Supported Titanium Catalysts Based on Magnesium Dichloride–Silicon Tetraethoxide Adduct for Propylene Polymerization

V. K. GUPTA, R. C. JAIN, M. RAVINDRANATHAN

Research Centre, Indian Petrochemicals Corporation Ltd., PO: Petrochemicals, Vadodara 391 346, India

ABSTRACT: Anhydrous magnesium dichloride was reacted with silicon tetraethoxide to form a solid adduct. The adduct was treated with titanium tetrachloride and an internal Lewis base to prepare supported titanium catalysts. Alkyl benzoate (PhCOOR, R = Me, Et, n − Bu) or dialkyl phthalate [Ph(COOR)$_2$, R = Me, Et, n − Bu] was used as an internal Lewis base. The prepared catalysts (MT) in combination with triethylaluminum as a cocatalyst polymerize propylene to yield polypropylene. The nature and concentration of internal Lewis base influence the composition, specific surface area, and performance of the catalysts. The addition of diphenyl dimethoxysilane into the MT/Et$_3$Al catalyst system increases the isotactic index of polypropylene from 75 to 97 at a Si/Al mol ratio of 0.05. The overall results indicate that a dialkyl phthalate-incorporated catalyst shows better physical, chemical, and polymerization characteristics compared to a corresponding alkyl benzoate catalyst. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64**: 1445–1450, 1997

Key words: magnesium dichloride; silicon tetraethoxide; alkyl benzoate; dialkyl phthlate

INTRODUCTION

Development of morphologically controlled high-performance catalysts has attracted much scientific attention due to their importance in the production of polyolefinic materials.[1–3] The composition of the catalyst system comprising a solid precatalyst (titanium tetrachloride supported on magnesium dichloride) and a cocatalyst (trialkylaluminum and external Lewis base) determines its performance for olefin polymerization. The physical and chemical characteristics of supported titanium species also provide a requisite three-dimensional shape to the catalyst which is replicated during polymerization by polymer particles. The above understanding has contributed significantly toward the development of present-generation catalysts.[3]

The selection of an appropriate synthetic methodology is important for the development of high-performance catalysts. One of the approaches for the preparation of supported titanium catalysts involves the reaction of magnesium dichloride and alcohol followed by treatment with titanium tetrachloride.[4–7] The liberation of a gaseous product, viz, HCl, during catalyst preparation leads to the generation of very fine particles which are undesirable in the subsequent steps. The replacement of alcohol by metal alkoxides will avoid formation of a gaseous product during catalyst synthesis and can, therefore, be a convenient route to prepare morphologically controlled catalysts. The literature reveals that metal alkoxides are used for the activation of magnesium dichloride in the synthesis of supported titanium catalysts.[8,9] However, there is no published information available on the

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Table I   Characteristics of Catalysts Prepared with Alkyl Benzoate

Catalyst	Lewis Base	Analysis (Wt %)			Surface Area (m^2/g)	Productivity	
		Mg	Cl	Ti		Yield (kg PP/g Ti)	Isotactic Index (%)
MT-1	—	12.0	41.1	4.2	48	1.10	52
MT-2	MeBz	14.2	50.3	3.6	105	1.89	71
MT-3	EtBz	15.1	56.0	2.9	136	2.10	74
MT-4	BuBz	16.0	58.1	2.5	148	2.21	75

Polymerization conditions: Pc_3 = 1 atm; catalyst = 50 ± 2 mg; Et_3Al = 5 mmol; temp = 25 ± 1°C; hexane = 200 mL; time = 2 h. MeBz = PhCOOMe, EtBz = PhCOOEt, BuBz = PhCOOBu.

composition–productivity relationship and polymerization behavior of catalysts.

The present article describes the preparation and characterization of supported titanium catalysts based on a magnesium dichloride–silicon tetraethoxide adduct. The performance of the catalysts was examined for propylene polymerization. The effect of an internal Lewis base (alkyl benzoate) was compared with the corresponding dialkyl phthalate. The influence of an external Lewis base on homopolymerization of propylene was also investigated.

