Ethylene/1-Hexene Copolymerization with Supported Ziegler–Natta Catalysts Prepared by Immobilizing TiCl$_3$(OAr) onto MgCl$_2$

Hongrui Yang, Biao Huang, Zhisheng Fu, Zhiqiang Fan

MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China
Correspondence to: Z. Fan (E-mail: fanzq@zju.edu.cn)

ABSTRACT: Five titanium complexes TiCl$_3$(OAr) (Ar = C$_6$H$_5$—, 2,6-Me$_2$C$_6$H$_3$—, 2,6-i-Pr$_2$C$_6$H$_3$—, 2,6-t-Bu$_2$C$_6$H$_3$—, 4-Me-2,6-t-Bu$_2$C$_6$H$_3$—) were immobilized, respectively, on MgCl$_2$ in semibatch reaction to form supported catalysts for olefin polymerization. Comparing with the catalysts prepared by immobilizing TiCl$_3$(OAr) onto MgCl$_2$ in batch reaction, the catalysts prepared by semibatch reaction have lower titanium content and higher ArO/Ti ratio. The aryloxy-containing catalysts studied in this work showed higher ethylene/1-hexene copolymerization activity and higher 1-hexene incorporation rate than the blank catalyst when activated by triisobutylaluminum. Similar effects of the aryloxy ligand were observed when the copolymerization is conducted in the presence of hydrogen. Introducing aryloxy ligand in the catalysts either by semibatch or batch reaction caused similar effects of enhancing copolymerization activity and α-olefin incorporation rate. Mechanism of the effects of aryloxy ligand has been discussed. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41329.

INTRODUCTION

In recent years, copolymerization of ethylene with α-olefins with Ziegler–Natta catalysts have been intensively studied, with aims of understanding the mechanism that control the copolymer chain structure and active center distribution of the catalytic system.[1–15] Meanwhile, various LTiCl$_3$ type organometallic complexes have been used to catalyze ethylene polymerization or its copolymerization with α-olefins, where the organic ligand L is bonded to Ti through an oxo, amino, or iminato bond.[16–38] Most of these complexes showed medium to high activity when activated by methyl aluminoxane (MAO), modified methyl aluminoxane (MMAO), or dried MAO, except ArOTiCl$_3$ type simple complexes.[10,11] Conversely, attempts have been made to support the LTiCl$_3$ type complexes on anhydrous MgCl$_2$ to form immobilized organometallic catalysts for olefin polymerization.[39–41] The immobilized LTiCl$_3$ catalysts, when activated by alkylaluminum like AlEt$_3$, can also catalyze ethylene/α-olefin copolymerization in high activity. Some LTiCl$_3$ type catalysts immobilized on silica gel have also been used for ethylene copolymerization, but the activity was much lower than the corresponding homogeneous catalysts.[23] Immobilization of organometallic catalyst on solid particles is a key step for controlling the morphology of the nascent polymer particles. This step is especially important when the organometallic catalyst is to be applied in industrial ethylene (co)polymerization processes like slurry and gas-phase processes.

In our previous work,[41] a series of aryloxy-containing MgCl$_2$ supported catalysts were prepared by batch addition of TiCl$_3$(OAr) into suspension of anhydrous MgCl$_2$ particles in toluene. It has been found that the ArO/Ti molar ratio in thus prepared supported catalyst was much lower than 1. The loss of organic ligand in the supported catalyst was ascribed to rapid exchanges of ArO— group of the immobilized Ti species with Cl of TiCl$_3$(OAr) in the solution. In this paper, similar TiCl$_3$(OAr) (Ar—C$_6$H$_5$—, 2,6-Me$_2$C$_6$H$_3$—, 2,6-i-Pr$_2$C$_6$H$_3$—, 2,6-t-Bu$_2$C$_6$H$_3$—, 4-Me-2,6-t-Bu$_2$C$_6$H$_3$—) complexes have been used to prepare MgCl$_2$-supported catalysts, but a semibatch reaction strategy has been adopted, namely, the TiCl$_3$(OAr) solution was slowly added into the suspension of MgCl$_2$. In such a reaction process, the concentration of TiCl$_3$(OAr) in the liquid phase kept at a very low level, leading to slower exchanges between ArO of the immobilized Ti species and Cl of TiCl$_3$(OAr) in the solution. To further depress such group exchanges, the temperature of the immobilization reaction was also lowered. A blank catalyst was prepared using TiCl$_4$ instead of TiCl$_3$(OAr) as the titanium compound to make comparative studies. Ethylene-1-hexene copolymerization with these catalysts has been studied, either in the absence or presence of molecular hydrogen (a chain-transfer agent). The supported catalysts containing aryloxy ligand prepared by the semibatch method showed much different polymerization behaviors from the catalysts prepared

by immobilizing TiCl$_3$(OAr) onto MgCl$_2$ in batch reaction.[41] Such strong influences of LTiCl$_3$ immobilization conditions on the catalyst structure and polymerization behaviors have not been reported in literatures before, and might be applied in developing new methods for regulating the catalytic properties of MgCl$_2$-supported Ziegler–Natta catalysts.

EXPERIMENTAL

Chemicals

All preparations and manipulations were carried out under dry oxygen-free nitrogen using standard Schlenk techniques for air sensitive substances. TiCl$_4$ (Shanghai Meixing Chemical Factory) and five ArOH compounds (Ar = C$_6$H$_5$—, 2,6-Me$_2$C$_6$H$_3$—, 2,6-iPr$_2$C$_6$H$_3$—, 2,6-tBu$_2$C$_6$H$_3$—, 4-Me-2,6-t-Bu$_2$C$_6$H$_3$—, purchased from Alfa Aesar) were distilled under reduced pressure and stored in N$_2$ atmosphere before use. Toluene (Hangzhou Chemical Reagent Corporation), n-heptane and n-hexane (Hangzhou Chemical Reagent Corporation) were distilled over sodium/benzophenone ketyl under N$_2$ atmosphere before use. Anhydrous MgCl$_2$ in fine granules was purchased from Alfa Aesar. Butyllithium (2.5 M solution in hexane, Alfa Aesar) was used as received. Ethylene (polymerization grade, a product of SINOPEC) was dried and purified by passing through columns of 4 Å molecular sieves and PEE deoxygenate catalyst (Dalian Samat Chemicals) before use. 1-Hexene (97%) from Acros was purified by distillation over Na and stored in a Schlenk flask containing 4 Å molecular sieves. The cocatalyst triisobutylaluminum (TIBA, 97%) purchased from Albemarle was diluted with n-heptane to make a 2 M solution before use.

