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Studies on magnesium dichloride-2,2-dimethoxypropane – titanium tetrachloride catalyst system for propylene polymerization*

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Magnesium dichloride supported titanium catalysts were prepared by solubilizing anhydrous magnesium dichloride in 2-ethyl-1-hexanol followed by treatment with titanium tetrachloride. 2,2-Dimethoxypropane was used as an internal Lewis base. Solid products were characterized by compositional analysis, and specific surface area. Titanium magnesium catalysts (Ti–Mg) in conjunction with triethylaluminium showed high activity (5110 g PP/g Ti) and high stereospecificity ($I.I = 92$) for propylene polymerization. The variation in the amount of 2,2-dimethoxypropane during catalyst synthesis governs the productivity of the catalyst. Furthermore, the increase in the chain length of the alkyl group from ethyl to hexyl of trialkylaluminum cocatalyst retards the activity of the catalyst system, with minor variation in the isotactic index of polypropylene. The addition of diphenyldimethoxysilane into triethylaluminum further improves the stereospecificity of the catalyst system. Copyright © 1996 Elsevier Science Ltd.

(Keywords: magnesium dichloride; 2,2-dimethoxypropane; dimethylphthalate)

INTRODUCTION

The polymerization of propylene catalysed by Ziegler Natta systems have progressed through self supported to supported titanium catalysts[1–5]. The continuing research in catalyst systems has led to improvements in the activity, stereospecificity and morphology of the solid catalyst. The present generation of supported titanium catalysts are composed of titanium tetrachloride supported on active magnesium dichloride. A combination of internal and external Lewis bases are used to improve the activity of the catalyst system, as well as to improve the isotacticity of polypropylene. An internal Lewis base is used during the preparation phase of the catalyst. The external Lewis base added along with alkylaluminium cocatalyst during the polymerization phase, gives complete control over the stereoregularity of polymers.

A number of Lewis bases with varied functionality, steric hindrance, and basic strength have been used[6,7]. Dialkyl phthalate (internal Lewis base) and alkoxysilane (external Lewis base) are found to be a very effective pair for achieving high activity and isotacticity in addition to lowering the consumption of the external Lewis base[8–10]. The interaction between the solid catalyst [$MgCl_2$-internal Lewis base-$TiCl_4$] and the cocatalyst [R_3Al + external Lewis base] causes complex exchange reactions of components. In this process, the Lewis base, in general, selectively poisons the non-stereospecific sites, at the same time activate and stabilize the stereospecific sites and/or increase the propagation rate constant[6,11]. The first and second effects depend not only on the specific internal or external Lewis base, but also on the pair of Lewis bases. These factors in turn also influence the catalyst performance and microstructure of polymeric products[12–18].

Recently, diethers have been reported in patent literature as an internal Lewis base for supported titanium catalysts[19–21]. However, very limited information is available concerning the performance of such catalysts towards propylene polymerization[22,23]. We have undertaken an investigation to study the synthetic and polymerization aspects of a $MgCl_2$-2,2-dimethoxypropane-$TiCl_4$ catalyst. Results have been compared with catalysts prepared using dimethylphthalate as an internal Lewis base.

EXPERIMENTAL

Anhydrous magnesium dichloride (Toho Titanium Corporation, Tokyo) triethylaluminium, triisobutylaluminium, tri-n-hexylaluminium (Ethyl Corporation, USA) and titanium tetrachloride (Riedel De Haen, Germany) were used as received. Diphenyldimethoxysilane, 2,2-dimethoxypropane, dimethylphthalate and 2-ethyl-1-hexanol were commercial products and used after distillation and drying. Hexane (polymerization grade), decane, and chlorobenzene were used after drying over sodium. Propylene (polymerization grade from a commercial plant) was used after passing through molecular sieve columns.

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All experimental manipulations were carried out under high purity nitrogen atmosphere. Standard Schlenk techniques and a vacuum atmospheres model HE-43 Dr-Lab equipped with a Model HE-491 Dri Train were used for handling of all air sensitive compounds.

Magnesium and chlorine estimations were performed by EDTA and argentometric titration, respectively[24]. Titanium content in the catalyst was determined by the u.v. technique[24] using Shimadzu (Model UV 160 A) spectrophotometer. The BET surface area measurements were carried out on a Sorptomatic 1900 model Carlo Erba instrument. The polymer samples were extracted with boiling heptane in a Soxhlet apparatus. The isotactic index (II) reported for each sample is the weight percentage of heptane insoluble polymer.

