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Highly active ethylene polymerization catalysts based on titanium complexes having two phenoxy-imine chelate ligands

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Abstract

Five titanium complexes having F(s) or CF_3(s) containing phenoxy-imine chelate ligands were prepared and investigated for their potential as ethylene polymerization catalysts using methylalumoxane (MAO) as a co-catalyst at 25 °C under atmospheric pressure. Polymerization results showed that the electrophilicity of the titanium center plays a dominant role in determining activity. These results clearly demonstrate, for the first time, the electron-withdrawing substituent effects on polymerization activity. The complexes possessing plural F(s) or CF_3(s) in the phenoxy-imine ligand displayed very high activities exceeding those for Cp_2TiCl_2 and Cp_2ZrCl_2. The activity, 43,300 kg polyethylene (PE) mol-cat^{-1} h^{-1}, exhibited by the complex having three fluorines in the ligand, represents the highest value reported to date for ethylene polymerization catalysts based on titanium complexes under atmospheric pressure at ambient temperatures. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Olefin polymerization catalyst; Post-metallocene; Phenoxy-imine ligand; Titanium; FI catalysts

1. Introduction

Historically, the development of highly active olefin polymerization catalysts has been a trigger for creating new polymers which impact on our daily lives in countless beneficial ways [1–5]. A recent instance is the development of group 4 metallocene catalysts which exhibit very high ethylene polymerization activities [4,5]. Based on the highly active group 4 metallocene catalysts, high performance linear low-density polyethylene (LLDPE), isotactic polypropylene (iPP), and syndiotactic polystyrene (sPS), etc. have been developed [6]. Therefore, much effort has been directed towards the development of highly active catalysts, following the group 4 metallocene catalysts. In consequence, quite a few highly active catalysts based on both early and late transition metal complexes have been developed [7,8]. There are, however, only a few examples of titanium complexes displaying high ethylene polymerization activities [9–11] though titanium metal is the major player in highly active heterogeneous Ziegler–Natta catalysts. As a result of ligand-oriented catalyst design research in our laboratories, we have developed a new family of group 4 transition metal complexes bearing two phenoxy-imine chelate ligands, named FI Catalysts, exhibiting high catalytic performance for olefin polymerization including living olefin polymerization [12–26]. Although we successfully obtained very active zirconium FI catalysts, we did not obtain highly active titanium FI catalysts [14]. Accordingly, we have conducted further research on titanium FI Catalysts with the intention of developing the highly active titanium catalysts and applying them to new polymers.

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In this paper, we would like to describe the catalytic performance of new titanium complexes having F(s) or CF₃(s) containing phenoxy-imine chelate ligands for ethylene polymerization in order to introduce a new method for acquiring highly active titanium complexes with phenoxy-imine chelate ligands.

2. Experimental

2.1. General

2.1.1. Solvents and reagents

Dried solvents (diethyl ether, toluene, dichloromethane, and hexane) used for ligand and complex syntheses were purchased from Wako Pure Chemical Industries, Ltd., and used as received. Toluene used as a polymerization solvent (Wako Pure Chemical Industries, Ltd.) was dried over Al_2O_3. 3-t-Butylsalicylaldehyde was obtained from Aldrich Chemical Company Inc. 4-Fluoroaniline, 3,5-difluoroaniline, 3,4,5-trifluoroaniline, 4-trifluoromethylaniline, and 3,5-bis(trifluoromethyl)aniline were purchased from Tokyo Kasei Kogyo Co., Ltd. An n-butyllithium hexane solution (Kanto Chemical Co., Inc.) were also used as received. $TiCl_4$ and ethylene were obtained from Aldrich Chemical Company Inc. and Sumitomo Seika Co., Ltd., respectively. Methylalumoxane (MAO) was purchased from Albemare as a 1.2 M toluene solution, and the remaining trimethylaluminum was evaporated in vacuo prior to use.