Preparation of MgCl$_2$-Supported Catalyst Containing Aryloxy Ligand

Five TiCl$_3$(OAr) complexes (Ar = C$_6$H$_5$—, 2,6-Me$_2$C$_6$H$_3$—, 2,6-i-Pr$_2$C$_6$H$_3$—, 2,6-t-Bu$_2$C$_6$H$_3$—, 4-Me-2,6-t-Bu$_2$C$_6$H$_3$—) were synthesized by the reactions of ArOH and TiCl$_4$ according to literature.[42] The operation procedures have been described in the previous paper.[41]

About 15-g anhydrous MgCl$_2$ was sealed in a 120 mL ball-milling can containing 35 vol % of steel balls that have diameters of 10 and 5 mm, and ball-milled at 250 r/min for 48 h under dry N$_2$ atmosphere. Then the activated MgCl$_2$ was transferred to a single-neck flask and stored in glove box before use.

Five grams (52.5 mmol) activated anhydrous MgCl$_2$ was added in a 100 mL Schlenk flask with a magnetic stirring bar, and 30 mL toluene was injected and stirred at 80°C. A solution of TiCl$_3$(Aro) (5.1 mmol) in 30 mL toluene was slowly added in 3 h to the toluene suspension of MgCl$_2$ under stirring. Then, the mixture was cooled to room temperature and filtered. The residue was repeatedly washed with toluene (20 mL × 2) and n-hexane (20 mL × 2), and finally dried under vacuum at 60°C for several hours. Five kinds of MgCl$_2$-supported catalysts containing ArO— ligand were prepared in this procedure using different TiCl$_3$(ArO). In the same procedure, a blank TiCl$_4$/MgCl$_2$ supported catalyst was prepared by using TiCl$_4$ instead of TiCl$_3$(ArO) as the titanium compound.

Ti content of the catalyst was determined by the standard photometric method. A known quantity (∼0.2 g) of catalyst was

Table I. Composition of Catalysts Prepared by Semibatch Reaction of Titanium Compounds and MgCl$_2$

Catalyst	Titanium compound	Ti content[a] (wt %)	ArO—/Ti[b]
Cat-**0'**[c]	TiCl$_4$	0.85	0
Cat-**1'**	(C$_6$H$_5$O)TiCl$_3$	0.84	1.00
Cat-**2'**	(2,6-Me$_2$C$_6$H$_3$O)TiCl$_3$	0.70	0.75
Cat-**3'**	(2,6-i-Pr$_2$C$_6$H$_3$O)TiCl$_3$	0.67	0.56
Cat-**4'**	(2,6-t-Bu$_2$C$_6$H$_3$O)TiCl$_3$	1.12	0.41
Cat-**5'**	(4-Me-2,6-t-Bu$_2$C$_6$H$_3$O) TiCl$_3$	1.07	0.39

[a] Titanium content in catalyst;
[b] Molar ratio of aryloxy ligand and titanium in the catalyst determined by GC analysis;
[c] Cat-**0'** was prepared by slow dripping of TiCl$_4$ solution into the suspension of MgCl$_2$ in toluene.

dissolved in 4 N sulfuric acid and treated with hydrogen peroxide to form a yellow solution. The concentration of Ti was calculated from the absorbance of the solution at 410 nm recorded by a UV-vis spectrophotometer (Cary 100 Bio).

The amount of aryloxy group in the aryloxy-containing catalysts was measured by the procedure as follows. 200–300 mg of catalyst was hydrolyzed by 0.5 N HCl and then extracted by toluene (5 mL × 4). The combined extract was transfered to a volumetric flask. Benzophenone was added into the volumetric flask as an internal standard. Additional toluene was added into the volumetric flask to make a 25 mL solution. The concentration of ArOH in the solution was quantitatively determined by gas chromatography (Shimadzu GC-8APF), and the content of ArO group in the catalysts was calculated.

Ethylene/1-Hexene Copolymerization

Ethylene (co)polymerization at 1 bar ethylene pressure was carried out in a 50 mL Schlenck flask equipped with a magnetic stirring bar. TIBA (Al/Ti = 100) was used as cocatalyst in all the polymerization runs. The copolymerization was conducted under 0.1 MPa ethylene pressure and 0.2 mol/L 1-hexene concentration at 60°C. Details of the experimental operations have been mentioned in the previous paper.[41]

Characterization

Each of the ethylene-1-hexene copolymer samples synthesized in this work was fractionated into boiling n-heptane soluble fraction and boiling n-heptane insoluble fraction according to the method described in the previous work.[41]

The molecular weights and molecular weight distributions of the fractions were measured by gel permeation chromatography (GPC) in a PL 220 GPC instrument (Polymer Laboratories) at 150°C in 1,2,4-trichlorobenzene. Three PL mixed B columns (500–10^7) were used. Universal calibration against narrow polystyrene standards was adopted.