SYNTHESIS OF CATALYSTS

Ti,Mg-1 *catalyst*

Magnesium dichloride (3.0 g) was reacted with 2-ethyl-1-hexanol in 1 : 3 molar ratio in decane at 130°C for 2 h. The solution was added dropwise into a titanium tetrachloride chlorobenzene mixture (1 : 1 by volume, Ti/Mg = 50). The temperature was raised to 100°C and the reaction mixture was heated for 2 h. Titanium tetrachloride was decanted off and the solid product was treated again with titanium tetrachloride (200 ml) for 1 h at 115°C. The final solid catalyst was washed with decane and hexane, respectively, at a higher temperature. The catalyst was stored as a slurry in hexane solvent (*Table 1*).

Ti, Mg-2,3,4 *catalysts*

The catalyst preparation was similar to Ti,Mg-1 except that 2,2-dimethoxypropane (DMP) was added at 100°C during the first phase of titanium tetrachloride treatment ($DMP/MgCl_2$ molar ratio = 0.10–0.30) (*Table 1*).

Ti,Mg-5,6,7 *catalysts*

The catalyst was prepared as reported for Ti,Mg-1 except that dimethylphthalate (DMPh) was added at 100°C during the first titanium tetrachloride treatment. ($DMPh/MgCl_2$ molar ratio = 0.10–0.30) (*Table 2*).

Polymerization of propylene

The reaction was carried out in a 500 ml glass reactor equipped with a magnetic stirrer. Calculated amounts of triethylaluminium and/or external Lewis base were added to the reactor containing hexane (200 ml). A solid catalyst was then mixed and propylene continuously supplied under a total pressure of 1 bar for a fixed period of time. Polymerization was terminated by the addition of methanolic hydrochloric acid. The polymer was separated and dried *in vacuo*.

RESULTS AND DISCUSSION

Anhydrous magnesium dichloride was treated with 2-ethyl-1-hexanol in decane to obtain a soluble adduct [equation (1)]. This adduct was

$$MgCl_2 + 3\ ROH \rightarrow MgCl_2.3\ ROH \qquad (1)$$

treated with excess of titanium tetrachloride. During this process, magnesium dichloride is regenerated with the incorporation of titanium compounds (*Scheme 1*).

$$MgCl_2.3\ ROH \xrightarrow{+\text{Excess } TiCl_4} 'MgCl_2' + TiCl_3OR + TiCl_4 + HCl$$

$$\downarrow$$

$$[MgCl_2\,(TiCl_3OR)_x(TiCl_4)_y \xleftarrow{+TiCl_4} [MgCl_2(TiCl_3OR)_a\ (TiCl_4)_b]$$

Scheme 1

Table 1 Evaluation of Ti-Mg catalysts prepared by using 2,2-dimethoxypropane for propylene polymerization

Catalyst	$DMP/MgCl_2$ molar ratio	Compositional analysis (wt%)			Specific surface area ($m^2\ g^{-1}$)	Productivity[a]	
		Mg	Cl	Ti		Polymer yield ($gPP\ gTi^{-1}$)	Isotactic index (%)
Ti,Mg-1	0.0	14.1	64.6	8.0	50	1750	56
Ti,Mg-2	0.10	15.8	58.5	5.5	111	4000	85
Ti,Mg-3	0.20	15.0	55.9	3.7	168	5110	92
Ti,Mg-4	0.30	14.5	52.1	4.3	150	4800	92

[a] Polymerization condition: $Pc^1/3 = 1$ atm, catalyst= 40 ± 2 mg, cocatalyst-Et_3Al, Al/Ti molar ratio= 100, time=2 h, temperature= 25 ± 1°C, hexane = 200 ml, DMP = 2,2-dimethoxypropane

Table 2 Polymerization of propylene with Ti-Mg catalysts containing dimethylphthalate

Catalyst	$DMP/MgCl_2$ molar ratio	Compositional analysis (wt%)			Specific surface area ($m^2\ g^{-1}$)	Productivity[a]	
		Mg	Cl	Ti		Polymer yield ($gPP\ gTi^{-1}$)	Isotactic index (%)
Ti,Mg-5	0.10	14.8	56.2	3.4	97	3100	76
Ti,Mg-6	0.20	13.9	52.9	3.8	90	2900	77
Ti,Mg-7	0.30	12.0	47.7	4.3	85	2700	76

