



Experimental and theoretical studies on ethylene polymerization using SiO₂-supported silyl chromate type catalysts prepared by a green method

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ABSTRACT

SiO₂-supported silyl chromate catalyst (UCC S-2 catalyst) is an important catalyst for the commercial production of polyethylene. Cann first reported a possible green synthesis route for the preparation of S-2 catalyst through transformation from Phillips catalyst by addition of triphenylsilanol (TPS) to avoid the use of toxic bis(triphenylsilyl) chromate (BC). In this work, this green synthesis route was further investigated by the combination of experimental and theoretical methods. The obtained catalyst was named as PS catalyst based on the incomplete conversion of Phillips catalyst to S-2 catalyst. Polymerization activity of PS1.5 catalyst was higher than that of S-2 catalyst with either TEA or MAO as cocatalyst. The existence of the simultaneously formed hydroxyl group and its coordination to the reduced Cr site was favorable to the PS catalyst, and this might attribute to the higher polymerization activity of PS catalyst than that of S-2 catalyst. A further modification of PS catalyst by a series of alkyl chlorosilane compounds showed that the role of the electron-withdrawing group only limited at a certain distance away from Cr active site. This preliminary study provided a solid basis for a further innovation of PS catalysts and final substitution of S-2 catalyst in commercial processes.

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1. Introduction

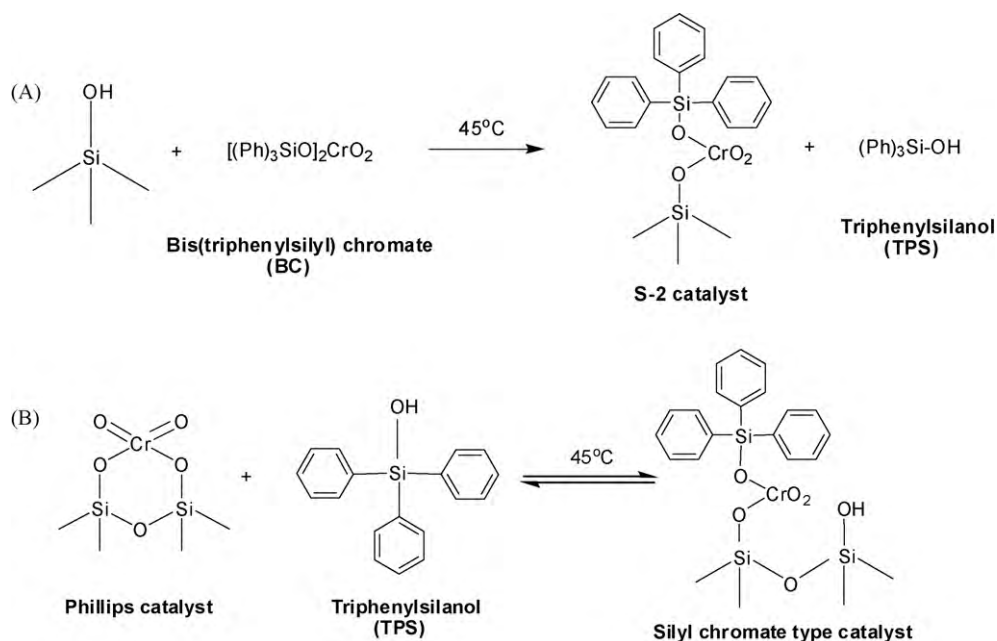
Polyethylene (PE) is a most commonly used plastic with the largest market. Chromium based catalyst systems, including Phillips (chromium oxide) and silyl chromate supported on silica, have long been among the most important catalysts for the production of PE [1–5]. The silyl chromate catalyst, namely S-2 catalyst, was commercialized by Union Carbide Corporation (UCC) with a gas phase UNIPOL process for HDPE production. Until now, S-2 catalyst still produces several millions tons of HDPE, which have desirable molecular weight characteristics meeting different market demanding [6].

However, compared with Phillips catalyst, S-2 catalyst has not been fully investigated during the past several decades. Traditionally, S-2 catalyst is directly prepared from bis(triphenylsilyl) chromate (BC) using thermal treated silica gel as support by wet impregnation method as shown in Scheme 1(A) [3]. It is well known that the catalytic activity is markedly increased when BC is supported on silica gel and then treated with aluminum alkyl [3]. And the unsupported BC is also an active catalyst for ethylene polymer-

ization under relatively high temperature and pressure [7]. Gaspar et al. found that S-2 catalyst showed lower polymerization activity than Phillips catalyst due to S-2 catalyst with less Cr⁶⁺ and Cr²⁺ active species in their calcined and reduced states, respectively [8,9]. However, S-2 catalyst using aluminum alkyl cocatalyst could produce polyethylene with broader molecular weight distribution (MWD) on both ends of high and low molecular weight than that of Phillips catalyst without using cocatalyst [5].

Generally, BC is prepared from triphenylsilanol (TPS) and chromium trioxide, and a higher BC product yield has been developed by Li et al. using triphenyl chlorosilane, potassium dichromate [10]. Nevertheless, the highly toxic BC does not meet the trend of the modern world with increasing concerns about environment and human health. In 2004, a pioneering work of a possible transformation from Phillips catalyst to silyl chromate catalyst through introduction of a silyl ligand from reaction with TPS was reported by Cann and co-workers [5,11]. It was found that the polymerization performance between the obtained catalyst and the silyl chromate catalyst tended to be similar in the case of two equivalents TPS to Cr on Phillips catalyst. The reaction was illustrated in Scheme 1(B). Furthermore, Liu et al. used different organo-silanol compound to modify Phillips catalyst and successfully developed a new SiO₂-supported Cr-based catalysts for olefin polymerization [6]. In our opinion, the reports mentioned above indicated a possible green synthesis route for the preparation of silyl chromate type

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Scheme 1. Two methods for preparation of silyl chromate type catalyst: (A) S-2 catalyst prepared from bis(triphenylsilyl) chromate (BC); (B) Conversion of Phillips catalyst to silyl chromate type catalyst by the addition of triphenylsilanol (TPS).

polyethylene catalyst. However, it was noticeable that a hydroxyl group appeared next to the Cr active site accompanied by the addition of TPS, while this kind of neighboring hydroxyl did not exist in the S-2 catalyst obtained through traditional preparation process. And also, this point was not considered within the previous work by Cann [5]. Considering the strong reverse correlation between the hydroxyl population on the silica surface and polymerization activity in Phillips catalyst [4], effect of the introduced hydroxyl group next to the Cr active site on the polymerization behavior of PS catalyst should be seriously considered.