^{13}C-NMR spectra of the fractions were measured on a Varian Mercury Plus 300 NMR spectrometer at 75 MHz. o-Dichlorobenzene-d$_4$ was used as the solvent to prepare the polymer solution of 10 wt %. The spectra were recorded at 120°C with

Table II. Ethylene/1-Hexene Copolymerization Catalyzed by Different Catalysts with no Hydrogen[a]

Sample	Catalyst	Activity (kg/g Ti·h)	M_w (10^4)	M_w/M_n	T_m (°C)	ΔH_m (J/g)
EHS-0	Cat-**0′**	14.6	35.6	5.63	120.9	72.4
EHS-1	Cat-**1′**	15.6	42.1	5.64	120.1	51.9
EHS-2	Cat-**2′**	20.6	37.8	5.61	121.8	51.4
EHS-3	Cat-**3′**	24.0	36.7	5.36	121.0	60.4
EHS-4	Cat-**4′**	14.3	38.2	4.94	120.2	60.8
EHS-5	Cat-**5′**	16.0	37.7	6.29	120.3	59.1

[a] Conditions of copolymerization: P_E = 0.1 MPa; [1-Hexene] = 0.2 mol/L; Weight of catalyst = 30–50 mg; Cocatalyst: TIBA, Al/Ti = 100; Solvent: n-heptane, 50 ml; T = 60°C; t = 0.5 h.

hexamethyldisiloxane as an internal reference. Chromium triacetylacetonate (about 2 mg) was added in each sample to shorten the relaxation time and ensure the quantitative results. Broadband decoupling with a pulse delay of 3 s was used. Typically, 5000 transients were collected.

Differential scanning calorimetry (DSC) measurements were carried out on a TA Q200 DSC calorimeter. About 5 mg of each sample was sealed in an aluminum sample cell. The sample was first melted at 170°C for 5 min to erase the thermal history, and then cooled to 40°C at a cooling rate of 10°C /min, followed by reheating to 170°C at a scanning rate of 10°C/min to observe the melting behavior.

RESULTS AND DISCUSSION

Composition of the Catalysts

Five $MgCl_2$ supported Ziegler–Natta catalysts containing aryloxy ligand were prepared by immobilizing $TiCl_3(OAr)$ onto $MgCl_2$ in semibatch reaction and were analyzed for titanium content and the content of aryloxy group. Table I lists the composition of these catalysts. It can be seen that titanium contents of these catalysts were much lower than the catalysts prepared by immobilizing $TiCl_3(OAr)$ onto $MgCl_2$ in batch reaction.[41] Ti contents of the catalysts prepared in semibatch reaction were about half of those prepared in batch reaction. The lower loading of Ti on semibatch immobilized catalysts could be attributed to lower [Ti] in the liquid phase than that of the batch reaction system.

Low [Ti] could depress formation of $(TiCl_4)_n$ ($n \geq 2$) clusters that are adsorbed on the $MgCl_2$ support. Lower temperature in the semibatch immobilization than that of the batch reaction system (80 vs. 120°C) may also cause lower Ti loading.

Conversely, the ArO/Ti molar ratio of the catalysts prepared by semibatch immobilization was higher than those prepared by batch immobilization. When the ArO group is a simple phenoxy (C_6H_5O), ArO/Ti ratio of Cat-**1′** reached 1 (see Table I), higher than the ratio 0.82 of the corresponding catalyst prepared by batch immobilization.[41] The influence of immobilization method on ArO/Ti ratio was even larger when the ArO group is bulkier. ArO/Ti ratio of Cat-**3′** (Ar = 2,6-i-$Pr_2C_6H_3$—) was 0.56, while that of the corresponding catalyst prepared by batch immobilization was only 0.13.[41] This means that group exchanges between the immobilized Ti species and $TiCl_3(OAr)$ in solution can be evidently depressed when the concentration of $TiCl_3(OAr)$ is lowered. The ArO/Ti ratio is also strongly affected by the bulkiness of ArO group. Table I show that the ArO/Ti ratio gradually decreased from 1 to 0.39 when the bulkiness of Ar increases. This means that the immobilized $TiCl_3(OAr)$ becomes unstable when the ArO group is bulky. The higher Ti content of Cat-**4′** and Cat-**5′** than the other catalysts in Table I is likely a result of their lower ArO/Ti ratio, because the bulky $TiCl_3(OAr)$ can approach to an immobilized $TiCl_4$ easier than to an immobilized $TiCl_3(OAr)$. In other words, higher Ti content of Cat-**4′** and Cat-**5′** could be ascribed to formation of more clustered Ti species on the surfaces of $MgCl_2$.

Table III. Fractionation Results of Copolymers Synthesized in the Absence of Hydrogen

Sample Catalyst Fraction	EHS-0 Cat-**0′**		EHS-1 Cat-**1′**		EHS-2 Cat-**2′**		EHS-3 Cat-**3′**		EHS-4 Cat-**4′**		EHS-5 Cat-**5′**	
	Insol.	Sol.	Insol.	Sol.	Insol.	Sol.	Insol.	Sol.	Insol.	Sol.	Insol.	Sol.
Content (wt %)	63.1	36.9	59.7	40.3	57.8	42.2	58.2	41.8	63.4	36.6	62.1	37.9
H content (mol %)[a]	1.9	9.4	2.1	12.5	2.3	16.8	1.8	11.7	2.3	13.2	2.0	13.0
T_m (°C)	121.9	113.2	120.3	86.2	122.0	112.8	121.8	112.8	120.6	109.2	120.1	110.5
ΔH_m (J/g)	90.3	35.5	86.8	20.7	86.5	19.6	92.9	32.5	84.6	28.1	87.2	30.1
M_w (10^4)	44.2	12.5	59.4	13.2	44.9	12.2	44.1	10.9	44.5	12.9	50.9	13.8
$(M_w)_I/(M_w)_S$[b]	3.54		4.50		3.68		4.04		3.45		3.69	
M_w/M_n	4.64	3.17	4.49	3.61	5.52	3.27	3.86	3.15	4.13	4.61	4.44	3.17