2.1.2. Ligand and complex analyses

NMR spectra were recorded on a JEOL270 spectrometer at ambient temperatures. Chemical shifts for the ^{1}H NMR were referenced to an internal solvent resonance and reported relative to tetramethylsilane (TMS). Elemental analysis for CHN was carried out by the CHNO type from the Helaus Co. The elemental analysis for Ti was carried out using the ICP method by a SHIMADZU ICPS-8000 after dry ashing and dilute nitric acid dissolution. The FD-MS spectra were recorded on a SX-102A from Japan Electron Optics Laboratory Co., Ltd.

2.1.3. Polymer characterization

Intrinsic viscosity (η) was measured in decalin at 135 °C using an Ubbelohde viscometer (polyethylene 25 mg/decalin 25 ml). Viscosity average molecular weight (Mv) values of polyethylenes were calculated from the following equation: $(\eta) = 6.2 \times 10^{-4} \, \text{Mv}^{0.7}$ [27].

2.2. General complex syntheses procedure

2.2.1. Ligand syntheses

Ligand syntheses were carried out under an atmosphere of nitrogen using oven-dried glassware. 3-t-Butylsalicylaldehyde reacted with a primary amine compound via Schiff base condensation in dried toluene to afford the corresponding phenoxy-imine ligand in approximately 70–98% yield [14].

2.2.2. Complex synthesis

All manipulations were performed with the exclusion of oxygen and moisture under argon using standard Schlenk techniques. A typical procedure for a complexation is as follows: to a stirred solution of a phenoxy-imine ligand (3.0 mmol) in dried diethyl ether (20 ml) at −78 °C, an n-butyllithium hexane solution (3.0 mmol) was added dropwise over a 5 min-period. The solution was allowed to warm to room temperature and stirred for 2 h, the resulting solution was added dropwise over a 30 min-period to a stirred solution of $TiCl_4$ (1.5 mmol) in dried diethyl ether (20 ml) at −78 °C. The mixture was allowed to warm to room temperature and stirred for 15 h. The resulting mixture was concentrated in vacuo to give a solid, to which dried dichloromethane (20 ml) was added, and the mixture was stirred for 5 min. The resulting mixture was filtered, and then the residue was washed with dried dichloromethane. The combined organic filtrates were concentrated in vacuo to afford the crude complex. To the crude complex, dried diethyl ether (3 ml) and dried hexane (10 ml) were added and stirred for 15 min. A titanium complex was collected by filtration, washed with dried hexane and dried in vacuo.

2.3. Bis(N-(3-t-butylsalicylidene)-4'-fluoroanilinato)titanium(IV)dichloride (**2**)

Reddish brown powder (22% yield). ^{1}H NMR (CDCl₃); δ. 1.33–1.50 (m, 18H, t-Bu), 6.71–7.67 (m, 14H), 7.96–8.06 (m, 2H, CH=N). Anal. found: C, 62.04; H, 5.30; N, 3.77; Ti, 6.93%. Calcd.:

$TiC_{34}H_{34}N_2O_2F_2Cl_2$; C, 61.93; H, 5.20; N, 4.25; Ti, 7.26%. FD-MS, 658 (M^+).

2.4. Bis(N-(3-t-butylsalicylidene)-3′, 5′-difluoroanilinato)titanium(IV)dichloride (3)

Reddish brown powder (69% yield). ^{1}H NMR (CDCl$_3$); δ. 1.32–1.62 (m, 18H, t-Bu), 6.33–7.33 (m, 10H), 7.52–7.70 (m, 2H), 8.03–8.10 (m, 2H, CH=N). Anal. found: C, 58.83; H, 4.91; N, 3.78; Ti, 6.86%. Calcd.:$TiC_{34}H_{32}N_2O_2F_4Cl_2$; C, 58.72; H, 4.64; N, 4.03; Ti, 6.89%. FD-MS, 694 (M^+).

