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# Notes

## An Unusually Stable Supported Bis(cyclopentadienyl)titanium Dichloride–Trialkylaluminum Catalyst System for Ethylene Polymerization[1]

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### Introduction

A homogeneous bis(cyclopentadienyl)titanium(IV) dichloride–dialkylaluminum chloride catalyst system was first shown by Breslow and Newburg to polymerize ethylene.[2] Kinetic studies by Chien established that the active tetravalent titanium species undergo bimolecular decay to inactive trivalent species.[3] Analogous zirconium compounds show no polymerization activity.[4] The basic kinetic and mechanistic features of soluble metallocene catalysts have been reviewed.[5] The distinguishing feature of this catalyst system is rapid decay as well as loss of catalyst activity within minutes of the start of polymerization and at temperatures higher than 30 °C.

One of the early attempts to heterogenize a soluble catalyst was due to Slotfeldt-Ellingsen and co-workers.[6] $Cp_2TiCl_2$ was supported on silica gel and used to polymerize ethylene using $Et_nAlCl_{3-n}$ as cocatalyst. The specific catalyst activity was found to be comparable for both homogeneous and supported catalysts. More recently, Soga and co-workers have studied supported ethylenebis(tetrahydroindenyl)zirconium(IV) dichloride for the isospecific polymerization of propylene.[7] $Al_2O_3$, $MgCl_2$, and $SiO_2$ pretreated with methylaluminoxane (MAO) were used as supports and trialkylaluminum as cocatalyst. $Al_2O_3$ and $MgCl_2$ gave low molecular weight polymers with broad polydispersity.[8] On the contrary, $SiO_2$ pretreated with MAO gave narrow polydispersities and lower catalyst activity. MAO-pretreated-silica supported metallocene catalyst has been shown to polymerize propylene with no change of stereospecificity.[9] All the above catalysts were prepared by physical mixing of the support with the zirconium compound in a diluent such as toluene.

We now report for the first time a simple synthesis of a $MgCl_2$ supported $Cp_2TiCl_2$ catalyst which shows significant activity for ethylene polymerization in the presence of trialkylaluminum and a kinetic behavior distinctly different from that of an unsupported metallocene catalyst.[10]

### Experimental Section

**Materials.** Grignard-grade Mg turnings (Loba Chemical, India), bis(cyclopentadienyl)titanium(IV) dichloride ($Cp_2TiCl_2$; Aldrich), triisobutylaluminum (TIBAL), and diethylaluminum chloride (DEAC; Schering A. G., Germany) were used as received. 1,2-Dichloroethane (SD Fine Chemicals, Bombay) was distilled over $CaH_2$ and stored over 3-Å molecular sieves. Tetrahydrofuran (THF), hexane, and xylene were purified by distilling over sodium. Polymer-grade ethylene was obtained from the Gas Cracker Complex of Indian Petrochemicals Corp., Ltd., at 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 $N_2$ (<5 ppm moisture) generated using a $N_2$ generator (Spantech Model NG 300-1, England) or under a positive pressure of high-purity $N_2$ using standard bench-top inert-atmosphere techniques.

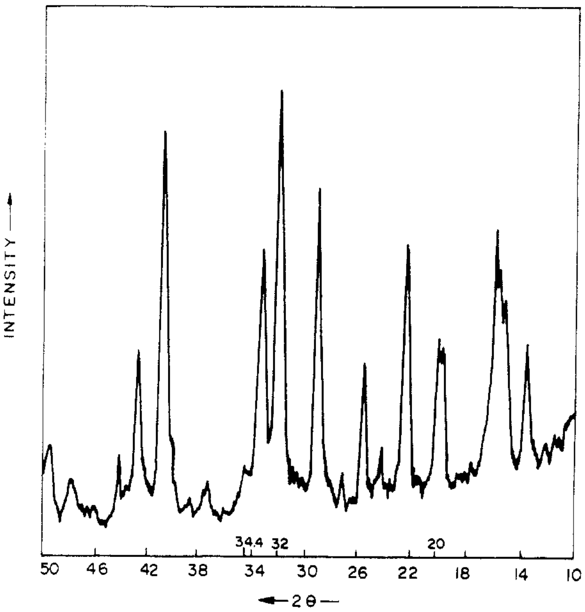

**Figure 1.** Powder XRD pattern of $Cp_2TiCl_2$ supported on $MgCl_2$.

**Catalyst Synthesis.** Two supported $Cp_2TiCl_2$ catalysts having 1.8 and 3.3% by weight of titanium were used in this study (catalysts A and B, respectively). A typical procedure for the synthesis of catalyst is as follows.