[a] 1-Hexene content of the copolymer fractions.
[b] Ratio of weight average molecular weight of the insoluble part and that of the soluble part.
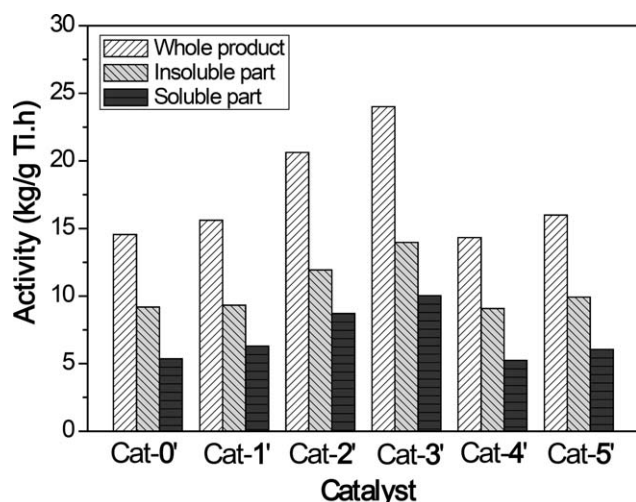
Figure 1. Ethylene/1-hexene copolymerization activity in the absence of hydrogen.

Ethylene/1-Hexene Copolymerization in the Absence of H_2

The results of ethylene/1-hexene copolymeriztion catalyzed by Cat-**0**′ ∼ Cat-**5**′ are summarized in Table II. It can be seen that the aryloxy-containing catalysts Cat-**1**′, Cat-**2**′, Cat-**3**′, and Cat-**5**′ have higher activity than the blank catalyst (Cat-**0**′). Because the Ti content of Cat-**4**′ is higher than the blank catalyst, its true activity expressed in the unit of (g product/g catalyst) is also higher than the blank system. Cat-**3**′ that contains 2,6-*i*-$Pr_2C_6H_3O$— ligand exhibited the highest catalytic activity among the six catalysts. This could be attributed to the electron effects caused by the ortho-isopropyl groups on the phenyl ring. Electron donation effects of the ortho-alkyl groups could stabilize the active species and result in increase in catalytic activity, as increasing electron density on Ti can enhance activity of the active center.[43] The higher catalytic activity of Cat-**5**′ than Cat-**4**′ could be attributed to the extra electron donating effect of the paramethyl substituent in Cat-**5**′. In comparison with the catalytic activity of catalysts prepared by batch process (16–23 kg copolymer/g Ti·h),[41] the activity of catalysts prepared by the semibatch process are only slightly lower.

The melting temperatures of copolymers synthesized with the six catalysts shown in Table II are roughly the same, but the products of five aryloxy-containing catalysts had lower melting enthalpy than that of the blank catalyst. The differences in molecular weight and molecular weight distribution of polymers synthesized with different catalysts are rather limited.

Each copolymer sample in Table II has been fractionated into two parts: boiling *n*-heptane insoluble fraction (Insol.) and *n*-heptane soluble fraction (Sol.). The fractionation results were summarized in Table III. Multiplying the copolymerization activity by the weight fraction of each fraction, the catalytic activities of both fractions were calculated and shown in Figure 1.

It is seen in Figure 1 that the activity of active sites producing soluble part was enhanced more than the insoluble part after introducing the aryloxy ligand in the catalysts. Especially, when the aryloxy ligand is not very bulky (Cat-**1**′, Cat-**2**′, and Cat-**3**′), the weight fraction of soluble part was higher than that of the blank catalyst. Although the melting temperature and melting enthalpy of the insoluble parts formed by different catalysts are quite close to each other, the melting enthalpy of the soluble part was evidently lowered by introducing the aryloxy ligand. This can be explained by evident increase in 1-hexene content of the soluble fraction by the aryloxy ligand. The molecular weight of the copolymer fractions was only slightly altered when different aryloxy ligands were introduced.

Table IV. Monomer Sequence Distribution of Copolymer Fractions Synthesized in the Absence of Hydrogen

Sample Catalyst Fraction	EHS-0 Cat-**0**′		EHS-1 Cat-**1**′		EHS-2 Cat-**2**′		EHS-3 Cat-**3**′		EHS-4 Cat-**4**′		EHS-5 Cat-**5**′	
	Insol.	Sol.	Insol.	Sol.	Insol.	Sol.	Insol.	Sol.	Insol.	Sol.	Insol.	Sol.
[EHE]	1.9	7.1	2.1	8.4	2.2	10.1	1.9	8.5	2.3	9.6	2.0	8.3
[EHH]	0	2.4	0	4.1	0	6.0	0	3.0	0	3.6	0	4.4
[HHH]	0	0	0	0	0	0	0	0	0	0	0	0
[HEH]	0	1.6	0	3.9	0	5.2	0	3.6	0	4.0	0	3.4
[EEH]	3.7	12.9	4.3	13.3	4.6	18.5	3.5	1.4	4.6	14.6	3.9	15.2
[EEE]	94.4	76.0	93.6	70.3	93.2	60.1	94.7	71.1	93.1	68.2	94.1	68.6
[EE]	96.2	82.5	95.8	77.0	95.5	69.4	96.4	78.0	95.4	75.5	96.0	76.2
[EH]	3.8	16.4	4.2	21.0	4.5	27.6	3.6	20.5	4.6	22.7	4.0	21.6
[HH]	0	1.2	0	2.1	0	3.0	0	1.5	0	1.8	0	2.2
[E]	98.1	90.6	97.9	87.5	97.7	83.2	98.2	88.3	97.7	86.9	98.0	87.0
[H]	1.9	9.4	2.1	12.5	2.3	16.8	1.8	11.7	2.3	13.2	2.0	13.0
$[H]_{sum}$[a]	4.6		6.3		8.4		6.0		6.3		6.2	
$[H]_S/[H]_I$[b]	5.0		5.9		7.4		6.6		5.8		6.5	

