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Various Activation Procedures of Phillips Catalyst for Ethylene Polymerization[1]

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Abstract—Nowadays, the Phillips CrO_x/SiO_2 catalyst is still attracting interest from both industrial and academic fields owing to its unique characteristics for HDPE production. Compared with other industrial catalysts for ethylene polymerization, the Phillips catalyst can be activated by ethylene monomer, CO or Al-alkyl cocatalyst after a simple calcination process (thermal activation). In this work, a brief review of our recent new understanding on various activation procedures, including thermal activation, monomer activation, and CO activation, on industrial Phillips catalyst was presented. A new initiation mechanism, ethylene metathesis mechanism, was proposed according to some experimental evidence during the induction period when ethylene monomer was used to activate the catalyst. Such an ethylene metathesis mechanism was also indirectly confirmed in CO-prereduced Phillips catalyst. The formation of short chain branches in polymer can be rationalized well by this newly proposed unique mechanism during ethylene homo- and copolymerization with hexene-1 using CO-prereduced Phillips catalyst in the presence of triethylaluminum cocatalyst.

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As one of the main industrial catalysts for ethylene polymerization, nowadays the Phillips CrO_x/SiO_2 catalyst is still responsible for nearly 7 million tons of commercial polyolefin production covering more than one-third of the world high-density polyethylene (HDPE) market. The Phillips CrO_x/SiO_2 catalyst shows quite competitive ability with two other kinds of catalysts, Ziegler–Natta and metallocene catalysts, owing to its production of HDPE with an ultrabroad molecular weight distribution and short chain branches as well as long chain branches, which contribute to some unique characteristics for commercial application like blow-molding HDPE production [1, 2].

Compared with the preparation process of other kinds of olefin polymerization catalysts, the Phillips $Cr(VI)O_x/SiO_2$ catalyst can be easily synthesized through a calcination procedure after impregnation of chromium compound on porous amorphous silica gel. The calcination procedure is also called thermal activation. The Phillips catalyst can be further activated to $Cr(II)O_x/SiO_2$ by ethylene monomer, CO or Al-alkyl cocatalysts for ethylene polymerization. But the reason why the Phillips catalyst has such unique properties is still unclear even after 50 years of great efforts since its discovery in the early 1950s [3–8].

Recently, our group carried out a series of studies on the various activation procedures, including thermal activation, ethylene monomer activation, and CO and Al-alkyl activation, in terms of catalyst characterization and polymerization [9–13]. In this paper, a brief review on such various activation procedures of the Phillips CrO_x/SiO_2 catalyst will be presented in order to obtain deeper and systematic understanding of this most important industrial catalyst.

EXPERIMENTAL

Catalyst preparation. The details about catalyst preparation of the calcined Phillips catalyst can be found in our previous report [9, 12, 14, 15]. A simplified introduction of the catalyst preparation process is given as follows. The Phillips catalyst precursor ES370X (defined as PCP120) was prepared through impregnation of an aqueous solution of chromium (III) acetate onto SiO_2 (Matthew Frosdyck ES70X) followed by drying in dry air at a fixed temperature of around 120°C for a certain period of time. About 15 g of Phillips catalyst precursor PCP120 was added into a spouted fluidized-bed quartz reactor followed by an isothermal calcination process at 200, 300, 400, 600, and 800°C, which was carried out in dry air for 6 h to obtain five Phillips catalysts named PC200, PC300, PC400, PC600, and PC800, respectively. The calcined catalyst was cooled down to room temperature in purified nitrogen and distributed into ampoule bottles. An industrial Phillips CrO_x/SiO_2 catalyst (S-1) (1 wt % of Cr loading) donated by Japan Polyolefin Co. Ltd. was used for ethylene monomer activation procedure, which is the same catalyst as we used in our previous study [16]. In the CO activation procedure, the calcined Phillips catalyst, PC600, was reduced by CO at 350°C for 1.5 h, which was named PC600/CO.

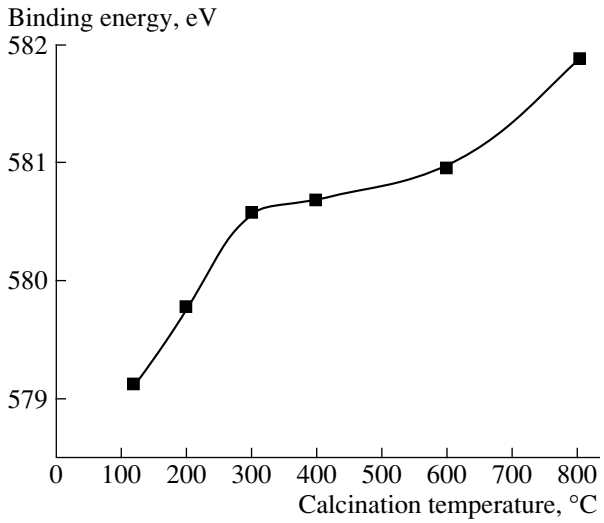


Fig. 1. Dependence of binding energy (Cr 2*p*(3/2)) of surface Cr^{6+} species of various Phillips catalysts on calcination temperature for preparation of the catalysts from PCP120 precursor.

