$.2THF supported Cp_2ZrCl_2 catalyst

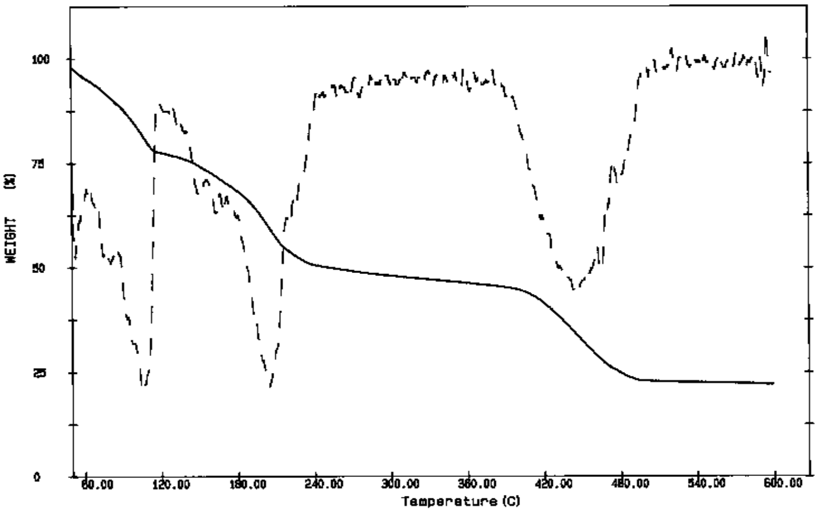


Fig 5.3 : TGA of $MgCl_2$ supported Cp_2ZrCl_2 catalyst.

5.3.2 Polymerization of ethylene under 1 bar pressure

5.3.2.1 Polymerization in xylene

Effect of pretreatment with trialkylaluminum

The solid catalyst $MgCl_2$-Cp_2ZrCl_2 was used for the polymerization of ethylene in xylene as diluent at 70°C using MAO as cocatalyst. The solid catalyst was pretreated with alkylaluminums by contacting a slurry of the catalyst in xylene with TMA or TIBAL at 70°C, for 2 minutes prior to adding monomer and MAO. The results are shown in **Table 5.1**. It is observed that the catalyst pretreated using TMA shows a higher catalyst activity when compared to a catalyst pretreated with TIBAL or without pretreatment. Resconi *et al.*[11] suggest that TMA is the actual cocatalyst, with MAO acting only as a soluble carrier of the ion pair formed. Tritto *et al.*[12] showed that MAO is a better alkylating agent than TMA and that the active centers are cation-like species produced by MAO. Chien et al[13] suggest that the activity and the molecular weight decreases when the TMA content increases but Reddy *et al.*[14] found that activities were enhanced by adding TMA to MAO. Chien *et al.*[15] on the other hand, reported that the effect of TMA in MAO on the activities of the ethylene polymerization and the molecular weight of the obtained polymers was small after replacing 90% of MAO with TMA. Michiels *et al.*[16] observed that catalyst activity for ethylene polymerization increase at low TMA concentrations with increasing the polymerization activity was observed at higher TMA/MAO ratios. Addition of TEAL or TIBAL to the MAO also brings about a decrease in the catalyst activities, TEAL being a stronger inhibitor than TIBAL. The specific role of TMA in activating the catalyst is not restricted to its general role as scavenger of impurities. If it were so, then, TIBAL should also activate the catalyst. The presence of additional TMA in solution, presumably, suppress the MAO deactivation process, occurring via a methane splitting reaction[17-19]. Additionally excess TMA also stabilizes the "cage-like" structure of MAO. Addition of TIBAL to MAO, on the contrary, leads to a destruction of MAO structure, leading to reduced activity in polymerization.

An increase in temperature from 70 to 80°C resulted in a two fold increase in catalyst activity (**Table 5.1, entry no. 3 & 4**). All the catalysts show similar kinetic curves with an increase in rate followed by steady decay (**Fig. 5.4**). The molecular weight and molecular weight distribution of the produced polyethylene was found to be high and narrow (**Table 5.2**)

Table 5.1: Polymerization of ethylene using $MgCl_2$ supported Cp_2ZrCl_2/MAO[a]

Entry no.	Zr x 10^7(mol)	Temp (°C)	Trialkyl-Aluminum	Wt of polymer (g)	Activity (Kg PE/ g Zr.h)	[η] (dL/g)
1	6.09	70	-	1.63	59	1.33
2	5.93	70	TIBAL	0.26	9.4	-
3	5.96	70	TMA	2.40	88	1.25
4[b]	5.9	80	“	1.90	143	0.73

[a] All polymerization were carried out in xylene (50 mL); Time = 30 min; Al/Zr = 5000; P = 1 bar; using 8-9 mg of catalyst; alkylaluminum added = 3 x 10^{-3} mol as Al. [b] Polymerization was conducted for 20 min.

Table 5.2 : Molecular weight and MWD of polyethylenes obtained from GPC using supported catalyst/MAO[a]

Entry no	Trialkylaluminum	Temp. (°C)	M_n	M_w	MWD
1	-	70	24, 564	61, 019	2.48
2	TIBAL	70	23, 394	43, 443	1.85
3	TMA	70	30, 097	63, 204	2.10
4[b]	"	80	20, 588	48, 383	2.35

[a] All polymerization were carried out in xylene (50 mL); Time = 30 min; Al/Zr = 5000; P = 1 bar; using 8-9 mg of catalyst. [b] Polymerization was conducted for 20 min.

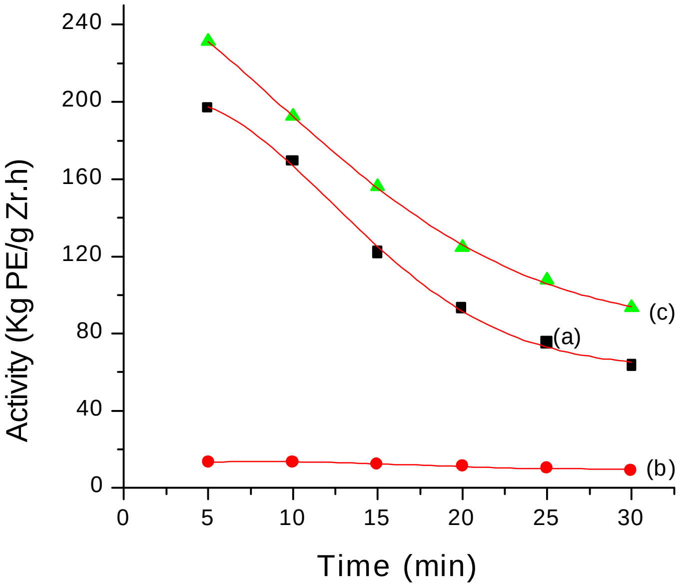


Fig. 5.4 : Kinetic profile of ethylene polymerization using supported catalyst/MAO at Al/ Zr = 5000, T = 70 °C, P = 1 bar; (a) catalyst without TMA; (b) catalyst pretreated with TIBAL; (c) catalyst pretreated with TMA.

5.3.2.2 Polymerization in n-heptane

Effect of Al/Zr ratio and temperature

In general aliphatic hydrocarbon diluents are preferred in olefin polymerization processes.

diluents, unlike the aromatic solvents needed for homogeneous catalysis. Ethylene polymerization using $MgCl_2$-Cp_2ZrCl_2 was studied in n-heptane in conjunction with MAO. The effect of Al/Zr mol ratio and temperature were examined. The results are shown in **Table 5.3 and 5.4**. In general the catalyst activity and the molecular weight of the polymer produced was lower in heptane than in xylene. In **Chapter-4**, it was shown that $MgCl_2$ supported Cp_2TiCl_2 catalyst exhibited a higher catalyst activity and produced higher molecular weight polyethylene in n-hexane. Thus the polymerization behavior of the zirconium metallocene is different from that of titanium metallocene in aliphatic solvent.

The supported catalyst is found to be active even at Al/Zr mol ratio of 1000 in n-heptane for more than half an hour. The catalyst activity increases with increase in Al/Zr ratio (**Fig 5.5**). The rate of polymerization and catalyst activity also increased when temperature increased from 50 to 70°C. Beyond 70°C, there was a decrease of both rate of polymerization and catalyst activity (**Fig. 5.6**). This behavior is distinctly different from the results obtained by Eskelinen and Seppala, where a two fold increase in ethylene polymerization activity was observed from 70 to 80°C using homogeneous Cp_2ZrCl_2/MAO catalyst in heptane[20].

Table 5.3 : Effect of Al/Zr ratio on ethylene polymerization using $MgCl_2$ supported Cp_2ZrCl_2/MAO in n-heptane[a]

Entry. No.	mol Zr x10^7	Al/Zr (mol)	Wt. of polymer (g)	Activity (Kg PE/ g Zr.h)	[η] (dL/g)	M_n	M_w	MWD
1[b]	9.9	1000	0.53	21	1.75	20, 205	46, 089	2.28
2	8.52	5000	1.85	38	1.24	18. 069	39, 021	2.15
3[c]	9.54	5000	1.66	45	0.81	n.d.	n.d.	n.d.

[a] Polymerization conditions: n-heptane = 50 mL; T = 70°C; time = 30 min. P = 1 bar (without adddition of TMA) using 11-14 mg of catalyst. [b] Reaction stopped after 15 min. [c] Polymerization was carried out using homogeneous Cp_2ZrCl_2 catalyst. n.d. = not determined

Cp_2ZrCl_2/MAO catalyst in n-heptane[a]

Entry. No.	mol Zr 10^7	Temp (^oC)	Wt. of polymer (g)	Activity (Kg PE/g Zr. h)	[η] (dL/g)
1	8.3	50	0.81	22	3.31
2	8.1	60	1.16	31	1.92
3	8.5	70	1.85	36	1.24
4	8.5	80	0.82	21	1.50

[a] Polymerization conditions : n-heptane = 50 mL; Al/Zr = 5000; P = 1 bar; time = 30 min (without addition of TMA) using 11-12 mg of catalyst.

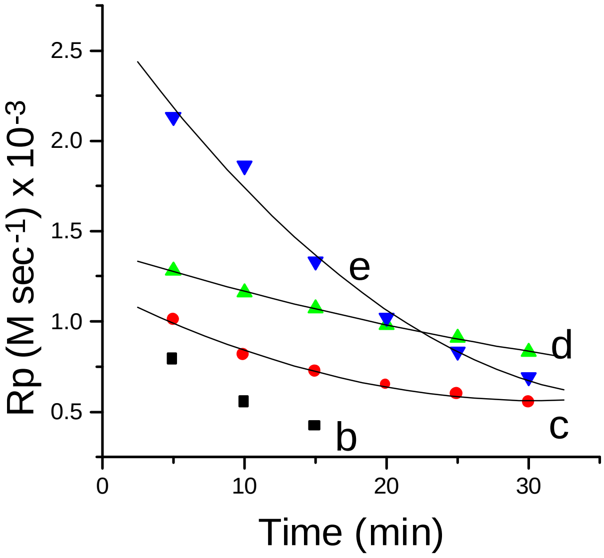


Fig 5.5 : Kinetic profile of ethylene polymerization using supported catalyst/MAO in n- heptane at 70 °C, P = 1 bar. (b) Al/Zr = 1000, (c) = 5000; (d) homogeneous Cp_2ZrCl_2/MAO, Al/Zr = 5000; (e) supported catalyst in xylene at 70 °C, Al/Zr = 5000.

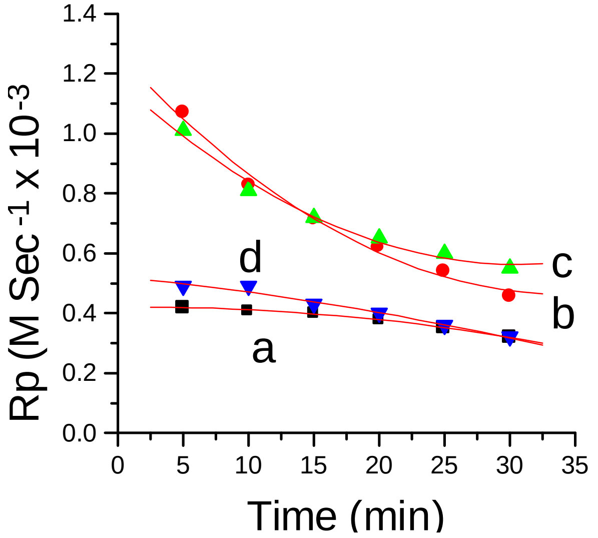


Fig 5.6 : Kinetic profile of ethylene polymerization using supported catalyst/MAO at Al/ Zr = 5000; P = 1 bar at different temperature. (a) 50 ℃; (b) 60 ℃; (c) 70 ℃; (d) 80 ℃.

5.3.2.3 Polymerization in xylene at 5 bar pressure

To explore the performance of the catalyst at high temperature and pressure, ethylene polymerization was carried out at 5 bar pressure using supported catalyst in conjunction with MAO. The results are shown in **Table 5.5**. The supported catalyst shows about 33 % higher catalyst activity when compared to unsupported Cp_2ZrCl_2 under comparable conditions. The supported catalyst also shows sensitivity to hydrogen as a chain transfer agent (**Table 5.6**).

Table 5.5 : Ethylene polymerization using $MgCl_2$ supported and unsupported Cp_2ZrCl_2 catalyst/MAO at high pressure[a]

Entry no.	Catalyst amount(mg)	mol Zr x 10^7	Temp (°C)	Wt. of polymer (g)	Activity (Kg PE/g Zr.h)	[η] (dL/g)
1	11.4	8.40	100	19.0	490	2.36
2	10.6	7.10	90	15.0	461	2.40
3[b]	-	9.54	90	13.3	306	1.02

[a] Polymerization conditions : xylene = 100 mL, P = 5 bar, Al/Zr = 5000, TMA added = 3 x 10^{-3} mol as Al, time = 30 min. [b] Polymerization using unsupported zirconocene.

Table 5.6 : Effect of hydrogen on the polymerization of ethylene using supported catalyst/MAO[a]

Entry no.	Cat. amount (mg)	mol Zr x 10^7	Temp. (°C)	Vol. of H_2 (mL)	Wt. of polymer (g)	Activity (Kg PE/g Zr.h)	[η] (dL/g)
1	9.5	6.35	90	200	8.0	276	1.37
2	9.2	6.75	85	100	13.3	455	1.53
3	8.8	6.46	80	400	12.4	403	1.29

[a] Polymerization conditions : xylene = 100 mL, P = 5 bar, Al/Zr = 5000, TMA added = 3 x 10^{-3} mol as Al, time = 30 min.

5.3.3 Molecular weight and molecular weight distribution of polyethylene

The polymer molecular weight obtained by using $MgCl_2$.2THF supported Cp_2ZrCl_2 catalyst was found to be higher as compared to unsupported Cp_2ZrCl_2 catalyst. The results are shown in **Table 5.7**. The polydispersities of the polymer obtained from catalyst A was found to be slightly broader in comparison to the homogeneous catalyst (**Fig 5.7**). Noteworthy, is the shape of the molecular weight distribution curve, which is not symmetrical, but instead possesses a “tail” of short polymer chains.

Table 5.7 : Molecular weight and MWD of polyethylenes obtained from GPC using $MgCl_2$ supported and unsupported Cp_2ZrCl_2 catalyst

Entry no.	Temp (°C)	Vol. of H_2 (mL)	M_n	M_w	MWD
1	100	-	28, 750	83, 537	2.90
2	90	-	49, 946	94, 850	1.89
3	80	400	13, 947	31, 814	2.28
4	85	100	20, 029	42, 015	2.09
Homo Zr	90	-	31, 744	59, 517	1.87

[a] Polymerization conditions : xylene = 100 mL, P = 5 bar, Al/Zr = 5000, TMA added = 3 x 10^{-3} mol as Al, time = 30 min.

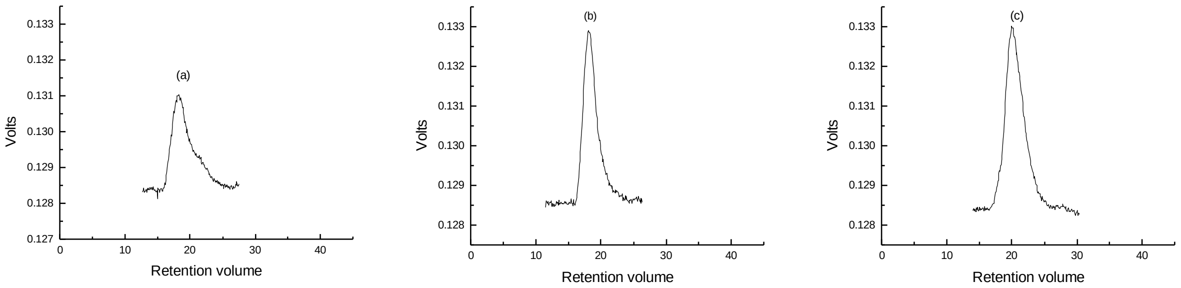


Fig 5.7 : GPC chromatogram of polyethylene samples obtained using supported catalyst/MAO at Al/Zr = 5000, P = 5 bar, in xylene at different temperatures; (a) at 100 °C; (b) at 90 °C; (c) at 80 °C.