[a] $[H]_{sum}$ is 1-hexene content of the whole copolymer sample;
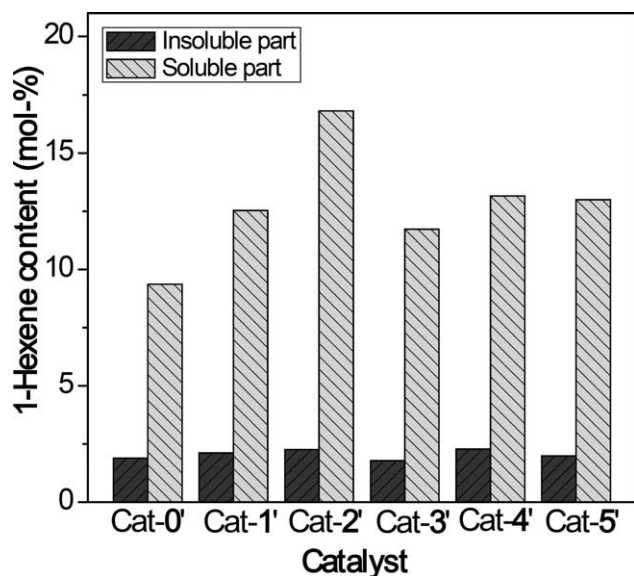[b] $[H]_S/[H]_I$ = [H] in Sol./[H] in Insol.

Figure 2. Composition of copolymer fractions synthesized in the absence of hydrogen.

The monomer sequence distribution of the copolymer fractions were determined by ^{13}C-NMR spectroscopy and the results were summarized in Table IV. The total amount of incorporated 1-hexene ($[H]_{sum}$) in copolymers produced by the aryloxy-containing catalysts was much higher than that of the blank system. This is mainly due to increase in 1-hexene content of the soluble parts.

The influences of aryloxy ligand on 1-hexene content of the copolymer fractions can be observed in Figure 2 more clearly. It shows that 1-hexene content of the insoluble parts changed only slightly by the organic ligand, but that of the soluble part was markedly increased. The 2,6-Me$_2$C$_6$H$_3$O— ligand (Cat-**2'**) caused the largest increment of 1-hexene content in the soluble part.

As reported in the previous work,[41] the catalysts containing C$_6$H$_5$O—, 2,6-Me$_2$C$_6$H$_3$O—, 2,6-i-Pr$_2$C$_6$H$_3$O—, or 2,6-t-Bu$_2$C$_6$H$_3$O—

ligand prepared by batch immobilization (named as Cat-**1**, Cat-**2**, Cat-**3**, and Cat-**4**, respectively) produced copolymers with 1-hexene content of about 6.4 mol % when activated by TIBA. In comparison, the catalyst containing 2,6-Me$_2$C$_6$H$_3$O— prepared by semibatch immobilization (Cat-**2'**) gave higher 1-hexene incorporation rate, but the other ArO-containing catalysts in Table IV gave comonomer incorporation rate similar to those of the previous catalysts. It is worth noting that the blank TiCl$_4$/MgCl$_2$ catalyst prepared by batch immobilization produced copolymer with 1-hexene content of 9.1 mol %, while Cat-**0'** prepared in this work produced copolymer with 1-hexene content of only 4.6 mol %. Possible reasons for this difference will be discussed later.

In Figure 3, the 1-hexene content of copolymer fractions produced by the batch immobilized catalysts (Cat-**0**, Cat-**1**, Cat-**2**, Cat-**3**, and Cat-**4**) and the semibatch immobilized catalysts (Cat-**0'**, Cat-**1'**, Cat-**2'**, Cat-**3'**, and Cat-**4'**) are compared (Cat-**0** is a blank catalyst prepared by batch method[41]). It is seen that the soluble copolymers produced by Cat-**0** and Cat-**2'** had higher 1-hexene content than the other samples, while 1-hexene content of the insoluble fraction produced by Cat-**0** was especially low. In comparison with the two blank catalysts (Cat-**0** and Cat-**0'**), the aryloxy-containing catalysts produced copolymers with higher 1-hexene content in the insoluble part.

Ethylene/1-Hexene Copolymerization in the Presence of Hydrogen

Hydrogen is an efficient chain-transfer agent for controlling the molecular weight of polyolefin. It is widely used in industrial production of ethylene copolymer with Ziegler–Natta catalysts. To investigate the influence of H$_2$ on catalytic behavior of the aryloxy-containing MgCl$_2$-supported Ziegler–Natta catalysts prepared in this work, a series of ethylene/1-hexene copolymerization runs were made in the presence of hydrogen (partial pressure of H$_2$ = 0.02 MPa), and the results were summarized in Table V.

Comparing with the data in Table II, introduction of H$_2$ slightly reduced the catalytic activity of Cat-**0'** ~ Cat-**5'**. Molecular
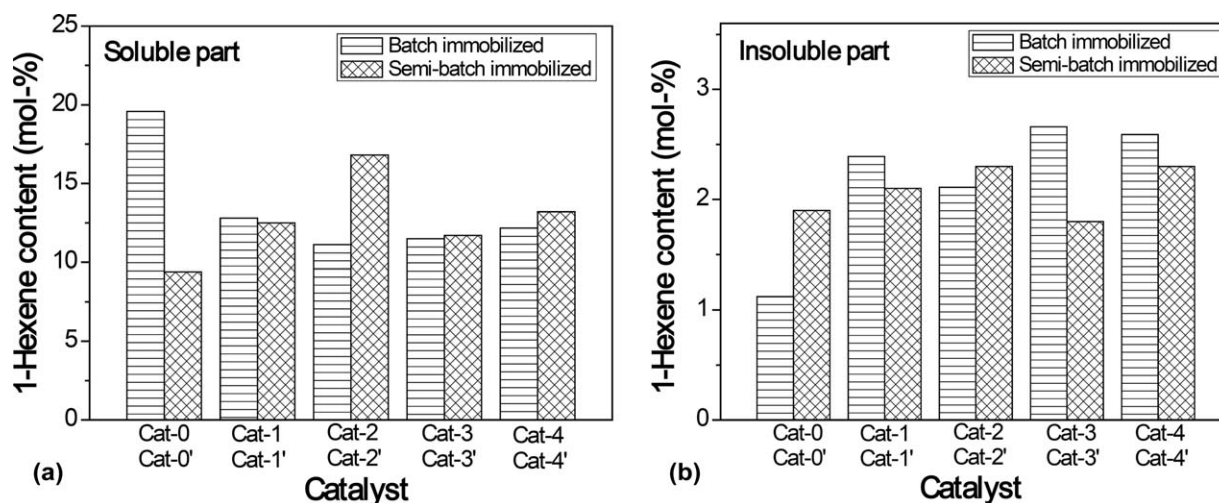

Figure 3. Comparisons of comonomer content in the soluble fraction and insoluble fraction of copolymer synthesized by batch immobilized and semi-batch immobilized catalysts.