[a] Polymerization conditions as mentioned in *Table 1*, DMPh = dimethylphthalate

The solid product was again treated with titanium tetrachloride to obtain the Ti,Mg-1 product. It is reported that the second treatment with titanium tetrachloride removes inactive titanium compounds resulting in the improvement of activity of the catalyst[25–27]. The Ti,Mg-1 solid product showed 8.0 wt% incorporation of titanium (*Table 1*). The specific surface area measurement of solid revealed a four-fold improvement as compared to the starting magnesium dichloride ($12\,m^2\,g^{-1}$). Efficiency of the catalyst was evaluated for propylene polymerization using triethylaluminium as a cocatalyst. The catalyst system produced 1750 g PP/g Ti with an isotactic index of 56.

During subsequent experiments, 2,2-dimethoxypropane (DMP) was used as an internal Lewis base. Catalysts were prepared at various $DMP/MgCl_2$ molar ratios (*Scheme 2*). The results are tabulated in *Table 1*. An increase in the $DMP/MgCl_2$ ratio up to 0.20 shows a lowering in titanium content and improvement in the specific surface area from $12\,m^2\,g^{-1}$ to $168\,m^2\,g^{-1}$ of the solid product. The decrease in the titanium content may be attributed to the effective removal of titanium compounds such as titanium alkoxide species. A further increase of ratio to 0.30 slightly increases the titanium content and lowers the specific surface area. This can be linked to the presence of titanium tetrachloride—dimethoxypropane adduct in the solid catalyst.

$$\begin{gathered} MgCl_2.3\ ROH \xrightarrow{+\text{Excess } TiCl_4} {}'MgCl_2{}' + TiCl_3OR \\ +TiCl_4 + HCl. \\ -TiCl_4.DMP \downarrow +DMP \\ [MgCl_2\ (DMP)_a\ (TiCl_3OR)_b\ (TiCl_4)_c] \\ +TiCl_4 \downarrow \\ [MgCl_2\ (DMP)_x\ (TiCl_4)_y\ (TiCl_3OR)_z] \\ DMP = 2,2\text{-dimethoxypropane.} \end{gathered}$$

Scheme 2

The polymerization data (*Table 1*) indicate that the addition of DMP into $MgCl_2$ initially increase the polymer yield by three-fold and the isotactic index. A further increase of ratio retards the activity with no change in the isotactic index. These results reveal that the concentration of 2,2-dimethoxypropane used during the preparation of the catalyst controls the composition, as well as the performance, of the catalyst system. The optimum performance of the catalyst is observed for the solid catalyst (Ti,Mg-3) prepared at $DMP/MgCl_2$ molar ratio of 0.20.

The supported titanium catalysts were also prepared using dimethylphthalate (DMPh) as an internal Lewis base. Results (*Table 2*) show that the variation of $DMPh/MgCl_2$ ratios bring changes in the composition, specific surface area as well as polymerization activity of catalysts. The lowest titanium content, highest surface area and high yield of polymer and isotactic index are observed for the catalyst prepared at $DMPh/MgCl_2$ ratio of 0.10 (Ti,Mg-5).

The comparison of both catalyst systems (*Tables 1* and *2*) indicate that a 2,2-dimethoxypropane incorporated catalyst (Ti,Mg-3) shows better productivity and isotactic index as compared to a dimethylphthalate containing catalyst (Ti,Mg-5). The high performance of Ti,Mg-3 catalyst may presumably be due to better physical as well as chemical characteristics leading to greater stability of active titanium species during polymerization. It is reported[22] that the bidentate nature of diether compound possibly blocks those magnesium atoms that have two coordination vacancies. It, therefore, prevents the formation of non-stereospecific titanium sites on the surface of the support. Furthermore, the inability of coordinated diether to interact with the triethylaluminium cocatalyst may be responsible for the slow deactivation of active species. Both these factors may be facilitating the catalyst containing 2,2-dimethoxypropane as a Lewis base with regard to productivity and stereospecificity, as compared to the dimethylphthalate incorporated catalyst.