5.3.4 Active site concentration[21,22]

It is well known that the polymerization reaction rate can be expressed by the **equation**

$R_p = K_p . [C^*_t].[M]$ (1)

Where,

R_p - polymerization rate, K_p - propagation rate constant, $[C_t^*]$ - concentration of active sites at time t, [M] - monomer (ethylene) concentration

The macromolecule creation rate equals the transfer rate, which can be expressed by equation :

$dN_t/dt = R_{tr} = K_{tr} . [C_t^*]. [M]$ (2)

After integration of equation (2) becomes

$[N_t] = [N_o] + K_{tr} . [C_t^*]. [M]. t$ (3)

Where,

$[N_o]$, $[N_t]$ - concentration of macromolecules at time t = 0 and t respectively

K_{tr} - transfer rate constant

When one macromolecule is formed on each active site, their initial number is equal to the concentration of active sites, which remains unchanged over the whole process due to the stable nature of the catalyst employed upto three minutes, i.e.

$$[N_o] = [C_o^*] = [C_t^*] = [C^*] \qquad (4)$$

The concentration of macromolecules after time t can be calculated from the experimental yield and the number average molecular weight of the polymer obtained by GPC. :

$$[N_t] = W_t / M_t \qquad (5)$$

Where

W_t - polyethylene yield after time t

M_t - number average molecular weight of polyethylene obtained after time t.

Hence,

$$W_t/M_t = [C^*] + K_{tr}.\ [C^*].\ [M]\ .\ t \qquad (6)$$

Using equation 6 and the experimental data of polymer yield and polymer average molecular weight versus time, one can calculate the concentration of active sites $[\overset{*}{C}]$ and the transfer rate constant K_{tr}. The corresponding experimental results are shown in **Table 5.8** and **Fig. 5.8**.

Table 5.8 : Kinetic parameters of the ethylene polymerization with $MgCl_2$ supported Cp_2ZrCl_2 catalyst/MAO[a]

Entry no.	Reaction Time (min)	mol Zr x 10^7	yield (mol)	M_n	N_t (mol)x10^7	N_t (mol/mol Zr)	$[C^*]$ x10^2 mol/mol Zr
1	1	5.97	5.89×10^{-3}	22,989	2.56	0.429	18.8
2	2	5.95	0.01	25,612	3.96	0.673	
3	3	5.93	0.015	27,671	5.42	0.913	

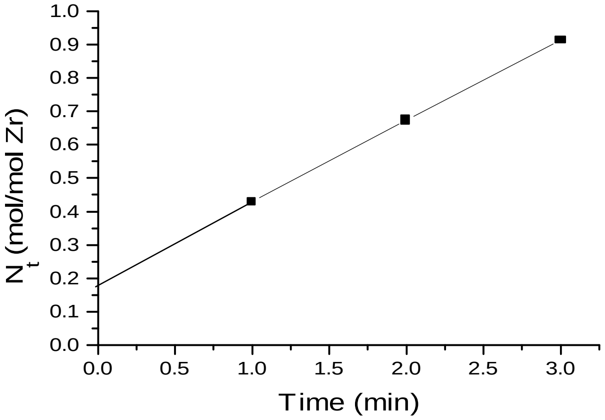


Fig 5.8 : Concentration of macromolecules N_t of the polyethylene in the polymerization medium as a function of polymerization time, t calculated according to the equation 6; $N_t = W_t/M_t = 0.194 + 0.194.\ K_{tr}.\ M.\ t$

From the intercept in **Fig. 5.8**, [C*] was found to be 19 mol % / mol of Zr

5.3.5 Copolymerization of ethylene with 1-hexene

Homogeneous metallocene/MAO catalysts offer unique advantages towards ethylene homo- and copolymerization[1-3,23]. Copolymers of ethylene and higher α-olefins such as propene, 1-butene, 1-hexene, 1-octene etc., are important commercial products. Metallocene catalysts have permitted the synthesis of ethylene/α-olefins with well defined structures compared to heterogeneous Ziegler-Natta catalysts.

Kaminsky *et al.* found that the homogeneous metallocene-MAO catalyst system can polymerize a variety of olefins with extremely high catalyst activities[24-26]. In contrast to the classical heterogeneous Ziegler-Natta catalysts[27-29] metallocene catalysts give very random copolymers[30]. Soga *et al.* found an influence of stereospecificity of the metallocene on the copolymerization of propene and 1-hexene[31]. The incorporation of comonomer increases in the following order aspecific < isospecific < syndiospecific catalyst and the stereospecificity retains during polymerization. Soga and Kaminaka[32] showed that the use of metallocenes supported on SiO_2, Al_2O_3 or $MgCl_2$ give random copolymers with much higher molecular weight, as compared to the homogeneous catalysts and that the content of comonomer does not appreciably depends on the catalyst carrier ($SiO_2 = Al_2O_3 > MgCl_2$).

Copolymerization of ethylene and 1-hexene was carried out using the solid $MgCl_2$.2THF-Cp_2ZrCl_2 and also with unsupported Cp_2ZrCl_2 with MAO as cocatalyst under 1 bar pressure by changing the monomer feed ratio and also at different temperatures. The results are shown in **Tables 5.9 and 5.10**. It can be seen that the catalyst activity increases with increase of 1-hexene concentration in the monomer feedupto a certain concentration of 1-hexene (0.24 M), beyond which the catalyst activity decreases. Further, the supported catalyst gives higher catalytic activity and higher comonomer incorporation in the copolymer compared to unsupported catalyst under identical polymerization conditions. With higher 1-hexene concentration in the monomer feed, thecomonomer incorporation in polymer is more.

Table 5.9 : Effect of 1-hexene concentration in the monomer feed on the co - polymerization of ethylene using $MgCl_2$ supported Cp_2ZrCl_2/MAO[a]

Entry no.	mol Zr x 10^7	Added 1-hexene Conc (M)	Yield (g)	1-hexene in copoly (mol %)	Activity (Kg Copoly./g Zr.h)	T_m (°C)		[η] (dL/g)	Crystallinity (%)
1	5.96	-	2.40	-	90	130.2		1.25	71.5
2	5.93	0.04	2.25	n.d	83	110.2	123.7	1.03	66
3	6.11	0.08	1.60	n.d.	57	108.6	121.6	-	51
4	5.93	0.16	1.75	5.1	65	93.0	111.3	0.42	44
5	6.00	0.24	2.10	6.2	77	92.5	108.4	0.20	33
6	5.93	0.48	1.45	8.6	53	-	82.8	-	-
7[b]	5.93	0.24	1.50	4.7	55	88.9	103.0	-	31

[a] All polymerization were carried out in xylene (50 mL); Al/Zr = 5000; T = 70°C; P = 1 bar; time 30 min; using 8-9 mg of solid catalyst. [b]Polymerization carried out using homogeneous Cp_2ZrCl_2 catalyst.

Increase of temperature from 40 to 70°C does not cause any significant change in

The molecular weight of the copolymer was found to be decrease with increasing comonomer concentration in the feed.

Table 5.10 : Effect of temperature on the copolymerization of ethylene and 1-hexene using $MgCl_2$ supported Cp_2ZrCl_2catalyst/MAO[a]

Entry no	mol Zr x 10^7	Temp (°C)	Yield (g)	1-hexene in copoly (mol %)	Activity (Kg Copoly/g Zr.h)	T_m (°C)		[η] (dL/g)	Crystallinity (%)
1	5.86	40	0.75	6.3	28	96.4	109.8	0.53	50
2	5.97	60	1.70	n.d	60	88.9	108.2	-	41
3	6.00	70	2.10	6.2	77	92.5	108.4	0.19	33
4	5.93	80	1.14	n.d	42	88.9	108.4	0.17	40

[a] All polymerization were carried out in xylene (50 mL); time = 30 min; Al/Zr = 5000; P = 1 bar; 1-hexene conc.in the monomer feed = 0.24mol; using 8-9 mg of catalyst.

5.3.5.2 Thermal behavior of the copolymer

Similar to Cp_2ZrCl_2/MAO catalysts syetem[33], the DSC analysis of the copolymers obtained by using supported catalyst exhibit two peaks implying that copolymers with different crystallinities are being formed (**Tables 5.9 & 5.10, Fig. 5.9**). The thermal behavior investigated by DSC shows strong influence of comonomer incorporation on polymer properties. Even at low levels of incorporation of 1-hexene in the copolymer, there is a sharp decrease in crystallinity and melting points of copolymers was observed. Due to the more homogeneous composition distribution of copolymers obtained usingmetallocene catalysts, the effect of comonomer incorporation on the thermal properties is much more pronounced than for a copolymer prepared using a heterogeneousZiegler-Natta catalysts[34].

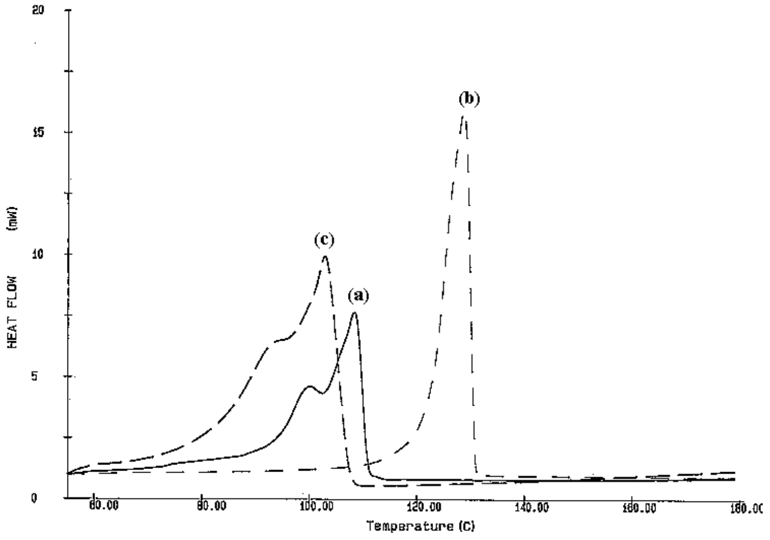


Fig. 5.9 : Thermal behavior of polyethylene and polyethylene-1-hexene copolymer obtained by using $MgCl_2$ supported and unsupported Cp_2ZrCl_2/MAO catalysts in xylene, T = 70 °C, Al/Zr = 5000, P = 1 bar; (a) copolymer obtained from $MgCl_2$ supported Cp_2ZrCl_2, (b) polyethylene obtained by using $MgCl_2$-Cp_2ZrCl_2, (c) copolymer obtained from unsupported Cp_2ZrCl_2.

5.3.5.3 Molecular weight and MWD of the copolymer

The results obtained from GPC of the copolymers are shown in **Tables 5.11 and 5.12**. The unsupported Cp_2ZrCl_2 catalyst shows a narrow molecular weight distribution whereas the copolymer obtained using supported catalyst shows a broad molecular weight distribution(**Fig. 5.10**). The extent of broadening increases with increasing comonomer content in the copolymer. The M_n is significantly reduced with increasing 1-hexene concentration.

It can be further seen that temperature has a significant effect on the polydispersities of the produced copolymers. At, 40°C the GPC chromatogram shows a narrow distribution of the molecular weight. But at 70°C the GPC chromatogram broaden with the appearance of a shoulder (**Fig. 5.11**). This is presuambly due to the severe chain transfer effect of the comonomer, depressing the M_n significantly compared to M_w. A plot of comonomer concentration in the feed against M_n shows an exponential decay (**Fig. 5.12**).

Table 5.11 : Molecular weight and MWD of poly(ethylene-co-1-hexene) obtained from GPC[a]

Entry no.	1-hexene in copolymer (mol%)	M_n	M_w	MWD
1	-	30, 097	63, 204	2.10
2[b]	4.7	3142	19183	6.10
3	6.2	4273	35, 726	8.36
4	8.6	1989	30, 812	15.49

[a] All polymerizations were carried out in xylene (50 mL); Al/Zr = 5000; T = 70°C; P = 1 bar; time 30 min; using 8-9 mg of solid catalyst. [b] Polymerization carried out using homogeneous Cp$_2$ZrCl$_2$ catalyst.

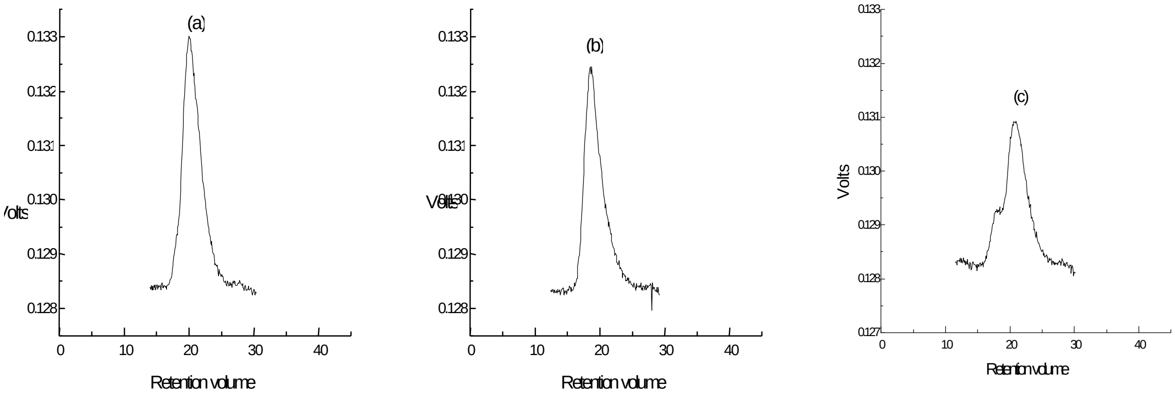


Fig 5.10 : GPC chromatogram of the ethylene homo and copolymer obtained by using supported and unsupported Cp$_2$ZrCl$_2$/MAO catalyst at Al/Zr = 5000, P = 1 bar, T = 70°C; (a) polyethylene obtained from supported catalyst/MAO (Table 5.11, entry no. 1); (b) copolymer using unsupported Cp$_2$ZrCl$_2$/MAO (Table 5.11, entry no. 2); (c) copolymer using supported catalyst (Table 5.11, entry no. 4).

obtained from GPC[a]

Entry no.	Temp (°C)	M_n	M_w	MWD
1	40	16, 422	39, 592	2.41
2	60	6177	31, 480	5.09
3	70	4273	35, 726	8.36
4	80	3660	29, 524	8.06

[a] All polymerization were carried out in xylene (50 mL); time = 30 min; Al/Zr = 5000; P = 1 bar; 1-hexene conc. = 0.24 mol; using 8-9 mg of catalyst.

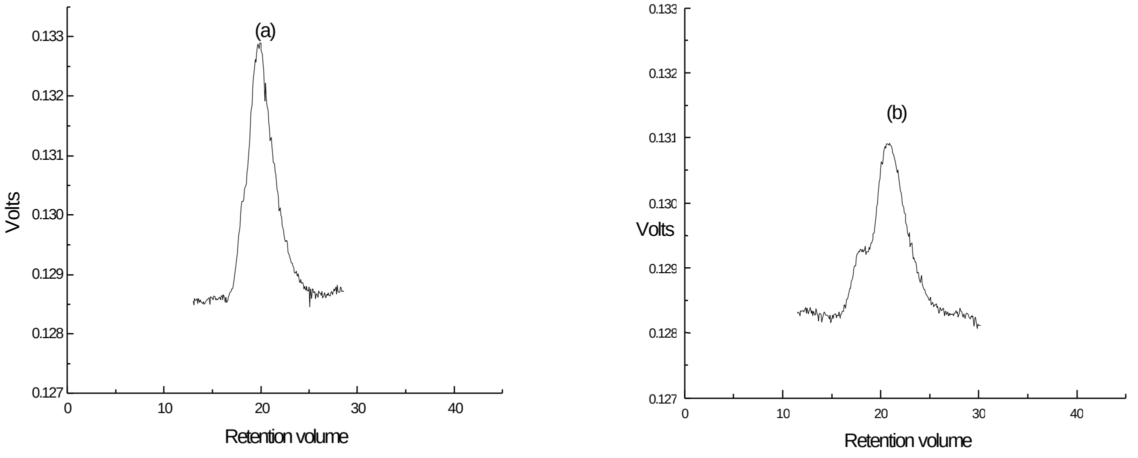


Fig. 5.11 : GPC chromatogram of the copolymer obtained from supported catalyst/MAO at Al/Zr = 5000, P = 1 bar, at different temperature; (a) at 40°C; (b) at 70 °C.

