

Novel SiO₂-supported chromium catalyst bearing new organo-siloxane ligand for ethylene polymerization

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Abstract

Nowadays, SiO₂-supported Cr-based catalysts mainly including oxo chromium (Phillips catalyst) and silyl chromate (UCC catalyst) systems are still important industrial catalysts for ethylene polymerization. It was found that the addition of triphenylsilanol could transform Phillips catalyst into silyl chromate catalyst. In this work, a new chiral organo-silanol was synthesized and subsequently introduced to modify the Phillips catalysts in order to develop a new SiO₂-support Cr-based catalyst with a chiral organo-siloxane ligand for ethylene polymerization. The new catalyst was characterized by X-ray photoelectron spectroscopy (XPS) and solid-state NMR methods. The new Cr-based catalysts with chiral organo-siloxane ligand presented as an active catalyst for ethylene polymerization, and their kinetic characteristic is found to be similar with that of calcined Phillips catalyst combined with TEA cocatalyst. It was very interesting to find the existence of short chain branches (SCBs) in these ethylene homo-polymers. The introduction of the new chiral organo-siloxane ligand was also found to produce polyethylene with bimodal molecular weight distribution and to enhance the amount of SCBs, which might be due to the steric and/or electronic effect of such chiral ligand, indicating a new method to improve the performance of Cr-based catalyst for polyethylene production.

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Keywords: Phillips catalyst; Ethylene polymerization; Chiral organo-siloxane ligand; Bimodal molecular weight distribution; Short chain branches (SCBs)

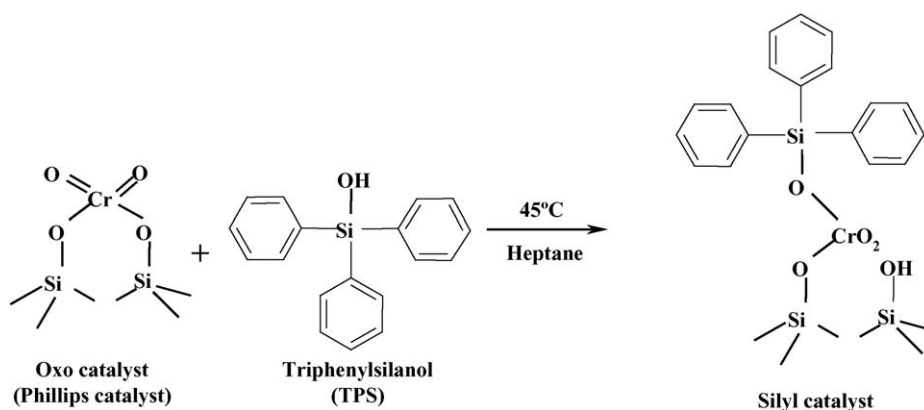
1. Introduction

Phillips CrO_x/SiO₂ catalysts, patented in 1958 by Hogan and Banks, are still responsible for more than one-third of the worldwide commercial high-density polyethylene (HDPE) production. The most unique performance of Phillips catalyst is contributed to production of HDPE with ultra-broad molecular weight distribution and chain branches including short and long chain branches, which is especially applied for blow-molding process. Until now, most work of the chromium-based catalyst for polyolefin has been focused on Phillips catalyst, commonly referred as oxo chromium supported on silica with high surface area [1,2]. However, a number of organo-chromium systems like chromocene and organo-silyl chromate, which are mainly synthesized by chemisorption of organo-chromium on dehydrated silica support, also show high activity for ethylene polymerization [3–6]. Of the organo-

chrome-based systems, silyl chromate derived catalysts are used extensively for commercial PE production according to some specific performances of silyl chromate catalyst. In comparison, Phillips catalyst shows much higher productivity than silyl chromate catalyst; however, silyl chromate catalyst shows not only less activity but also prolonged induction period. However, silyl chromate catalyst can produce polyethylene with broader molecular weight distribution (MWD) on both high and low molecular weight ends meeting different market demanding.

Recently, Cann et al. [6] found that the Phillips catalyst can be transformed into the silyl chromate catalyst through introduction of silyl ligand from triphenylsilanol (TPS) as shown in Scheme 1 [6,7]. It was further confirmed that the polymerization performance observed with oxo chromium-based catalysts could be converted to that observed with silyl chromate type catalysts by the addition of TPS into the former. In our opinion, this report also indicates a general method for developing various new SiO₂-supported Cr-based catalysts for olefin polymerization through modification of the Phillips catalyst using various organo-silanol compounds. Since the

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Scheme 1. Conversion of Phillips catalyst to silyl chromate catalyst.

catalyst structures are similar in nature, it is also possible to synthesize another type silyl chromate catalyst by direct conversion of the chromium oxide catalyst through the introduction of a novel chiral organo-siloxane ligand. Such chiral organo-siloxane bonded on chromium site via an oxygen atom was expected to result in a novel Cr catalyst with some specific performances.

In this work, a new chiral organo-silanol species, methyl (1-naphthyl) phenylsilanol, was synthesized and subsequently used to react with calcined Phillips $\text{CrO}_x/\text{SiO}_2$ catalyst in order to develop a novel SiO_2 -supported Cr-based catalyst. The physico-chemical states of the new synthesized chromium catalyst were characterized by solid-state NMR and X-ray photoelectron spectroscopy (XPS) methods. The ethylene homo-polymerization was carried out using the new catalyst in the presence of triethylaluminum (TEA) cocatalyst. The microstructures of the obtained polymers were investigated by solution NMR method. A general method for developing new SiO_2 -supported Cr-based catalyst with improved performance for ethylene polymerization has been demonstrated.