A three-neck round-bottomed flask equipped with a magnetic stirring bar, $N_2$ inlet, addition funnel, and reflux condenser was flame dried and cooled under a $N_2$ atmosphere. Iodine (5 mg) activated magnesium turnings (0.4 g) were placed in the flask, and THF (30 mL) was added. The slurry was stirred for 30 min at 40 °C. A mixture of 1,2-dichloroethane and THF (1:1) (40 mL) was transferred into the addition funnel using a cannula and added dropwise at 40–50 °C. It was observed that all the Mg turnings slowly dissolved in THF with the formation of a clear solution. Steady evolution of ethylene gas was observed, indicating decomposition of the intermediate β-chloroethylmagnesium chloride to a complex of $MgCl_2$ and THF and its dissolution in THF. The clear solution was further diluted by addition of 20 mL of THF, separated from traces of unreacted magnesium, and transferred into another flame-dried three-neck flask equipped with a magnetic stirring bar, $N_2$ inlet, addition funnel, and septum.

$Cp_2TiCl_2$ (3.36 mmol) was dissolved in THF in a flame-dried round-bottomed flask. The clear dark-red solution was then transferred into an addition funnel using a cannula. The $Cp_2TiCl_2$–THF solution was added dropwise into the $MgCl_2$–THF solution. It was observed that no separation of layers or any solid material occurred. This red solution was then added slowly to 300 mL of dry hexane. A solid precipitate having a whitish pink color separated out. The solid was dried under vacuum at 40 °C. The dried solid was transferred into vials and stored in the glovebox. Yield: 4.2 g. Anal. Calcd: Mg, 10.8; Ti, 3.3; Cl, 35.9.

**Polymerization.** Ethylene polymerization was performed in a stirred glass reactor at 1 atm in xylene using about 100–120 mg

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**Table I. Ethylene Polymerization with Unsupported and Supported Catalyst**[a]

| sample no. | catalyst | cocatalyst | time (min) | PE (g) | convn (%) | $R_p$ (M s$^{-1}$) | activity (kg of PE/ mol of Ti) | $[\eta]^c$ (dL/g) |
|---|---|---|---|---|---|---|---|---|
| 1 | $Cp_2TiCl_2$ | TIBAL | 60 | no polymerization activity | | | | |
| 2[b] | $Cp_2TiCl_2$ | DEAC | 10 | 0.30 | 100 | 1.37 | 0.9 | 0.3 |
| 3 | catalyst B | TIBAL | 60 | 0.48 | 100 | 0.39 | 2.4 | 3.5 |
| 4 | catalyst B | DEAC | 60 | 0.61 | 100 | 1.69 | 6.4 | 0.9 |

[a] All polymerizations were performed at 40 °C in xylene medium at Al/Ti = 50 at a total pressure of 1 atm. [b] Ethylene absorption ceased after a lapse of 10 min. [c] Intrinsic viscosities were determined in *o*-dichlorobenzene at 135 °C.

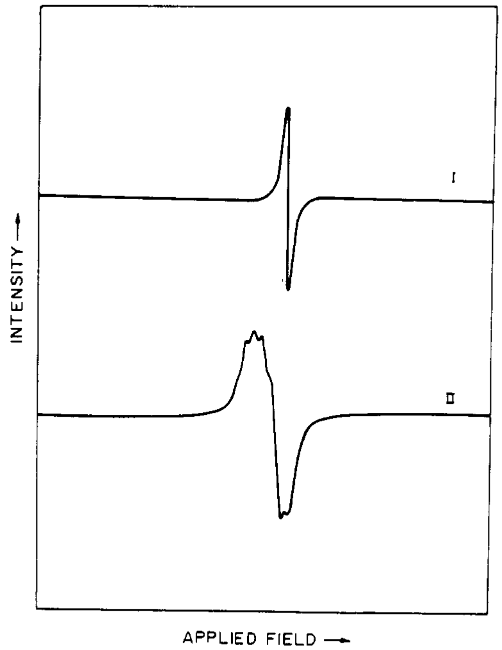


**Figure 2.** ESR spectra of (I) $Cp_2TiCl_2$–TIBAL and (II) $Cp_2TiCl_2/MgCl_2$–TIBAL in xylene at 25 °C; [Ti] = 1.25 × 10$^{-4}$ mol, Al/Ti = 50.