Fig. 5.12 : Plot of 1-hexene concentration in the monomer feed vs M_n of the copolymer obtained from GPC.

5.3.5.4 Sequence and structure

Chemical shift assignments in the ^{13}C NMR spectra of the copolymers were taken from the literature[35,36]. The triad distributions were evaluated from the spectra following Randall's methodology[37]. Triad results are given in **Table 5.13**. The experimental values of conceptually equal integrals were averaged in order to minimize their uncertainties. The monomer reactivity ratios were calculated from the ^{13}C NMR sequence data[31] using the following relationship[31]:

$$r_E = \frac{2[EE]}{[EH]X} \qquad r_H = \frac{2[HH]X}{[EH]}$$

where, r_E = ethylene reactivity ratio and r_H = 1-hexene reactivity ratio.

$[EE] = [EEE] + 1/2\ [HEE]$

$[EH] = [HEH] + 1/2[HEE] + [EHE] + 1/2[EHH]$

$[HH] = [HHH] + 1/2[EHH]$

X = [E]/[H] in the feed = concentration of ethylene (mol/L)/ concentration of comonomer (mol/L) in the feed. The results are shown in **Table 5.13**.

Fig. 5.13 shows the spectra of three ethylene-1-hexene copolymers which differ in the content of 1-hexene incorporated (a) 5.1 (b) 6.2 (c) 8.6 mol %. The absence of peaks at cases. Resonance at 34.9 and 24.5 ppm is due to HEHE (1,5-dibutyl branches) and 30.9 ppm due to sequences HEEH (1,7-dibutyl branches) which is present only in case of C. These spectra show that the most of the 1-hexene units were isolated in the copolymer between polyethylene block. As the concentration of the 1-hexene in the copolymer increased, butyl branches became closer. Some of the butyl branches were separated only by one or two units of ethylene, as indicated by the presence of 1,5 and 1,7 dibutyl branches (**Table 5.13**). It can be further observed that in case of supported catalyst, HHE/EHH, HH sequences appear which enables calculation of reactivity ratios (**Table 5.14**).

Table-5.13 : Monomer sequence distributions of poly(ethylene-co- hexene) using supported catalyst and unsupported Cp_2ZrCl_2/MAO catalyst

Entry No.	Polymn Temp (°C)	1-hexene in copoly. (mol %)	[EHE]	[HHE] [EHH]	[HHH]	[HEH]	[HEE] [EEH]	[EEE]	[EE]	[EH]	H
1	70	-	0.0	0.0	0.0	0.0	0.0	100	100	0.0	0.
2[b]	70	4.7	4.3	0.0	0.0	0.4	11.9	83.4	89.35	10.65	0.
3	“	.5.1	5.06	0.0	0.0	0.0	10.74	84.19	89.56	10.43	0.
4	“	6.2	5.34	0.84	0.0	0.0	5.34	86.9	89.57	8.65	0.4
5	“	8.6	7.2	1.37	0.0	2.20	16.67	72.54	80.88	18.12	0.6
6			6.27	0.0	0.0	3.62	12.81	77.28	83.68	16.29	0.

[a] All polymerization were carried out in xylene (50 mL); Al/Zr = 5000; T = 70°C; P = 1 bar; time 30 min; using 8-9 mg of solid catalyst. [b] Polymerization carried out using homogeneous Cp_2ZrCl_2 catalyst

Table 5.14 : Reactivity ratio and average sequence length of ethylene and

1-hexene of the copolymer[a]

Entry no.	1-hexene in copolymer (mol %)	Monomer conc.(M)		r_E	r_H	$r_E.r_H$	$\bar{n}_E$	$\bar{n}_H$
		E	H					
1	6.2	0.042	0.24	119.62	0.017	2.03	23.78	1.09
2	8.6	0.042	0.48	101.1	0.006	0.60	8.68	1.09

[a] All polymerization were carried out at 70°C, P = 1 bar, Al/Zr = 5000, for 30 min; n_E and n_H are the average sequence length of ethylene andhexene.

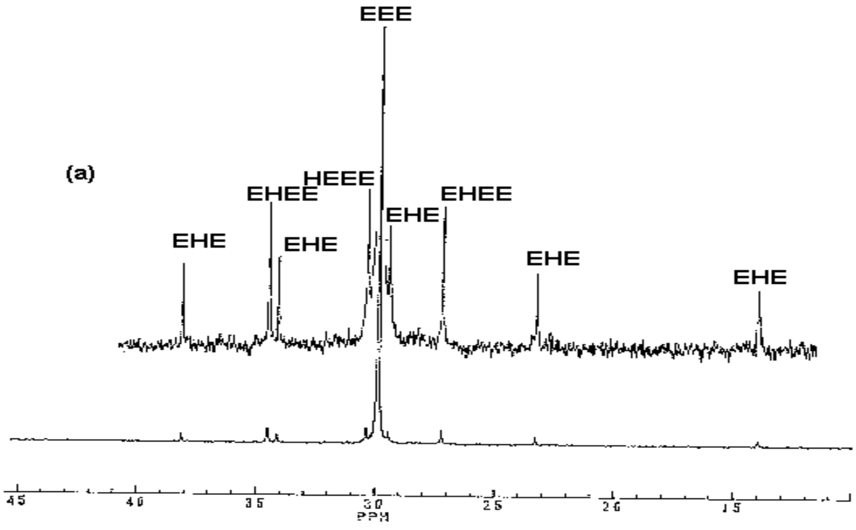
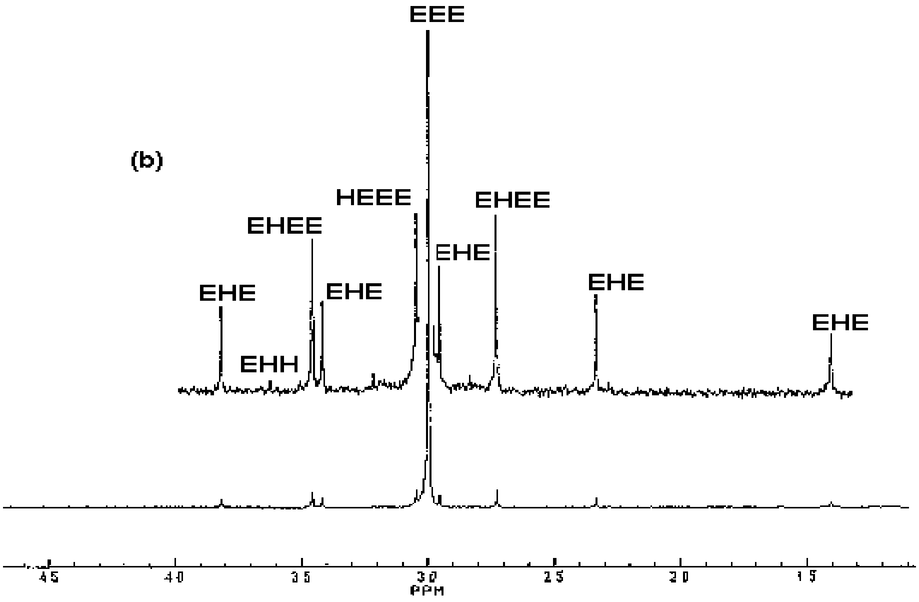
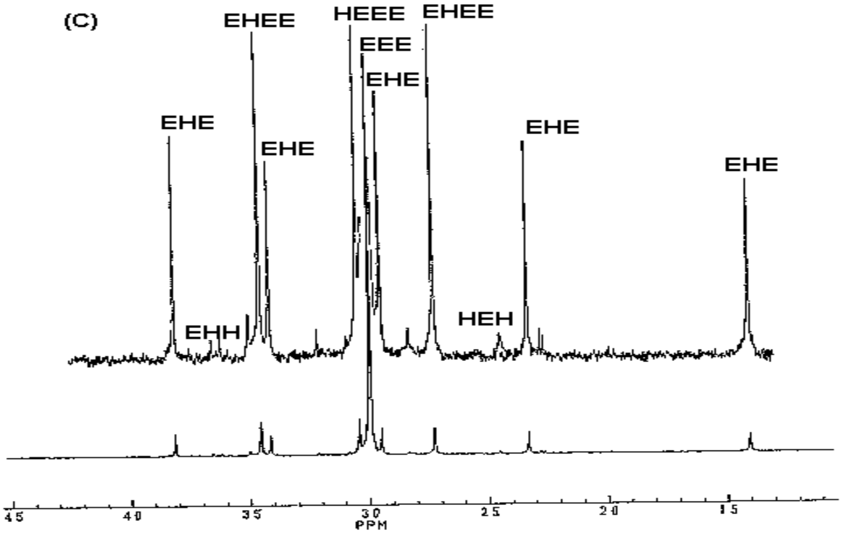


Fig. 5.13 : ^{13}C NMR of the copolymer obtained by using $MgCl_2$ supported Cp_2ZrCl_2 catalyst at Al/Zr = 5000, T = 70°C, P = 1 bar; (a) 1-hexene content 5.1 mol %, (b) 1-hexene content 6.2 mol %, (c) 1-hexene content 8.6 mol % (b and C in the next page).


(b)
EEE
HEEE
EHEE
EHEE
EHE
EHE
EHE
EHE
EHE
EHH
45
40
35
30
25
20
15
PPM


(C)
EHEE
HEEE
EHEE
EEE
EHE
EHE
EHE
EHE
EHE
EHH
HEH
45
40
35
30
25
20
15
PPM

5.3.6 Mechanism of ethylene polymerization using $MgCl_2$.2THF supported Cp_2ZrCl_2 catalyst

The support $MgCl_2$.2THF examined in the present study significantly modulates the reactivity of the cationic zirconium center towards homo- and copolymerization of ethylene. The supported catalyst enhances the catalytic activity and also increases the molecular weight of polymer as compared to unsupported Cp_2ZrCl_2. Although no direct evidence exist, we can speculate that the increased stability of the active center is due to the interaction of the cationic zirconium center with the weakly Lewis basic support. A mechanistic scheme similar to that proposed for $MgCl_2$.2THF-Cp_2TiCl_2 (**Scheme 4.1**, **Chapter-4**) can also be written for the supportedzirconocene system.

5.4 CONCLUSION

By exploiting the mutual solubility of $MgCl_2$.2THF and Cp_2ZrCl_2 in THF, it was possible to prepare a supported catalyst by precipitating the complex from a homogeneous solution. The solid catalyst thus prepared shows high catalyst activity and good catalyst life times at temperatures as high as 100°C in xylene for ethylene polymerization. This is attributed to the fact that the active cationic zirconium centers are anchored on the surface of magnesium chloride and thus are highly stabilized. The supported catalyst shows a lower catalyst activity in n-heptane than in xylene. The supported catalyst exhibit a higher catalyst activity with increase in temperature from 70 to 80°C in xylene, at 1 bar ethylene pressure and from 90-100°C at 5 bar ethylene pressure. The supported catalyst does not lead to broadening of molecular weight distribution. The supported catalyst shows response to hydrogen as chain transfer agent and reactivity towards copolymerization. Only about 20 mol % of zirconium is active for polymerization in the supported catalyst. When one corrects for the relative active center concentration, the catalyst activity difference between $MgCl_2$.2THF-Cp_2ZrCl_2 and Cp_2ZrCl_2 is further enlarged. This is a clear indication of the enhanced stability to the active center provided by the support.

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6.1 INTRODUCTION

Anhydrous magnesium chloride is commonly used as a support in titanium based heterogeneous polymerization catalysts. These catalyst systems are characterized by high catalytic activities and lead to the formation of polymer with relatively narrow molecular weight distributions. They are useful for slurry and gas phase polymerization processes and thus form the basis of the commercial polyolefin processes[1-3]. Anhydrous magnesium chloride, however, is brittle and undergoes easy attrition. In addition it has a relatively low surface area even after activation. On the contrary, silica is a well known support for gas phase fluidized bed polymerization of olefins using titanium based Ziegler-Natta catalysts. However, when used with metallocene type catalysts silica support shows reduced polymerization activities[4-6] and causes broadening of molecular weight distribution, presumably because of the multiplicity of bonding sites on the surface of silica, which change the electronic and steric environment of the transition metal center.

One of the early attempts to support a soluble metallocene catalyst was due to Slotfeldt-Ellingsen and co-workers. Cp_2TiCl_2 was supported on silica-gel and used to polymerize ethylene with $AlEt_nCl_{3-n}$[7]. Ihm *et al.* used a slightly modified procedure in order to support Cp_2TiCl_2 on SiO_2 pretreated with MAO[8]. The catalyst thus produced gave bimodal molecular weight distribution polyethylene, which was explained due to an interaction between silica and aluminoxane. On the other hand, $SiO_2/MgCl_2/TiCl_4$ bisupported catalysts have been well studied in case of homo- and copolymerization of olefins. Pasquet *et al.*[9] described a SiO_2-$MgCl_2$ supported $TiCl_4$ catalyst used for the polymerization of ethylene. The preparation method was improved by the use of an additive, stabilizing $MgCl_2$, namely, ammonium chloride. Best supports contain less than 5 wt. % Mg with about 2/3 of Mg as $MgCl_2$, thus maintaining the porous properties of silica. Nowlin *et al.*[10] describe a method of impregnating a Ziegler-Natta catalyst onto silica. Geoke *et al.*[11], Karol *et al.*[12], Wagner *et al.*[13,14] have described high activity catalysts prepared by forming a precursor from a titanium compound, a magnesium compound and an electron donor compound such as tetrahydrofuran, and depositing the precursor onto silica. Catalysts prepared by this method were useful for gas phase polymerization of olefins.

supporting anhydrous magnesium chloride and a titanium based metallocene catalyst precursor from a homogeneous solution onto an inert carrier material such as high surface area silica. It was hoped that catalyst prepared by this method would offer a good balance of properties such as high activity, narrow molecular weight distribution and acceptable catalyst life times. This chapter discusses the preparation of a SiO_2-$MgCl_2$ supported titanium based metallocene catalysts prepared by the deposition of a homogeneous solution of anhydrous magnesium chloride and a titanocene onto high surface area SiO_2. The broad objective is to understand the combined effect of both silica and magnesium chloride on factors such as catalytic activity, rate of polymerization, molecular weight and molecular weight distribution of polyethylene.

6.2 EXPERIMENTAL SECTION

6.2.1 Synthesis of the catalysts

Catalyst A: A three neck r.b. flask equipped with magnetic needle, reflux condenser, addition funnel, N_2 inlet and outlet was flame dried and cooled under N_2. Anhydrous $MgCl_2$ (176.1 mg) was placed in the flask followed by addition of 30 mL THF. The temperature of the flask was maintained at 60-65^{0}C with constant stirring until all $MgCl_2$ dissolves in the THF. Cp_2TiCl_2 (503.3 mg) dissolved separately in 35 mL of THF and was added to the solution of $MgCl_2$ over a period of 15 min and stirred for 30 min at 60-65^{0}C. SiO_2 (2.56 g, previously calcined at 550^{o}C for 12 h, free -OH content after calcination 1.1 mmol/g) was taken in another flask followed by addition of 75 mL of THF and the slurry was stirred at 60-65^{0}C. The previously prepared magnesium chloride and metallocene solution in THF was then added to this slurry and stirred for 2 h at 60-65^{0}C. The mixture was cooled, THF distilled under vacuum and the solid catalyst dried under vacuum. The solid catalyst thus prepared contains Ti = 3.5 wt. %; Mg = 1.5 wt. %; Cl = 8.56 wt. %.

Catalyst B: A three neck r.b. flask equipped with magnetic needle, reflux condenser, addition funnel, N_2 inlet and outlet was flame dried and cooled under N_2. Anhydrous $MgCl_2$ (277.6 mg) was placed followed by addition of 40 mL THF. The temperature of the flask was maintained at 60-65^{0}C with constant stirring until all $MgCl_2$ dissolves in THF. Cp_2TiCl_2 (503.5 mg) dissolved separately in 40 mL of THF and was added to the solution previously calcined at 550^{o}C for 12 h, free -OH content after calcination 1.1 mmol/g) was taken in another flask followed by addition of 300 mL of n-hexane and the slurry was stirred at 60-65^{0}C. The previously prepared magnesium chloride and metallocene solution was then added to this slurry and stirred for 3 h at 60-65^{0}C. The mixture was cooled and the precipitate was washed 3-4 times by n-hexane (using 50 mL each time) and dried under vacuum. The solid catalyst thus prepared contains Ti = 2.64 wt. %; Mg = 2.3 wt. %; Cl = 11.2 wt. %.