2. Experimental

2.1. Raw materials

α -Bromonaphthalene, sodium sulfate, lithium aluminum hydride, methanol, benzene, diethyl ether (Et_2O) and tetrahydrofuran (THF) were purchased from Kanto Chemical Co. Industries. Phenylmethyldimethoxysilane was obtained from Shin-Etsu Chemical. (–)-Menthol was obtained from Nacalai Tesque Inc. Solid potassium hydroxide, cyclohexane and pentane were purchased from Wako Pure Chemical Industries. Di-*n*-butyl ether was obtained from TCI. THF, Et_2O , hexane and benzene were purified by distillation after drying over sodium metal prior to use. Such materials were used for the preparation of the chiral organo-silanol compound.

Nitrogen of G3-grade (total impurity < 5 ppm) and pure air of G1-grade (total impurity < 1 ppm) were purchased from Uno Sanso Corp. Molecular sieves 4A and molecular sieves 13X, which were purchased from Wako Pure Chemical Industries Ltd., were used as moisture scavengers for gas purification. Q-

5 reactant catalyst (Aldrich) was used as oxygen scavenger for gas purification. A Phillips catalyst precursor (Crosfield ES370X donated from Asahi Kasei Corp.) with 1.0 wt.% of Cr loading (surface area: 280–350 m^2/g , pore volume: 1.45 cm^3/g) was used for preparation of Phillips $\text{CrO}_x/\text{SiO}_2$ catalysts.

2.2. Preparation of novel chiral organo-silanol compound

2.2.1. Preparation of racemic α -naphthylphenylmethylmethoxysilane

The Grignard reagent was prepared from 0.10 mole of α -bromonaphthalene in a solvent mixture containing benzene (100 ml), and tetrahydrofuran (100 ml). It is important to avoid the presence of β -bromonaphthalene in more than trace amounts. Substantial contamination by β -naphthylsilanes may cause great difficulty in the subsequent separation of diastereoisomers. And then the Grignard reagent was added dropwise to the solution of phenylmethyldimethoxysilane (0.10 mole, obtained from Shin-Etsu Chemical) in Et_2O (50 ml) for 1 h. This solution was stirred overnight at 55 °C and followed by treatment with cold aqueous ammonium chloride, washing with water, drying over sodium sulfate, and subsequent removal of solvents. Distillation gave 22.3 g (80% yield) of α -naphthylphenylmethylmethoxysilane, b.p. 143–146 °C (0.15 mmHg) and m.p. 62.5–63.5 °C (after recrystallization from hexane).

2.2.2. Preparation of diastereomeric α -naphthylphenylmethyl-(–)-menthoxysilanes

Distillation flask were placed 13.9 g (0.05 mole) of α -naphthylphenylmethylmethoxysilane, 7.8 g (0.05 mole) of (–)-menthol, 0.093 g of solid potassium hydroxide, and 100 ml of toluene. The reaction mixture was maintained at 145–155 °C for 10 h, while the methanol–toluene azeotrope (69% methanol, b.p. 63.8 °C) was distilled through a fractionating column. After removal of the basic catalyst by passing the product through a short column of silica gel, fractional distillation gave a 90.5% yield (18.2 g) of the diastereomeric α -naphthylphenylmethyl-(–)-menthoxysilane as a viscous syrup having b.p. 173–177 °C (0.07 mmHg). This material had an infrared spectrum virtually identical with that of the crystalline, separated diastereoisomers described below.

2.2.3. Separation of the diastereoisomers

The syrupy mixture of diastereoisomers was diluted with twice its own volume of pentane and chilled overnight in -78°C . This gave 10.1 g of crude crystals, recrystallization from pentane gave 8.37 g of material, m.p. $82\text{--}84^{\circ}\text{C}$. This material comprised 46% of the original (–)-mentoxysilane syrup and had a specific rotation of $[\alpha]_{\text{D}} -53.9^{\circ}$ (c11.32 in cyclohexane). The infrared spectrum clearly showed the presence of the $\alpha\text{-NpPhMeSi}$ -group.

The (–)-mentoxysilane syrup (9.83 g) remaining after removal of the less soluble diastereomer was evacuated free of pentane and then taken up in twice its volume of absolute ethanol. Refrigeration for several days gave a deposit of 6.9 g of crude crystals, m.p. $50\text{--}55^{\circ}\text{C}$. One of many recrystallizations produced large well-formed crystals, m.p. $56.5\text{--}59^{\circ}\text{C}$, $[\alpha]_{\text{D}} -47^{\circ}$ (c1.40 in cyclohexane). It is fairly difficult to free the lower-melting isomer from admixture with the higher-melting diastereomer.

The diastereomeric relationship of the higher- and lower-melting isomers is indicated by their infrared spectra, and by the enantiomeric relationship of the silanes resulting from their reduction with lithium aluminum hydride.