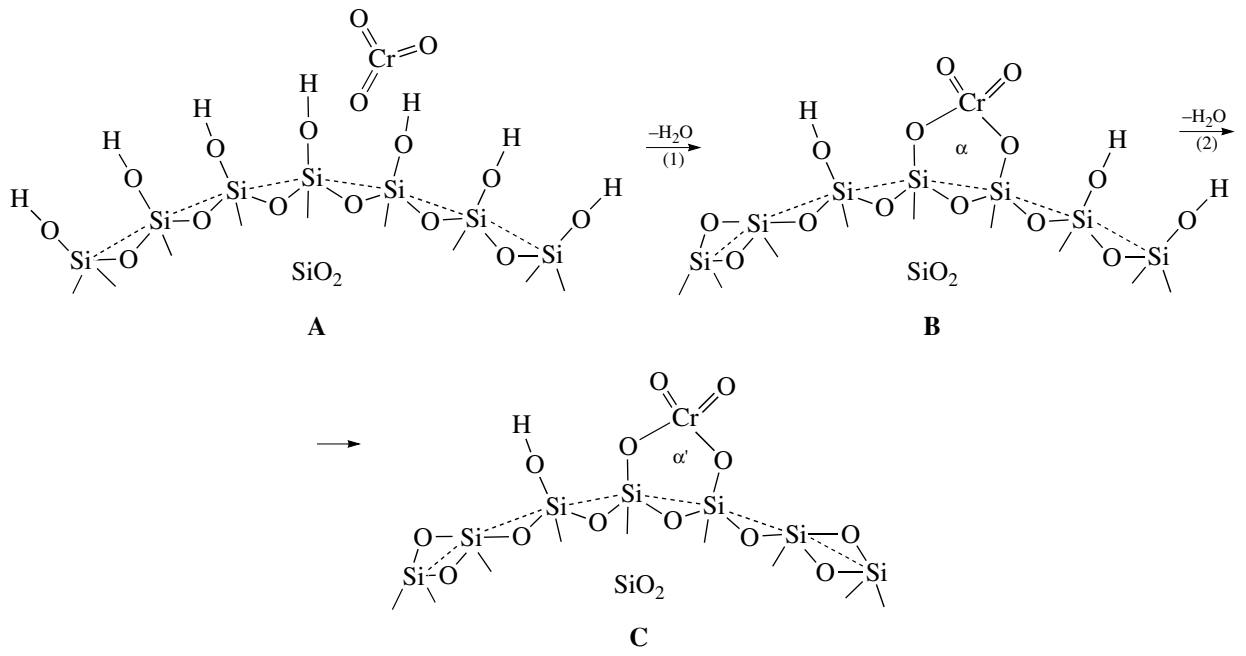
Ethylene activation and polymerization. The S-1 catalyst was activated by ethylene monomer at room temperature (r.t.) for 2 h in a glove box. The activated S-1 catalyst was named S-2. The CO-prereduced PC600/CO catalyst was used for ethylene homo- and copolymerization with hexene-1 in the presence of triethylaluminum (TEA) cocatalyst. The details of polymerization were described in our papers [12, 13]. A simple introduction is shown here. An ampoule bottle with about 100 mg of Phillips catalyst was fixed on the top part of a glass polymerization reactor with a water jacket and a magnetic stirrer inside. Purified heptane solvent and TEA cocatalyst (in the case of copolymerization, purified hexene-1 comonomer was subsequently introduced into the reactor) were added to the reactor under nitrogen atmosphere after system purification by vacuum for 2 h. Ethylene monomer under a pressure of 0.13 MPa was introduced into the polymerization reactor after purification. Polymerization started after breaking the ampoule bottle with catalyst by screwing of a steel bar and was carried out at 60°C for 90 min. An on-line mass flowmeter was used to record the real-time ethylene consumption profile for both homo- and copolymerization. An Ethanol/HCl solution was used as the terminator of polymerization. The obtained polymer was washed and dried under vacuum at 60°C for 6 h.