Catalyst C : A three neck r.b. flask equipped with magnetic needle, reflux condenser, addition funnel, N_2 inlet and outlet was flame dried and cooled under N_2. Anhydrous $MgCl_2$ (190 mg) was placed in the flask followed by addition of 40 mL THF. The temperature of the flask was maintained at 60-65^{0}C with constant stirring until all $MgCl_2$ dissolves in THF. Cp_2TiCl_2 (434 mg) dissolved separately in 35 mL of THF and was added to the solution of $MgCl_2$ over a period of 15 min and stirred for 30 min at 60-65^{0}C. SiO_2 (2.50 g, calcined as before) and 100 mL of xylene were taken in another flask and treated with MAO (0.0339 mol as Al), and stirred for 30 min and washed several times with xylene, followed by addition of 75 mL of THF and stirred at 60-65^{0}C. The magnesium chloride and metallocene solution in THF was then added to the slurry of MAO treated silica, stirred for 2 h at 60-65^{0}C. The mixture was cooled, THF removed by distillation under vacuum and catalyst dried in vacuo. The solid catalyst thus prepared contains Ti = 2.65 wt. %; Mg = 1.26 wt. %; Cl = 9.01 wt. %.

Catalyst D: A three neck r.b. flask equipped with magnetic needle, reflux condenser, addition funnel, N_2 inlet and outlet was flame dried and cooled under N_2. SiO_2 (1.5 g, calcined as before) was placed in it followed by addition of 300 mL of n-hexane and the slurry was heated to 60-65^{0}C with stirring. Cp_2TiCl_2 (253.6 mg) was dissolved separately in 90 mL of xylene and was added to the slurry of silica in hexane over a period of 15 min and stirred for 1 h at 60-65^{0}C. The mixture was cooled, filtered and the filtrate washed by n-hexane for 3-4 times and dried under vacuum and kept for further studies. The solid catalyst thus prepared contains Ti = 3.4 wt. %.

6.2.2 Determination of hydroxyl group on SiO_2[9]

A weighed sample of silica (0.5-0.8 g) was suspended in dry n-heptane (50 mL) in a dry three neck flask connected to a gas burrette of capacity 100 mL. A solution of triethylaluminum (0.073 mol) was added by a hypodermic syringe at room temperature. The mixture was vigorously stirred, and the amount of ethane gas evolved was measured. A blank measurement with pure heptane allows one to eliminate the contribution of heptane vapor (diluent of triethylaluminum). This method is similar to the other methods[18,19] employing other reagents with metal carbon or metal halogen bonds, CH_3MgI or $TiCl_4$.

Number of hydroxyl group before calcination was 2.8 mmol/g silica and after calcination was 1 mmol/g silica.

6.3 RESULTS AND DISCUSSION

6.3.1 Characterization of catalysts

FT-IR spectra of all the catalysts A, B and C are nearly identical and shown in **Fig 6.1**. Silica calcined at 550^0C shows a single peak at 3664 cm^{-1}, which has been previously assigned to isolated hydroxyl groups on silica[20]. The broad absorption 3150-3850 cm^{-1} may be due to the interaction of neighboring hydroxyl groups on the silica surface. Both the FT-IR spectra of cat A and B are same. After treatment with Cp_2TiCl_2 and $MgCl_2$ this sharp singlet peak is no longer observed and part of the broad -OH stretching region is still discernible. Again the peaks at 1630 cm^{-1} corresponding to $MgCl_2$ is shifted to 1614 cm^{-1}. This may be due to the interaction of silica with $MgCl_2$.nTHF. After treatment with MAO the peaks at 3664 cm^{-1} is broadened indicating the absence of free hydroxyl group on silica. The presence of cyclopentadienyl ligand on the solid catalysts was evidenced by the presence of peaks at 1462 and 820 cm^{-1}.

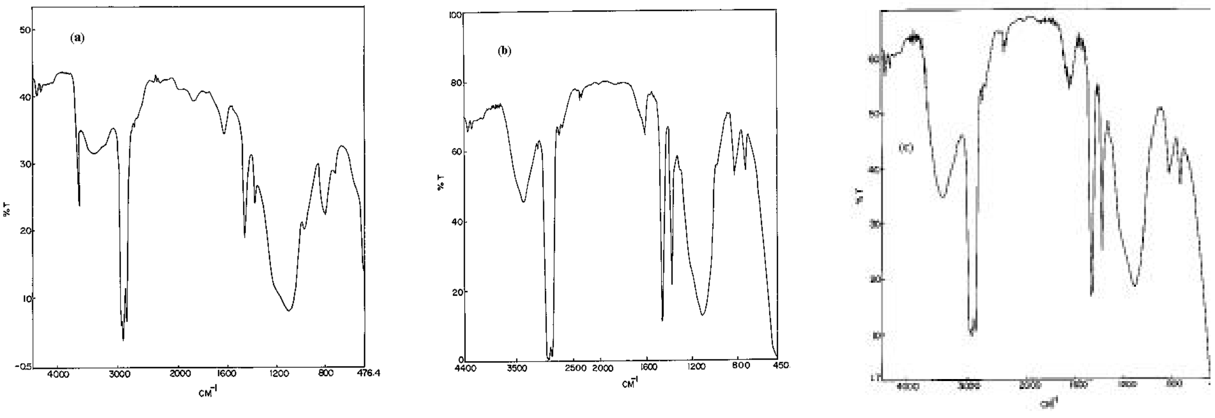


Fig. 6.1 : FT-IR spectra of SiO_2-$MgCl_2$ supported Cp_2TiCl_2 catalysts; (a) silica calcined at 550 °C, (b) catalyst A; (c) catalyst C.

6.3.2 Polymerization of ethylene

6.3.2.1 Effect of cocatalysts

Catalysts A, B and C were used for the polymerization of ethylene in xylene as diluent at 50^0C using different cocatalysts. The results are shown in **Table 6.1**. Catalysts A, B and C showed higher activity compared to catalyst D. In all cases catalyst activity was superior with MAO as cocatalysts. Of the three catalysts A, B and C, B and C showed comparable catalyst activity while the same for A was slightly lower. The molecular weight of polyethylene obtained from Si-Mg-Ti/MAO was found to be higher than obtained from Si-Ti catalyst. The MAO treated silica supported catalyst C gave the highest molecular weight. It is reported that Mg^{+2} stabilizes the active titanium centers in case of Mg-Ti catalyst systems resulting in increases of molecular weight of polyolefins[3]. The presence of THF as a Lewis base also increases the propagation rate constant (k_p) relative to transfer rate (k_{tr}) thus increasing the molecular weight. This observation has also been made in case propylene polymerization using Mg-Ti/TEAL catalyst in presence of ethylbenzoate as an internal electron donor[2,21].

Table 6.1 : Polymerization of ethylene by SiO_2-$MgCl_2$ supported and SiO_2 supported

Entry No.	Catalyst	mol Ti x 10^6	Cocat.	Al/Ti (mol)	Polymn. time (min)	Wt.. of polymer (g)	Activity (Kg PE/ g Ti.h)	[η] (dL/g)
1	A	5.1	MAO	500	20	0.80	10	2.31
2	“	75	DEAC	100	25	0.35	0.2	1.42
3	“	56	TIBAL	100	-	-	-	-
4	B	4.3	MAO	500	20	0.78	14	3.02
5	“	50	DEAC	100	25	0.49	0.5	0.754
6	“	60	TIBAL	100	-	-	-	-
7	C	5.14	MAO	500	20	1.04	13	4.11
8	“	55.4	DEAC	100	25	0.23	0.2	1.17
9	“	53.5	TIBAL	100	25	0.05	0.04	n.d.
10	D	4.9	MAO	500	30	0.65	5.5	1.82

[a] All polymerization were conducted inxylene (50 mL) at 50^0C, P = 1 bar.

6.3.2.2 Effect of Al/Ti ratio

The effect of Al/Ti mole ratio were examined with the catalysts A, B and C. In these experiments, MAO was added as a 5.4 wt. % (as Al) solution in xylene. The results are shown in **Table 6.2**. All the three catalysts showed a progressive increase in activity and a decrease in molecular weight with increase in Al/Ti ratio. All the catalysts show similar kinetic curves with an increase in rate followed by a steady decay (**Fig 6.2**). The peak rate attained by SiO_2-$MgCl_2$ supported catalyst is higher than SiO_2 supported Cp_2TiCl_2 catalyst.

Table 6.2 : Effect of Al/Ti ratio on the polymerization of ethylene using

Entry No	Catalyst	mol Ti x 10^6	Al/Ti (mol)	Polymn. time(min)	Wt. of polymer (g)	Activity (Kg PE/g Ti.h)	[η] (dL/g)
1	A	6.4	500	25	0.81	6	2.98
2	"	5.1	1000	25	0.83	8	2.58
3	"	2.5	2000	25	0.81	16	1.76
4	B	4.8	500	25	0.82	8.5	3.30
5	"	4.0	1000	25	0.88	11	3.01
6	"	2.9	2000	15	0.78	22	2.88
7	C	4.4	500	30	1.05	10	4.22
8	"	4.8	1000	30	1.37	12	3.61
9[b]	"	2.6	2000	30	0.95	15	2.78

[a] All polymerization was conducted in xylene (50 mL) at 30^0C, P = 1 bar. [b] Polymerization was conducted at 50^0C.

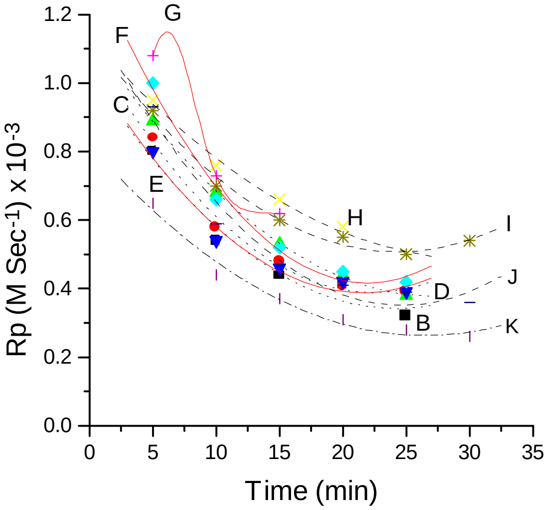


Fig. 6.2 : Kinetic profiles of ethylene polymerization using supported metallocene catalysts. B, C, D using catalyst A/MAO at Al/Ti = 500, 1000, 2000; E, F, G using catalyst B/MAO at Al/Ti = 500, 1000, 2000; H, I, J using catalyst C/MAO at Al/Ti = 500, 1000 and 2000; K using catalyst D/MAO at Al/Ti = 500.

6.3.2.3 Effect of temperature

The three catalysts A, B and C show an increase in catalyst activity with an increase in temperature from 30 to 50^{0}C beyond which the catalyst activities decreases (**Table 6.3**).

Table 6.3 : Effect of temperature on ethylene polymerization using SiO_2-$MgCl_2$ supported Cp_2TiCl_2 /MAO catalysts[a]

Entry No	Catalyst	mol Ti x10^6	Temp (^{0}C)	Polymn. Time (min)	Wt. of polymer (g)	Activity (Kg PE/g Ti.h)	[η] (dL/g)
1	A	6.4	30	25	0.81	6.4	2.98
2	“	5.1	50	25	0.80	10	2.31
3	“	4.8	70	25	0.62	6.4	1.36
4	B	4.8	30	25	0.82	8.5	3.30
5	“	4.3	50	15	0.78	14	3.02
6	“	4.5	70	25	0.64	7	2.94
7	C	4.4	30	25	1.05	12	4.22
8	“	5.1	50	25	1.2	12	4.11
9	“	4.98	70	25	0.67	6.7	3.92

[a] All polymerization were carried out in xylene (50 mL), P = 1 bar, Al/Ti = 500.

This behavior is different from that of homogeneous Cp_2TiCl_2 catalyst which rapidly lose their activity at higher temperature. In addition, all the catalysts showed significantly lesser rate decay at higher temperatures (**Fig. 6.3**). Furthermore the molecular weight of polyethylene obtained from catalyst C is higher compared to catalyst A and B. These results are different from that previously observed by Kaminsky *et al.*[4] and Sacchi *et al.*[23] in case of propylene polymerization using zirconium based metallocene catalysts. It was observed that silica pretreated with MAO led to lowering in molecular weight when compared to silica support without treating with MAO. The observation was explained by the fact that when MAO is absorbed on silica surface, the zirconocene can easily float on these MAO groups, and hence is mobile and similar to a homogeneous catalyst. It is further observed that molecular weight decreases more rapidly with increasing temperature in case of

THF present in catalyst A which might causes faster deactivation of the catalyst, especially at higher temperatures.

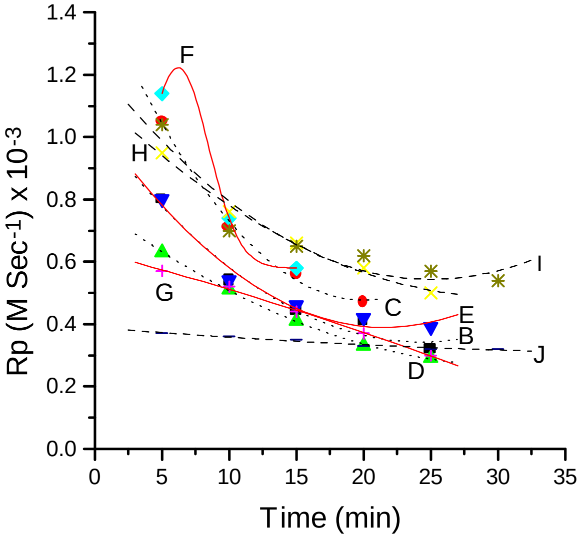


Fig. 6.3: Kinetic profiles of ethylene polymerization using SiO_2-$MgCl_2$ supported Cp_2TiCl_2/MAO catalysts at different temperatures. B, C, D catalyst A/MAO at 30, 50, 70 °C respectively; E, F, and G catalyst B/MAO at 30, 50, 70 °C; H, I, J catalyst C/MAO at 30, 50, 70 °C respectively.

6.3.2.4 Polymerization at 5 bar pressure

Catalysts B and C were used for polymerization of ethylene at 5 bar pressure using xylene as diluent. The results are shown in **Table 6.4**.

Table 6.4 : Polymerization of ethylene using SiO_2-$MgCl_2$ supported Cp_2TiCl_2/MAO catalysts at 5 bar pressure[a]

Entry No	Catalyst	mol Ti $x10^6$	Al/Ti (mol)	Wt. of polymer (g)	Activity (Kg PE/g Ti.h)	[η] (dL/g)
1	B	6.83	1000	3.35	20	4.44
2	"	2.20	5000	2.11	41	3.80
3	C	10.4	500	2.3	9	3.08

[a] All polymerization were carried out in xylene (100 mL) for 30 min, P = 5 bar, T = 50°C, TMA added = 3 $x10^{-3}$ mol as Al.

The GPC chromatograms of polyethylene samples obtained by using catalysts A to D are shown in **Fig. 6.4** and the analytical data are shown in **Table 6.5**. Under similar polymerization conditions SiO_2 supported Cp_2TiCl_2 (catalyst D) shows a bimodal molecular weight distribution in the GPC chromatograms while catalyst A, B, and C produce unimodal and narrow molecular weight distribution. Recently, Ihm *et al.* has shown that ethylene polymerization using Cp_2TiCl_2 supported on SiO_2 result in the formation of a broad and bimodal molecular weight distribution polyethylene[8].

Supporting a $MgCl_2$-Cp_2TiCl_2 complex on silica narrows molecular weight distribution. Thus, when Cp_2TiCl_2 is supported on silica a multisite catalyst is generated presuambly due to the different electronic and steric environment around titanium caused by the different types of hydroxyl groups on the surface of silica. However, once complexed with $MgCl_2$ the effect due to surface heterogeniety of silica is considerably reduced. SiO_2 pretreated with MAO gave the most narrow molecular weight distribution (catalyst C) which further substantiates this argument as this further reduces the hydroxyl content in SiO_2.

Table 6.5 : Molecular weight MWD of polyethylenes obtained with SiO_2-$MgCl_2$ supported and SiO_2 supported Cp_2TiCl_2/MAO catalysts[a]

Entry no.	Catalyst	Temp (°C)	M_n	M_w	MWD
1	Cat A	50	95,749	3,02,391	3.16
2	Cat B	50	78,408	2,05,948	2.62
3	Cat C	50	1,30,460	2,97,688	2.28
4	Cat D	50	35,765	2,59,742	7.25
5	Cat A	70	69,654	1,92,504	2.76
6	Cat B	70	54,614	1,53,798	2.81
7	Cat C	70	72,061	1,45,098	2.01

[a] All polymerization were carried out in xylene (50 mL), P = 1 bar, Al/Ti = 500.