EXPERIMENTAL

All experimental manipulations were carried out under a high-purity nitrogen atmosphere. Standard Schlenk techniques and a vacuum atmosphere Dri Lab Model HE-8/85 equipped with a Dri Train Model HE-493-7/80 were used for the handling of all compounds. Magnesium dichloride (surface area 12 m^2/g, Toho Titanium Co., Japan) and triethylaluminum (Ethyl Corp., USA) were commercially procured and used without further purification. Titanium tetrachloride, silicon te-

traethoxide, methyl benzoate, ethyl benzoate, butyl benzoate, dimethyl phthalate, diethyl phthalate, dibutyl phthalate, and diphenyl dimethoxysilane were used after distillation. Decane, toluene, and hexane were dried over a sodium wire and distilled before use. Propylene received from a commercial plant was used after passing through a molecular sieve column.

Preparation of Catalysts

MT-1 Catalyst

Magnesium dichloride was reacted (4.0 g) with silicon tetraethoxide (STE) in a 1 : 2 molar ratio. The obtained solid was treated with a titanium tetrachloride–toluene mixture (Ti/Mg molar ratio = 30). The temperature of the reaction mixture was increased to 115°C and the reaction was continued for 2 h. The solid mass thus obtained was washed with decane after removal of excess titanium tetrachloride. The product was further washed with hexane and stored in hexane (Table I).

MT-2,3,4 Catalyst

The method of preparation of the catalysts was similar to that of MT-1 except that alkyl benzoate

Table II   Influence of $BuBz/MgCl_2$ Molar Ratios on the Characteristics of Catalysts

Catalyst	$BuBz/MgCl_2$ Ratio	Analysis (Wt %)			Surface Area (m^2/g)	Productivity	
		Mg	Cl	Ti		Yield (kg PP/g Ti)	Isotactic Index (%)
MT-5	0.0	12.0	41.1	4.2	48	1.10	52
MT-6	0.15	14.0	51.5	3.1	97	1.64	61
MT-7	0.30	16.0	58.1	2.5	148	2.21	75
MT-8	0.45	15.6	55.2	2.7	128	1.90	78

BuBz = butyl benzoate. Polymerization conditions similar to those reported in Table I.

Table III   Characteristics of Catalyst Prepared with Dialkyl Phthalate

| Catalyst | Lewis Base | Analysis (Wt %) | | | Surface Area (m²/g) | Productivity | |
		Mg	Cl	Ti		Yield (kg PP/g Ti)	Isotactic Index (%)
MT-9	DMePh	13.8	48.0	4.4	99	2.20	70
MT-10	DEtPh	15.1	53.0	3.3	124	3.00	74
MT-11	DBuPh	16.9	59.0	2.0	165	3.40	76

Polymerization conditions as stated in Table I. DMePh = dimethyl phthalate; DEtPh = diethyl phthalate; DBuPh = dibutyl phthalate.

(PhCOOR, R = Me, Et, n-Bu) was added into a $MgCl_2$–STE–$TiCl_4$ mixture at 115°C (ester/ $MgCl_2$ molar ratio = 0.30; Table I).

MT-5,6,7,8 Catalyst

The catalyst synthesis was similar to that of MT-4 except that the $BuBz/MgCl_2$ (BuBz = butyl benzoate) molar ratio was varied from 0.0 to 0.45 (Table II).

MT-9,10,11 Catalyst

The preparation of the catalysts was similar to that of MT-1 except that dialkyl phthalate [Ph$(COOR)_2$, R = Me, Et, n-Bu] was added to the $MgCl_2$–STE–$TiCl_4$ mixture at 115°C (ester/ $MgCl_2$ molar ratio = 0.15; Table III).

MT-12,13,14,15,16 Catalyst

The catalysts were prepared the same as in case of MT-11 except that the molar ratio of DBPh/ $MgCl_2$ was varied from 0.0 to 0.30 (DBPh = dibutyl phthalate; Table IV).