Characterization of catalysts and polymers. Some modern analytic methods, including X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption mass spectroscopy (TPD-MS), were utilized to investigate the Phillips catalyst. The microstructures of the polymer samples were investigated by ^{13}C NMR. A more precise description about the measurement and spectrum analysis was given in our previous reports [10, 11, 13, 16].

RESULTS AND DISCUSSION

Thermal Activation (Calcination)

In this part of work, the specific surface physicochemical states on Phillips catalysts isothermally calcined at different temperatures have been elucidated by high-resolution XPS spectra. The successive increase in binding energy (BE) values for Cr 2*p*(3/2) level of hexavalent chromium species with increasing calcination temperature from PCP120 to PC800 was plotted in Fig. 1. Compared with the BE of bulky CrO_3 in PCP120, a significant increase of 2.8 eV in the BE value was observed for PC800. A similar tendency toward such a BE increase from bulky CrO_3 to chromate species of calcined Phillips catalysts has also been observed by Thune et al. [17] and Merryfield et al. [18], as well as in our previous report [16]. Such a significant increase in binding energy of Cr species before and after grafting of chromium trioxide on the silica gel surface is considered to originate mainly from the following three factors. Firstly, weak acidity of the silica gel surface creates a stronger electron-extracting effect on the Cr atoms in chromate species of the catalyst than that from the CrO_3 lattice itself [16]. Secondly, successive dehydroxylation of the catalyst surface corresponds to removal of electron-donating hydroxyl ligands for the Cr atoms in chromate species of the catalyst. Thirdly, the increasing surface tension in the surface siloxane groups due to successive dehydroxylation of the catalyst surface may indirectly induce the decrease in electron density of Cr atoms in chromate species of the catalyst [5]. The surface reactions supporting bulky CrO_3 on the silica gel surface (reaction (1)) and successive dehydroxylation of the catalyst surface (reactions (1) and (2)) are shown in Scheme 1. The dominant supporting of bulky CrO_3 on the silica gel surface and simultaneous dehydroxylation of the silica gel surface at a temperature between 120 and 300°C account for the drastic increase in BE values of hexavalent chromate species in this temperature range for isothermal calcination (Fig. 1). The slow increase in BE values of chromate species from 300 to 600°C is solely derived from dehydroxylating residual surface hydroxyl groups (Fig. 1). Another enhancement of the increase in BE values of chromate species from 600 to 800°C can be observed in Fig. 1. This was considered to stem from further dehydroxylation of residual hydroxyl groups, as well as the enhanced surface tension from easier relaxation of surface siloxane groups induced by high temperature [5]. It could be expected that the bond angle α'(O–Cr–O) of chromate species on surface C formed at higher temperature should be larger than α(O–Cr–O) of chromate species on surface B formed at lower temperature as shown in Scheme 1.



Scheme 1. Surface reaction diagram of the dehydration of residual hydroxyl groups, simultaneous formation of surface siloxane bridges, and transformation of bulky CrO_3 into chromate species (using monochromate as an example) during calcination for preparation of Phillips catalyst from PCP120 precursor.

Ethylene Monomer Activation

In this part of work, an industrial Phillips CrO_x/SiO_2 catalyst (S-1) (1 wt % of Cr loading) donated by Japan Polyolefin Co. Ltd. is the same catalyst that we used in our previous study [16]. Another sample (S-2) was prepared from treatment of the catalyst S-1 at room temperature for 2 h in ethylene atmosphere in a glove box. The oxidation states of surface Cr species on catalysts S-1 and S-2 were investigated by the XPS method, and the information on the Cr 2*p*(3/2) core level for S-1 and S-2 corresponding BE and FWHM values were tabulated in Table 1.

According to the assignments in our previous report [16], the surface Cr species in two oxidation states on catalyst S-1 were the surface chromate species in an oxidation state of +6 (expressed as $Cr(VI)O_{x,\,surf}$ with an atomic concentration of 70.4%) with a BE of 581.81 eV and a FWHM of 9.62 eV and the surface-stabilized (i.e., chemically bonded to the silica surface) trivalent Cr species in an oxidation state of +3 (expressed as $Cr(III)O_{x,\,surf}$ with an atomic concentration of about 29.6%) with a BE of 577.21 eV and a FWHM of 4.43 eV, respectively. The $Cr(III)O_{x,\,surf}$ species on S-1 was assumed to be derived from thermal-induced partial reduction of some chromate species in the calcination process during catalyst preparation [16]. After S-1 was treated in ethylene atmosphere at r.t. for 2 h, deconvolution of the spectrum of Cr 2*p* core level of S-2 by multiplet curve fitting revealed the coexistence of three oxidation states. The first Cr species with a Cr 2*p*(3/2)