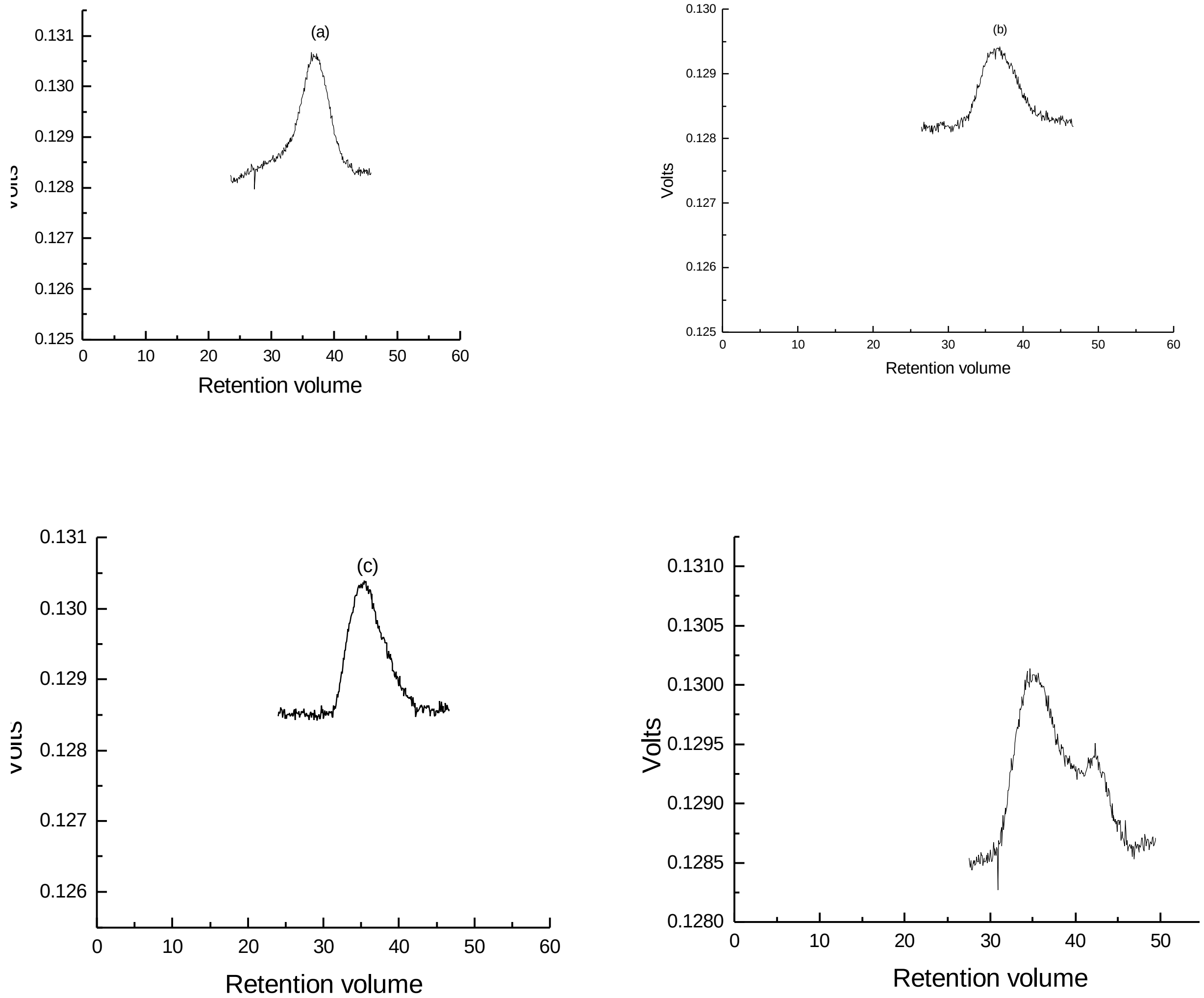


Fig 6.4 : GPC chromatogram of poly(ethylene)s obtained from SiO_2-$MgCl_2$ supported Cp_2TiCl_2 catalysts; (a) catalyst A; (b) catalyst B; (C) catalyst C; (d) catalyst D

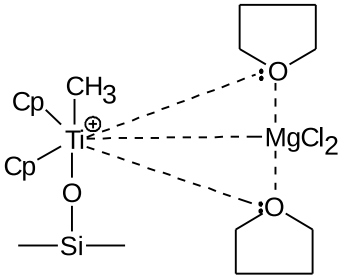
6.3.4 Mechanism of ethylene polymerization on SiO_2-$MgCl_2$ supported Cp_2TiCl_2 catalysts

Low amounts of $MgCl_2$ (< 3 wt. %) incorporation as a complex with metallocene in silica results in a modulation of the catalyst behavior. All the three catalysts Si-Mg-Ti showed a higher rate of polymerization compared to Si-Ti catalyst. The activity of Si-Mg-Ti catalysts were higher than Si-Ti catalyst. Amongst catalyst A, B and C, the activity of catalyst A was found to be the lowest. This could be due to the presence of excess THF which decreases

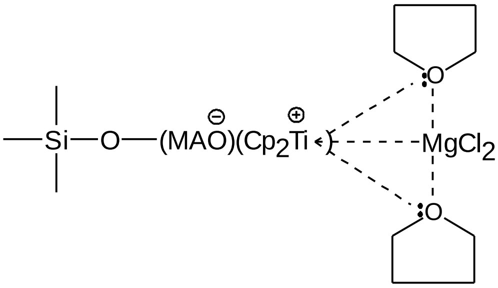
The molecular weight of polyethylene obtained from catalyst A, B and C are also higher when compared to catalyst D. Interestingly, the molecular weight distribution of the polyethylene obtained from Si-Mg-Ti was found to be narrow while that obtained from Si-Ti was found to be broad. This reflects a change in the nature of the active site when Cp_2TiCl_2 is precomplexed with $MgCl_2$ prior to supporting on SiO_2.

Of the four catalysts examined catalyst C was the most effective. Catalyst C gave the maximum catalyst activity and highest polymer molecular weight as well as narrow molecular weight distribution.

A tentative structure of active center for catalyst A, B and C is shown in **Scheme 6.1** and **Scheme 6.2**.



Scheme 6.1 : Cationic active species in case of SiO_2-$MgCl_2$ supported Cp_2TiCl_2 catalysts (catalyst A or B)



Scheme 6.2 : Cationic active species in case catalyst C

6.4 CONCLUSION

Supporting of a precomplexed $MgCl_2$-Cp_2TiCl_2 on SiO_2 causes major improvement of the catalyst such as an increase in catalyst activity, higher polymer molecular weight and narrow molecular weight distribution. The catalysts also show reduced rate decay at temperatures as high as 70^0C in xylene. These observations demonstrates the beneficial role of $MgCl_2$ as a component of SiO_2 supported metallocene catalysts.

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7.1 INTRODUCTION

Homogeneous metallocene/methylaluminoxane (MAO) catalysts, offer unique possibilities in tailoring molecular structure of polyolefins through modification of ligand structure at the transition metal center[1,2]. However, homogeneous catalysts have some drawbacks from a practical point of view. Most commercial processes use solid catalyst, which are easy to feed and produce polymers with superior particle morphology with reduced reactor fouling. Therefore, increasing attention has been devoted in the recent years to the transformation of homogeneous metallocene catalysts to heterogeneous catalysts by supporting them onto suitable inorganic carriers such as silica, alumina and magnesium chloride[3-6].

Silica is an inert support and having negligible interaction with the active metal center. However, silica supported metallocene show reduced catalyst activity and broader molecular weight distribution relative to the homogeneous catalyst. On the contrary, anhydrous magnesium chloride has been extensively examined as an efficient support for titanium based heterogeneous catalyst for ethylene and propylene polymerization and forms the basis of commercial polyolefin processes[7-9]. Detailed studies have established the presence of significant modulation of the catalytically active titanium center by anhydrous magnesium chloride support[9]. Earlier work from this laboratory had shown when bis(cyclopentadienyl) titanium(IV)dichloride was supported on a magnesium chloride.THF complex a cationic titanium species with unusal stability was observed[10]. This was attributed to the ability of the weak lewis base, $MgCl_2$, to stabilize the counter anion.

Therefore, it was thought that supporting a soluble complex of anhydrous $MgCl_2$-group IV metallocene on a high surface area silica may offer the combined advantages of active center stabilization and high polymerization activity.

Silica supported anhydrous magnesium chloride-titanium (IV) chloride have been previously studied for ethylene polymerization[11,12]. A number of patents from Union Carbide corporation describes high activity catalysts prepared from a soluble complexes of $MgCl_2$-$TiCl_4$ in tetrahydrofuran and silica and their utility in gas-phase polymerization processes[13-16].

This chapter discusses the synthesis of a SiO_2-$MgCl_2$-Cp_2ZrCl_2 catalyst and the evaluation of this catalyst. An objective of this study was assess the role of silica and magnesium chloride as supports for zirconium based metallocene catalysts.

7.2 EXPERIMENTAL SECTION

7.2.1 Synthesis of the catalyst

Catalyst A (Si-Mg-Zr) : A three neck round bottom flask equipped with magnetic needle, reflux condenser, addition funnel, N_2 inlet and outlet was flame dried and cooled under N_2. Anhydrous $MgCl_2$ (277.6 mg) was placed in the flask and 40 mL THF added to it. The mixture was heated to 60-65^{0}C with constant stirring until all $MgCl_2$ dissolved in THF. Cp_2ZrCl_2 (503.5 mg) dissolved separately in 40 mL of THF was added to the solution of $MgCl_2$ in THF over a period of 15 min and stirred for 30 min at 60-65^{0}C. SiO_2 (2.91 g, previously calcined at 550^{o}C for 12 h, free -OH content after calcination 1.1 mmol/g) was taken in another flask followed by addition of 300 mL of n-hexane and the slurry was stirred at 60-65^{0}C. The magnesium chloride and metallocene solution in THF was then added to this slurry and stirred for 3 h at 60-65^{0}C. The slurry was cooled, filtered, washed 3-4 times with n-hexane (using 50 mL each time) and dried under vacuum.

Catalyst B (Si-Zr) : A three neck round bottom flask equipped with magnetic needle, reflux condenser, addition funnel, N_2 inlet and outlet which was flame dried and cooled under N_2. SiO_2 (1.95 g, calcined as before) was placed in the flask followed by addition of 150 mL n-hexane and heated to 60-65^{0}C with stirring. Cp_2ZrCl_2 (200.9 mg) dissolved separately in 25 mL of THF was added to the slurry of silica in n-hexane over a period of 15 min and stirred for 1 h at 60-65^{0}C. The slurry was cooled, filtered, washed with n-hexane for 3-4 times (using 50 mL each time) and dried under vacuum.

7.2.2 Determination of hydroxyl group on SiO_2

The procedure has been described in **chapter-6**, **section 6.2.2**.

7.2.3 Removal of electron donor from the solid catalyst precursor

About 1 g of the solid catalyst was taken in three neck round bottom flask equipped with magnetic stirring bar, N_2 inlet and outlet. The solid catalyst was heated by means of an oil bath at the desired temperature under a continuous flow of N_2. After a specified time of heating the catalyst was cooled under N_2, and the loss in weight was calculated.

7.3 RESULTS AND DISCUSSION

7.3.1 Characterization of the catalysts

The elemental analysis of both the catalysts are shown in **Table 6.1**. In case of catalyst B, the wt % of Zr was 0.53 wt %, which is more than catalyst A (0.36 wt. %). The low amount of Zr in the latter case may be due to the presence of $MgCl_2$ on SiO_2. The low surface area in case of catalyst A may be due to higher amount of THF present on the silica.

Table 7.1 : Elemental analysis of supported catalysts (A, B)

Catalyst	Zr (wt. %)	Mg (wt. %)	Cl (wt. %)	THF (wt. %)	S. A. (m^2/g)	Empirical formula
Cat. A	0.36	2.4	10.04	15	247	$MgCl_{2.75}Zr_{0.039}THF_{2.25}Cp_{0.078}$
Cat. B	0.53	-	n.d.	-	n.d.	-

The FT-IR spectra of the catalyst A is shown in **Fig 7.1**. The presence of cyclopentadienyl ligand on the solid catalysts was inferred by the presence of peaks at 1462 and 820 cm^{-1}. Silica calcined at 550^0C shows a single peak at 3664 cm^{-1}, which has been previously assigned to isolated hydroxyl groups on this silica[17] (**Fig 7.2**). The broad absorption 3150-3850 cm^{-1} may be due to the interaction of neighbouring hydroxyl groups on the silica surface. After treatment with Cp_2ZrCl_2 and $MgCl_2$ this sharp singlet peak is no longer observed and part of the broad -OH stretching region is still discernible. Again the peaks at 1632 cm^{-1} correspond to $MgCl_2$.

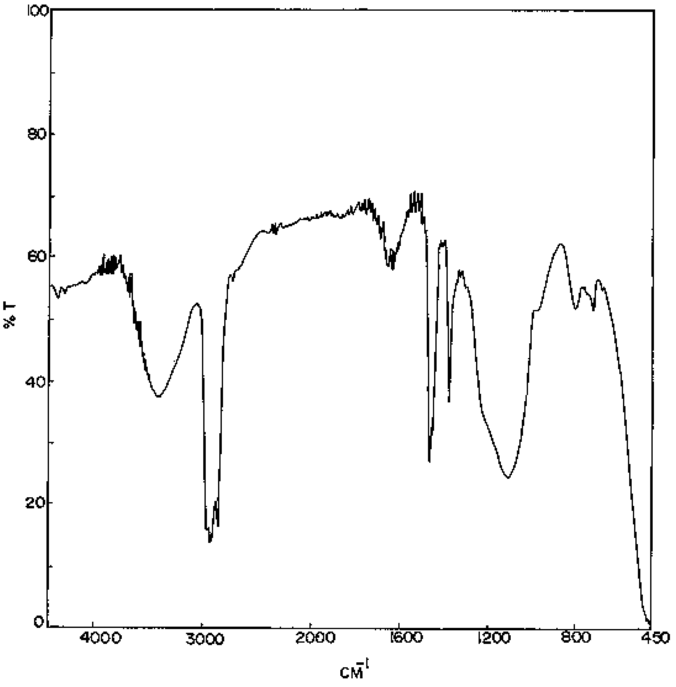


Fig. 7.1 : FT-IR spectra of catalyst A

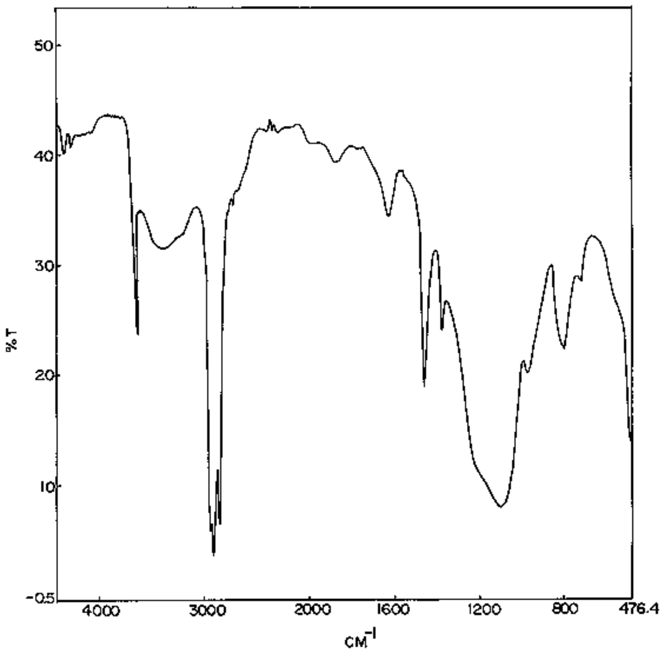


Fig 7.2 : FT-IR spectra of silica calcined at 550 °C

7.3.2 Polymerization of ethylene

7.3.2.1 Polymerization of ethylene at 1 bar pressure

Catalysts A & B were used for the polymerization of ethylene in xylene as diluent at 70^0C in conjunction with MAO as cocatalyst (**Table 7.2**). It was found that catalyst B shows lower activity when compared to catalyst A.

Table 7.2 : Ethylene Polymerization using SiO_2 supported and SiO_2-$MgCl_2$ supported Cp_2ZrCl_2/MAO catalyst[a]

Entry no.	Catalyst	Cat. Wt (mg)	mol Zr $x10^7$	Wt of polymer (g)	Activity (Kg PE/g Zr.h)	[η] (dL/g)	M_n	M_w	MWD
1	Cat. A	16.0	6.50	2.10	69	1.81	39450	108209	2.74
2	Cat. B	10.3	5.98	1.2	44	1.45	26,450	92,575	3.57

[a] All polymerization were carried out in xylene (50 mL); Al/Zr = 5000; T = 70°C; time = 30 min; P = 1 bar.

All these catalysts (A & B) show similar kinetic curves, with an initial increase in rate followed by steady decay (**Fig. 7.3**). The polymer molecular weight and molecular weight distribution obtained from Catalyst A was found to be higher and narrower when compared to catalyst B **(Fig 7.4)**.