Table V. Ethylene/1-Hexene Copolymerization Catalyzed by Different Catalysts in the Presence of Hydrogen[a]

Sample	Catalyst	Activity (kg/g Ti·h)	M_w (10^4)	M_w/M_n	T_m (°C)	ΔH_m (J/g)
EHS-6	Cat-**0'**	11.3	11.4	5.51	123.7	65.2
EHS-7	Cat-**1'**	14.6	12.4	6.70	122.9	65.2
EHS-8	Cat-**2'**	18.0	9.9	7.20	124.6	61.3
EHS-9	Cat-**3'**	18.5	10.1	6.99	124.0	66.5
EHS-10	Cat-**4'**	11.4	9.7	5.67	122.8	51.7
EHS-11	Cat-**5'**	14.7	8.7	6.32	124.0	63.4

[a] Conditions of polymerization: the same as Table II, with addition of hydrogen (P_{H2} = 0.02 MPa).

weight of the copolymers was evidently lowered, owing to chain transfer with hydrogen.

Each of the copolymer samples in Table V was fractionated into boiling *n*-heptane soluble and insoluble parts, and the results were summarized in Table VI. In comparison with the fractionation data of the copolymers synthesized in the absence of hydrogen (Table III), the introduction of H_2 resulted in significant increase (with increment of 20–95%) of the content of soluble part. This can be mainly attributed to strong deactivation effect of hydrogen on the active centers producing high molecular weight copolymer chains. As shown in Figures 1 and 4, the activity of insoluble parts formed by Cat-**0'** $\sim$ Cat-**5'** were lowered for about 45% by introducing hydrogen, while the activity of soluble parts were increased. Increase in the amount of soluble parts can be partly explained by reduction of their molecular weight by chain-transfer with H_2, because shorter chains have higher solubility.

By comparing Table VI with Table III, it can be found that the ratio of molecular weights of the two fractions $[(M_w)_I/(M_w)_S]$ was evidently lowered after introducing H_2, because the molecular weights of insoluble part was reduced more than that of the soluble part.

The monomer sequence distributions of the copolymer fractions synthesized in the presence of hydrogen were summarized in

Table VII. Comparing with the data in Table IV, introduction of H_2 significantly increased the total 1-hexene content in the copolymer. This can be mainly attributed to evident increase in the content of boiling *n*-heptane soluble fraction by hydrogen. Among the six catalysts, the blank catalyst Cat-**0'** and the catalysts containing bulky aryloxy ligands (Cat-**3'**, Cat-**4'**, and Cat-**5'**) experienced stronger increase of 1-hexene incorporation. This might reflect their similarity in words of active center structure.

As shown in Figure 5, the 1-hexene content of the insoluble part was hardly changed by introducing ayloxy ligand in the catalyst, while that of the soluble part was markedly increased by the ayloxy ligand, similar to the situations of copolymerization in the absence of H_2.

Discussions on Catalyst Structure and Catalytic Mechanism
Summarizing the results of ethylene/1-hexene copolymerization with five aryloxy-containing catalysts and the blank catalyst, it can be concluded that the aryloxy-containing catalysts produce copolymer with higher 1-hexene incorporation rate. Figure 6 shows the amount of 1-hexene incorporated in the copolymer fractions formed by Cat-**0'**, Cat-**1'**, Cat-**2'**, Cat-**3'**, and Cat-**4'**. Both the soluble and insoluble parts of the copolymer contained more 1-hexene when the catalyst had an aryloxy ligand, and introducing methyl groups in the ortho-positions of the phenyl ring further enhanced comonomer incorporation rate of the catalyst.

The mechanism of this effect of organic ligand cannot be simply deduced from the present experiment results, but some hints can be obtained when we carefully compare the copolymerization behaviors of catalysts that have been prepared under different conditions or carry different aryloxy ligand. First, when we compare the amount of incorporated 1-hexene comonomer in copolymers produced by the semibatch immobilized catalysts and that by the batch immobilized catalysts (see Figure 6), it becomes clear that the two series of aryloxy-containing catalysts have similar ability of incorporating 1-hexene in the copolymer chains. As ArO/Ti molar ratios of the semibatch series of catalysts were higher than that of the batch series, it means that higher ArO/Ti ratio cannot further improve the comonomer incorporation rate. To trace the presence of ArO ligand in the

Table VI. Fractionation Results of Copolymers Synthesized in the Presence of Hydrogen