In recent years, molecular modeling based on density functional theory (DFT) method was increasingly used for the study of the Phillips catalyst [12–19]. Most work was focused on achieving a deeper understanding of the polymerization mechanisms on Phillips-type catalyst. Espelid and Borve [19] compared different routes of initiation and chain propagation with respect to structural, thermodynamic and kinetic properties, and concluded that only a three-coordinate mono-alkylchromium species was found to support chain propagation with the reaction barrier compatible with catalytic activity based on the model of disiloxanochromium site. Liu et al. [15] used a novel silsesquioxane-supported Phillips Cr catalyst as realistic model to elucidate the effects of surface chemistry of silica gel in terms of ligand variation on the catalytic properties of Phillips catalyst. And also, possible reaction mechanisms of olefin polymerization catalyzed by surface supported Cr(IV) species have been investigated using DFT method by Ziegler [13]. However, up to now, there has no theoretical study using DFT method on the silyl chromate type catalyst.

In order to achieve the green synthesis of S-2 catalyst, the preparation of Phillips catalyst in a green method is principal. As a matter of fact, from about 1978, trivalent Cr compound, mostly basic chromium(III) acetate with much weaker toxicity, has been developed as raw material instead of chromium(VI) trioxide for the preparation of Phillips catalyst owing to the environmental and health considerations [9,10,20–25]. Ruddick et al. [22] studied the calcination process of Phillips catalysts using basic chromium(III) acetate and chromium(III) acetylacetonate, and concluded that chromium(III) acetate supported on silica decomposed in a way similar to that observed for bulk chromium acetate. A mecha-

nism for the activation of silica-supported basic chromium acetate in oxidizing, inert, and reducing environments was proposed by Augustine and Blitz [25]. Liu et al. [24] utilized XPS to elucidate the specific transformation process of chromium(III) acetate into bulky CrO_3 and subsequently into $\text{Cr(VI)O}_{x,\text{surf}}$ as a function of calcination temperatures between 120 and 800 °C.

Thus, in this work, the silica supported Phillips catalyst was first prepared from basic chromium(III) acetate with much lower toxicity compared with the commonly used chromium(VI) trioxide according to our previous report [26]. Subsequently, TPS was added to react with oxo chromate species in Phillips $\text{CrO}_x/\text{SiO}_2$ catalyst to form the silyl chromate type catalyst system, which was denoted as PS catalyst. Therefore, in this green synthesis route, highly toxic bis(triphenylsilyl) chromate(VI) (BC) was replaced by chromium(III) compound and TPS. Series PS catalysts and the obtained PE products were characterized. The ethylene polymerization kinetics of the PS1.5 catalysts was compared with those of Phillips catalyst and traditional S-2 catalyst. Specially, the simultaneously formed hydroxyl group next to the Cr active site during the preparation of PS catalyst was investigated by the theoretical method. This was the first theoretical investigation using DFT method for the silyl chromate type catalyst. Additionally, a further modification of the PS catalyst by alkyl chlorosilane compound to remove the nearby surface hydroxyl group was carried out by the combination of theoretical and experimental methods. Much deeper understanding on the SiO_2 -supported silyl chromate type catalyst for ethylene polymerization has been demonstrated.

2. Experimental

2.1. Raw materials

Chromium(III) acetate hydroxide (with 24 wt% Cr) was purchased from Johnson Matthey Company. Bis(triphenylsilyl) chromate (>96%) was obtained from Aldrich. Silica gel (Davison 955, surface area 270.4 m^2/g , pore volume 1.65 cm^3/g and average pore size 24.5 nm) was donated by Qilu Branch Co., SINOPEC. Triphenylsilanol (TPS, >98%) and triethylaluminum (TEA, 25%, w/w, in hexane, >95%) were purchased from Alfa Aesar. Methylalumox-

ane (MAO) in toluene (MAO 9.1 wt%, TMA 1.7 wt%) were purchased from Shanghai Qigele Co. Chlorotrimethylsilane ((CH₃)₃SiCl, AR), dichlorodimethylsilane ((CH₃)₂SiCl₂, AR) and methyltrichlorosilane (CH₃SiCl₃, 99%) were purchased from Aladin. Pure air (>99.999%) was supplied by Shanghai Wetry.

n-Hexane and *n*-heptane were purified by distillation after drying over sodium metal slices prior to use. Silver molecular sieves and Q5 reactant catalyst (13 wt% of Cu(II) oxide on alumina) purchased from Aldrich (St. Louis, MO) were used as oxygen scavenger for gas purification. Nitrogen was further purified by passing through columns of silver molecular sieves and 13X molecular sieves before use. Ethylene monomer was further purified by subsequently passing through columns of 4A molecular sieves, Q5 reactant catalyst, and 13X molecular sieves.

2.2. Catalyst preparation and characterization

2.2.1. Catalyst preparation

Phillips catalyst (CrO_x/SiO₂) with a loading of 0.5 wt% Cr was prepared by wet impregnation of aqueous solutions of chromium (III) acetate hydroxide on silica gel. After impregnation, the slurry was slowly dried at 120 °C for 12 h. Thereafter, about 10 g of obtained sample was added into a fluidized-bed quartz reactor followed by an isothermal calcination process at 700 °C in dried air with a flow rate of 600 mL/min for 6 h to obtain the Phillips catalyst.

A stoichiometric amount of TPS was reacted with 1 g Phillips catalyst in 150 mL *n*-hexane for 2.5 h at 45 °C under inert atmosphere, and the molar ratios of TPS/Cr were 0.5, 1.0, 1.5, 2.0, 3.0, respectively. The series of TPS-modified Phillips catalysts were denoted as PS_x (*x* = 0.5, 1.0, 1.5, 2.0, 3.0). After reaction, the modified catalyst was washed by 50 mL *n*-hexane for three times followed by vacuum drying at 70 °C. The other two PS1.5 catalysts prepared from Phillips catalysts calcined at 500 and 600 °C respectively were also carried out in similar way to investigate the effect of calcination temperatures.

Afterwards, 2 mol equivalents of (CH₃)_xSiCl_y to Cr, chlorotrimethylsilane ((CH₃)₃SiCl), dichlorodimethylsilane ((CH₃)₂SiCl₂), and trichloromethylsilane (CH₃SiCl₃) were added respectively to 1 g PS1.5 catalysts in 50 mL *n*-hexane at room temperature for 2 h. After reaction, the catalyst was dried by vacuum at 70 °C for 1 h. Here, the (CH₃)_xSiCl_y-modified PS1.5 catalysts were denoted as PS1.5-Cl, PS1.5-2Cl, and PS1.5-3Cl, respectively.

For comparison, a traditional S-2 catalyst with a Cr loading of 0.5 wt% Cr was directly prepared from BC using silica gel as support by wet impregnation method. The pretreatment of silica gel was conducted through an isothermal calcination process at 700 °C in nitrogen with a flow rate of 600 mL/min for 6 h. The chemisorption of BC on dehydrated silica gel was carried out at 45 °C in 150 mL purified *n*-hexane for 4 h. After reaction, the catalyst was washed by 50 mL *n*-hexane for three times followed by vacuum drying at 70 °C.