2.2.4. Preparation of (+)- α -naphthylphenylmethylsilane

A solution of 0.35 g (3.7 equiv.) of lithium aluminum hydride in 20 ml of ether was prepared and then 3 g (0.0075 mole) of (–)- α -naphthylphenylmethyl-(–)-mentoxysilane (m.p. $82\text{--}84^{\circ}\text{C}$) and 20 ml of di-*n*-butyl ether were added. Diethyl ether was removed by distillation until the reaction temperature reached 80°C . Heating at $80\text{--}90^{\circ}\text{C}$ was continued for 18 h. After decomposition of excess metallic hydride with acetone, treatment with crushed ice and concentrated hydrochloric acid, was followed by drying over sodium sulfate. Solvents and (–)-menthol were removed by distillation up to a head temperature of 151°C (1.5 mmHg) and a still temperature of 170°C . Crystallization of the product gave 1.78 g (96% yield) of (+)- α -naphthylphenylmethylsilane, m.p. $60\text{--}62^{\circ}\text{C}$. Recrystallization from pentane yielded 1.69 g (91% yield) of material, m.p. $61.5\text{--}63^{\circ}\text{C}$, $[\alpha]_{\text{D}} +33.4^{\circ}$ (c8.00 in cyclohexane). Repeated recrystallization of a portion from hexane raised the melting point to $63.5\text{--}64.5^{\circ}\text{C}$. The specific rotation of this latter material was determined in cyclohexane at three concentrations: $[\alpha]_{\text{D}} +33.7^{\circ}$ (c4.00), $+34.3^{\circ}$ (c10.9), and $+35.0^{\circ}$ (c15.6); from this, the above 1.69 g are seen to be 98% optically pure

(racemic α -naphthylphenylmethylsilane, m.p. 42°C , comprises a low-melting eutectic which is separable from active silane by crystallization); it is assumed that at least half of the silane not recovered (i.e., the theoretical yield of 1.85 g less the above 1.69 g), or 0.08 g, was also dextrorotatory. This means that about 1.74 g (i.e., 98% of the 1.69 g plus the additional 0.08 g) of (+)- α -naphthylphenylmethylsilane was formed and that the reduction is at least 94% stereospecific. The infrared spectrum provided positive proof of structure since it showed an absorption band characteristic of the $\alpha\text{-NpPhMeSi}$ -group as well as the strong band at $4.70\ \mu\text{m}$ characteristic of the Si–H group.

2.2.5. Preparation of $\alpha\text{-NpPhMeSi}^*\text{-OH}$ by palladium carbon

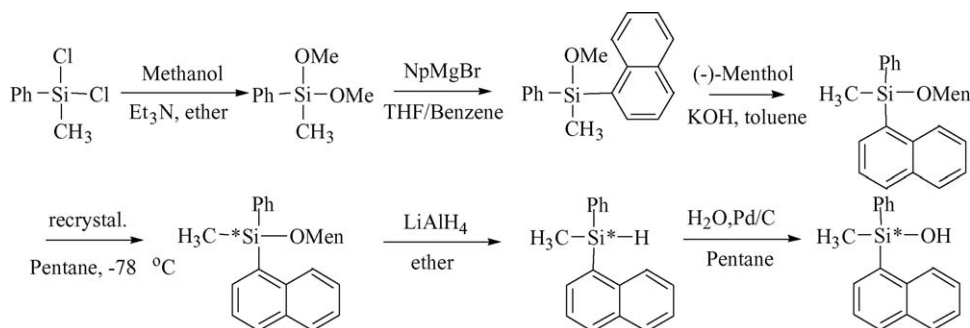
The 10% palladium on carbon catalysts 0.06 g, was mixed with a solution of 1.24 g of optically active $\alpha\text{-NpPhMeSi}^*\text{-OH}$ in 10 ml of the pentane. An equimolar amount of water was added and the reaction was allowed to proceed at room temperature for 6 h in an atmosphere of dry nitrogen. After evolution of hydrogen had ceased, products were isolated in 95% yields. The product was formed with 96% inversion of configuration. The whole preparation process of naphthylphenylmethylsilanol was shown in Scheme 2.

NMR spectrum of the naphthylphenylmethylsilanol was obtained in CDCl_3 on a Varian Gemini-2000 300 MHz spectrometer, model Unity INOVA. Chemical shifts are reported in ppm relative to CHCl_3 (δ 7.26 for ^1H). ^1H NMR (δ): $-\text{CH}_3$ 0.829(s, 3H), phenyl or naphthyl 8.138–8.110(d, 1H), 7.944–7.916(d, 1H), 7.882–7.857(d, 1H), 7.828–7.806(d, 1H), 7.654–7.622(m, 2H), 7.509–7.369(m, 6H), $-\text{OH}$ 1.9–2.1(br, 1H) [8].