2.5. Bis(N-(3-t-butylsalicylidene)-3′,4′, 5′-trifluoroanilinato)titanium(IV)dichloride (4)

Reddish brown powder (33% yield). ^{1}H NMR (CDCl$_3$); δ. 1.17–1.62 (m, 18H, t-Bu), 6.41–7.69 (m, 10H), 8.03–8.09 (m, 2H, CH=N). Anal. found: C, 55.96; H, 4.00; N, 3.56; Ti, 6.48%. Calcd.:$TiC_{34}H_{30}N_2O_2F_6Cl_2$; C, 55.83; H, 4.13; N, 3.83; Ti, 6.55%. FD-MS, 730 (M^+).

2.6. Bis(N-(3-t-butylsalicylidene)-4′-trifluoromethylanilinato)titanium(IV)dichloride (5)

Reddish brown powder (27% yield). ^{1}H-NMR (CDCl$_3$); δ. 1.18–1.59 (m, 18H, t-Bu), 6.78–6.93 (m, 4H), 7.05–7.17 (m, 4H), 7.31–7.69(m, 6H), 8.09 (s, 2H, CH=N). Anal. found: C, 56.47; H, 4.85; N, 3.50; Ti, 6.45%. Calcd.:$TiC_{36}H_{34}N_2O_2F_6Cl_2$; C, 56.94; H, 4.51; N, 3.69; Ti, 6.30%. FD-MS, 758 (M^+).

2.7. Bis(N-(3-t-butylsalicylidene)-3′, 5′-bis(trifluoromethyl)anilinato)titanium(IV) dichloride (6)

Reddish brown powder (51% yield). ^{1}H NMR (CDCl$_3$); δ. 1.06–1.47 (m, 18H, t-Bu), 6.99–7.11 (m, 4H), 7.33–7.39 (m, 4H), 7.53–7.70 (m, 4H), 8.28 (s, 2H, CH=N). Anal. found: C, 50.86; H, 3.55; N, 2.93; Ti, 5.12%. Calcd.:$TiC_{38}H_{32}N_2O_2F_{12}Cl_2$; C, 50.97; H, 3.60; N, 3.13; Ti, 5.35%. FD-MS, 894 (M^+).

2.8. Ethylene polymerization

Ethylene polymerization was carried out under atmospheric pressure in toluene using a 500 ml glass reactor equipped with a mechanical stirrer and a temperature probe. Toluene (250 ml) was introduced into the nitrogen-purged reactor and stirred vigorously (600 rpm). The toluene was kept at 25 °C, and then the ethylene gas feed (100 l/h) was started. After 15 min, polymerization was initiated by the addition of a toluene solution of MAO and then a toluene solution of a complex into the reactor with vigorous stirring (600 rpm). After 5 min, isobutyl alcohol (10 ml) was added to terminate the polymerization, and the ethylene gas feed was stopped. The resulting mixture was added to the acidic methanol (1000 ml including 2 ml of conc. HCl). The polyethylene was isolated by filtration, washed with methanol (200 ml × 2), and then dried in vacuo to constant weight (80 °C, vacuum oven).

2.9. HOMO energy level calculation

Highest Occupied Molecular Orbital (HOMO) energy level calculations for anionic phenoxy-imine chelate ligands were performed using MNDO-PM3 method (HyperChem Ver. 5.1).

3. Results and discussion

A general synthetic route for titanium complexes used in this study is depicted in Scheme 1. The synthesis of complex **1** has already been reported [14]. The phenoxy-imine ligands, A–E, are prepared in high yields (A: 98%, B: 89%, C: 98%, D: 70%, E: 72%) from an aniline having F(s) or CF$_3$(s) and 3-t-butylsalicylaldehyde in dried toluene. The titanium complexes are obtained in moderate to good yields (**2**: 22%, **3**: 69%, **4**: 33%, **5**: 27%, **6**: 51%) by the reaction of TiCl$_4$ with two equivalents of the lithium salt of the phenoxy-imine ligand in dried diethyl ether, followed by the purification using dried diethyl ether and dried hexane.