| Sample	EHS-6		EHS-7		EHS-8		EHS-9		EHS-10		EHS-11	
Catalyst	Cat-**0'**		Cat-**1'**		Cat-**2'**		Cat-**3'**		Cat-**4'**		Cat-**5'**	
Fraction	Insol.	Sol.	Insol.	Sol.	Insol.	Sol.	Insol.	Sol.	Insol.	Sol.	Insol.	Sol.
Content (wt %)	43.3	56.7	37.3	62.7	39.6	60.4	48.8	51.2	28.3	71.7	34.3	65.7
H content (mol %)	2.0	11.0	1.4	10.0	1.7	14.3	1.8	15.3	2.0	14.5	1.9	10.8
T_m (°C)	124.0	113.8	123.8	115.6	124.6	117.6	123.9	112.2	122.2	114.0	124.2	114.3
ΔH_m (J/g)	103.3	39.7	105.3	36.6	117.0	29.2	108.8	36.0	106.8	34.4	111.8	42.1
M_w (10^4)	15.5	6.7	17.6	7.3	12.0	5.1	15.6	5.3	11.9	6.2	12.5	5.2
$(M_w)_I/(M_w)_S$	2.31		2.41		2.35		2.94		1.92		2.40	
M_w/M_n	4.32	3.93	5.18	3.60	4.26	3.35	4.91	4.49	4.66	3.87	4.32	3.30
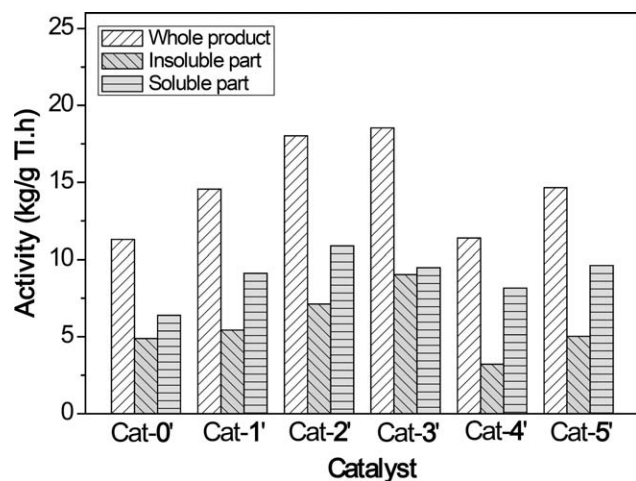
Figure 4. Ethylene/1-hexene copolymerization activity in the presence of hydrogen.

catalytic system, we measured ArO/Ti molar ratios of Cat-**1**′, Cat-**2**′, and Cat-**3**′ that had reacted with TIBA (Al/Ti = 100) at 60°C for 30 min in *n*-heptane, and found that about 60% of the immobilized ArO group was leached into the solution. This means that the ArO ligand fixed on the catalyst surface can be easily removed by exchanging with alkyl groups of the cocatalyst. The number of ArO ligand remaining on the activated catalyst is quite small. Therefore, direct influence of the ArO ligand on catalytic properties of active centers is unlikely the main reason for the improved copolymerization behavior.

Among possible indirect routes of the aryloxy ligand effects, one possible route is that the ArO ligand changes the spatial distribution of Ti species on the surface of MgCl$_2$ support. It has been recognized long ago that supported Ti species on

TiCl$_4$/MgCl$_2$ catalysts exist in either isolated or clustered states.[44–47] The two groups of Ti species form active centers with much different copolymerization behavior. The isolated Ti species tend to produce ethylene/α-olefin random copolymer, but the clustered Ti species produce blocky copolymer chains.[46] When the titanium compound is changed from TiCl$_4$ to TiCl$_3$(OAr), its adsorption on the surface of MgCl$_2$ will favor the formation of isolated Ti species rather than the clustered species, because the bulky ArO group will hinder the close contacts of multiple Ti compounds on the catalyst surface. This tendency will become more evident when the bulkiness of ArO group increases from phenyl to substituted phenyls. According to literature results,[46] the soluble part of ethylene/1-hexene copolymer is more likely to be produced by isolated Ti species, as they have relatively more open environment to accommodate bulky α-olefin, favoring formation of random copolymer. The clustered Ti species have more crowded environment, thus can incorporate much less α-olefin and produce the insoluble part. The evident increase of 1-hexene incorporation rate in the soluble fraction by introducing ArO group in the catalyst can thus be reasonably explained by increased distances between the active sites. However, the ArO group also caused moderate increase of 1-hexene incorporation rate in the insoluble fraction. This may mean that even when the Ti compound carry a bulky aryloxy group, clustered Ti species can still be formed in the immobilization process. Such clustered Ti species might be formed by conversion of an isolated TiCl$_3$(OAr)/MgCl$_2$ surface species into TiCl$_4$/MgCl$_2$ species through ligand exchange, and adsorption of another TiCl$_3$(OAr) on the same site to form bimetallic species. Continuation of this circle of adsorption/ligand exchange may lead to formation of various clustered Ti species. Because of the steric hindrance from the ArO group, clustered Ti species formed in a TiCl$_3$(OAr)/MgCl$_2$ catalyst may

Table VII. Monomer Sequence Distribution of Copolymer Fractions Synthesized in the Presence of Hydrogen

| Sample | EHS-6 | | EHS-7 | | EHS-8 | | EHS-9 | | EHS-10 | | EHS-11 | |
| Catalyst | Cat-**0**′ | | Cat-**1**′ | | Cat-**2**′ | | Cat-**3**′ | | Cat-**4**′ | | Cat-**5**′ | |
Fraction	Insol.	Sol.	Insol.	Sol.	Insol.	Sol.	Insol.	Sol.	Insol.	Sol.	Insol.	Sol.
[EHE]	2.0	8.1	1.4	7.3	1.7	9.3	1.8	9.8	1.9	9.8	1.9	8.3
[EHH]	0	2.9	0	2.4	0	4.9	0	5.4	0	4.6	0	2.4
[HHH]	0	0	0	0	0	0	0	0	0	0	0	0
[HEH]	0	3.1	0	2.5	0	3.7	0	3.7	0	3.6	0	2.3
[EEH]	3.8	13.0	2.9	13.3	3.4	16.4	3.5	17.9	4.0	17.1	3.7	15.0
[EEE]	94.1	72.9	95.7	74.5	94.9	65.6	94.7	63.2	94.0	64.8	94.4	72.1
[EE]	96.1	79.4	97.1	81.2	96.6	73.8	96.4	72.1	96.0	73.3	96.3	79.5
[EH]	3.9	19.1	2.9	17.6	3.4	23.7	3.6	25.2	4.0	24.4	3.7	19.3
[HH]	0	1.5	0	1.2	0	2.5	0	2.7	0	2.3	0	1.2
[E]	98.0	89.0	98.6	90.0	98.3	85.7	98.2	84.7	98.0	85.5	98.1	89.2
[H]	2.0	11.0	1.4	10.0	1.7	14.3	1.8	15.3	2.0	14.5	1.9	10.8
[H]$_{sum}$[a]	7.1		6.8		9.3		8.7		11.0		7.8	
[H]$_S$/[H]$_I$[b]	5.5		7.1		8.4		8.5		7.3		5.7	