Table 3 The effect of the nature of trialkylaluminium on the polymerization of propylene using a $MgCl_2$-2,2-dimethoxypropane-$TiCl_4$ catalyst (Ti,Mg-3)

Cocatalyst	Cocatalyst volume (A^{03})	Specific charge of aluminium atoms in electrons	Polymer yield (gPP gTi^{-1})	Isotactic index (%)
Et_3Al	99	0.6864	5110	92
$^iBu_3Al$	183	0.6677	4880	92
Hex_3Al	331	0.6767	3000	91

Et_3Al=triethylaluminium, $^iBu_3Al$ = triisobutylaluminium
Hex_3Al = trihexylaluminium, polymerization conditions as mentioned in *Table 1*

Table 4 The effect of Al/Ti ratios on the polymerization of propylene with a Ti,Mg-3/Et_3Al catalyst system

Al/Ti molar ratio	Polymer yield (gPP gTi^{-1})	Isotactic index (%)
50	3100	92
100	5100	92
150	6200	89
200	5700	86

Polymerization conditions as mentioned in *Table 1*

The polymerization behaviour of the $MgCl_2$-2,2-dimethoxypropane-$TiCl_4$ catalyst was investigated by varying the nature of cocatalyst and polymerization parameters. The results of polymerization studies as a function of the nature of alkylaluminium cocatalyst is shown in *Table 3*. The polymer yield decreases as the bulkiness of the alkylaluminium is increased. The isotacticity of polypropylene is, however, not changed significantly from ethyl to hexylaluminium. The correlation of activity with the nature of alkylaluminium[28] indicates that the polymer yield is lowered with increasing size of the alkyl group. The long alkyl group in the cocatalyst may be preventing the aluminium from coming closer to the titanium for active species formation. The Ti,Mg-3/Et_3Al catalyst system was also studied at different Al/Ti molar ratios. The results indicate (*Table 4*) that an increase of Al/Ti ratio from 50 to 150 enhances the polymer yield by two-fold, with approximately 4% decrease in the isotactic index of polypropylene. Furthermore, an increase of ratio to 200 retards the formation of polymer and also lowers the isotactic index. This behaviour may be attributed to the deactivation of the active Ti(III) species[29,30].

The effect of external Lewis base, diphenyldimethoxysilane, used in conjunction with a triethylaluminium cocatalyst was investigated (*Table 5*). The addition of a

Table 5 Polymerization of propylene with a Ti,Mg-3/Et_3Al + $Ph_2Si(OMe)_2$ catalyst system as a function of Al/Si ratios

Al/Si molar ratio	Polymer yield (gPP gTi^{-1})	Isotactic index (%)
no donor	5110	92
40	4900	95
30	4710	97
20	4100	97
10	3800	97

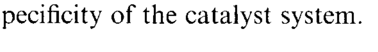
Polymerization conditions as mentioned in *Table 1*

small quantity of Lewis base (Al/Si = 30) increases the isotacticity of polypropylene from 92 to 97 with a reduction in polymer yield by 8 wt%. A further decrease in Al/Si ratio upto 10 leads to a decrease in the polymer yield, without affecting the isotacticity of polymer. This trend indicates that the addition of diphenyl dimethoxysilane at low concentrations improves the stereospecific characteristics of the system[7,15,31].

Present studies indicate that the Ti,Mg-3 catalyst can be considered as consisting of a Lewis acid ($MgCl_2$) on the surface of which a second Lewis acid ($TiCl_4$) and a Lewis base (2,2-dimethoxypropane) are chemisorbed[6,32]. During the synthesis, magnesium dichloride crystallites are most probably cleaved along (100) and (110) planes having five coordinate and four coordinate magnesium atoms[33–36]. These unsaturated magnesium sites coordinate with titanium tetrachloride and/or internal Lewis base to form titanium species with different structural features[7,32–39]. For example, there may exist three types of titanium species on the (100) cut of magnesium dichloride crystallites (*Figure 1*), namely mononuclear species (I), binuclear species (II) and Lewis base coordinated titanium species (III). The mixing of cocatalyst, triethylaluminium, with a Ti,Mg catalyst results in both structural and compositional changes due to complexation and exchange of chemical groups between Lewis acids and Lewis bases[7,37]. The titanium species on the (100) cut of $MgCl_2$ may undergo alkylation and reduction processes to generate reduced titanium species (*Figure 1*, Ia, IIa and IIIa). Ti^{3+} species are only reported to be active for propylene polymerization[29,30]. These species interact with propylene monomer to produce polypropylene[40]. Titanium species having two vacant sites (Ia) may produce atactic polypropylene and the species with one vacant site (IIa and IIIa) may be responsible for isotactic polypropylene[37].