**Table II. Effect of the Al/Ti Ratio on Ethylene Polymerization with the Mg–Ti/TIBAL Catalyst System**[a]

| sample no. | Ti (wt %) | Al/Ti wt ratio | convn (%) | $R_p$ (M s$^{-1}$) | activity (kg of PE/ mol of Ti) | $[\eta]^b$ (dL/g) |
|---|---|---|---|---|---|---|
| 1 | 3.3 | 50 | 95 | 0.39 | 2.5 | 2.6 |
| 2 | 3.3 | 100 | 97 | 0.51 | 2.5 | 3.6 |
| 3 | 3.3 | 200 | 99 | 0.68 | 2.0 | 4.7 |
| 4 | 1.8 | 50 | 99 | 0.18 | 0.8 | 2.2 |
| 5 | 1.8 | 100 | 98 | 0.48 | 1.0 | 3.4 |
| 6 | 1.8 | 200 | 98 | 0.61 | 2.0 | 4.0 |

[a] All polymerizations were performed at 40 °C for 60 min in xylene at a total pressure of 1 atm. [b] Intrinsic viscosities were determined in *o*-dichlorobenzene at 135 °C.

of solid catalyst in conjunction with cocatalyst. The reactor assembly and manner of conducting polymerization has been described elsewhere.[11]

**Analysis.** Titanium estimation was performed using a Hitachi Model 220 UV–visible spectrophotometer. Mg and Cl estimations were performed by EDTA and argentometric titrations. ESR spectra were run on a Bruker Model ER-200D ESR spectrometer at room tmperature (9.72 GHz). Powder XRD was recorded on a Philips PW 1730 spectrometer using nickel-filtered Cu $K_\alpha$ radiation. FT-IR spectra were run on a Perkin-Elmer 16PC FT-IR in Nujol mull using NaCl cells (1600–400 cm$^{-1}$). Viscosities of the polymer samples were determined using an Ubbelohde viscometer in *o*-dichlorobenzene as solvent at 135 °C.

## Results and Discussion

Two heterogeneous magnesium–titanium catalysts, having 1.8 and 3.3% of titanium, synthesized in the present study, were observed to have the empirical formulae $MgTi_{0.05}Cl_{2.0}Cp_{0.1}(THF)_{0.5}$ and $MgTi_{0.15}Cl_{2.09}Cp_{0.3}(THF)_{1.2}$ as calculated from the corresponding elemental analysis. The FT-IR spectrum of the solid catalyst showed distinct bands at 1460 and 820 cm$^{-1}$ characteristic of C–C stretching and C–H deformation bands of the cyclopentadienyl ring.[12] It also showed at 1036 and 888 cm$^{-1}$ characteristic vibration bands of THF bound to the solid surface.[13] The powder XRD pattern of the Mg–Ti catalyst showed the absence of a strong reflection at 2$\theta$ = 34.4° and a reduction in the intensity of a reflection at 2$\theta$ = 20° both of which were originally present in $Cp_2TiCl_2$. A new reflection at 2$\theta$ = 32° appeared in the Mg–Ti catalyst (Figure 1) corresponding to that of the $MgCl_2$–THF complex. $MgCl_2$–THF is formed by the in situ Grignard decomposition of the intermediate $\beta$-chloroethylmagnesium chloride. Upon reduction with TIBAL, the Mg–Ti catalyst showed a splitting in the spectrum in contrast to a sharp single peak at $g$ = 1.98 for $Cp_2TiCl_2$ (Figure 2). This indicates that the metallocene is heterogenized on the support.[6]

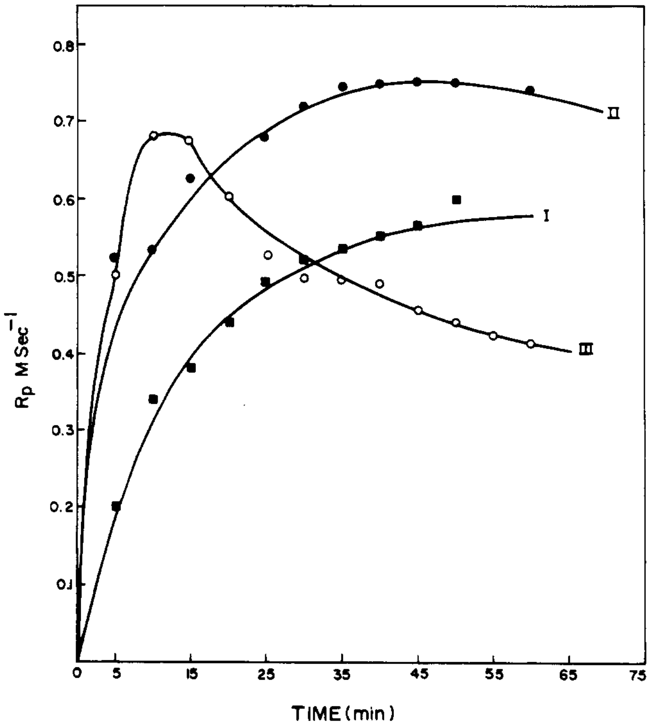


**Figure 3.** Plot of rate of polymerization versus time for the $Cp_2TiCl_2/MgCl_2$–TIBAL catalyst system in xylene at 40 °C; [Ti] = 1.84 × 10$^{-4}$ mol; (I) Al/Ti = 50, (II) Al/Ti = 100, and (III) Al/Ti = 200.