[a] [H]$_{sum}$ is 1-hexene content of the whole copolymer sample;
[b] [H]$_S$/[H]$_I$ = [H] in Sol./[H] in Insol.

have structure different from that of a classical $TiCl_4/MgCl_2$ catalyst. The former may have sterically more open environment than the latter, thus can incorporate more α-olefin comonomer. Dupuy and Spitz proposed similar explanation on enhancement of ethylene polymerization activity caused by introducing cyclopentadienyl ligand in $MgCl_2$-supported Z-N catalyst.[48]

This explanation cannot be satisfactorily applied to the two blank $TiCl_4/MgCl_2$ catalysts (Cat-**0** and Cat-**0**′) prepared by batch and semibatch methods (see Figure 6). Because Cat-**0** was prepared under higher $TiCl_4$ concentration as compared with the conditions of Cat-**0**′, and the Ti content of Cat-**0** is about twice of Cat-**0**′, more clustered and less isolated Ti species should be formed in Cat-**0** than in Cat-**0**′. However, the actual fraction distributions of the two catalysts (Figure 6) showed the opposite trend: Cat-**0** incorporated much more 1-hexene in the soluble part and much less 1-hexene in the insoluble part than Cat-**0**′. A possible factor related to this phenomenon is that Cat-**0** was prepared under much higher temperature (120°C) than Cat-**0**′ (80°C). This may cause changes in structure and catalytic properties of both the isolated and clustered active species. Further investigations are needed to disclose the relationship between the conditions of $TiCl_4$ immobilization and the microstructure of the active centers.

In summary, the aryloxy-containing catalysts prepared by immobilizing $TiCl_3(OAr)$ on $MgCl_2$ in semibatch reaction showed improved 1-hexene incorporation rate. This effect is more likely to be caused by the influence of aryloxy group on spatial distribution of the supported Ti species. Therefore, these catalysts are basically a kind of $MgCl_2$-supported Ziegler–Natta catalyst with modified structure and distribution of Ti species. However, the present experiment data cannot unambiguously exclude the possibility that a part of active centers are directly influenced by one or more aryloxy groups that are chemically bonded to the supported Ti species.
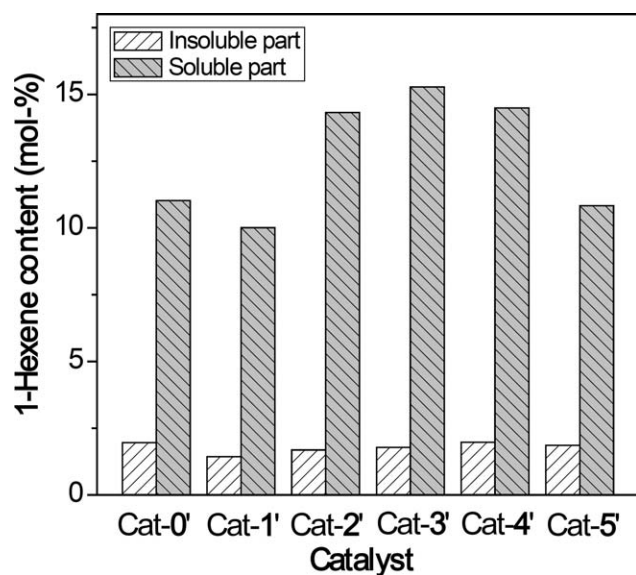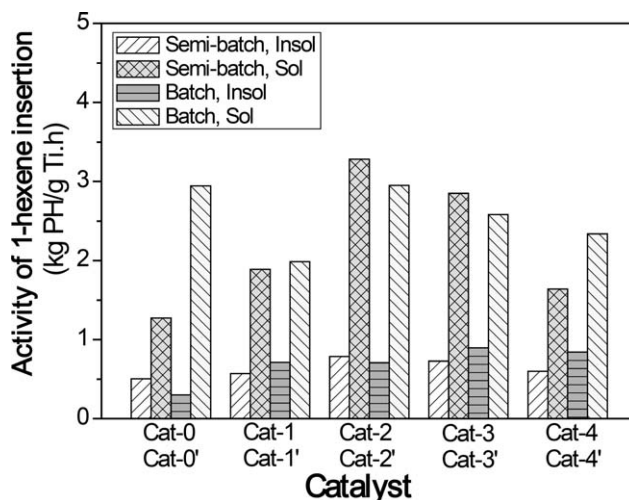

Figure 6. Comparisons of 1-hexene insertion rate in the soluble fraction and insoluble fraction of copolymer synthesized by batch immobilized and semibatch immobilized catalysts.

CONCLUSIONS

The catalytic behavior of the supported catalysts prepared by semibatch reaction of (aryloxyl)$TiCl_3$ with $MgCl_2$ was different from the $TiCl_4/MgCl_2$ blank catalyst prepared under the same conditions. The ArO/Ti ratios of the catalysts prepared by semibatch process are higher than those prepared by batch process, but the former series of catalysts has lower Ti content. The aryloxy-containing catalysts studied in this work show higher ethylene/1-hexene copolymerization activity and higher 1-hexene incorporation rate than the blank catalyst when activated by TIBA. Similar effects of the aryloxy ligand were observed when the copolymerization is conducted in the presence of hydrogen. Both the two series of aryloxy-containing catalysts prepared by semibatch and batch processes show similar characteristics like higher activity and enhanced α-olefin incorporation rate.

Figure 5. Composition of copolymer fractions synthesized in the presence of hydrogen.

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