2.2.2. Characterization of catalysts and polyethylene products

Inductively-coupled plasma (ICP) characterization of Phillips, PS_x, and S-2 catalysts were carried out to determine the Cr loadings on the support before and after washing by *n*-hexane on IRIS 1000 Iris Plasma Spectrometer.

X-ray photoelectron spectroscopy (XPS) data of the Phillips, PS_x (after being washed by *n*-hexane and dried), and S-2 catalysts were obtained on an Axis Ultra DLD X-ray Photoelectron Spectrometer with monochromated Al K radiation in order to study the changes of elemental composition on the surface of catalysts. The vacuum in the main chamber was kept below 1 × 10⁻⁹ Torr. Voltage was 15 kV and current was 10 mA during XPS data acquisitions. Scanning frequency of Cr 2p regions were performed for each sample 12 times

while other elements only 1 time in a cycle during high resolution XPS data acquisitions.

Molecular weight (MW) and molecular weight distribution (MWD) of the polyethylene from Phillips, PS_x, and S-2 catalysts were obtained by a Polymer Labs PL220 Gel Permeation Chromatograph using 1,2-dichlorobenzene as solvent with a flow rate of 1.0 mL/min at a temperature of 135 °C. Two PLGel mixed B columns were used.

2.3. Ethylene polymerization

Ethylene polymerization was carried out in a 3-mouth flask, which was placed at a thermostatic bath keeping at 90 °C. One small ampoule tube with about 160 mg catalysts, which was previously weighed and sealed in nitrogen at a glove box, was carefully transferred to the flask. The reactor system was heated and vacuumed for 0.5 h, and then 60 mL *n*-heptane was added followed by introducing a certain amount of aluminum alkyl (Al/Cr molar ratios at 10.0–90.0). Then, ethylene was introduced up to the total pressure of 0.15 MPa. The polymerization was initiated after opening the sealed catalyst tube. The real-time ethylene consumption was continuously monitored by an on-line mass flowmeter (Brooks Instrument 0150E). After 1 h, the polymerization was stopped by adding 100 mL ethanol/HCl solution. The obtained polymer was washed and dried in vacuum at 60 °C for 6 h before weighted.

3. Computational

Geometry optimizations and energy calculations for model compounds were performed with Gaussian 03, using the non-local three-parameter hybrid density functional method B3LYP [27–29]. The Gaussian basis set LANL2DZ (Los Alamos National Laboratory Second Double-Zeta) was used for Cr, and the basis set 6-31G(d, p) was used for all other elements [30]. All transition states were verified using Intrinsic Reaction Coordinate (IRC) calculations, which indicated the transition state was directly connected to the involved reactant and product geometries [31]. All energies reported refer to Gibbs free energy corrections to the total electronic energies at 25.15 °C in gas phase. The Mulliken charge of chromium atom was also calculated by Gaussian 03 program for analysis of the charge distribution on each center.

4. Results and discussion

4.1. Characterization of catalysts and polyethylene products

The series of PS_x, Phillips, and S-2 catalysts were characterized by ICP and XPS methods. During the PS catalyst preparation process, each catalyst was washed by 50 mL *n*-hexane for three times after the reaction of Phillips catalyst with TPS. Table 1 shows the chemical analysis data on catalysts detected by ICP method before and after the *n*-hexane washing. The Cr loadings of Phillips and

Table 1
Amount of Cr on catalyst before and after washing with *n*-hexane.

Cat.	Color of eluate	Cr (wt%) ^a	
		Before washing	After washing
Phillips	Colorless	0.51	0.51
PS0.5	Colorless	0.51	0.50
PS1.0	Light yellow	0.51	0.46
PS1.5	Yellow	0.51	0.45
PS2.0	Yellow	0.51	0.45
PS3.0	Dark yellow	0.51	0.37
S-2	Dark yellow	0.47	0.23

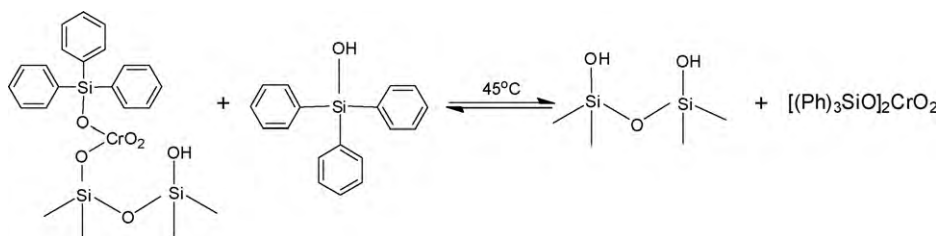
^a Determined by ICP (inductively-coupled plasma).

Table 2
Effects of TPS/Cr ratio on catalysts and polyethylene products.

Cat.	Atomic percentage (%) ^a			Si/C molar ratio	Mn ($\times 10^{-5}$) ^b	Mw ($\times 10^{-5}$) ^b	Mw/Mn ^b
	Si	C	O				
Phillips	22.61	5.57	71.61	4.06	1.10	26.50	24.30
PS1.0	19.77	11.04	68.85	1.79	0.86	16.56	19.34
PS1.5	18.21	10.74	70.58	1.70	1.04	24.80	23.76
PS2.0	20.03	11.78	67.76	1.70	1.68	29.38	17.52
S-2	17.76	20.18	61.59	0.88	2.27	32.05	14.14

^a The atomic percentage of the catalysts washed by *n*-hexane was measured by XPS.

^b The polyethylene was characterized by GPC method. Polymerization conditions: catalyst amount, 160 mg; polymerization temperature, 90 °C; polymerization time, 60 min; ethylene pressure, 0.15 MPa; solvent, heptane, 70 mL; cocatalyst TEA, Al/Cr molar ratio = 20.0.



Scheme 2. Further plausible reaction between the obtained PS catalyst and TPS.

PS0.5 catalysts were maintained as the original 0.5 wt% loading after washing. For the PS1.0, PS1.5, and PS2.0 catalysts, the Cr loadings were similar and slightly decreased to 0.45 wt%. However, the Cr loading for PS3.0 was obviously decreased to 0.37 wt%. As for S-2 catalyst, the Cr loading was dramatically decreased from 0.47% to 0.23% after *n*-hexane washing, thus only less than half of Cr was remained on the surface after washing. It was also consistent with the experimental evidence that the eluate gradually changed from colorless for PS0.5 to dark yellow for PS3.0, indicating that the increase of TPS amount seemed to accelerate the removal of surface hexavalent chromium species from Phillips catalyst by *n*-hexane washing.