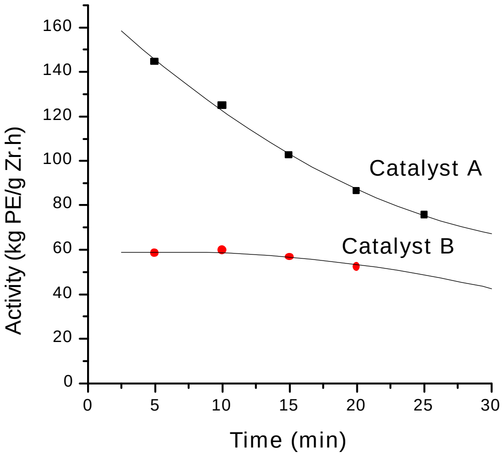


Fig. 7.3 : Kinetic profile of ethylene polymerization using Supported catalyst; xylene = (50 mL); Al/Zr = 5000; T = 70 °C; time = 30 min; P = 1 bar.

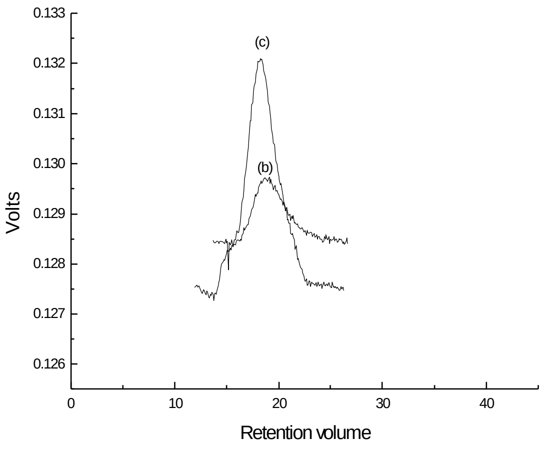


Fig. 7.4 : GPC of polyethylene obtained from supported catalyst; (b) catalyst A; (c) catalyst B.

a) Effect of pretreatment with trialkylaluminums

The solid catalyst B was pretreated with different aluminum alkyls prior to the addition of MAO and used for polymerization of ethylene (**Table 7.3**). The results show that catalyst pretreated with TMA shows higher activity when compared to that without pretreatment. Pretreatment with TIBAL was unsatisfactory. With TEAL, no polymerization activity was observed. A similar behavior was observed in **chapter-5**, with $MgCl_2$ supported Cp_2ZrCl_2 catalyst.

b) Effect of Al/Zr mol ratio

The effect of Al/Zr ratio was examined with the catalyst A in conjunction with MAO. The results are shown in **Table 7.4**. Catalyst activity increased with increase in Al/Ti mole ratio. The catalyst was found to be active for more than 1/2 h at a low Al/Zr ratio mole i.e. at 1000. This behavior is different from that of homogeneous Cp_2ZrCl_2 which rapidly lose their activity within 5 minutes of start of polymerization under similar conditions[18]. With increase in Al/Zr ratio there is a gradual decrease in molecular weight. The rate of polymerization increases with increase in Al/Zr ratio (**Fig. 7.5**).

Table 7.3 : Pretreatment of catalyst A with trialkylaluminums and its effect towards polymerization of ethylene in conjunction with MAO

Entry no.	Trialkylaluminums	Cat. amount (mg)	mol Zr x 10^7	Wt. of polymer (g)	Activity (Kg PE/g Zr.h)	[η] (dL/g)	M_n	M_w	MWD
1[b]	-	15.8	6.23	1.5	53	1.73	25137	67094	2.67
2	TEAL	15.6	6.15	-	-	-	-	-	-
3	TIBAL	15.5	6.12	0.53	19.0	0.99	23392	49509	2.11
4	TMA	16.0	6.5	2.1	69	1.81	39450	108209	2.74

[a] All polymerization were carried out in xylene (50 mL); T = 70^0C; time = 30 min; Al/ Zr = 5000; P = 1 bar. [b] Polymerization without adding trialkylaluminums.

Table 7.4: Effect of Al/Zr ratio on ethylene polymerization using catalyst A/MAO[a]

Entry no.	Cat. amount (mg)	mol Zr x 10^7	Al/Zr (mol)	Wt. of polymer (g)	Activity (Kg PE/ g Zr. h)	[η] (dL/g)
1	15.0	5.90	1000	1.45	54	2.22
2	15.3	6.04	2000	1.60	58	1.90
3	16.0	6.50	5000	2.10	69	1.81

[a] Polymerization conditions: Xylene = 50 mL; Temp. = 70^0C; Time = 30 min; P = 1 bar; TMA added = 1.7 x 10^{-3} mol. as Al.

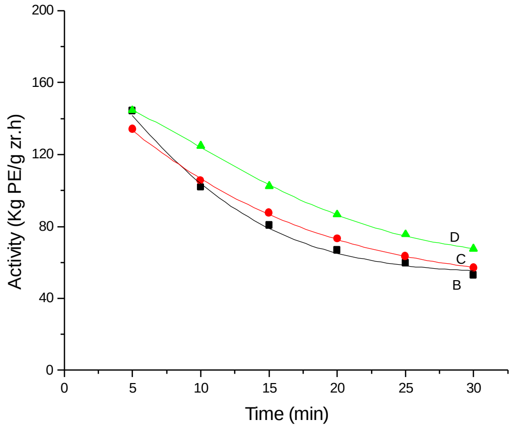


Fig 7.5 : Kinetic profiles of ethylene polymerization at different Al/Zr mol ratio using catalyst A/MAO at 70 °C, P = 1 bar; B at Al/Zr = 1000; C at Al/Zr = 2000; D at Al/Zr = 5000.

c) Effect of temperature

The solid catalyst A showed an increase rate of polymerization as well as catalyst activity with increase in temperature (**Table 7.5**). The kinetic profile shows lesser decay with increase in temperature (**Fig. 7.6**) and at a temperature of 80°C the kinetic curve changes almost to a steady state. An increase in temperature results in a decrease in molecular weight.

Table 7.5 : Effect of temperature on ethylene polymerization using catalyst A/MAO[a]

Entry no.	Cat. amount (mg)	mol Zr x 10^7	Temp. (^{o}C)	wt. of polymer (g)	Activity (Kg PE/ g Zr. h)	[η] (dL/g)
1	15.1	5.9	60	1.5	55	2.61
2	16	6.5	70	2.1	69	1.81
3	15.3	6.04	80	1.8	64	0.88

[a] Polymerization conditions : xylene = 50 mL; Al/Zr = 5000; time = 30 min; P= 1 bar. TMA added = 1.7 x 10^{-3} mol as Al.

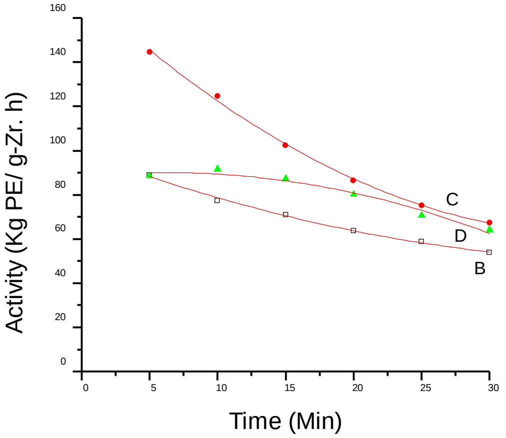


Fig. 7.6 : Kinetic curves of ethylene polymerization using catalyst A/MAO at different temperatures keeping Al/Zr mole ratio of 5000, P = 1 bar. B at 60 °C; C at 70 °C; D at 80 °C.

d) Effect of solvent

Aliphatic hydrocarbon is the preferred solvent for Mg-Ti based Ziegler-Natta catalysts while aromatic solvents are extensively used in the case of homogeneous metallocene catalysts. Ethylene polymerization was carried out using catalyst A in conjunction with MAO in aliphatic hydrocarbon diluents such as n-heptane. The catalyst activity was found to be very low. Eskelinen and Seppala reported ethylene polymerization using Cp_2ZrCl_2/MAO catalyst system. It was observed that catalyst activity decreases in n-heptane than in toluene[19].

7.3.2.2 Polymerization of ethylene at 5 bar pressure

Effect of temperature and hydrogen

To examine the performance of the catalyst under pressure, ethylene polymerization was carried out at 5 bar pressure using solid catalyst A in conjunction with MAO. The results are shown in **Table 7.6**. Catalyst A was found to be active even at 110°C. The activity was sustained for more than one hour. This behavior is distinctly different from that of a homogeneous Cp_2ZrCl_2, which shows higher activity only at a relatively high Al/Zr ratio (Al/M mole ratio > 10^5). Furthermore, at a temperature 95°C, only oligomers produced[20]. The polymer molecular weights and molecular weight distribution was found to be in the range of 2.5-3.1 (**Fig. 7.7**). Noteworthy is the shape of the molecular weight distribution which is symmetrical but instead possesses a “tail” of short polymer chains. Catalyst A was also sensitive to hydrogen (**Table 7.7)**

Table 7.6 : Effect of temperature on ethylene polymerization using catalyst A/MAO in xylene at 5 bar pressure[a]

Entry no.	Cat. amount (mg)	mol Zr x 10^7	Temp (°C)	Wt. of polymer (g)	Activity (Kg PE/ g Zr. h)	[η] (dL/g)	M_n	M_w	MWD
1	15.8	6.2	60	5.0	177	n. d.	-	-	-
2	21.3	8.4	70	7	183	2.60	-	-	-
3	15.7	6.2	80	9.5	334	2.44	33106	101796	3.07
4	21.3	8.4	100	25	670	1.81	26348	77329	2.89
5	21.2	8.4	105	21	806	1.75	24748	75511	3.05
6[b]	18.8	7.4	110	30	886	1.73	27310	75935	2.78

[a] Polymerization conditions : xylene = 100 mL; P = 5 bar; Al/ Zr = 5000; TMA added = 3 x 10^{-3} mol as Al ; time = 30 min. [b] Polymerization was carried out for 20 min.

Table 7.7 : Effect of hydrogen on ethylene polymerization using catalyst A/MAO in xylene at 5 bar pressure[a]

Entry no.	Cat. amount (mg)	mol Zr x 10^7	Temp (°C)	Wt. of polymer (g)	Activity (Kg PE/ g Zr. h)	[η] (dL/g)	M_n	M_w	MWD
1[b]	17.2	6.8	80	3.5	113	1.48	-	-	-
2[c]	18	7.1	90	17	525	1.10	15977	42215	2.64

[a] Polymerization conditions : xylene = 100 mL; P = 5 bar; Al/ Zr = 5000; TMA added = 3 x 10^{-3} mol as Al ; time = 30 min. [b] 100 mL of hydrogen was introduced into the reservoir.[c] 50 mL of hydrogen was introduced into the reservoir.

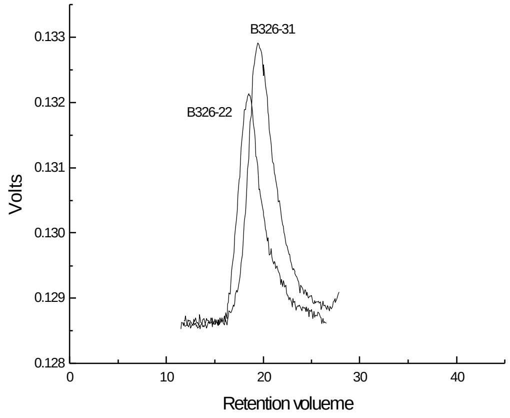


Fig 7.7 : GPC chromatogram of polyethylene samples obtained by using catalyst A/MAO at Al/Zr = 5000; P = 5 bar; t = 30 min.

7.3.3 Effect of removal of electron donor from the solid catalyst

The solid catalyst A was subjected to heat treatment in order to reduce the THF content in the catalyst precursor. The results are shown in **Table 7.8**. Upon heating catalyst A under a stream of N_2 the catalyst activity decreased. Such observation has been earlier reported by Choi *et. al.*[21].

Table 7.8 : Heat treatment of the solid catalyst A and its effect towards polymerization of ethylene[a].

Entry no.	Activation Temp (°C)	Activation time (min)	Wt loss (Wt %)	mol Zr x 10^7	Wt. of polymer (g)	Activity (Kg PE/g-Zr. h)
1	-	-	-	6.52	1.91	67
2	85-90	30	3.4	6.49	1.7	57
3	115-120	30	1	6.5	1.55	52

[a] Polymerization was carried out in xylene (50 mL); Temp = 70°C; Al/Zr = 5000; P = 1 bar; Time = 30 min; using 12- 13 mg of catalyst A in combination with MAO.

7.3.4 Active site concentration determination

The concentration of active site on the catalyst A was determined asdiscusssed in **chapter-5** and was found to be 17 mol per mol of zirconium (**Table 7.9 and Fig. 7.8**).

Table 7.9 : Kinetic parameters of the ethylene polymerization using catalyst A/MAO[a]

Entry no.	Reaction Time (min)	mol Zr x 10^7	Yield (Mol)	M_n	N_t (mol)x10^7	N_t (mol/mol Zr)	[C^*] x10^2 mol/mol Zr	K_{tr} (M sec^{-1})
1	1	7.63	0.0075	44, 997	1.66	0.217	17.0	9.1x 10^{-2}
2	2	7.73	0.114	64, 765	1.76	0.227		
3	3	7.57	0.016	71, 459	2.25	0.297		

[a] All polymerization were carried out in xylene (50 mL); Al/Zr = 5000; T = 70°C; P = 1 bar.

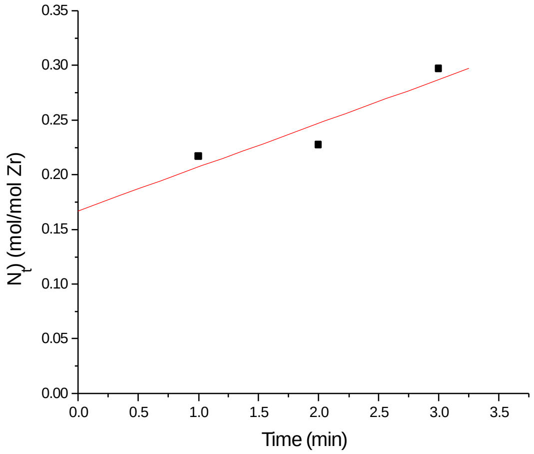


Fig. 7.8 : Concentration of macromolecules N_t of polyethylene in the polymerization medium as a function of polymerization time, t calculated according to the equation (6); $N_t = W_t/M_t = 0.170 + 0.170 . K_{tr} . M.t$

7.3.5 Copolymerization of ethylene with 1-hexene

An unbridged metallocene, such as, Cp_2ZrCl_2 is not suitable for the copolymerization of ethylene with higher α-olefins. Nevertheless, a supported Cp_2ZrCl_2 was used for the copolymerization of ethylene and 1-hexene, purely as a model, to examine the differences, if any, in the behavior of supported and unsupported zirconocenes on the copolymerization behavior.

7.3.5.1 Catalyst activity

It was observed that the activity of catalyst A was higher than catalyst B and unsupported Cp_2ZrCl_2. All the catalysts show two melting temperatures, but catalyst B shows higher melting transition than catalyst A and unsupported catalyst. Amongst the three catalysts catalyst B shows greater incorporation of comonomer and higher crystallinity of the copolymer however, in case of catalyst A and unsupported catalyst they are comparable (**Table 7.10**).

Table 7.10 : Copolymerization of ethylene and 1-hexene using catalyst A, B and unsupported Cp_2ZrCl_2/MAO catalysts[a]

Entry no.	mol Zr x 10^7	Catalyst	Yield (g)	1-hexene in copoly (mol %)	Activity (Kg Copoly./ g Zr.h)	T_m (°C)		[η] (dL/g)	Crystall -inity (%)
1[b]	6.52	A	1.91	-	67	131.2		1.81	71
2	5.93	Cp_2ZrCl_2	1.50	4.3	55	80.9	103.0	0.38	31
3	6.63	A	2.14	4.7	71	88.7	106.6	0.68	34
4	6.16	B	1.26	6.7	45	94.7	109.9	0.74	43

[a] All polymerization were carried out in xylene (50 mL); T= 70°C; time = 30 min; Al/Zr = 5000; P = 1 bar; TMA = 3 x 10^{-3} mol as Al; 1-hexene conc. in the monomer feed = 0.24mol/l.

[b] homopolymerization of ethylene using catalyst A.