MT-17 Catalyst

The MT-14 catalyst was treated with an excess of titanium tetrachloride at 115°C for 2 h. It was washed with decane followed by hexane. The solid was kept in hexane (Table V).

Polymerization Procedure

The polymerization of propylene was carried out in a 500 cm³ glass reactor equipped with a stirrer and an oil bath. A calculated amount of triethylaluminum and/or diphenyl dimethoxysilane were added into the reactor containing 200 cm³ hexane. The solid catalyst was added into the flask and propylene was continuously supplied up to a pressure of 1 bar. Polymerization was terminated by the addition of methanolic hydrochloric acid. The polymer was dried in a vacuum.

Characterization

Magnesium and chloride contents were estimated titrimetrically and titanium was estimated by a spectrophotometric method.[10] The BET surface area of the samples was measured on a Carlo-

Table IV   Effect of DBPh/MgCl₂ Molar Ratios on the Characteristics of Catalysts

| Catalyst | DBPh/MgCl₂ Ratio | Analysis (Wt %) | | | Surface Area (m²/g) | Productivity | |
		Mg	Cl	Ti		Yield (kg PP/g Ti)	Isotactic Index (%)
MT-12	0.0	12.0	41.1	4.2	48	1.10	52
MT-13	0.10	15.0	54.1	3.8	110	2.62	71
MT-14	0.15	16.9	59.0	3.5	165	3.48	76
MT-15	0.20	15.1	53.0	3.0	130	2.84	76
MT-16	0.30	14.4	51.2	2.5	82	2.00	76

DBPh = dibutyl phthalate; polymerization conditions as stated in Table I.

Table V   Characteristics of Catalysts Prepared with Single and Double Treatment of Titanium Tetrachloride

Catalyst	TiCl$_4$ Treatment	Analysis (Wt %)			Surface Area (m^2/g)	Productivity	
		Mg	Cl	Ti		Yield (kg PP/g Ti)	Isotactic Index (%)
MT-14	Single	16.9	59.0	3.5	165	3.48	76
MT-17	Double	18.8	64.0	1.9	182	5.40	75

Polymerization conditions as stated in Table I.

Erba Sorptomatic 1900 model. Polypropylene 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 polypropylene.

RESULTS AND DISCUSSION

Anhydrous magnesium dichloride was reacted with silicon tetraethoxide (STE) to prepare a MgCl$_2$–STE adduct. The treatment of the product with excess titanium tetrachloride gives a solid catalyst. The characterization data show 4.2 wt % incorporation of titanium and a four times higher BET surface area than that of the starting magnesium dichloride (Table I). These results indicate that magnesium dichloride reacts with silicon tetraethoxide to form a MgCl$_2 \cdot$ STE adduct (Scheme 1). The treatment of the obtained product with excess titanium tetrachloride gives titanium chloroethoxide and active magnesium dichloride. Simultaneously, the titanium species react with regenerated magnesium dichloride to yield a supported titanium catalyst. This catalyst (MT-1) in combination with triethylaluminum polymerizes propylene to give polypropylene with an isotactic index of 52.
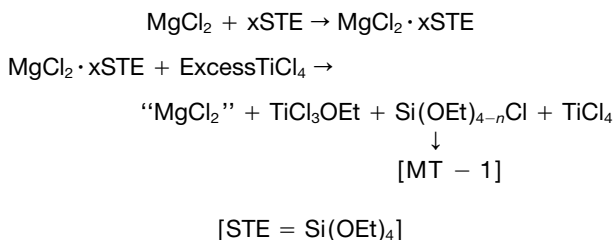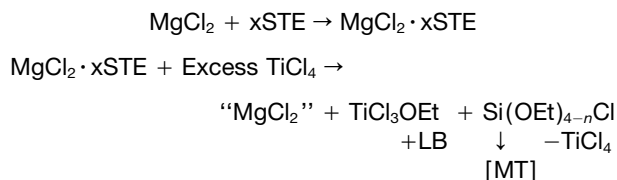
Influence of Internal Lewis Base