XPS method was applied to study the change of the elemental composition on PS_x catalysts surface after being washed by *n*-hexane and dried. The results were summarized in Table 2. The carbon content for Phillips catalyst was 5.57%, which might be due to the impact of contamination carbon in the sample preparation (from solvent). For PS_x ($x = 1.0, 1.5, 2.0$) catalysts, the carbon contents were increased up to about 11% after the modification of the Phillips catalyst by TPS, indicating that the reaction between TPS and oxo chromate species were likely occurring. The normalization atomic ratios of Si/C for PS_x ($x = 1.0, 1.5, 2.0$) catalysts implied the similar tendencies on these catalyst surfaces.

Cann et al. reported that two equivalents of TPS were needed to complete the transformation of all oxo chromate species into silyl chromate species [5]. As shown in Table 1, the loading of Cr on PS_x catalyst decreased with the increasing addition of TPS, suggesting a further reaction of the formed silyl chromate species and the TPS could occur even in the case of less than one equivalent addition of TPS (as shown in Scheme 2). With the increase of additional TPS amount, the degree of the conversion presented in Scheme 2 enhanced resulting into the loss of chromium loading. Therefore, the surface chromium species might be largely removed off from the surface of silica in form of BC with large amount of TPS. It could be concluded that the conversion from Phillips catalyst to S-2 catalyst by the addition of TPS could not occur completely because the reactions shown in Schemes 1(B) and 2 were simultaneous and reversible.

Ethylene slurry polymerization using the Phillips, PS_x ($x = 1.0, 1.5, 2.0$), and S-2 catalysts was carried out at 90 °C and 0.15 MPa for 1 h using heptane and TEA (Al/Cr = 20) as solvent and cocata-

lyst, respectively. The polyethylene products were characterized in order to investigate the variations of the polymer molecular weight (MW) and molecular weight distribution (MWD). The corresponding MW and MWD were shown in Table 2, and the corresponding GPC curves of polyethylene were shown in Fig. 1. As shown in Table 2 and Fig. 1, the MWD of the PEs obtained from Phillips and S-2 catalyst were the highest (Mw/Mn = 24.30) and the lowest (Mw/Mn = 14.14) values, respectively, although all the polymer products showed broad MWD. The MWD of polymers from PS_x catalysts are between Phillips and S-2 catalyst. After the reaction of TPS (TPS/Cr = 1.0) with Phillips catalyst, the GPC curve of PS1.0 catalyst significantly shifted to low MW region. With the further increase of TPS/Cr ratio, the GPC curves of the PS_x catalysts gradually moved back to the high MW region analogous to that of S-2 catalyst. This could also be seen in Table 2 from the gradual increase of the average Mw with the increase of TPS/Cr ratio. Due to the use

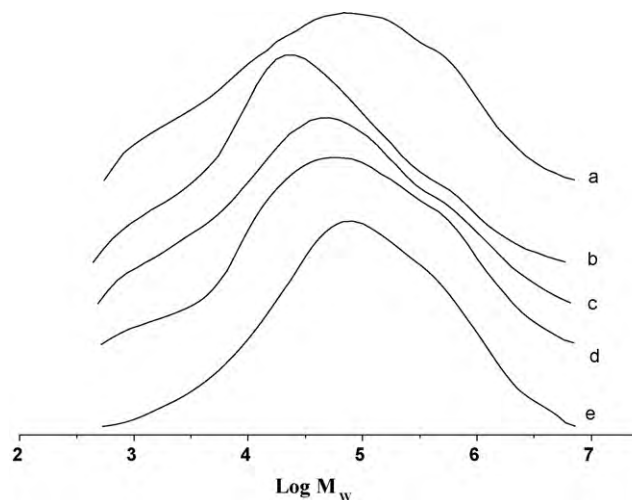


Fig. 1. Effect of TPS/Cr ratio on molecular weight distribution for polyethylene obtained from (a) Phillips; (b) PS1.0; (c) PS1.5; (d) PS2.0; and (e) S-2 catalysts. (Polymerization conditions: catalyst amount, 160 mg; polymerization temperature, 90 °C; polymerization time, 60 min; ethylene pressure, 0.15 MPa; solvent, heptane, 70 mL; cocatalyst TEA, Al/Cr molar ratio = 20.0).

of cocatalyst, the Phillips catalyst produced the polyethylene with very broad MWD.

According to the characterization results of PSx catalysts and their corresponding products, the PS1.5 catalyst was selected as a typical representative of the series of PSx catalysts for ethylene polymerization in the following sections investigation.

4.2. Ethylene polymerization kinetics of catalysts

The ethylene polymerization kinetic of PS1.5 catalyst was investigated and compared with those of Phillips and traditional S-2 catalysts. Fig. 2 presents the polymerization kinetics curves of Phillips, PS1.5, and S-2 catalysts with TEA or MAO as cocatalyst, respectively, and the molar ratio of Al/Cr was selected according to the optimum condition of catalyst. The polymerization kinetics curve of PS1.5 catalyst declined obviously compared with that of Phillips catalyst, and the polymerization activity of PS1.5 catalyst was much lower than that of Phillips catalyst. For PS1.5 and S-2 catalysts, the kinetics curves for the two catalysts with the same cocatalyst were similar, and a higher activity of PS1.5 catalyst was obtained than that of S-2 catalyst. However, significantly different kinetics curves were observed when the two catalysts were treated with different cocatalysts. When TEA was chosen as cocatalyst (shown in Fig. 2(b)), the kinetics curves of PS1.5 and S-2 catalysts characterized with a tendency of fast built up and then fast decay. In the case of MAO (shown in Fig. 2(c)), an obvious changes were found that the kinetics curves reached to a relatively lower peak but stabilized at a higher rate level accompanied by an increased induction period. The similar type of kinetics curves for PS1.5 and S-2 catalysts implied the similar active site properties of the two catalysts. Different polymerization kinetics with different cocatalyst may be explained that the reducing and alkylation capability of MAO was weaker than that of TEA leading to a prolonged induction period for the formation of active site. However, the active sites formed with MAO might be stable due to the weaker reduction power of MAO, while active site formed with TEA could be easily deactivated owing to the over-reduction by TEA with much stronger reduction power [32].

There may be several reasons for the significant decline of polymerization activity from Phillips catalyst to PS1.5 catalyst. Firstly, coordinated ligands of Cr active site for PS1.5 catalyst were quite different from that of Phillips catalyst. The phenyl, electron-donating group, which was introduced through the addition of TPS, resulted in the decline of Cr electron-deficiency and greater steric hindrance for ethylene coordination and insertion. Secondly, during the addition of TPS, the opening of Si–O–Cr–O–Si–O ring of Phillips catalyst led to the release of surface ring strain and decline of the electron-deficiency of Cr. The ethylene polymerization of Phillips catalyst and PS1.5 catalyst calcined at different temperatures was conducted subjected to the release of surface ring strain, and the results would be discussed in Section 4.3. Thirdly, it was noteworthy that a hydroxyl group was introduced next to the Cr active site after the reaction between Phillips catalyst and TPS. Considering the strong reverse correlation between the hydroxyl population on the silica surface and polymerization performance of Phillips catalyst [4], the plausible effect of the introduced hydroxyl on polymerization performance of PS catalyst was discussed in Section 4.4.