In the presence of TIBAL, $Cp_2TiCl_2$ is inactive toward polymerization of ethylene. Substitution of TIBAL with DEAC causes initiation of polymerization; however, the catalyst system is short lived and rapidly decays. Ethylene absorption ceases within 10 min of mixing the catalyst components. In contrast, $Cp_2TiCl_2$ supported on $MgCl_2$ shows a significant polymerization activity even with TIBAL and a 3-fold increase in activity with DEAC (Table

**Table III. Effect of Temperature on Ethylene Polymerization with the Mg–Ti/TIBAL Catalyst System**[a]

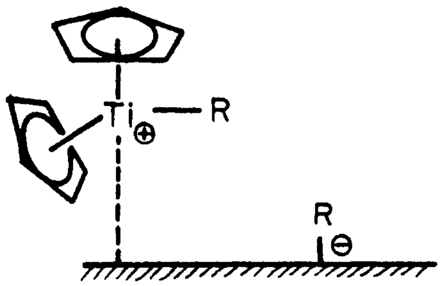
| sample no. | Ti (wt %) | temp (°C) | PE (g) | convn (%) | $R_p$ (M $s^{-1}$) | activity (kg of PE/mol of Ti) | $[\eta]$[b] (dL/g) |
|---|---|---|---|---|---|---|---|
| 1 | 3.3 | 40 | 0.25 | 93.6 | 0.51 | 2.5 | 3.52 |
| 2 | 3.3 | 60 | 0.16 | 33.3 | 0.76 | 1.2 | 1.47 |
| 3 | 3.3 | 70 | 0.08 | 22.2 | 1.29 | 0.7 | 0.79 |
| 4 | 1.8 | 40 | 0.18 | 99.0 | 0.18 | 0.7 | 3.42 |
| 5 | 1.8 | 60 | 0.08 | 60.0 | 0.19 | 0.5 | 2.20 |
| 6 | 1.8 | 70 | 0.07 | 50.0 | 0.33 | 0.4 | 1.40 |

[a] All polymerizations were performed at Al/Ti = 100 in xylene for 60 min at a total pressure of 1 atm. [b] Intrinsic viscosities were determined in *o*-dichlorobenzene at 135 °C.

I). More interestingly, the catalyst system shows a steady-state kinetic behavior. The increase in molecular weight upon heterogenization shows that the propagation is faster or that the chain-transfer process is slowed down relative to the soluble catalyst or that different chain-transfer processes are operating.

The effect of the Al/Ti weight ratio on the polymerization behavior was studied with the two Mg–Ti catalysts. The results are shown in Table II (Figure 3). The catalyst activity increased with increasing Al/Ti ratio for a catalyst containing a lower titanium content. The polymer molecular weights showed a steady increase with increasing Al/Ti ratio, indicating the organoaluminum compound did not contribute significantly to the chain-transfer process. Conversion and molecular weight decreased with increasing reaction temperature (Table III). The decrease was more severe in the case of the catalyst containing a higher titanium content.

These results suggest that $MgCl_2$ confers unusual stability to an otherwise unstable active polymerization center. Dramatic enhancement in catalytic activity has been reported for $Cp_2'Th(CH_3)_2/MgCl_2$ for propylene hydrogenation.[14] On the basis of a $^{13}C$ CP-MAS NMR study of $Cp_2'Th(CH_3)_2/MgCl_2$, it was concluded that the active center was a "cation-like" complex formed by the transfer of methide anion from the actinide center to the Lewis acidic sites on the surface of $MgCl_2$.[15] A similar mechanism can be invoked to explain the unusual activity as well as stability of the $Cp_2TiCl_2/MgCl_2$–trialkylaluminum catalyst system for ethylene polymerization. Although we have no experimental evidence at the present time, we presume that the active site is a cation-like complex of $Cp_2TiR^+$ adsorbed on $MgCl_2$ (A), where the reactive sites are isolated on the support, thereby stabilizing the coordinatively unsaturated monomeric titanium species. Matrix isolation of catalytically active sites in the case of $Cp_2TiCl_2$ chemically anchored to rigid polymeric support has been shown to be responsible for higher rates of olefin hydrogenation observed with supported $Cp_2TiCl_2$ compared to $Cp_2TiCl_2$ in solution.[16]



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