The use of external Lewis base in conjunction with triethylaluminium as a cocatalyst generates new chemical species. It is reported that diphenyldimethoxysilane reacts with triethylaluminium to yield a mixture of $Et_3Al.Ph_2Si(OMe)_2$ complex

$$n(Et_3Al)_2 + Ph_2Si(OMe)_2 \rightarrow n - 1/2(Et_3Al)_2$$



$$+ \ {}^{Et}_{Et}{>}Al{<}^{Et}_{\underset{Me}{O}} \text{---} {}^{Ph}Si{<}^{Ph}_{OMe} \qquad (2)$$

and dimeric triethylaluminium[31,40,41], as shown in equation (2). The complex shifts the dynamic equilibria existing between the components of the catalyst and cocatalyst towards reduction in the concentration of titanium species responsible for non-stereospecific products[6,8,43]. This is in good agreement with our observation that the addition of diphenyldimethoxysilane into the triethylaluminium / Ti,Mg system decreases the yield of atactic polymer, thereby improving the stereospecificity of the catalyst system.

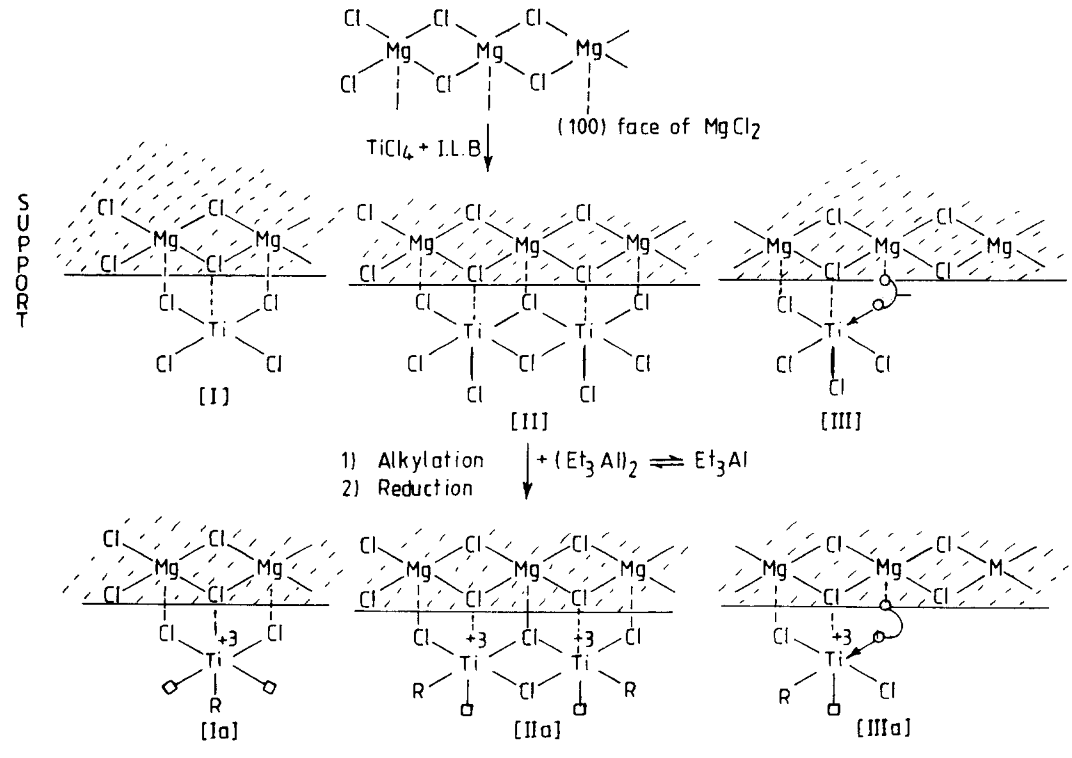


Figure 1 Plausible nature of titanium species on (100) face of $MgCl_2$ (R = Et)

CONCLUSIONS

The treatment of a soluble $MgCl_2$-2-ethyl-1-hexanol adduct with titanium tetrachloride and 2,2-dimethoxypropane gives a catalyst with high surface area and low titanium content under optimized experimental conditions. The catalyst in conjunction with triethylaluminium as a cocatalyst, shows a high yield and high stereospecificity for propylene polymerization. The addition of a small amount of diphenyldimethoxysilane as an external Lewis base (Al/Si=30) further increases the isotactic index of polypropylene. The nature of trialkylaluminium influences the activity of the catalyst in the order: $Et_3Al >^{i} Bu_3Al > Hex_3Al$.

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