Ethylene polymerization behavior of complexes **1–6** was investigated at 25 °C in toluene with MAO as a co-catalyst under ethylene at atmospheric pressure. Polymerization results are compiled in Table 1. All complexes are active toward ethylene polymerization and in all cases, high molecular weight polyethylenes were obtained (viscosity average molecular weight

Scheme 1. Synthetic route for titanium complexes.
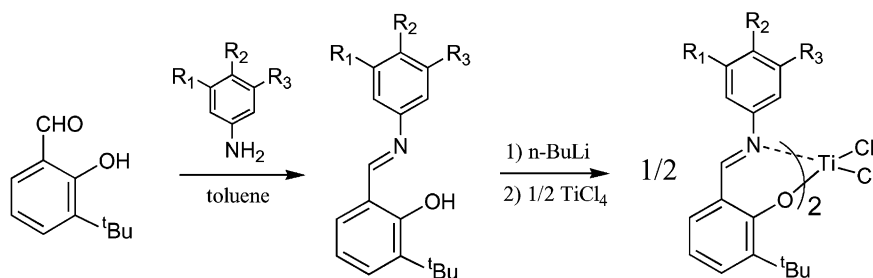
2: R$_1$ = R$_3$= H, R$_2$ = F
3: R$_1$ = R$_3$= F, R$_2$ = H
4: R$_1$ = R$_2$ = R$_3$= F
5: R$_1$ = R$_3$ = H, R$_2$ = CF$_3$
6: R$_1$ = R$_3$ = CF$_3$, R$_2$ = H

Table 1
Ethylene polymerization results[a]

Entry	Complex	Catalyst (μmol)	Yield (g)	Activity (kg-PE mol-cat^{-1} h^{-1})	Mv[b] $\times$ 10^{-4}
1	**1**	0.2	0.06	3,580	32.6
2	**2**	0.2	0.07	3,960	41.9
3	**3**	0.2	0.58	34,800	62.3
4	**4**	0.2	0.72	43,300	37.8
5	**5**	0.2	0.06	3,600	54.2
6	**6**	0.2	0.67	40,320	136.5
7	Cp$_2$TiCl$_2$	1.0	1.39	16,700	125.4
8	Cp$_2$ZrCl$_2$	0.5	1.16	27,900	104.0

[a] Polymerization conditions: solvent; toluene, 250 ml, MAO, 1.25 mmol; ethylene, atmospheric pressure 100 l/h; Polymerization time, 5 min; Polymerization temperature, 25 °C.
[b] $(\eta) = 6.2 \times 10^{-4} \, Mv^{0.7}$.

(Mv) 326,000–1,3700,00).[1] A comparison of catalytic performance in Table 1 shows that the introduction of F(s) or CF$_3$(s) in the ligand had profound effects on activities whereas it had relatively small effects on molecular weight (Mv) values. Considering that a molecular weight value is determined by the relative rate of chain growth and chain termination, the introduction of F(s) or CF$_3$(s) in the ligand had similar effects on chain growth and on chain termination. Although the introduction of one F(s) or CF$_3$(s) in the ligand (complexes **2** and **5**) gave rise to no sig-

nificant increase in activity, the introduction of plural F(s) or CF$_3$(s) in the ligand (complexes **3**, **4**, and **6**) resulted in a great increase in catalytic activity, unlike the group 4 metallocene catalysts whose activity is decreased by the introduction of electron-withdrawing substituent(s) in cyclopentadienyl (Cp) ligand [28,29]. Complexes **3** and **4**, having two or three fluorines, showed 34,800 (complex **3**) and 43,300 (complex **4**) kg-PE mol-cat^{-1} h^{-1} of activities, on the order of one digit larger than that exhibited by the non-fluorinated parent complex **1**. Likewise, complex **6**, possessing two CF$_3$(s), displayed 40,320 kg-PE mol-cat^{-1} h^{-1} of activity.