An internal Lewis base such as alkyl benzoate or dialkyl phthalate was incorporated into the support during the synthesis of the catalyst (Scheme 2). A compositional analysis of the catalysts prepared with alkyl benzoate shows (Table I) that a change of methyl benzoate to the butyl derivative reduces the titanium content. It can be due to the removal of titanium chloroethoxide from the solid product in the presence of an internal Lewis base and titanium tetrachloride.[6] A specific surface area of the solid product also improves with the incorporation of alkylbenzoate. The highest surface area (148 m^2/g) was observed for the n-butyl benzoate-treated catalyst. Polymerization data (Table I) indicate that the incorporation of alkyl benzoate improves both polymer yield and the isotactic index of polypropylene. The change of methyl benzoate to an ethyl derivative leads to an increase in polymer yield of 11 wt % and an isotactic index of 4 wt %. Fixation of a higher homolog, i.e., butyl benzoate, brings a marginal increase in the yield and isotactic index of polypropylene.

Supported titanium catalysts were synthesized with varied amounts of butyl benzoate. Results are shown in Table II. Compositional analysis shows that increase in the BuBz/MgCl$_2$ ratio from 0.0 to 0.30 leads to a lowering of titanium content from 4.2 to 2.5 wt %. Increasing the ratio of BuBz/

$$\text{MgCl}_2 + x\text{STE} \rightarrow \text{MgCl}_2 \cdot x\text{STE}$$

$$\text{MgCl}_2 \cdot x\text{STE} + \text{Excess TiCl}_4 \rightarrow$$

$$\text{``MgCl}_2\text{''} + \text{TiCl}_3\text{OEt} + \text{Si(OEt)}_{4-n}\text{Cl} + \text{TiCl}_4$$
$$\downarrow$$
$$[\text{MT} - 1]$$

$$[\text{STE} = \text{Si(OEt)}_4]$$

Scheme 1

$$\text{MgCl}_2 + x\text{STE} \rightarrow \text{MgCl}_2 \cdot x\text{STE}$$

$$\text{MgCl}_2 \cdot x\text{STE} + \text{Excess TiCl}_4 \rightarrow$$

$$\text{``MgCl}_2\text{''} + \text{TiCl}_3\text{OEt} + \text{Si(OEt)}_{4-n}\text{Cl}$$
$$+\text{LB} \quad \downarrow \quad -\text{TiCl}_4$$
$$[\text{MT}]$$

$$[\text{LB} = \text{PhCOOR, Ph(COOR)}_2, \text{MT} = \text{MT-2 to 16}]$$

Scheme 2

MgCl$_2$ up to 0.30 improves the specific surface area of the catalyst from 48 to 148 m^2/g. Further increase of the ratio is found to reduce the specific surface area to 128 m^2/g. Polymerization activity of the catalysts showed the following order: MT-5 (0.0) < MT-6(0.15) < MT-7 (0.30) > MT-8(0.45). The stereospecificity of the catalyst system, however, showed an increasing trend with a higher BuBz/MgCl$_2$ ratio up to 0.45.

A bifunctional ester, dialkyl phthalate, was also used as an internal Lewis base in the synthesis of supported titanium catalysts (Scheme 2). The data show (Table III) that a change of dimethyl phthalate to a dibutyl derivative decreases the titanium content and improves the specific surface area, activity, and stereospecificity of the catalyst system. The concentration-dependent studies of dibutyl phthalate (Table IV) reveal that the optimum activity of the catalyst system is observed at a DBPh/MgCl$_2$ ratio of 0.15. The isotactic index of polypropylene is not affected above this ratio.