Table 1. XPS data from multiplet fitting of Cr 2*p* spectra for the Phillips CrO_x/SiO_2 catalyst (S-1) and the ethylene-treated catalyst sample (S-2)*

Sample	Cr 2*p*(3/2)		Atomic percentage**, %	Oxidation state assignment
	BE, eV	FWHM, eV		
S-1	581.81	9.62	70.4	6+
	577.21	4.43	29.6	3+
S-2	580.64	7.75	47.8	6+
	577.00	4.18	39.3	3+
	576.00	3.29	12.9	2+

* XPS measurements were carried out under high resolution acquisition mode within 2 h.
** Percentage of the fitted peak areas of each valence component vs. the whole area of the Cr 2*p* spectrum.

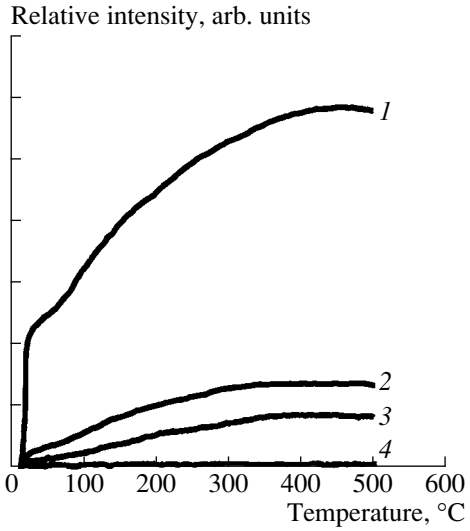


Fig. 2. TPD-MS evolution curves of three new species, including formaldehyde and two new short olefins, from the Phillips catalyst treated in ethylene at ambient conditions for 2 h: (*1*) propene ($m/z = 42$); (*2*) formaldehyde ($m/z = 30$); (*3*) butene ($m/z = 56$); (*4*) pentene ($m/z = 70$). TPD conditions: temperature elevation rate 2 K/min; $RT \sim 500$°C; helium gas flow rate 50 ml/min.