2.3. Catalyst preparation

2.3.1. Conversion of oxo to $\alpha\text{-NpPhMeSi}^*\text{-OH}$ chromate catalyst

The oxo chromium catalyst is well known and prepared by thermal oxidation of silica impregnated with a variety of chromium compounds in air between 600 and 800°C . In this work, the details about catalyst preparation of the calcined Phillips catalyst could be found in our recent papers [9,10]. A simplified introduction of catalyst preparation process was given as follows. About 15 g of catalyst precursor was added into a spouted fluidized-bed quartz reactor followed by an isother-



Scheme 2. Preparation of methyl (1-naphthyl)phenylsilanol.

mal calcination process at 600 °C in pure air with a flow rate of 200 ml/min for 6 h. Dry air was further purified by passing through a 13X molecular sieve column before entering the catalyst preparation system. The calcined catalyst was cooled down to room temperature in nitrogen (200 ml/min). Nitrogen was further purified by passing through a Q-5 catalyst column and a 13X molecular sieve column before entering the catalyst preparation system. The calcined Phillips catalysts named as PC600 was stored in ampoule glass bottle. Then, ca. 500 mg of PC600 catalyst was reacted with 25.4 mg (0.096 mmol, 1:1 Cr/Si mole ratio) α -NpPhMeSi^{*}-OH and 101.5 mg (0.384 mmol, 1:4 Cr/Si mole ratio) α -NpPhMeSi^{*}-OH, respectively, in 400 ml purified heptane for 2 h at 45 °C. The two modified catalysts were named as PC600-S and PC600-4S, respectively. After reaction, the modified catalyst was washed by 20 ml heptane for 30 min followed by decantation of the upper solvent. After three times of washing, the catalyst was dried by vacuum at room temperature. During the modification, no color change in the solvent was found for PC600-S, however, for PC600-4S, the solvent became light yellow indicating some hexavalent chromium was removed from catalyst surface. The color turned into greenish yellow after a period of time most probably due to photo-reduction of some hexavalent into trivalent chromium. Each catalyst was further distributed and sealed in some small glass ampoule bottles in nitrogen and the amount of catalyst in each ampoule bottle was regulated to about 100 mg, which was weighed precisely.

2.4. Characterization of catalysts

2.4.1. Solid-state NMR measurement

The samples of catalyst and silica were characterized by a Varian UNITY-400 spectrometer at room temperature with a Varian Room Temperature/Cross Polarization Magic Angle Spin (RT/CP MAS) probe. Each sample (ca. 80 mg) was put and pressed tightly into a 7 mm zirconia rotor under N₂ atmosphere. The ¹H MAS NMR spectra were obtained operating at 400.47 MHz with a 30° pulse of 3 μ s and a relaxation delay of 1 s under rotating at ca. 3 kHz. All ¹H MAS spectra of the samples were referenced relative to external tetramethylsilane (TMS).

2.4.2. XPS characterization of catalysts

The details concerning the XPS measurements of catalysts, PC600, PC600-S and PC600-4S, could be found in our previous report [9–11]. XPS data were obtained on a Physical Electronics Perkin-Elmer Model Phi-5600 ESCA spectrometer with monochromated Al K radiation (1486.6 eV) operated at 300 W. The vacuum in the main chamber was kept above 3×10^{-9} Torr during XPS data acquisitions. High resolution XPS scan measurements for Si 2p and Cr 2p regions were performed for each sample within 10 min. All binding energies (BE) were referenced to the Si 2p peak of silica gel at 103.3 eV for the charging effect correction. Multiplet fitting of the Cr 2p XPS curves by the Gaussian–Lorentzian method was conducted after the measurement to obtain the precise oxidation states of surface chromium species in each catalyst. The fitting for each curve was repeated for several times to ensure a reproducible result.

2.5. Ethylene polymerization and characterization of polymers

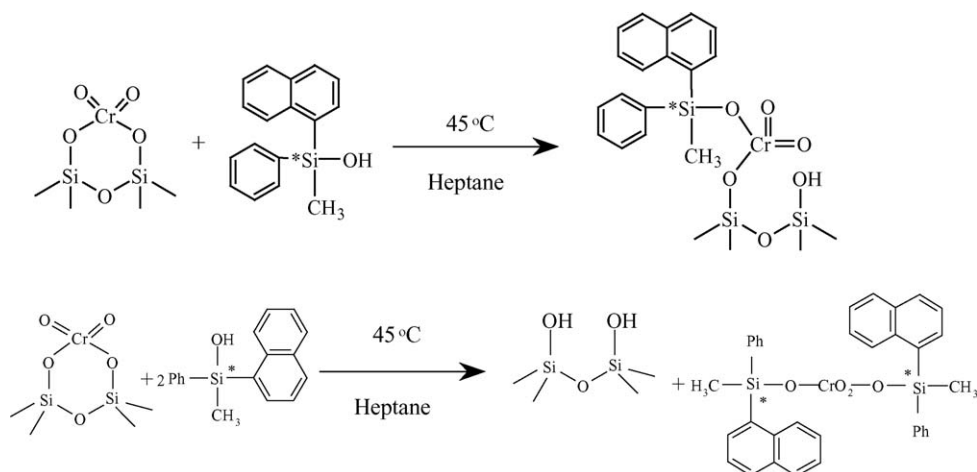
The experimental system for semi-batch slurry ethylene polymerization using the catalysts was the same as our previous work [9,12,13]. N₂ was further purified by passing through a Q-5 catalyst column and a 13X molecular sieve column before entering the polymerization system. Heptane was passed through a column of 13X molecular sieve followed by 24 h bubbling by high purity N₂ before use. One ampoule bottle with ca. 100 mg of PC600-S or PC600-4S was set in the top part of the glass polymerization reactor (volume ca.100 ml). Then, the reactor system was vacuumed for 2 h before introduction of heptane solvent, TEA cocatalyst and ethylene. The polymerization was initiated after breaking of the catalyst ampoule bottle by a steel bar. Ethylene monomer was further purified by passing through a 4A molecular sieve column, a Q-5 catalyst column and a 13X molecular sieve column before entering the polymerization reactor. The polymerization conditions are shown as follows: ethylene pressure 0.13 MPa, polymerization temperature: 60 °C, 20 ml purified heptane, Al/Cr molar ratio at 15.0–22.5 using 1 M TEA heptane solution. The real-time ethylene consumption was continuously monitored by an on-line mass flowmeter. The polymerization was stopped by adding 20 ml ethanol/HCl after 1.5 h. The polymer was washed and dried in vacuum at 60 °C for 6 h.