Comparison of the compositional analysis and performance data of dialkyl phthalate containing a catalyst with the corresponding alkyl benzoate containing catalysts indicate that the dialkyl phthalate system is more efficient than is the analogous alkyl benzoate. Furthermore, an optimum ester/MgCl$_2$ ratio in dialkyl phthalate case is approximately half of that of the alkyl benzoate system. The better performance of dialkyl phthalate systems indicates that bifunctionality offers a higher stability to the titanium species during polymerization.[11]

Effect of Titanium Tetrachloride Treatment

The catalysts were prepared with single and double treatment of titanium tetrachloride for examining their compositional and performance characteristics. Results are given in Table V. It is observed that the second treatment of titanium tetrachloride helps in lowering the titanium content and improving the specific surface area of the catalyst (MT-17). Polymerization studies indicate that double treatment of the catalyst with titanium tetrachloride resulted in enhancing its activity for propylene polymerization. The activity profile of the catalyst as a function of time shows a higher polymerization rate which tends to decrease with increasing time (Fig. 1).

Influence of External Lewis Base

The supported titanium catalyst (MT-17) was evaluated for studying the influence of an exter-
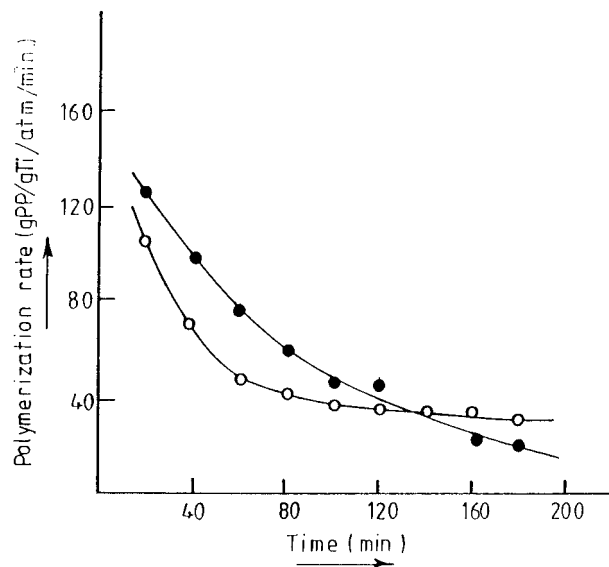
Figure 1 Polymerization rate vs. time: (●) MT-17/Et$_3$Al catalyst system; (○) MT-17/Et$_3$Al + Ph$_2$Si(OMe)$_2$ catalyst system; polymerization conditions as mentioned in Table I, Si/Al = 0.05.

nal Lewis base. The data indicate that the addition of diphenyl dimethoxysilane into the cocatalyst (triethylaluminum) significantly increases the isotactic index of polypropylene (Table VI) to 97 from 75 at a low Si/Al ratio of 0.05. However, the productivity of the system is lowered due to the reduction in the rate of polymerization (Fig. 1). The results show that diphenyl dimethoxysilane in combination with triethylaluminum improves the stereospecificity of the catalyst system at an optium ratio of Si/Al by deactivation of atactic sites and/or also act as an activator for titanium sites forming isotactic polypropylene.[12-15]

CONCLUSIONS

The present study reveals that silicon tetraethoxide can be used for the activation of crystalline magnesium dichloride through formation of an adduct. The treatment of the product with titanium tetrachloride and an internal Lewis base results in the synthesis of a supported titanium catalyst. The nature and concentration of an internal Lewis base influence the chemical composition, specific surface area, and polymerization characteristic of the catalysts. The incorporation of dialkyl phthalate onto a solid catalyst results in a higher performance of the catalyst system as compared to the corresponding alkyl benzoate.

Table VI Performance of MT-17 (MgCl$_2$–DBPh–TiCl$_4$) Catalyst with Diphenyl Dimethoxysilane as an External Lewis Base and Triethylaluminum as Cocatalyst

Sample No.	Si/Al Ratio	MT-17/Et$_3$Al + Ph$_2$Si (OMe)$_2$	
		Polymer Yield (kg PP/g Ti)	Isotactic Index (%)
1	0.0	5.40	75
2	0.05	4.48	97
3	0.10	3.56	98
4	0.20	3.24	98

Polymerization conditions as stated in Table I.

Moreover, the addition of diphenyl dimethoxysilane with the triethylaluminum cocatalyst further enhances the stereospecificity of the catalyst system.

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