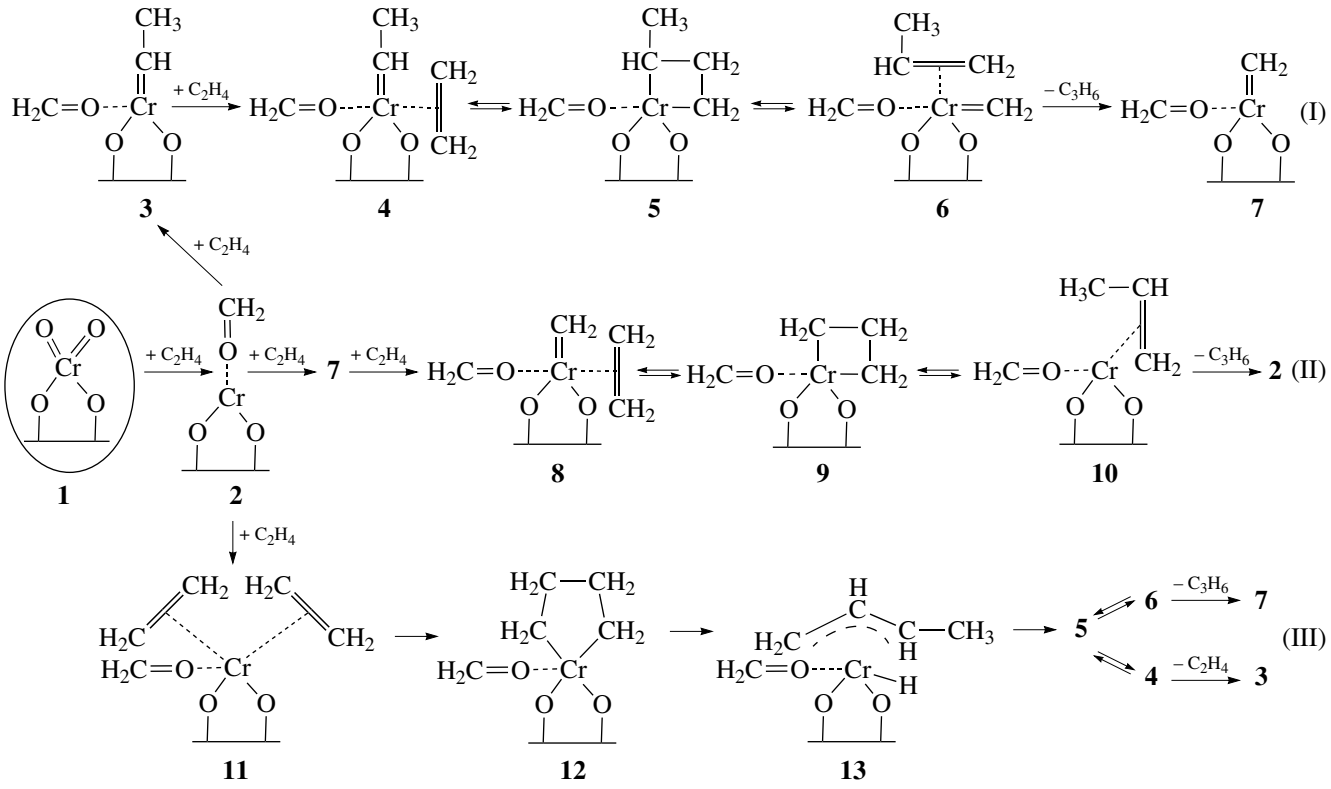
BE of 580.64 eV and FWHM of 7.75 eV (atomic concentration 47.8%) on S-2 can be ascribed to surface chromate $Cr(VI)O_{x,\,surf}$ species [19]. It means that about one-third of the chromate $Cr(VI)O_{x,\,surf}$ species in S-1 was reduced to Cr species in lower oxidation states during the ethylene treatment. The second Cr species with a Cr 2*p*(3/2) BE of 577.00 eV and FWHM of 4.18 eV (atomic concentration 39.3%) on S-2 was assigned to be surface-stabilized trivalent $Cr(III)O_{x,\,surf}$ species, indicating an increase of 9.7% Cr on the whole as $Cr(III)O_{x,\,surf}$ species on S-2 after the ethylene treatment to S-1. The decrease in the Cr 2*p*(3/2) BE value of $Cr(III)O_{x,\,surf}$ species from 577.21 to 577.0 eV after ethylene treatment (from S-1 to S-2) can be rationalized mainly by the fact that the by-product formaldehyde, which was usually generated from the redox reaction between surface chromate species and ethylene [19], might coordinate with the $Cr(III)O_{x,\,surf}$ species and create an electron-donation effect. The third Cr species with a Cr 2*p*(3/2) BE of 576.00 eV and FWHM of 3.29 eV (atomic concentration 12.9%) on S-2 was ascribed to surface-stabilized (chemically bonded to silica surface) divalent chromium species (expressed as $Cr(II)O_{x,\,surf}$, with atomic concentration of 12.9%). Therefore, it seems evident that the redox reaction between the surface chromate $Cr(VI)O_{x,\,surf}$ species and ethylene already occurred during the induction period on the Phillips catalyst under interaction with ethylene at r.t., resulting in the formation of some $Cr(III)O_{x,\,surf}$ and $Cr(II)O_{x,\,surf}$ species.

According to the TPD–MS characterization of the calcined Phillips $Cr(VI)O_x/SiO_2$ catalyst before and after the treatment under ethylene atmosphere at r.t. for 2 h, the evolution of three new species, i.e., propene ($m/z = 42$), butene ($m/z = 56$), and formaldehyde ($m/z = 30$), besides ethylene ($m/z = 28$) was confirmed without detection of any other higher olefins. The TPD–MS desorption spectra of those newly formed species, namely, propene, butene, and formaldehyde, from the ethylene-treated catalyst are shown in Fig. 2.

According to a typical quadrupole mass spectroscopic measurement [20], the formation of a propene fragment ($m/z = 42$) from butene can be completely ruled out. According to the literature [21] and XPS results, ethylene first reduces the hexavalent chromate species into divalent chromium species accompanied by the formation of the by-product formaldehyde. Subsequently, the divalent chromium species coordinatively adsorbed with formaldehyde molecules, which cannot be desorbed under mild conditions, might act as the active precursor to produce the three new short olefins. Judging from the relative ratios of ethylene (56%), propene (32%), and butene (7%) in the desorbed gases from the ethylene-treated catalyst sample, it can be concluded that the first hydrocarbon species formed on the Phillips catalyst during the induction period is propene instead of the expected dimer of ethylene—butene (according to the most generally accepted Cossee–Arlman mechanism). Butene is in fact the second hydrocarbon species formed after propene. This new experimental evidence obtained from the induction period of ethylene polymerization cannot be rationalized well by most of the conventional mechanisms proposed for olefin polymerization up to now. A new initiation mechanism during the induction period, which might be different from that during the normal polymerization period, for the Phillips catalyst has to be taken into consideration.