4.3. Effect of calcination temperatures on ethylene polymerization kinetics

As mentioned above, PS1.5 catalyst was prepared from the reaction between TPS and silica supported Phillips catalyst, which had been calcined at high temperatures. Silica gel, being the most commonly used support for heterogeneous olefin polymerization

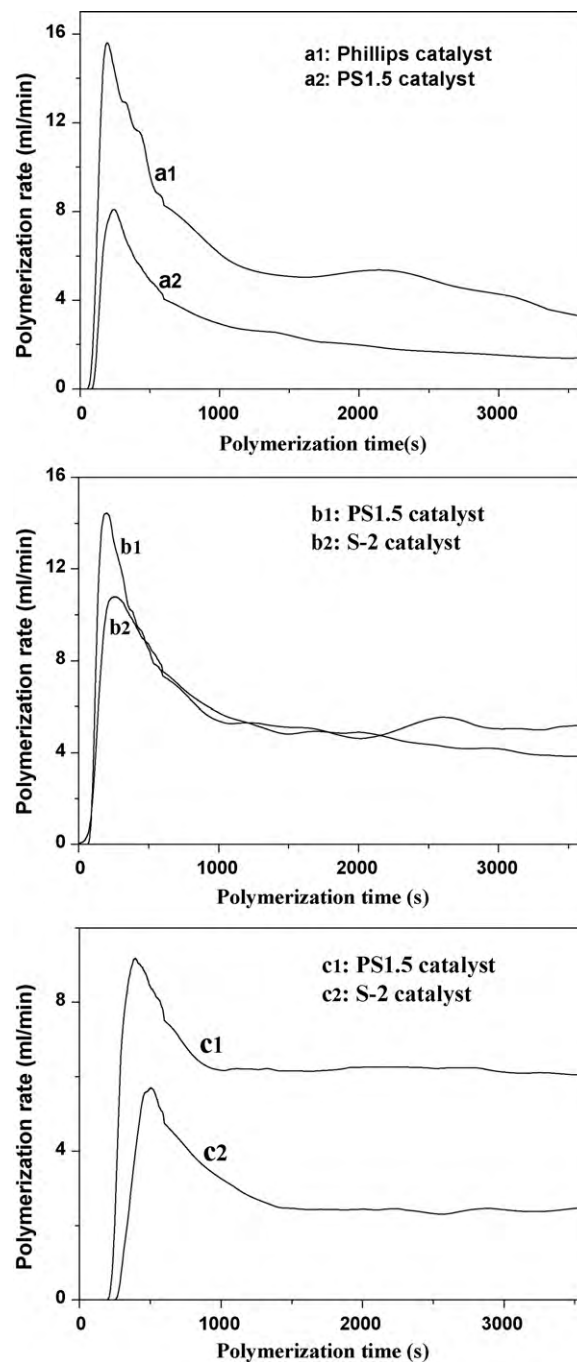


Fig. 2. Ethylene polymerization kinetics curves of catalysts (a) Phillips catalyst and PS1.5 catalyst with TEA cocatalyst (Al/Cr molar ratio = 20.0); (b) PS1.5 catalyst and S-2 catalyst with TEA cocatalyst (Al/Cr molar ratio = 15.0); (c) PS1.5 catalyst and S-2 catalyst with MAO cocatalyst (Al/Cr molar ratio = 90.0). (Polymerization conditions: catalyst amount, 160 mg; polymerization temperature, 90 °C; polymerization time, 60 min; ethylene pressure, 0.15 MPa; solvent, heptane, 70 mL.)

catalysts, contains surface Si–OH groups of varying structures and concentrations depending on the calcination temperatures. Considering the effect of the calcination temperature, PS1.5 catalyst was prepared based on the Phillips catalysts calcined at 500, 600, and 700 °C, respectively, and the ethylene polymerization performances of PS1.5 and Phillips catalyst counterparts were compared in Fig. 3. The activities for Phillips catalyst linearly increased with the increasing calcination temperatures from 500 to 700 °C. The reasons for the increased activity with increased calcined temperature for Phillips catalyst were the decreasing amount