Characterization of the obtained polymer by ¹³C NMR measurement was carried out with a Varian Gemini-300 spectrometer at 75.46 MHz. The detail was the same as our previous work [13]. The polymer samples were added into sample tube (a diameter of 10 mm) with the mixture of 1,2,4-trichlorobenzene, 1,1,2,2-tetrachloroethane-d₂ and hexamethyldisiloxane (volume ratio: 40/10/1) as the solvent (sample concentration: ca. 18 mg/ml). The ¹³C NMR spectrum of each polymer sample was obtained with 6 s pulse repetition at 140 °C for 40 h. The backbone carbon of the polymer chain was regarded as the internal reference at 30.00 ppm. The amount of branches was normalized as the number of branching carbon per 1000 CH₂ in the main chain. Molecular weight (MW) and MWD of all the polymer samples were determined by GPC (Waters Alliance GPC V2000CV) with a polystyrene gel column (Shodex UT-806M) at 140 °C, using 1,2,4-trichlorobenzene as solvent. The catalyst residue was removed from obtained polymers by filtration before characterization by ¹³C NMR and GPC methods.

3. Results and discussion

In this work, a novel organo-silanol compound namely naphthylphenylmethylsilanol was successfully synthesized and subsequently used to react with calcined Phillips CrO_x/SiO₂ catalyst with 1:1 and 1:4 of Cr/Si mole ratio, which was named as PC600-S and PC600-4S, respectively. According to literature [6], the plausible reactions between oxo chromate and naphthylphenylmethylsilanol are shown in Scheme 3.

The synthesized catalysts, PC600-S and PC600-4S, were investigated by solid-state NMR in ¹H spectra. The ¹H MAS NMR spectra of the catalysts, PC600-S and PC600-



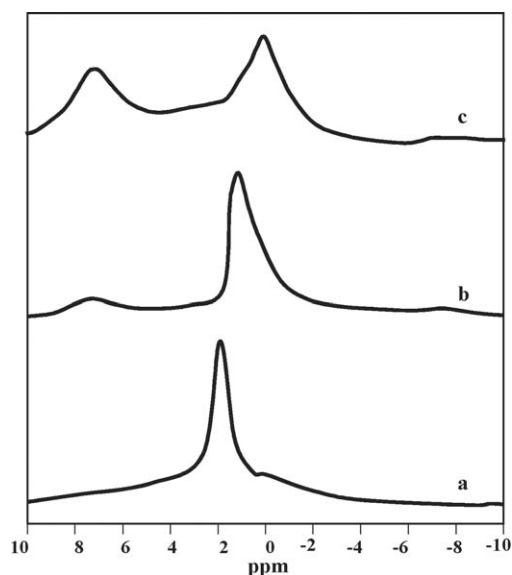
Scheme 3. Plausible reactions between methyl (1-naphthyl)phenylsilanol and Phillips catalyst.

Table 1
Chemical shift of ^1H peak in the synthesized catalyst

Catalyst	Chemical shift of peak (ppm)	
PC600	1.77	
PC600-S	0.79	7.13
PC600-4S	0.30	7.13

4S, were compared with that of catalyst, PC600, as shown in Fig. 1. The precise chemical shift of ^1H peaks was shown in Table 1.

In Fig. 1, the peak at 1.77 ppm in ^1H MAS NMR spectra of PC600 could be assigned to the residual isolated hydroxyl group even after calcination at 600 °C [14]. According to the data of ^1H NMR characterization of the novel chiral organo-silanol, the broad peak at 7.13 ppm in ^1H MAS NMR spectra of PC600-S and PC600-4S catalysts was attributed to the proton of phenyl or naphthyl groups. The proton of Si–CH₃ in organo-siloxane ligand accounts for the shifting of the H peak from 1.77 to 0.79 and 0.30 ppm for PC600-S and PC600-4S, respectively. The peak at 0.79 ppm in the ^1H spectrum of catalyst, PC600-S, was assigned to combination of proton in Si–CH₃ and in Si–OH (hydroxyl groups on silica surface). With increase of reaction ratio between organo-silanol compound and PC600 catalyst, the intensity of peak at 7.13 increased, and the peak at 0.79 ppm was shifted to 0.30 ppm. According to the above-mentioned results, it could be confirmed by the ^1H solid-state NMR that the chiral organo-siloxane ligand has been successfully introduced onto the calcined catalyst surface.

Fig. 1. ^1H MAS NMR spectra of catalysts: (a) PC600; (b) PC600-S; (c) PC600-4S.