Copolymerization of ethylene with 1-hexene was carried out using catalyst A at 1 bar pressure with Cp_2ZrCl_2, catalyst A and catalyst B as well as at different feed ratio of hexene-1 and at different temperatures in conjunction with MAO. The results are shown in **Table 7.11 & 7.12**. The activity of the supported catalyst is higher compared to Cp_2ZrCl_2-MAO. Catalyst B shows an activity equivalent to the homogeneous catalyst. However, the comonomer incorporation is higher in case of catalyst B, whereas they are comparable in case of catalyst A and Cp_2ZrCl_2. The catalyst activity increases with temperature whereas comonomer incorporation decreased with increasing temperature. Addition of comonomer causes a depression in molecular weight indicating that the comonomer promotes chain transfer However for equivalent comonomer content the reduction in molecular weigh

Table 7.11 : Effect of 1-hexene concentration in the monomer feed in the co - polymerization of ethylene using catalyst A/MAO[a]

Entry no.	mol Zr x 10^7	1- hexene conc. (M)	Yield (g)	1-hexene in copoly (mol %)	Activity (Kg Copoly./g Zr.h)	T_m (°C)		[η] (dL/g)	Crystallinity (%)
1	6.52	0.16	1.85	2.4	62	101.1	113.7	1.47	45
2	6.63	0.24	2.14	4.7	71	88.72	106.6	0.68	34
3	6.52	0.48	2.10	8.3	73	83.4		0.23	19

[a] All polymerization were carried out in xylene (50 mL); Al/Zr = 5000; T = 70°C; P = 1 bar; time 30 min; using 12.4-12.6 mg of solid catalyst A.

Table 7.12 : Effect of temperature on the copolymerization of ethylene and 1-hexene using catalyst A/MAO[a]

Entry no.	mol Zr x 10^7	Temp (°C)	Yield (g)	1-hexene in copoly (mol %)	Activity (Kg Copoly./g Zr.h)	T_m (°C)		[η] (dL/g)	Crystallinity (%)
1	6.00	40	0.73	7.3	27	95.3		0.86	31
4	6.63	70	2.14	4.7	71	88.7	106.6	0.68	34

[a] All polymerization were carried out in xylene (50 mL); time = 30 min; Al/Zr = 5000; P = 1 bar; 1-hexene conc. = 0.24 mol; using 12.2-12.5 mg of catalyst A.

7.3.5.2 Thermal behavior of the copolymer

The thermal behavior investigated by Differential Scanning Calorimetry (DSC) shows the strong influence of the comonomer incorporation on polymer properties. Even small amounts of 1-hexene in the polymer chain cause a sharp decrease in crystallinity and melting point of the coopolymer. Due to a homogeneous chemical structure of the poly(ethylene-co-1-hexene) obtained with the metallocene catalysts the effect of comonomer on the properties is much stronger compared to copolymers produced with heterogeneous catalysts with broad comonomer distribution[22]. The DSC of polyethylene obtained from catalyst A, B and unsupported catalyst exhibit two melting temperatures

(**Fig. 7.9**). When the 1-hexene content was higher than 5 mol % a broad single peak was observed (**Fig. 7.10**).

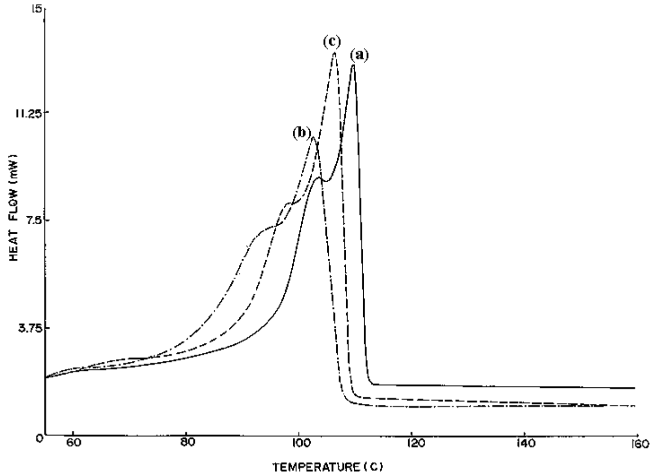


Fig 7.9 : Thermal behavior of poly(ethylene-co-1-hexene obtained by using supported and unsupported catalyst, T = 70 °C, P= 1 bar, Al/Zr = 5000. (a) using catalyst B, (b) using unsupported Cp_2ZrCl_2 catalyst, (c) using catalyst A.

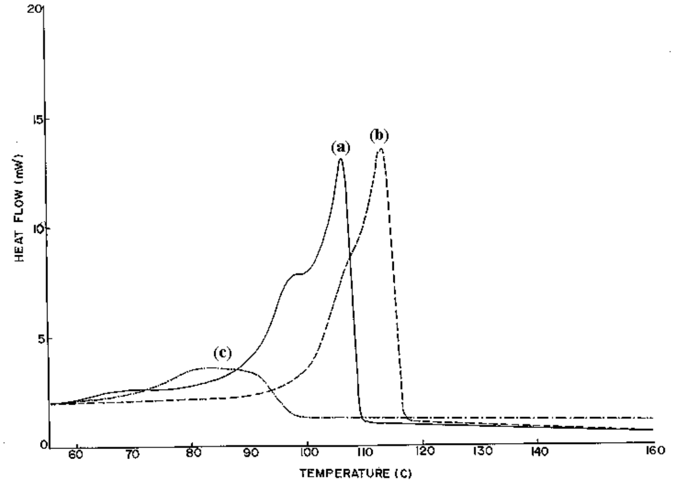


Fig 7.10 : Thermal behavior of the copolymer poly(ethylene-co-1-hexene) obtained by using catalyst A with different comonomer content. (a) 4.7 mol %, (b) 2.4 mol %, (c) 8.3 mol %

7.3.5.3 Molecular weight and MWD of the copolymer

The GPC results of the copolymers obtained from catalysts A, B and unsupported Cp_2ZrCl_2 catalysts are shown in **Table 7.13**. The number average molecular weight was found to be very low in case of catalyst A and unsupported catalyst while for catalyst B is somewhat higher. Nevertheless, MWD was found to be broad when catalyst A and unsupported

Table 7.13 : Molecular weight and MWD data of poly[ethylene-co(1-hexene)] obtained from GPC

Entry no.	Catalyst	1-hexene in copoly.(mol %)	M_n	M_w	MWD
1	Cp_2ZrCl_2	4.3	3, 142	19, 183	6.10
2	A	4.7	5, 800	28, 716	4.95
3	B	6.7	17, 362	61, 517	3.54

[a] All polymerization were carried out in xylene (50 mL); T= 70°C; time = 30 min; Al/Zr = 5000; P = 1 bar; TMA = 3 x 10^{-3} mol as Al; 1-hexene conc. in the monomer feed = 0.24mol/l.

With increase in 1-hexene concentration in GPC chromatogram shows an interesting observation (**Fig. 7.12**). For low 1-hexene incorporation the nature of the molecular weight distribution curve was found to be a narrower. When the incorporation is more than4 mol % it becomes broader with the appearance of a shoulder. When thecomonomer is more than 8 mol %, a braod distribution was obtained (**Table 7.14**). The observation can be attributed to very low M_n value of the copolymers.

Table 7.14 : Molecular weight and MWD of polyethylene-co-1-hexene obtained from GPC

Entry no.	1-hexene in copolymer (mol %)	M_n	M_w	MWD
1	1.20	11, 346	33, 698	2.97
2	2.96	5800	28, 716	4.95
3	7.22	3235	20, 480	6.33

[a] All polymerization were carried out in xylene (50 mL); Al/Zr = 5000; T = 70°C; P = 1 bar; time 30 min; using 12.4-12.6 mg of solid catalyst A.

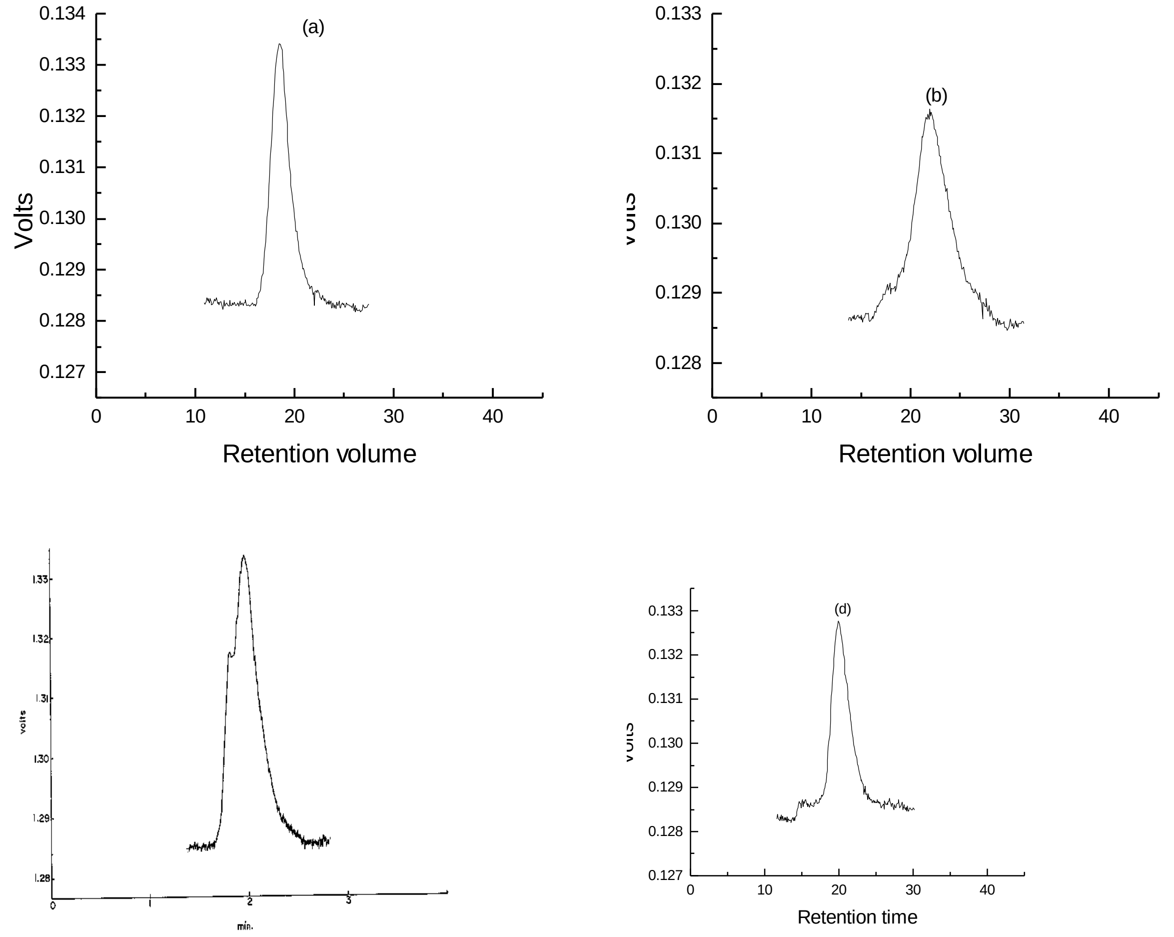


Fig. 7.11 : GPC chromatogram of poly(ethylene-co-1-hexene) obtained by using supported and unsupported Cp_2ZrCl_2 catalyst (as mentioned in Table 7.13); (a) chromatogram of polyethylene obtained from catalyst A; (b) chromatogram of the copolymer obtained from unsupported Cp_2ZrCl_2; (c) chromatogram of copolymer obtained from catalyst A; (d) chromatogram of copolymer obtained from catalyst B.

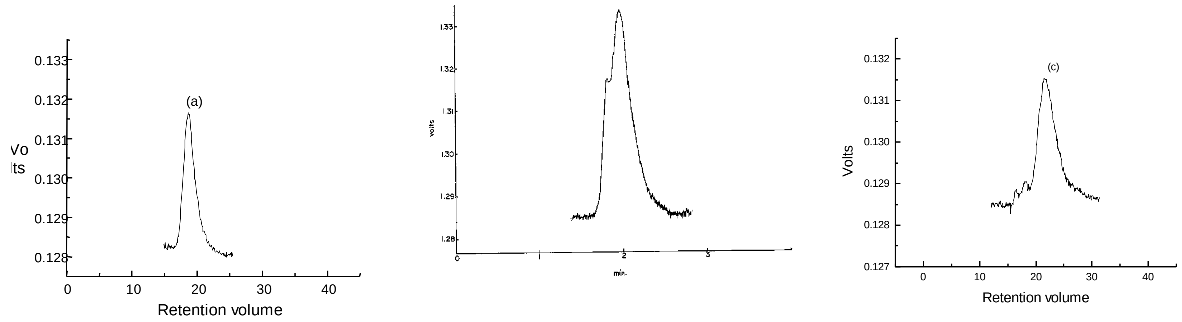


Fig 7.12 : GPC chromatogram of copolymer obtained by using catalyst A/MAO with different

7.3.5.4 Sequence and structure

The triad distributions were evaluated from the spectra following Randall's methodology as described in **chapter-5**. The triad concentrations and sequence distribution are shown in **Table 7.15** and the reactivity ratios are shown in **Table 7.16**.

Fig 7.13 shows the spectra for three types of ethylene-1-hexene copolymers which differ in the content of 1-hexene incorporated (a) 2.30, (b) 4.7, (c) 8.3mol % . The absence of peaks at 40.18-41.40 ppm indicates that the HH diads (1,3-dibutyl branches were absent in the three cases. Resonance at 34.9 and 24.5 ppm is due to HEHE (1,5-dibutyl branches) and 30.9 ppm due to sequences HEEH (1,7-dibutyl branches) which is present only in case of B. These spectra show that the most of the 1-hexene units were isolated in the copolymer between polyethylene block. As the concentration of the 1-hexene in the copolymer increased, butyl branches became closer. Some of the butyl branches were separated only by one or two units of ethylene, as indicated by the presence of 1,5 and 1,7 dibutyl branches. It can be observed that in case of catalyst B, [HHE]/[EHH] and [HHH] triads are appeared which is absent in case of catalyst B and unsupported catalyst. Nevertheless, catalyst B gives HH diad fractions also. From reactivity ratio calculations it can be said that catalyst B has both greater reactivity towards ethylene and 1-hexene than catalyst B and unsupported catalyst.

Table 7.16 : Reactivity ratio and average sequence length of ethylene and 1-hexene of the copolymer[a]

Entry no.	Monomer conc.(M)		r_E	r_H	$r_E.r_H$	$\bar{n}_E$	$\bar{n}_H$
	E	H					
1[b]	0.042	0.48	104.86	0.004	0.45	9.24	1.05
2[c]	0.042	0.24	116	0.021	2.43	30.82	1.09

[a] All polymerization were carried out at 70°C, P = 1 bar, Al/Zr = 5000, 1-hexene added = 0.24 M.
[b] using catalyst A; [c] using catalyst B.