The conversion of ethylene into higher olefins with both odd and even numbers of carbon atoms is a well-established phenomenon that is believed to proceed by metathesis over metal alkylidene species [22]. This indicates that coordination of formaldehyde on surface-stabilized divalent chromium species results in the formation of a new kind of active precursor for olefin metathesis, rather than a polymerization active precursor. By considering propene as the first hydrocarbon species formed during the induction period, a metathesis initiation mechanism on the $Cr(VI)O_x/SiO_2$ catalyst is proposed in Scheme 2, including the three most plausible routes of the formation of Cr-alkylidene species and the first hydrocarbon species propene.

As a common initial reaction stage within Scheme 1, surface chromate species **1** is reduced by ethylene, resulting in the formation of **2**, which is coordinately adsorbed with a formaldehyde molecule owing to the high coordination unsaturation of surface-stabilized divalent chromium species as well as the mild conditions [16, 21]. The surface-stabilized divalent chromium species is believed to be the final active pre-



Scheme 2. Plausible mechanistic routes of the formation of the first hydrocarbon species propene during the induction period over the non-prereduced Phillips Cr(VI)O_x/SiO_2 catalyst through interaction with ethylene at ambient conditions.

cursor of the Phillips catalyst for ethylene polymerization by most researchers [5, 7]. This indicates that coordination of formaldehyde on the surface-stabilized Cr(II) species results in **2** appearing to be an olefin metathesis precursor, rather than a polymerization active precursor. In the first possible route (I) as shown in Scheme 2, the first coordination of ethylene on **2** with a subsequent 1,2-hydrogen shift leads to a Cr(IV)-ethylidene **3** [23]. Further reaction of the Cr(IV)-ethylidene **3** with ethylene gives rise to a Cr(IV)-methylidene **7** and the first hydrocarbon species propene through a metallacyclobutane **5** [24]. As shown in Scheme 2, the second possible route (II) shows the formation of the Cr(IV)-methylidene **7** through direct splitting of the double bond of ethylene over two neighboring **2** [25], and propene is made through the reductive decomposition of a metallacyclobutane **9** [26]. The simultaneous formation of Cr(IV)-methylidene **7** and Cr(IV)-ethylidene **3** is depicted in the third possible route (III) showing that the π-allyl Cr(II)-hydride species **13**, formed through the metallacyclopentane **12**, is converted into metallacyclobutane **5**. The metallacyclobutane species **5** is subsequently subjected to metathesis, generating either Cr(IV)-methylidene **7** and the first hydrocarbon species propene or Cr(IV)-ethylidene **3** and a new ethylene monomer [27]. The subsequent metathesis of the first hydrocarbon species propene on Cr(IV)-ethylidene **3** and/or Cr(IV)-methylidene **7** in either route will lead to the formation of the second hydrocarbon species butene through similar mechanisms as Scheme 2 during the induction period. Further investigation of the induction period of the Phillips catalyst under various reaction conditions is still in progress in order to completely elucidate which route within routes (I), (II), and (III) is really in function during the induction period.

Another important implication from the new evidence obtained in this work is that a transformation of olefin metathesis active sites into normal polymerization active sites should proceed when the formaldehyde is desorbed from the Cr-alkylidene species at higher temperature accompanied by the start of ethylene polymerization on the Phillips catalyst, which rationalizes well the typical accelerating kinetics for ethylene polymerization over the Phillips catalyst. This speculation is supported by a previous report of the interconversion of catalysis between olefin metathesis and olefin polymerization using various transitional metal catalysts, which still remains a mystery worth exploring further [28].

CO Activation

In this part of the work, the Phillips catalyst, PC600, was reduced by CO at 350°C for 1.5 h, which was