The atomic percentage of surface species on PC600, PC600-S and PC600-4S catalysts was measured by XPS method as shown in Table 2.

Theoretically, if one chromium site reacts with one chiral organo-silanol compound, the molar ratio of C/Cr should be 17. For PC600-S catalyst, the C/Cr molar ratio was only 7.9 (as shown in Table 2), which indicated 46.5% of chromate species on the Phillips catalyst surface had been transformed into silyl

Table 2
Conversion from oxo chromate into silyl chromate

Catalyst	Atomic percentage ^a (%)				C/Cr	Conversion	Cr loss (%)
	Si	Cr	C	O			
PC600	33.10	0.84	0	66.06	0	0	0
PC600-S	31.87	0.79	6.24	61.10	7.9	46.5	0
PC600-4S	30.85	0.70	11.46	56.99	16.4	96.3	6

^a Atomic percentage of surface species on catalysts was determined by XPS analysis under high resolution scans.

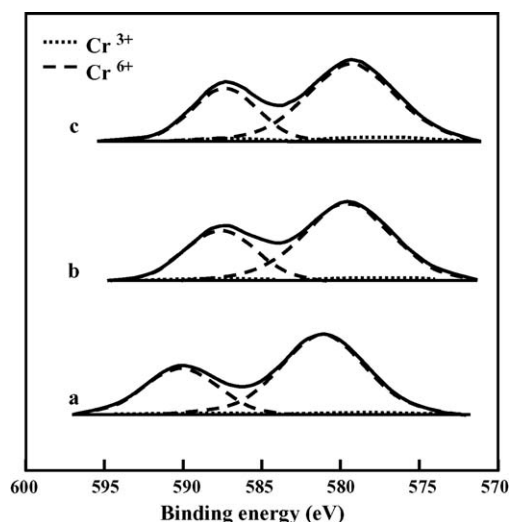


Fig. 2. Cr 2p fitting curves of catalyst: (a) PC600; (b) PC600-S; (c) PC600-4S with acquisition time of 10 min.

chromate species, and no Cr loss from PC600-S catalyst was found compared with PC600. According to experimental evidence, no color change was found in the upper solvent for PC600-S after reaction. For PC600-4S catalyst, the C/Cr molar ratio was 16.4, which is very near to 17 and indicated 96.3% of surface chromium site was connected with a chiral organo-siloxane ligand. Moreover, about 6% of hexavalent chromium species ($\text{Cr(VI)}\text{O}_{x,\text{surf}}$) were lost from the Phillips catalyst surface, which could be further confirmed by the light yellow color of the upper solvent.

In this work, multiplet fitting of the Cr 2p XPS curves by the Gaussian–Lorentzian method was conducted after the measurement to obtain the precise oxidation states of surface chromium species in each catalyst. The obtained Cr 2p XPS spectra of PC600-S and PC600-4S are shown in Fig. 2. The XPS results of PC600 with 10 min XPS acquisition, which have been fully discussed in our previous report [10], were used again just for a comparison with the results from the synthesized catalyst, PC600-S and PC600-4S, in this work. In our previous report [10,11], we reported that high resolution XPS characterizations with acquisition time of 10 min can neglect the photo-reduction of surface chromate species induced by soft X-ray irradiation during XPS measurement.

The specific details relating to the assignments of oxidation states for all surface chromium species (binding energy (BE) values of Cr 2p_{3/2} level, etc.) of the samples, PC600, PC600-S and PC600-4S, can be found in Table 3. The corresponding BE, full width at half maximum (FWHM) values of Cr 2p_{3/2} level, assignment and atomic percentage of different oxidation states of Cr species for all samples obtained from peak deconvolution and multiplet fitting have also been shown in Table 3.

It can be observed from Table 3 that the Cr(VI) species of PC600-S significantly shifted to lower binding energy (BE = 579.3 eV) together with a slight broadening (FWHM = 6.59 eV) compared with that of calcined Phillips catalyst PC600 (BE = 581.0 eV, FWHM = 6.30 eV). This can be explained from two aspects, one is the electron donation effect of the new chiral organo-siloxane ligand for chromium site; the other is that some hydroxyl groups were formed after the reaction between oxo chromate and chiral organo-silanol compound, which can release the strong surface tension on silica support formed during high-temperature calcination according to our recent report [10].

The BE values of the Cr(VI) species on PC600-4S (as shown in Table 3) were found to further slightly decrease to 579.1 eV (FWHM = 6.60 eV). This decreasing of BE values of hexavalent chromium species with increasing molar rate of chiral ligand from 1:1 to 1:4 has been explained by the electron donation effect of chiral organo-siloxane ligand, which can be further confirmed that the chiral organo-siloxane ligand has been introduced onto the Cr sites.

In Table 3, 3.52% of $\text{Cr(III)}\text{O}_{x,\text{surf}}$ with a BE value of 577.3 eV was observed on PC600-S, which is similar with that of PC600 (3.10% of $\text{Cr(III)}\text{O}_{x,\text{surf}}$). However, the percentage of $\text{Cr(III)}\text{O}_{x,\text{surf}}$ on PC600-4S was found to increase up to 5.66%. According to Scheme 3, 6% of chromium loss on PC600-4S catalyst (as shown in Table 2) should be chromate species ($\text{Cr(VI)}\text{O}_{x,\text{surf}}$). Therefore, the relative increase of percentage of $\text{Cr(III)}\text{O}_{x,\text{surf}}$ on PC600-4S was mainly due to the loss of chromate species ($\text{Cr(VI)}\text{O}_{x,\text{surf}}$).