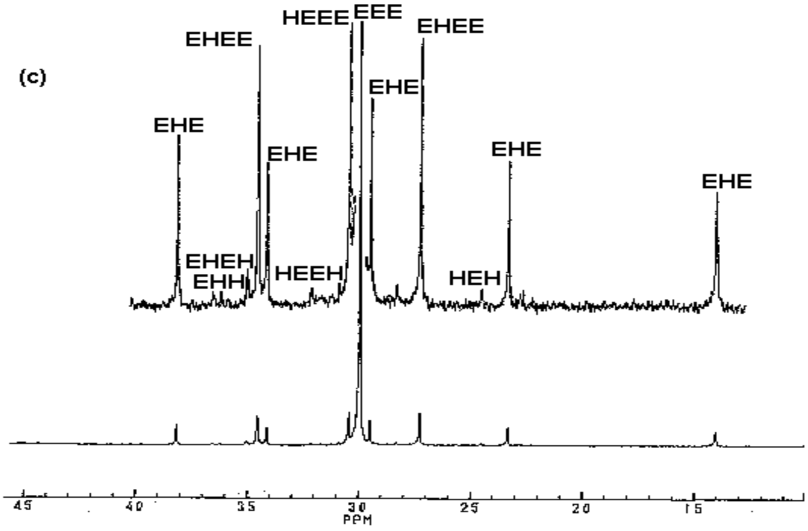
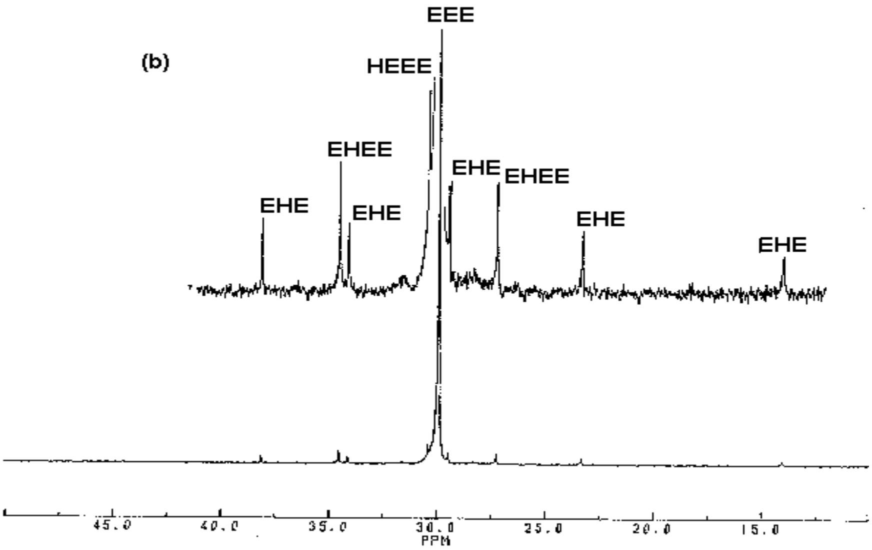


Fig. 7.13 : ^{13}C NMR spectra of of poly[ethylene-co(1-hexene)] copolymer with different percentages of 1-hexene incorporated using catalyst A/MAO; (a) 2.4 mol %; (b) 4.7 mol %; (c) 8.3 mol %.(Spectra of a & b in next page)


(b)
EEE
HEEE
EHEE
EHE
EHE
EHE
EHEE
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EHE
45.0
40.0
35.0
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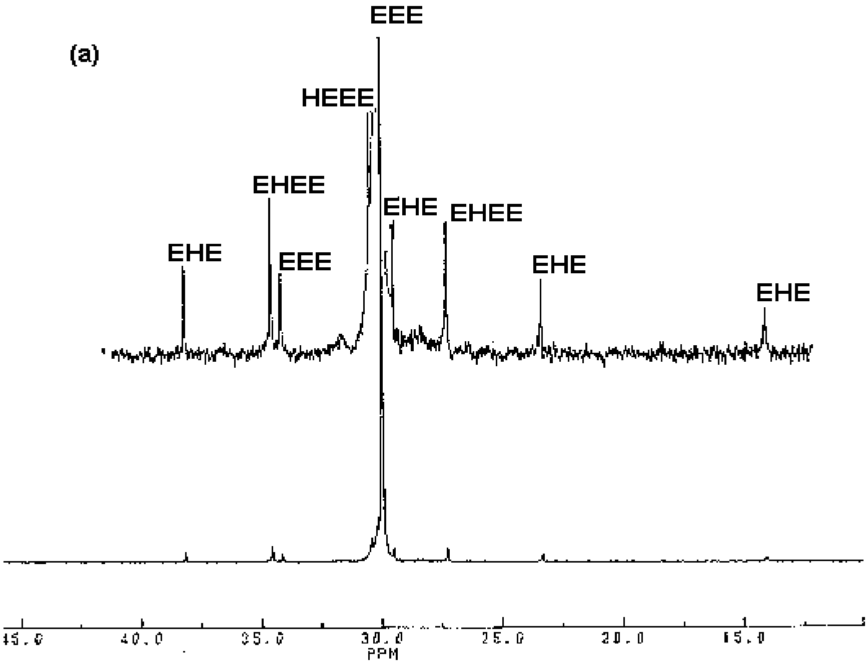
25.0
20.0
15.0
PPM


(a)
EEE
HEEE
EHEE
EHE
EEE
EHE
EHEE
EHE
EHE
45.0
40.0
35.0
30.0
25.0
20.0
15.0
PPM

7.4 CONCLUSION

Incorporation of low amounts of $MgCl_2$ onto SiO_2 support enhances the catalytic performance of zirconocene catalyst towards polymerization of ethylene. Cp_2ZrCl_2 supported on SiO_2-$MgCl_2$ shows a higher catalyst activity compare to SiO_2 supported Cp_2ZrCl_2 catalyst. The supported catalyst also responds to hydrogen.

The silica-magnesium chloride supported catalyst shows reduced rate decay at temperatures as high as 110^0C in xylene. This is in contrast to unsupported Cp_2ZrCl_2 which gives only oligomers at similar temperature.

The Si-Mg-Zr catalyst produces polymer with higher molecular weight and narrower molecular weight distribution as compared to Si-Zr catalyst. This fact can be attributed to the fact that when metallocene is supported on silica different kind of active species are formed due to different kinds of hydroxyl groups present on the silica, thus causing the broadening of MWD. Upon supporting a magnesium chloride/metallocene complex on silica the electronic environment around the transition metal is altered, presumably, due to the presence of Mg^{+2} ions, causing a narrowing of molecular weight distribution. A study of copolymerization of ethylene with 1-hexene using Si-Mg-Zr catalyst shows that the comonomer incorporation and the molecular weight of the copolymer is low when compared to Si-Zr catalyst. However, supporting Cp_2ZrCl_2 does not change the copolymerization activity and comonomer incorporation of the copolymer significantly. The copolymer produced using Si-Mg-Zr at 70°C exhibits two melting endotherms.

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The research embodied in this **thesis** describes the preparation of supported metallocenes derived from titanium and zirconium and their performance in polymerization of ethylene. Supported metallocene catalysts, being solids, simplify catalyst handling and improve reactor performance. Two supports have been examined in the course of this study, namely, a $MgCl_2$.2THF complex and SiO_2-$MgCl_2$.2THF complex. Anhydrous $MgCl_2$ is well recognized as a support of choice for heterogeneous titanium based Ziegler-Natta catalysts.

The results of the research demonstrate the beneficial role of $MgCl_2$ as a component of support for homogeneous metallocene catalysts. A comparison of the key performance characteristics of homogeneous titanium and zirconium metallocenes with those of the supported catalysts is shown in **Table 8.1**. Mg-Ti catalyst is active even at 70 °C, a temperature where homogeneous Cp_2TiCl_2 shows negligible polymerization activity. Mg-Zr catalyst shows reduced activity at 70°C compared to Cp_2ZrCl_2 at 1 bar ethylene pressure. However, at 5 bar pressure, Mg-Zr shows a higher activity compared to Cp_2ZrCl_2.

In general, polymer molecular weights are higher with magnesium supported metallocenes compared to unsupported Cp_2ZrCl_2. Magnesium supported metallocenes show a slightly broad molecular weight distribution compared to homogeneous metallocenes.

$MgCl_2$ supported catalysts, enable use of aliphatic hydrocarbon as diluent for slurry phase polymerization of poly(ethylene). In general, aliphatic hydrocarbon reduces catalyst activity, but increases molecular weights.

Silica is well known catalyst support for heterogeneous metallocenes. However, silica catalysts generally lead to reduced catalyst activity and broad molecular weight distribution. However, supporting a preformed complex of $MgCl_2$.2THF.metallocene on silica results in an increase in catalyst activity and polymer molecular weight and narrowing of molecular weight distribution. The key performance characteristics of SiO_2-$MgCl_2$ supported titanium and zirconium metallocenes are given in **Table 8.2**. Si-Mg-Zr catalyst was active for polymerization even at 110 °C, a temperature at which homogeneous Cp_2ZrCl_2, generates only oligomeric products. Unlike, Mg-Zr, Si-Mg-Zr showed negligible polymerization activity in aliphatic solvent.

The copolymerization of ethylene and hexene-1 was studied with homogeneous Cp_2ZrCl_2 and three types of supported Cp_2ZrCl_2, namely, Mg-Zr, Si-Zr and Si-Mg-Zr and the results are shown in **Table 8.3**. In general presence of $MgCl_2$ increased copolymerization activity. However, Mg-Zr catalyst caused a much greater reduction in molecular weight of the copolymer. The copolymer molecular weight distribution was relatively broader than corresponding homopolymer molecular weight distribution.

In conclusion, the results presented in this thesis demonstrate the remarkable role of the support in metallocene based catalyst systems. The support imparts an unusal stability to the metallocene catalysts. Upon heterogenization of Cp_2MCl_2 (M = Ti or Zr) on $MgCl_2$ or a complex of Cp_2MCl_2-$MgCl_2$ (M= Ti or Zr) onto silica results a significant modulation of the M^{+4} cationic center. Supported catalysts show high catalyst activity towards polymerization of ethylene and a greater catalyst life time in conjunction with MAO. These results are even more striking when one considers the fact that the active center concentration in supported catalysts is only about one fifth of the homogeneous catalysts. The polymer molecular weight obtained using supported catalysts is higher when compared to unsupported catalysts. The supported catalysts can be used at temperatures greater than 100°C with high catalytic activity. Copolymerization of ethylene with 1-hexene using these supported catalysts establish that the support has negligible effect on comonomer incorporation (< 8 mol %).

The thesis entitled " *A study of ethylene polymerization using supported metallocene catalyst systems*" is divided into eight chapters.

INTRODUCTION

Metallocene catalysts such as Cp_2MCl_2 (M = Ti, Zr, Hf) in the presence of aluminum alkyl reagents constitute a group of homogeneous catalyst for Ziegler-Natta olefin polymerization[1]. Catalyst system based on bis(cyclopentadienyl)titanium (IV) dichloride in conjunction with dialkyl aluminum chlorides was first shown by Breslow and Newburg to polymerize ethylene[2]. However, these catalysts show rapid rate decay and loss of catalyst activity within minutes of start of polymerization and at temperature higher than 30°C[3]. The discovery of homogeneous, highly active and stereospecific matallocene-methylaluminoxane (MAO) catalysts have stimulated renewed commercial and scientific interest in this area[4,5,6]. The significance of these catalysts arise because they contain single active site and, thus, offer potential advantages over traditional multisite Ziegler-Natta polymerization catalyst. These advantages include high catalyst activities, good copolymerization behavior, uniform comonomer distribution, narrow polydispersities and excellent control on stereoregularity[7-9]. However, from the point of practical catalysis, it has some drawbacks. Homogeneous catalysts need a large excess of MAO (Al/Metal mol ratio > 10^5) for obtaining reasonable polymerization activities, inability to use the catalyst in the gas-phase or slurry processes, excessive reactor fouling leading to poor heat transfer and poor control on polymer morphology. Three different strategies are evident in the literature to overcome these problems.

In one approach, a single two component catalyst based on group IV metallocene dialkyls with a stoichiometric or near stoichiometric amount of an activator such as $[C_6H_5(CH_3)_2NH^+][B(C_6F_5)_4^-]$[10], $[(C_6H_5)_3C^+][B(C_6F_5)_4^-]$[11] or $[B(C_6F_5)_3^-]$[12] were developed to generate a single site cationic species. Jordan and co-workers found that ethylene polymerization proceeds effectively in presence of dicyclopentadienyl zirconium alkyl complexes in absence of cocatalyst[13]. Ewen *et al.* showed that cationic zirconium complexes such as $Et[IndH_4]_2ZrMe^+$, i-Pr$[Flu(Cp)_2]ZrMe^+$ show very high activity for propylene polymerization[14]. These single site cationic species of d^0, 14 e^- metallocenes unstable at higher temperatures, difficult to handle and very sensitive to light.

The second approach involves, supporting the metallocene on a support such as silica, alumina and magnesium chloride with or without aluminum alkyls or aluminoxanes such as MAO. One of the early attempts in this direction was made by Slotfeldt-Ellingsen and co-workers. Cp_2TiCl_2 supported on silica gel was used to polymerize ethylene using Et_nAlCl_{3-n} as cocatalyst[15]. Soga and co-workers reported supported ethylenebis(tetrahydroindenyl) zirconium (IV)dichloride for the isospecific polymerization of propylene[16]. SiO_2, Al_2O_3 and $MgCl_2$ pretreated with MAO were used as supports and trialkylaluminums as cocatalyst. Al_2O_3 and $MgCl_2$ gave low molecular weight polymers with broad polydispersities. On the contrary, SiO_2 gave narrow polydispersities and low catalyst activity. Collins *et al.* and Chien *et al.* have shown that isospecific polymerization of propylene can be performed with supported chiral ansa-metallocene in conjunction with MAO[17, 18]. The most active supports were those derived from partially dehydroxylated SiO_2 or Al_2O_3 that has been pretreated with excess of trialkylaluminums. Kaminsky *et al.* have disclosed a refined route for preparation of silica supported ansa-metallocene catalyst which yields high molecular weight and high melting polypropylene with a performance similar to heterogeneous catalysts[19]. Recently, Ihm *et al.* used a slightly modified procedure in order to support Cp_2MCl_2 (M = Ti, Zr, Hf) catalysts on silica. They replaced MAO by $Al(C_2H_5)_3$ and by C_2H_5MgCl during the SiO_2 pretreatment[20]. Lee et al[21] developed another method to synthesize Cp_2ZrCl_2 supported on SiO_2. Hydrated silica was prepared by two procedures. In the first one silica was fully hydrated in deionized water, filtered and fluidized in a column under N_2 gas flow, yielding silica with 45 wt % of water. In the second method, SiO_2 was fluidized with wet N_2. Silica with 16 wt % of water was obtained. The catalyst support was then prepared by bringing in contant the hydrated silica ($H\text{-}SiO_2$) with a solution of TMA in toluene. The supported catalysts was then synthesized by addition of metallocenes onto the support by direct impregnation method and used for the polymerization of ethylene. More recently, Jin *et al.* prepared SiO_2 supported neodymocene catalyst and used it for the polymerization of ethylene [22].

In the present work, we propose to examine various methods for effectively supporting a homogeneous catalyst and study of their polymerization behavior. The work includes synthesis, characterization of supported metallocene catalysts and the study of their polymerization behavior in conjunction with different aluminum alkyls or aluminoxane cocatalysts.

OBJECTIVE OF THE PRESENT INVESTIGATION

1. Synthesis of heterogeneous metallocene catalysts (Ti or Zr) supported on SiO_2, SiO_2-$MgCl_2$ and $MgCl_2$ by direct immobilization of metallocenes onto the support or preparation of the support via Grignard decomposition and immobilization of metallocenes onto the support.

2. To study the effect of supported metallocene catalysts under different reaction conditions such as temperature, Al/M ratio, pressure, solvent, pretreatment with aluminum alkyls, concentration of the catalyst, on the polymerization and copolymerization of ethylene.

3. Determination of active site concentration as well as polymer properties.

CHAPTER-1

This chapter provides a historical background of the Ziegler-Natta catalyst systems, a detailed literature survey of supported metallocene catalysts synthesis, characterization, and a critical survey of heterogeneous metallocene catalyst for the polymerization and copolymerization of ethylene and higher α-olefins.

CHAPTER-2

The objective and the scope of the present invention is described in this chapter.

CHAPTER-3

This chapter deals with the materials used, purification of the reagents, methods of polymerization and analytical techniques used to characterize catalysts and polymers.

CHAPTER-4

This chapter deals with the

a) preparation of a bis(cyclopentadienyl)titanium (IV) dichloride supported on $MgCl_2$

tetrahydrofuran (THF). This $MgCl_2$ has been shown to exist in δ active form.

b) Characterization of the solid catalyst by means of FT-IR, XRD, TGA, surface area, ^{13}C NMR.

c) Polymerization of ethylene using this synthesized catalyst in conjunction with MAO as cocatalyst, in xylene or n-hexane as diluents at one atmosphere ethylene pressure will be investigated.

d) Mechanism of ethylene polymerization using this solid catalyst and catalyst structure will be studied.

CHAPTER-5

This chapter deals with the

a) preparation of a bis(cyclopentadienyl) zirconium (IV) dichloride supported on $MgCl_2$ by exploiting the solubility of $MgCl_2$ into THF.

b) Characterization of the solid catalyst by means of FT-IR, XRD, surface area, TGA.

c) Polymerization of ethylene and higher α-olefins using this solid catalyst in conjunction with MAO as cocatalyst, in xylene or n-heptane as doluents at 1 atmosphere as well as 5 bar ethylene pressure will be investigated.

d) Mechanism of ethylene polymerization, active site concentration and catalyst structure will also be studied.

CHAPTER-6

This chapter deals with the

a) Preparation of bis(cyclopentadienyl) titanium(IV) dichloride supported on SiO_2-$MgCl_2$ will be studied.

b) Characterization of the catalysts by means of FT-IR, surface area.

c) Polymerization of ethylene using these solid catalysts in conjunction with at 5 bar ethylene pressure will be investigated.

d) Mechanism of ethylene polymerization and catalyst structure will be studied.

CHAPTER-7

This chapter deals with the

a) Preparation of a bis(cyclopentadienyl) zirconium(IV) dichloride supported on SiO_2-$MgCl_2$ will be studied.

b) Characterization of the catalysts by means of FT-IR, surface area.

c) Polymerization of ethylene using these solid catalysts in conjunction with aluminum alkyls or aluminoxanes as cocatalysts, in xylene as diluent at 1 atmosphere and 5 bar ethylene pressure will be investigated.

d) Mechanism of ethylene polymerization, active site concentration, and catalyst structure will also be studied.

CHAPTER-8

This chapter summarizes the results and described the salient conclusions of the investigation disclosed in this thesis.

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