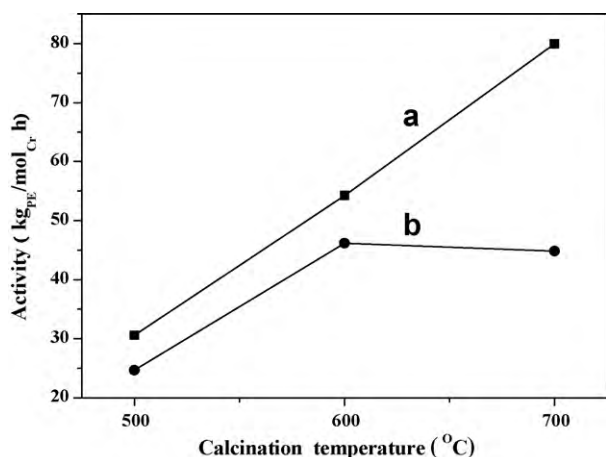


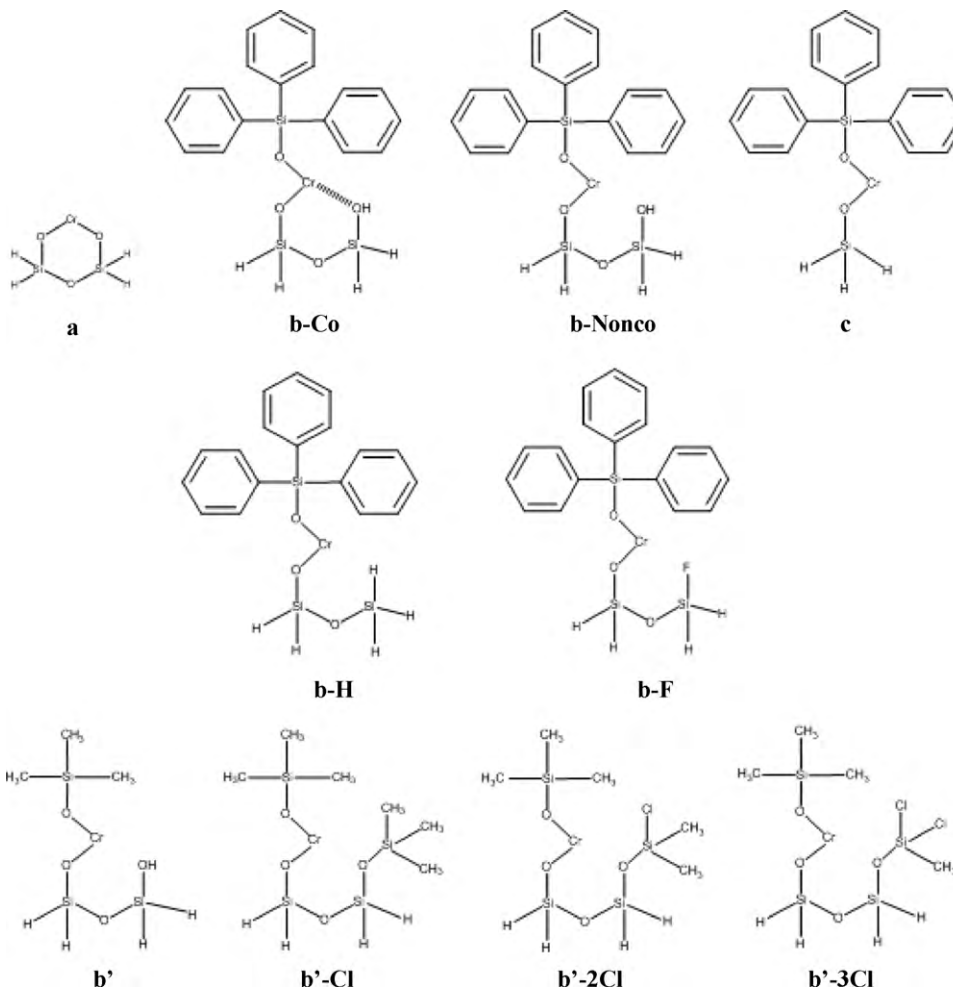
Fig. 3. Ethylene polymerization activities of (a) Phillips catalyst and (b) PS1.5 catalyst prepared at different calcination temperatures (500, 600, 700 °C). (Polymerization conditions: catalyst amount, 160 mg; polymerization temperature, 90 °C; polymerization time, 60 min; ethylene pressure, 0.15 MPa; solvent, heptane, 70 mL; cocatalyst TEA, Al/Cr molar ratio = 15.0).

of residual hydroxyl groups and introduced surface ring strain into Si–O–Cr–O–Si bonds making the electron-deficient Cr center more active [24,33–35]. Conversely, the activity for PS1.5 catalyst obtained from Phillips catalyst calcined at 700 °C was even slightly

lower than that at 600 °C, suggesting the activity of PS catalyst was not directly related with that of the corresponding Phillips catalyst. And a significant activity decline was found between Phillips and PS1.5 catalysts calcined at 700 °C, while the differences were smaller at 500 and 600 °C, respectively. This might be rationalized well as follows. On the one hand, the increasing of calcination temperature could decrease the surface residual hydroxyl groups and increase the electron-deficiency of Cr center and thus favor the polymerization reaction on PS catalyst. On the other hand, the opening of Si–O–Cr–O–Si ring accompanied with the release of ring strain during the formation of PS catalyst in Scheme 1(B) and decline of electron-deficiency of Cr center could become dominant for PS catalyst calcined at higher temperature. Therefore, the highest polymerization activity for PS1.5 was achieved at 600 °C calcination temperature.

4.4. Effect of hydroxyl on ethylene polymerization

Hydroxyl was another important factor to affect the catalytic performance of Phillips catalyst, and there was a strong reverse correlation between the hydroxyl population on the silica surface and the polymerization activity for Phillips catalyst [4]. However, there was still no clear explanation [36–40]. One of the explanations was that the hydroxyl might coordinate to the reduced Cr site and thus poison the active Cr center [37]. Another explanation was that the Cr(II) active center might be reoxidized by hydroxyl into



Scheme 3. Computational models for catalysts (a) Phillips catalyst; (b-Co) PS catalyst with coordination between Cr and –OH; (b-Nonco) PS catalyst without coordination between Cr and –OH; (c) S-2 catalyst; (b-H) PS catalyst with –OH replaced by –H; (b-F) PS catalyst with –OH replaced by –F; (b') simplified PS catalyst with phenyl replaced by methyl; (b'-Cl) PS catalyst modified by $(\text{CH}_3)_3\text{SiCl}$; (b'-2Cl) PS catalyst modified by $(\text{CH}_3)_2\text{SiCl}_2$; (b'-3Cl) PS catalyst modified by CH_3SiCl_3 .

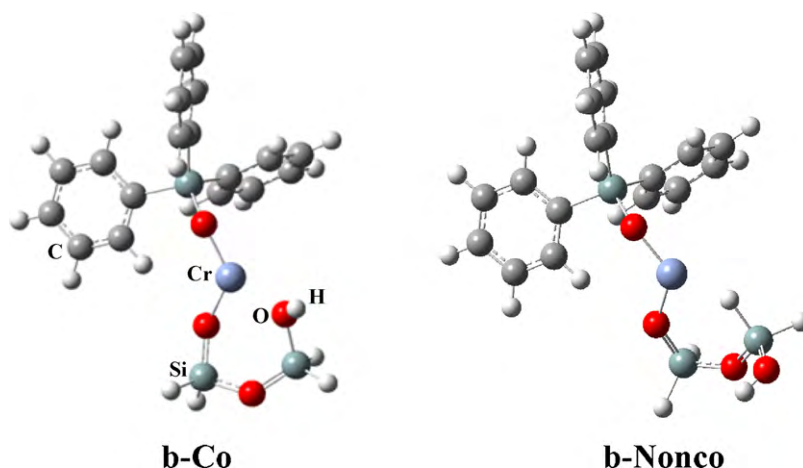
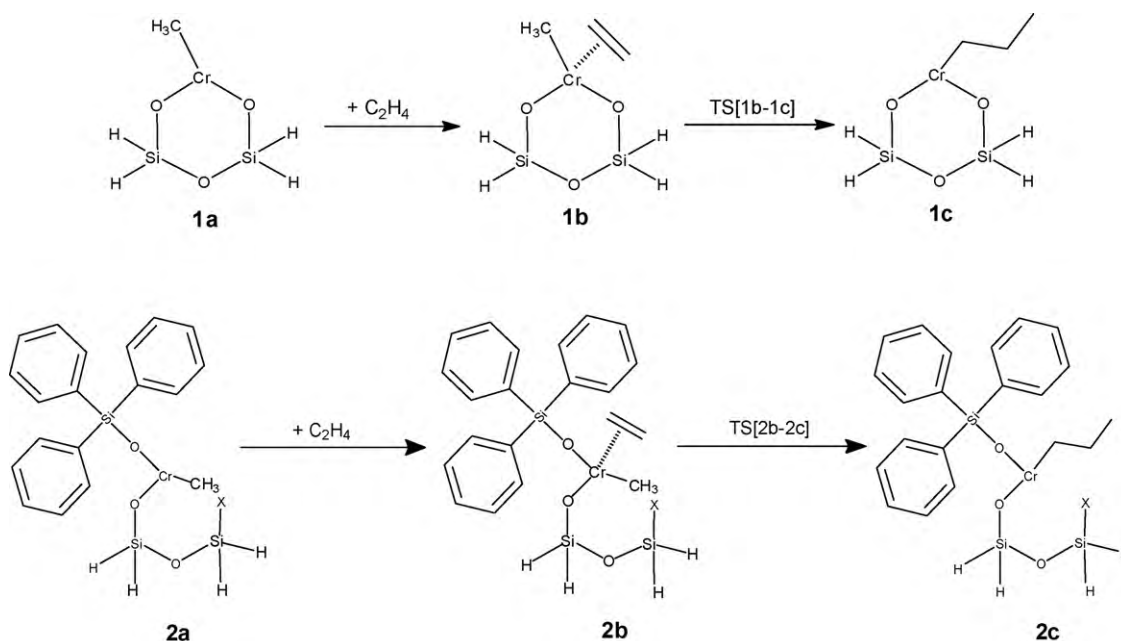