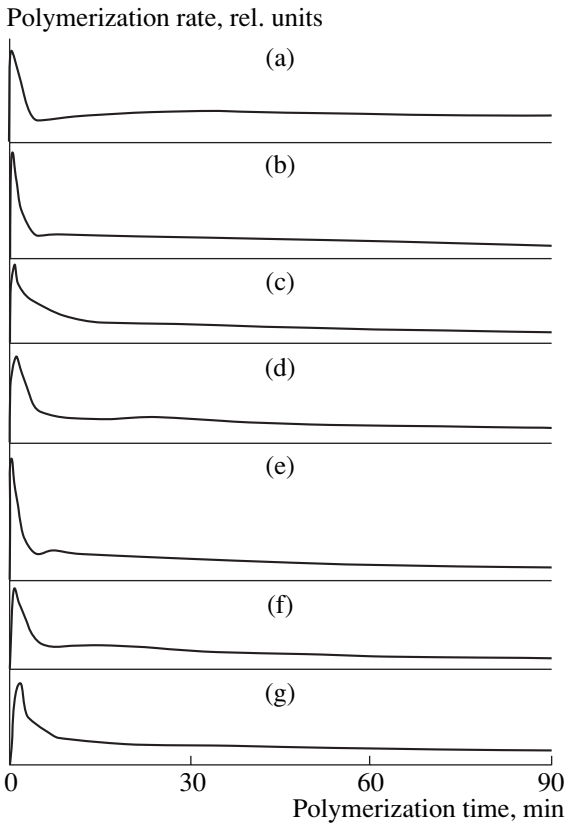


Fig. 3. Kinetics of ethylene homopolymerization with Al/Cr mole ratio of 7.5 (a), 15.0 (b), and 22.5 (c) and ethylene copolymerization under Al/Cr ratio of 7.5 with 10 vol % of hexene-1 (d), Al/Cr ratio of 15.0 with 5 vol % of hexene-1 (e), Al/Cr ratio of 15.0 with 10 vol % of hexene-1 (f), and Al/Cr ratio of 22.5 with 10 vol % of hexene-1 (g). 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).

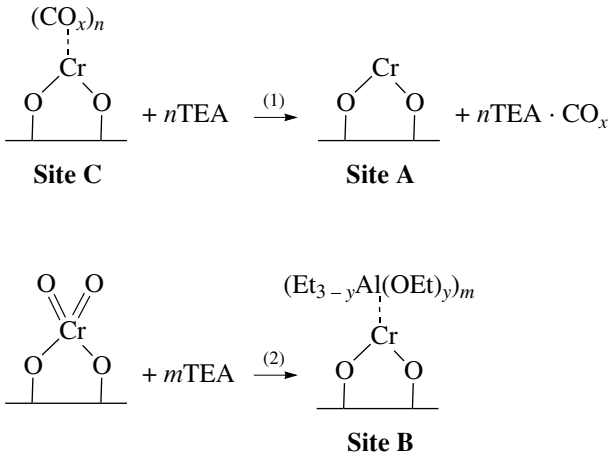
named PC600/CO. The oxidation states of surface Cr species on PC600 (calcined) and PC600/CO (CO-prereduced) catalysts were measured by the XPS method. It was observed that about 97% (atomic percentage) of the surface Cr species is chromate species with a binding energy of 581 eV (Cr 2*p*(3/2)) in the PC600 catalyst. Only about 3% of the surface Cr species was thermally reduced into surface-stabilized Cr(III) species with a BE of 577.6 eV [11]. For the PC600/CO catalyst, about 63% of the surface Cr species was reduced into surface-stabilized Cr(II) species with a BE of 576.6 eV by CO. It was interesting to find that there still existed about 37% of the residual chromate species, which had not been reduced by CO in the PC600/CO catalyst. It was clearly confirmed by TPD-MS results that CO and CO_2 were still strongly adsorbed on the surface Cr(II) species and could not be desorbed even at high temperature (up to 600°C) in the absence of ethylene monomer.

On the basis of this experimental evidence, ethylene homo- and copolymerization with hexene-1 using the PC600/CO catalyst in the presence of an alkyl-Al cocatalyst were carried out. The alkyl-Al cocatalyst was expected to enhance the formation of active sites through fast removal of CO or CO_2 from Cr(II) species and further reduction of residual chromate Cr(VI) species on the PC600/CO catalyst.

It was most interesting and important that quite unique polymerization kinetics was found in both homo- and copolymerization in this study, which has never been reported for the Phillips Cr-based catalysts up to now. As shown in Fig. 3, the real-time polymerization kinetic curves seem to be a hybrid type comprising two basic types of polymerization kinetics: one is a fast formation and fast decay type and the other is a slow formation and slow decay type. According to the surface physicochemical state of the PC600/CO catalyst clarified by XPS and TPD-MS, it is reasonable to ascribe the origins of the two basic types of polymerization kinetics to two different types of active sites produced on PC600/CO by TEA, namely, Cr(II) species after desorption of CO or CO_2 by TEA (Site A in Scheme 3) and Cr(II) species from reduction of residual chromate Cr(VI) species by TEA (Site B in Scheme 3). Site A is very exposed and can be easily deactivated owing to overreduction from further contact with TEA cocatalyst, while Site B might be protected and/or stabilized by the coordination with Al-alkoxyl groups. This is also consistent with previous polymerization kinetics reports relating to organometal-modified Phillips CrO_x/SiO_2 catalysts by McDaniel et al. [29]. The Al-alkoxyl ligands coordinated on Site B were not a poisonous by-product of polymerization as indicated by McDaniel et al. [29].