Above all, the specific surface components in various catalyst samples versus chiral organo-siloxane ligand were clarified. It was evident that the chiral organo-siloxane ligand could be displaced into surface chromium site on catalyst during the preparation process. The chiral organo-siloxane ligand could be stabilized on silica gel surface as an active site by ligand

Table 3
XPS data from multiplet fitting of Cr 2p spectra for PC600, PC600-S and PC600-4S catalysts

Sample	Measurement time (min)	Cr 2p _{3/2}		Oxidation state assignment	Atomic percentage (%)
		BE (eV)	FWHM (eV)		
PC600	10	581.0	6.30	Cr ⁶⁺	96.90
		577.6	6.49	Cr ³⁺	3.10
PC600-S	10	579.3	6.59	Cr ⁶⁺	96.48
		577.3	6.23	Cr ³⁺	3.52
PC600-4S	10	579.1	6.60	Cr ⁶⁺	94.34
		577.3	6.88	Cr ³⁺	5.66

XPS acquisition time: 10 min.

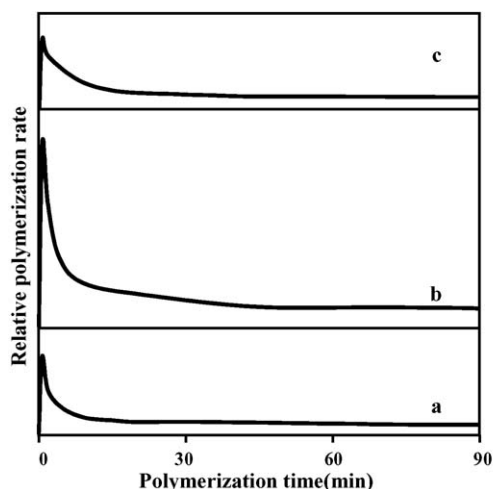


Fig. 3. Polymerization kinetics curves of catalysts with TEA cocatalyst: (a) PC600-S catalyst with 15.0 of Al/Cr molar ratio; (b) PC600-S catalyst with 22.5 of Al/Cr molar ratio; (c) PC600-4S catalyst with 22.5 of Al/Cr molar ratio.

displacement on the compound. As the precursor of chiral silyl chromate active site on calcined Phillips catalyst PC600, the chromate species ($\text{Cr(VI)O}_{x,\text{surf}}$) was found to be gradually becoming more and more electron-sufficient with increasing the chiral ligand ratio of the catalyst from 1:1 to 1:4.

In this work, the novel silyl chromate catalysts with chiral organo-siloxane ligand, PC600-S and PC600-4S, were used for ethylene homo-polymerization in the presence of TEA cocatalyst with different Al/Cr molar ratio. The real-time kinetic curves of catalysts, PC600-S and PC600-4S, under different Al/Cr molar ratio shown in Fig. 3 illustrated the hybrid type kinetics behavior including two kind of basic type, one was high activity and fast decay, and the other was relative low activity and slow decay. It was similar with that of calcined PC600 catalyst in our recent report [15].

The catalytic activities and the microstructures of the obtained polymers are shown in Table 4. It is very interesting and important to find the existence of short chain branches (SCBs) in the ethylene homo-polymers. According to our previous report [13,15], the formation of SCBs in ethylene homo-polymers is one of the most unique features of Phillips $\text{CrO}_x/\text{SiO}_2$ catalyst. It was speculated to be derived from the coexistence of ethylene metathesis sites together with polymerization sites during a transformation of the former into the latter [16]. Similar mechanism can be considered for the formation of SCBs

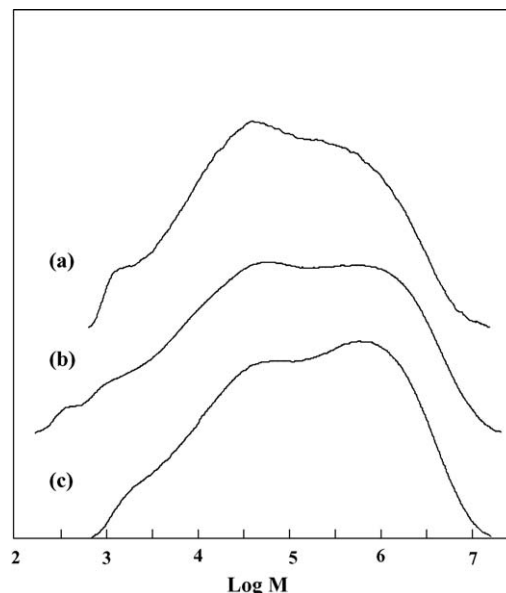


Fig. 4. GPC curves of polymers obtained from: (a) PC600-S catalyst with 15.0 of Al/Cr molar ratio; (b) PC600-S catalyst with 22.5 of Al/Cr molar ratio; (c) PC600-4S catalyst with 22.5 of Al/Cr molar ratio.

in ethylene homo-polymers using the novel catalysts in this work. It was found that the relative amount of methyl and *n*-butyl branches of the polymers obtained from PC600-S catalyst decreased when the cocatalyst concentration increased, which was also similar with those from calcined PC600 catalyst as mentioned in our recent work [13]. The relative amounts of methyl and *n*-butyl branches of PC600-4S are higher than those of PC600-S at the Al/Cr molar ratio of 22.5. According to analysis of atomic percentage by XPS, more amount of silyl chromate with the chiral organo-siloxane ligand was formed in PC600-4S than PC600-S. Therefore, the introduction of the chiral organo-siloxane ligand seemed to promote the formation of methyl and *n*-butyl short chain branches plausibly due to the steric and/or electronic effect of the novel chiral organo-siloxane ligand.