Fig. 4. Optimized structures for **b-Co** and **b-Nonco** models by DFT method.

Cr(III) [38,39]. Another possibility was that the hydroxyls might not be directly involved in the polymerization reaction, but be merely removed through an annealing of the surface which better exposed the Cr sites and induced some important change in terms of the surface strain by the condensation of surface hydroxyl groups during the annealing [36]. Some reports even suggested the favorable effect of hydroxyl for Phillips catalyst was that surface hydroxyl groups might be a necessary source of the active site by providing the first proton during the initiation stage of polymerization [39,40]. Therefore, during the preparation of PSx catalysts (Scheme 1(B)), a simultaneously formed hydroxyl group next to the Cr center should be seriously considered and investigated.

Firstly, FTIR characterizations of the PSx, Phillips, and S-2 catalysts were carried out in order to obtain some information about the hydroxyl groups on the catalyst surface. As shown in Fig. SI-1 (in the supporting information), the gradual increase of surface hydroxyl groups with increase of TPS/Cr molar ratios could be observed, which provided the direct evidence of the formation of surface hydroxyl groups on the PSx catalysts. The effect of the neighboring hydroxyl groups on the catalytic properties of the

Cr centers was further investigated by molecular modeling using DFT method. DFT calculations were performed on three site models (Scheme 3), **a** model for Phillips catalyst was taken as a comparison, and active site **b** model for PS catalyst and **c** model for S-2 catalyst were established, respectively. Two cases for model **b** were considered involving the coordination (model **b-Co**) or non-coordination (model **b-Nonco**) between Cr active site and the neighboring hydroxyl group for PS catalyst. Taking **b-Co** and **b-Nonco** models as examples, the optimized structures were shown in Fig. 4. In Scheme 4, the chain propagation based on the popularly accepted Cossee mechanism [41] on heterogeneous coordination polymerization catalysts was shown. And, the DFT calculations for the chain propagation with the growing polymer chain simplified as methyl group on several models were presented in Table 3. The energy barrier for ethylene insertion significantly increased from 19.22 kcal/mol for **a** model (Phillips catalyst) to 22.03 kcal/mol for **b** model (PS catalyst). The consistency with the experimental result in Fig. 2(a) suggested that the models were somewhat reasonable. Also, it was interesting to note that the calculated free energy of -1953.70 hartree for the model **b-Co** involved Cr and $-OH$ coordination



Scheme 4. Ethylene chain propagation over **1a** and **2a** models through Cossee mechanism.

Table 3
Mulliken charge on Cr(*q*), geometry parameters, and ethylene insertion energy barrier of cluster models.

Models ^a	q_{Cr}^b	q_{Cr}^c	Cr–O ^b (Å)	Cr–O ^c (Å)	Barrier (kcal/mol)
a	+0.609	+0.738	–	–	19.22
b-Co	+0.781	+0.735	2.136	2.220	22.03
b-Nonco	+0.671	+0.757	4.328	4.173	23.66
b-H	+0.694	+0.757	2.014 (Cr–H)	4.662 (Cr–H)	23.93
b-F	+0.784	+0.731	2.152 (Cr–F)	2.333 (Cr–F)	20.63
b'	+0.844	+0.733	2.076	2.225	21.59
b'-Cl	+0.686	+0.758	2.153	4.907	23.24
b'-2Cl	+0.668	+0.753	2.236	5.250	23.44
b'-3Cl	+0.686	+0.777	2.261	5.033	23.58
c	+0.784	+0.760	–	–	23.75

^a Refer to models description in Scheme 3.

^b Before ethylene insertion.

^c After ethylene insertion.

dination was lower than that of model **b-Nonco** with Cr and –OH non-coordination of –1953.68 hartree, primarily indicating that the PS catalyst was more likely to be existed in the coordinated form between Cr and –OH. The insertion energy barrier for the case of **b-Co** (Cr and –OH coordination) was even lower than that of model **b-Nonco** (non-coordination between Cr and –OH) in Table 3. Moreover, Mulliken charge of Cr for model **b-Co** was higher than that of model **b-Nonco**, indicating an increased electron-deficiency of Cr active center for **b-Co**, which would be beneficial to the ethylene insertion. The insertion energy for model **c** with non-vicinal hydroxyl coordination presented 23.75 kcal/mol, which was similar with the case of model **b-Nonco** and higher than that of model **b-Co**. Above calculation results were also consistent with the activity decline from PS1.5 catalyst to S-2 catalyst as shown in Fig. 2(b) and (c).

Furthermore, **b-H** and **b-F** models referred as hydroxyl group replaced by hydrogen and fluorine atoms, respectively, were established in order to further determine the role of surface hydroxyl. In Table 3, the Mulliken charge of Cr for **b-H** (+0.694) was obviously lower than those for **b-F** (+0.784) and **b-Co** (+0.781), respectively. And the insertion energy barriers for **b-H** (23.93 kcal/mol) were also higher than those for **b-F** (20.63 kcal/mol) and **b-Co** (22.03 kcal/mol). It indicated that the introduced hydroxyl group in PS catalyst behaving similar electron-withdrawing effect as F-ligand was beneficial to the ethylene insertion, which is quite different with the case of Phillips catalyst. This difference from the surface hydroxyl groups between Phillips and PS catalysts might be derived from the completely different ligand environment of the two catalyst systems.