All obtained homo- and copolymers were characterized through the ^{13}C NMR method. The microstructure of polymer was described by the numbers of carbons of methyl and *n*-butyl branches per 1000 backbone carbons in the main polymer chain, as shown in Table 2.

It was most important and interesting to confirm that a relatively large number of methyl branches were found even in the ethylene homopolymers. According to the previous section about monomer activation, it was found that some short α-olefins, especially propene, could be formed through an ethylene metathesis reaction on a chromium(II) site coordinated with formaldehyde, the by-product from a direct reaction of ethylene with chromate(VI) species. The metathesis site can be converted into the polymerization site by desorption of the coordinated formaldehyde. The propene formed in situ can insert itself into the polymer chain to form methyl branches. Owing to the similar electron properties of CO and CO_2, especially CO, with formaldehyde, the chromium(II) site coordinated with CO or CO_2 might also be a metathesis site (Site C as shown in Scheme 3) that contributed to the formation of some short α-olefins, especially propene. It was clearly



Scheme 3. Plausible mechanism of the formation of two kinds of active sites on the CO-prereduced Phillips catalyst in the presence of TEA cocatalyst for ethylene polymerization (x = 1 or 2; n = 1 or 2; y = 1 or 2; m = 1 or 2).

shown in Table 2 that the relative number of methyl branches is much higher than that of butyl branches even in copolymers with hexene-1 (around 5–14 and 1.2 times for homopolymerization and copolymerization, respectively).

It was obviously demonstrated that the relative number of *n*-butyl branches increased with an increase in the concentration of hexene-1 as shown for the polymers of runs 4 and 6. It was very interesting to notice that the butyl branches were also found in polymers obtained from ethylene homopolymerization, runs 2 and 3. On the basis of our previous explanation in the last section, this could be explained by the fact that the relative amount of polymer obtained from Site A also increased when the concentration of hexene-1 increased, as shown in Table 2. From Fig. 3, it was further demonstrated that the kinetic curves of Site A became broader when the concentration of hexene-1 was increased, which indicated that the existence of hexene-1 might slow the transformation from the metathesis site (Site C) to the polymerization site (Site A). Therefore, it can be rationalized that the relative number of methyl branches increased with an increase in 1-hexene concentration. Therefore, the formation of methyl, butyl, and other SCBs can be rationalized well through an in situ ethylene metathesis reaction on the chromium(II) site coordinated with CO or CO_2 as a newly proposed unique mechanism.

CONCLUSIONS

In this work, our recent new understanding on various activation procedures, including thermal activation, monomer activation, and CO activation, on industrial Phillips catalyst was elucidated. During the thermal activation procedure (an isothermal calcination process), the physicochemical natures of surface chromium species as well as their transformation on the

Table 2. Activities of PC600/CO catalyst in homo- or copolymerization and microstructures of polymers obtained

Run	Al/Cr molar ratio	Hexene-1, vol %	Activity, kg (mol Cr)$^{-1}$ h^{-1}	Methyl branches*	*n*-Butyl branches*	Polymer from Site A, wt %**
1	7.5	0	44.0	–	–	9.7
2	15.0	0	37.5	0.558	0.098	12.3
3	22.5	0	16.4	1.425	0.100	12.9
4	15.0	5	39.5	0.911	0.521	13.4
5	7.5	10	34.5	–	–	12.0
6	15.0	10	36.3	1.200	0.946	13.6
7	22.5	10	26.6	1.629	1.276	13.8

Note: 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), comonomer hexene-1.

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

** Weight percentage of polymer obtained from active Site A was determined by the integral area of the kinetic curve of Site A and Site B after deconvolution.

Phillips catalyst were clarified clearly. The first hydrocarbon species formed in ethylene monomer activation was unexpectedly found to be propene instead of butene. This evidence strongly implied that the initiation in terms of Cr–carbon bond formation on the Phillips catalyst occurs through an ethylene metathesis mechanism during the induction period. The transformation from a metathesis site into a polymerization site is expected. As for CO-activated Phillips catalyst, CO and subsequently formed CO_2 were found to be strongly adsorbed on the Cr(II) site. It was indirectly confirmed by ethylene polymerization in the presence of TEA cocatalyst that the Cr(II) site coordinated with CO or CO_2 is also a metathesis site according to similar electron properties between CO or CO_2 and formaldehyde. The formation of SCBs can be rationalized well by a newly proposed unique mechanism.

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