The GPC curves of polymers obtained from PC600-S and PC600-4S catalyst are shown in Fig. 4. Table 4 showed the MW, MWD and microstructure of obtained polymers. It was obviously found both of the PC600-S and PC600-4S catalyst systems produced polymers with bimodal MWD. For PC600-S catalyst, MW and MWD of polymer obtained at Al/Cr molar ratio of 22.5 are larger than those obtained at Al/Cr molar ratio of 15.

Table 4
Ethylene polymerization of PC600-S or PC600-4S catalysts with TEA cocatalyst^a

Catalyst	Amount of catalyst (mmol)	Al/Cr	Yield (mg)	Activity (kg PE/mol Cr-h)	Methyl branches ^b	<i>n</i> -Butyl branches ^b	MW ^c ($\times 10^5$)	MW/ M_n ^c
PC600-S	0.020	15.0	105.7	3.5	1.37	0.50	5.03	35.1
	0.023	22.5	309.7	9.0	0.98	0.34	7.88	101.1
PC600-4S	0.012	22.5	72.4	5.8	2.63	0.66	7.85	39.1

^a Polymerization conditions: catalyst amount 100 mg, polymerization temperature 60 °C, polymerization time 1.5 h, ethylene pressure 0.13 MPa, solvent heptane (20 ml), cocatalyst TEA in heptane (1 M).

^b Number of methyl or *n*-butyl branches per 1000 backbone carbon determined by ¹³C NMR method.

^c Characterized by GPC method.

MW and MWD of polymer might be determined by two chain transfer effects. One is polymer chain transfer from active sites to Al-alkyl. MW of polymers decreases with increase of Al/Cr mole ratio. The other is the β -H elimination (or β -H transfer) to monomer. For PC600-S catalyst, the relative amount of SCBs including methyl and butyl branches decreased with increase of Al/Cr mole ratio as shown in Table 4. The proton in the tertiary β -carbon can be easily transferred or β -eliminated leading to chain transfer to monomer. So the MW of polymers increases with decrease of the comonomer insertion. For PC600-S catalyst, the low MW fraction of polymer obtained at Al/Cr molar ratio of 22.5 is less than that obtained at Al/Cr molar ratio of 15. For PC600-S and PC600-4S catalysts at Al/Cr molar ratio of 22.5, the average MW of polymers obtained is similar but the MWD of polymer obtained from PC600-4S is less than that from PC600-S. That can be explained that for PC600-S catalyst, solely 46.5% of chromate species on the Phillips catalyst surface were transformed into silyl chromate species. For PC600-4S catalyst, 96.3% of surface chromium sites were connected with a chiral organo-siloxane ligand. For PC600-S catalyst, almost half of the PC600 catalyst was transformed silyl chromate species, however for PC600-4S catalyst, almost all the PC600 catalyst was transformed to silyl chromate species. The active sites of PC600-S catalyst are more complex than those of PC600-4S catalyst. So the MWD of polymer obtained from PC600-S is much broader than that from PC600-4S at the same Al/Cr molar ratio. For PC600-S catalyst, the low-MW fraction is more than high-MW fraction. For PC600-4S catalyst, the low-MW fraction is less than high-MW fraction. It was speculated that the novel chiral organo-siloxane ligand seemed to promote the formation of the high-MW fraction.

4. Conclusion

In this work, a newly synthesized chiral organo-silanol compound, (*R*)-methyl-(1-naphthyl)-phenylsilanol, was used to react with Phillips $\text{CrO}_x/\text{SiO}_2$ catalyst to synthesize a novel SiO_2 -supported chromium catalyst for ethylene polymerization. Formation of the catalytic chromate species bearing novel organo-siloxane ligand was confirmed by XPS and solid-state

NMR methods, and then the catalysts were used for ethylene homo-polymerization in presence of triethylaluminum cocatalyst. The new silyl chromate catalysts with the chiral organo-siloxane ligand showed similar kinetic behavior as that of calcined Phillips catalyst combined with TEA. It was very interesting and important to find the existence of short chain branches in these ethylene homo-polymers. The relative amount of methyl and *n*-butyl SCBs of the obtained polymers decreased with increase of Al/Cr molar ratio. Both of the PC600-S and PC600-4S catalyst systems produced polymers with bimodal MWD. The introduction of the novel chiral organo-siloxane ligand leads to the formation of polymers with bimodal MWD as well as higher amount of methyl and *n*-butyl SCBs, which indicates a general method to improve the catalytic performance of SiO_2 -supported Cr-based catalyst for polyethylene production after further exploration with various other organo-silanol compounds.

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