All above computational and experimental results suggested that the existence of the introduced hydroxyl and its coordination to the reduced Cr site was favorable to the polymerization activity of PS catalysts. The Cr active site in model **b-Co** mainly including three phenyl ligands (strong electron-donating group) may lead to the change of hydroxyl role from an electron-donating group into electron-withdrawing group resulting in the increase of electron-deficiency of Cr, which was beneficial to the ethylene insertion. Also, it can be seen that the decreased activity from Phillips cata-

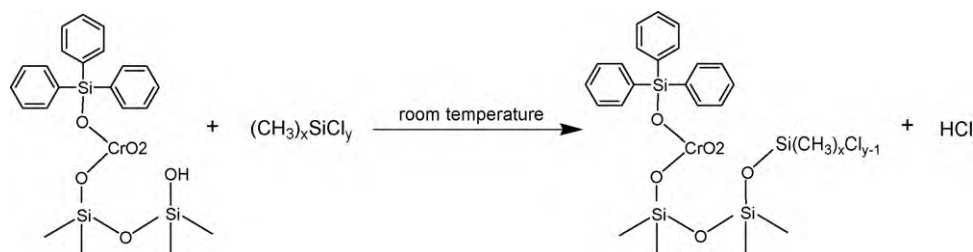
lyst to PS1.5 catalyst might be due to the presence of phenyl ligands and the release of surface ring strain in PS catalysts decreasing the electron-deficiency of the Cr active site, but not the introduction of the hydroxyl group next to the Cr active site.

4.5. Modification of PS catalyst by alkyl chlorosilane

As a consequence of the above considerations, due to the positive effect of F modification of PS1.5 catalyst obtained from the prediction of theoretical calculation, it is necessary to carry out a detailed experiment. In practice, high temperature is necessary for the F modified Phillips catalyst by (NH₄)SiF₆ to remove the ammonia ion [42–44]. Unfortunately, the introduction of F was impracticable due to the loss of remaining TPS ligand under high temperature. Alternatively, three different kinds of alkyl chlorosilane, chlorotrimethylsilane (CH₃)₃SiCl, dichlorodimethylsilane (CH₃)₂SiCl₂, and trichloromethylsilane CH₃SiCl₃ were studied systematically. The reaction of surface silanol of the silica gel with alkyl chlorosilane was applied as a typical method to quantification of the silanol number [45]. A plausible reaction between the surface hydroxyl group on PS1.5 catalyst and alkyl chlorosilane is shown in Scheme 5.

Firstly, DFT method was used to gain basic understanding on the influence of the modification of PS catalyst by alkyl chlorosilane, and a set of simplified models were presented in Scheme 3. Model **b'** was derived from model **b** with replacement of phenyl by methyl ligand. Models **b'-Cl**, **b'-2Cl** and **b'-3Cl** were derived from model **b'** modified by alkyl chlorosilane compounds with one, two, and three chlorine atoms, respectively. As shown in Table 3, there was a significant decline for Mulliken charge of Cr but an increase of bond length (r_{Cr-O}) from **b'** to **b'-Cl**, **b'-2Cl**, and **b'-3Cl**. The energy barriers of ethylene insertion for alkyl chlorosilane modified PS models were all around 23 kcal/mol, which was higher than **b'** with 21.59 kcal/mol, indicating that the modification of PS catalyst by alkyl chlorosilane was unfavorable for ethylene polymerization.

Next, ethylene polymerization experiments using the corresponding PS catalysts were carried out in order to further confirm the above computational results. And 2 mol equivalents of alkyl



Scheme 5. Plausible reaction between PS catalyst and (CH₃)_xSiCl_y.

Table 4
Ethylene polymerization over PS1.5, PS1.5-Cl, PS1.5-2Cl, and PS1.5-3Cl catalysts with TEA cocatalyst^a.

Cat.	Cocatalyst	Al/Cr mol ratio	Activity (kg _{PE} /mol _{Cr} h)
PS1.5	TEA	15	38.9
PS1.5-Cl	TEA	15	33.9
PS1.5-2Cl	TEA	15	34.3
PS1.5-3Cl	TEA	15	34.8

^a Polymerization conditions: catalyst amount 120 mg; polymerization temperature 90 °C; ethylene pressure 0.15 MPa; polymerization time 60 min; solvent heptanes; 70 mL.

chlorosilane were excessively added to PS1.5 obtained by the reaction of TPS and Phillips catalyst. Table 4 shows the activity of alkyl chlorosilane-modified PS1.5 catalysts. Compared with the original PS1.5 catalyst, the chlorosilane-modification resulted in a decrease in activity. And the activity difference between three different kinds of chlorosilane compounds was small, which was consistent with the computational results.

Both computational and experimental results showed that the modification of PS catalyst by alkyl chlorosilane compounds was unfavorable for polymerization activity, which further verified that the coordination of hydroxyl with the reduced Cr site was favorable for PS1.5 catalyst (Table 3). We also found that PS catalyst modified by three different kinds of chlorosilane compounds made very small difference despite of the introduction of electron-withdrawing group Cl in models **b'-2Cl** and **b'-3Cl**, indicating that the electron-withdrawing group may play the role only limited at a certain distance away from the Cr active site as model **b-F** did. Further investigation using other modification reagents is still being carried out by experiments combined with molecular modeling in order to improve the performance of PS catalysts.

5. Conclusion

A green synthesis route for the preparation of silica gel supported silyl chromate type catalysts namely PS catalysts for ethylene polymerization through a transformation reaction between Phillips catalyst and TPS was systematically investigated by combined theoretical and experimental methods. The element analysis of the catalysts demonstrated that the conversion from Phillips catalyst to the UCC S-2 catalyst could not occur completely suggesting the chromium might be partially removed off from the surface of silica gel in the form of BC especially at high TPS/Cr molar ratio. Though the PS1.5 and S-2 catalysts presented similar kinetics curves for the same kind of TEA or MAO cocatalyst, the corresponding polymerization activity of PS1.5 catalyst was higher than that of S-2 catalyst. Compared with the Phillips catalyst, the activity of the PS1.5 was not increased with the increasing calcination temperature, and the highest activity was obtained at 600 °C. The decreased activity from Phillips catalyst to PS1.5 catalyst may be due to the presence of phenyl ligands and the release of surface ring strain in PS catalyst decreasing the electron-deficiency of the Cr active site. The simultaneous formation of a hydroxyl group next to the Cr active site during the preparation of PS catalyst was investigated. The existence of the introduced hydroxyl and its coordination to the reduced Cr active site seemed favorable to the polymerization activity for PS catalysts, and this might be the reason for the higher activity of PS catalysts than that of S-2 catalyst. Further modification of PS catalyst by three different kinds of alkyl chlorosilane compounds presenting similarly computational and experimental results indicated that the effect of the electron-withdrawing group was limited at a certain distance away from Cr active site. This preliminary study with combination of theoretical and experimental methods provided a solid basis for the further innovation of silica gel supported silyl chromate type

catalysts and final substitution of UCC S-2 catalyst in commercial processes.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2010.07.002.

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