For the purposes of having a quantitative discussion on the effects of introducing F(s) or CF$_3$(s) in the ligand, the HOMO energy level of anionic

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[1] The molecular weight distribution (Mw/Mn) values exhibited by complexes **1–6** are ca. 2.0 under the conditioned employed in Table 1, confirming that complexes **1–6** work as single-site catalysts.
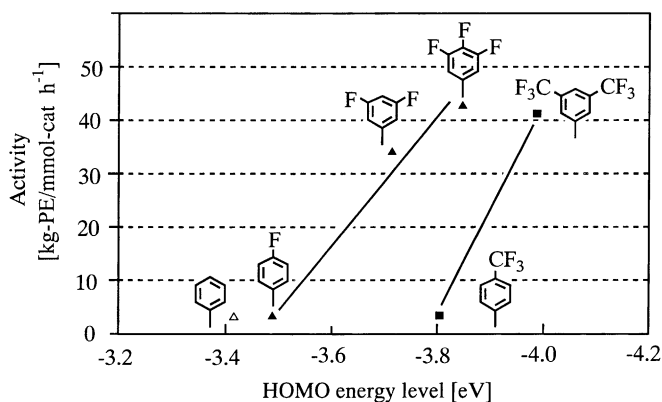
Fig. 1. Relationship between activity and HOMO energy level of anionic phenoxy-imine chelate ligand.

phenoxy-imine chelate ligand (an indication of electron donation ability of the ligands) was calculated using MNDO-PM3 method. As shown in Fig. 1, the basic trend observed is that decreases in HOMO energy level of anionic phenoxy-imine chelate ligand resulted in increased activity. These results provide the first clear demonstration that the electrophilicity of the titanium center in active species plays a dominant role in determining the catalytic activity. A different trend vis-à-vis activity—HOMO energy level relationship observed for F(s) containing complexes (complexes **2**, **3**, and **4**) and CF$_3$(s) containing complexes (complexes **5** and **6**) may result from the difference in steric factors between F(s) and CF$_3$(s), which probably causes the structural difference of the active species.

A possible explanation for the activity increase as a result of introducing electron-withdrawing F(s) or CF$_3$(s) is that a more electrophilic titanium center, generated by a more electron-withdrawing ligand, results in an increase in metal-carbon reactivity, leading to reduced activation energy for ethylene insertion. The activities obtained with complexes **3** (34,800 kg-PE mol-cat^{-1} h^{-1}), **4** (43,300 kg-PE mol-cat^{-1} h^{-1}), and **6** (40,320 kg-PE mol-cat^{-1} h^{-1}) are much larger than those for Cp$_2$TiCl$_2$ (16,700 kg-PE mol-cat^{-1} h^{-1}) and Cp$_2$ZrCl$_2$ (27,900 kg-PE mol-cat^{-1} h^{-1}) under the same polymerization conditions. Therefore, highly active new titanium catalysts have been developed. To the best of our knowledge, the activity displayed by complex **4** (43,300 kg-PE mol-cat^{-1} h^{-1}) represents the highest value reported to date for titanium-based ethylene polymerization catalysts including titanocenes under atmospheric pressure at ambient temperatures. Highly active titanium FI catalysts for the polymerization of α-olefins and co-polymerization of ethylene and α-olefins are currently being applied with the purpose of producing polymers possessing novel properties and uses.

4. Conclusions

In conclusion, titanium complexes having electron-withdrawing F(s) or CF$_3$(s) containing phenoxy-imine chelate ligands have been developed, which represent the first titanium catalysts displaying ethylene polymerization activities exceeding those for the group 4 metallocene catalysts under mild conditions. The results described herein together with our previous results [30] may provide a catalyst design guideline for developing highly active non-metallocene titanium complexes.

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