

New aspects of the induction period of ethene polymerization using Phillips $\text{CrO}_x/\text{SiO}_2$ catalyst probed by XPS, TPD and EPMA

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Abstract

In this work, an industrial Phillips $\text{CrO}_x/\text{SiO}_2$ catalyst engaged in the induction period through interaction with ethene at room temperature (RT) was studied by the combination of surface analytical methods: X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD) and electron probe microanalysis (EPMA). XPS method disclosed the reduction of surface chromate species (expressed as $\text{Cr(VI)O}_{x,\text{surf}}$) into surface-stabilized Cr^{3+} and Cr^{2+} species (expressed as $\text{Cr(III)O}_{x,\text{surf}}$ and $\text{Cr(II)O}_{x,\text{surf}}$, respectively) by monomer during the induction period and the simultaneous formation of two kinds of surface carbon species, namely, formaldehyde and unsaturated hydrocarbons. The hydrocarbon species were supposed to be composed of not only coordinated ethene, but also adsorbed longer olefin chains. TPD measurement confirmed the formation of formaldehyde. EPMA characterization revealed that the surface Cr aggregation occurred in a low extent during the induction period resulting in a few Cr islands in sizes of several microns on catalyst surface. It was demonstrated that reduction and alkylation of Cr species as well as initiation of ethene insertion had already occurred even in the induction period. A mechanism concerning the reactions occurred during the induction period on the Phillips catalyst was proposed. The $\text{Cr(II)O}_{x,\text{surf}}$ species coordinated with one formaldehyde and one ethene is postulated to be the active sites precursor for the alkylation as well as initiation of the ethene insertion. The coordinatively-adsorbed formaldehyde molecules on the catalyst are supposed to be the very reason for the hindered ethene oligomerization rather than normal polymerization, as well as for the induction of the surface Cr aggregation. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Phillips catalyst, which was discovered by Hogan and Banks at Phillips Petroleum Company in the early 1950s, is one of the most important industrial polyolefin catalysts. In the world polyolefin market, it is still producing more than one third of HDPE (ca. 7

million tons per year). The Phillips HDPE products have many unique properties and applications due to the unique polymer chain conformation such as long chain branching (LCB, about one LCB per 10,000 of ethene units) and broad molecular weight distribution (typical polydispersity is between 10 and 30), etc. [1–3]. Unfortunately, after almost half century of research efforts, the main academic aspects concerning this catalyst, e.g. understanding of the state of active sites and polymerization mechanism, etc. still remain ambiguous and controversial [3–11]. Especially, the

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incorporation of the first ethene, i.e. the initiation of the first polymer chain on the active sites, is poorly understood [3,4,7,11].

Phillips catalyst is known to be highly active for ethene polymerization with or without a preliminary activation step using organometallic cocatalysts [12–15] or other reducing agents e.g. CO [16–19] and H₂ [20,21]. In the absence of using any reducing agents, the ethene polymerization on Phillips catalyst at low temperature (ca. <150 °C) usually presents an induction period (also called “dormant period” without measurable activity) [3,4,22,23]. The ethene has to play three important roles namely reduction agent (to reduce the chromate species in an oxidation state of +6 into coordinatively-unsaturated potential active chromium species in a lower oxidation state), alkylation agent (to alkylate the potential active chromium species resulting in the formation of active sites) and propagation agent (to act as monomer for chain propagation on the active sites) simultaneously and/or successively, which might accounts for the presence of the “induction period” for Phillips catalyzed ethene polymerization without using any other reducing agents [3,22]. The lower the polymerization temperature the longer the induction period. When the polymerization temperature goes below ca. 50–60 °C, there is almost no activity whatever how long the catalyst contacts with ethene atmosphere, so to speak the induction period will become infinitely long in this case [3,22]. In whatever cases, which reaction among the reduction, alkylation and propagation actually occurred and whether the incorporation of the first ethene was initiated or not during the induction period are still unclear [3,4,22,23]. The reason is that the induction period has never been specifically studied before (according to our knowledge). In our viewpoint, this period is most probably tightly related with the formation of active sites or even the incorporation of the first ethene on Phillips catalyst. The insufficient understanding of the induction period also hindered the real comprehension of the mechanisms concerning the polymerization process. For example, the reason for explaining the successively increasing of activity during a typical Phillips catalyzed ethene polymerization process in the absence of any reducing agents still remains disputable [3,22–25]. Furthermore, Phillips catalyst engaged in induction period (without using any other reducing agents) is

expected to be the most simple [2] and suitable system for studying the surface species (e.g. Cr, C) by utilizing modern surface science analytical methods with high surface sensitivity and resolution, because encapsulation of the catalytic species on the catalyst surface by polymer layer is not achieved yet within the induction period [3,4,22,23]. Moreover, the reactions, e.g. reduction, alkylation and propagation, if possibly exist during the induction period, would proceed much slowly and thus controllable unlike a normal polymerization process.

X-ray photoelectron spectroscopy (XPS) is a powerful surface science method for measuring the oxidation states of the transition metal on polyolefin catalysts including Phillips catalysts [10,22,26–44], Ziegler–Natta catalysts [45–47] and Metallocene catalysts [48]. As for Phillips catalysts, the binding energy (BE) of the Cr 2p level, which increases with increasing Cr oxidation state and for a certain oxidation state with increasing electronegativity of the surrounding atoms, is frequently used as a criterion for identifying the oxidation state of the surface Cr species [10,22]. On the other hand, the full width at half maximum (FWHM) value of the Cr 2p spectrum reflects the distribution state of the Cr species in its corresponding oxidation state, which also gives valuable information especially for discriminating aggregated and bulky chromium oxide from surface-stabilized and highly dispersed Cr species [43]. By utilizing high-resolution acquisition mode and proper curve fitting method, both qualitative and quantitative information of surface Cr species in mixed oxidation states can be obtained by XPS method [27–30,32,33,40–44]. Electron probe microanalysis (EPMA) method with high resolution makes it possible to directly map the distribution state of the Cr species on an industrial Phillips catalyst with relatively low Cr loading ca. 1 wt.%. In our previous studies, it has been demonstrated that the combination of modern surface science analytical methods, namely, XPS and EPMA is most powerful for basic approaches in investigating the physico-chemical states (including oxidation state and distribution state) of surface Cr species on Phillips catalyst [42,43]. In this work, temperature programmed desorption (TPD), which is suitable for detecting adsorbed species on the catalyst surface, is jointly applied with XPS and EPMA methods to probe the possible reactions in the induction period of the industrial Phillips CrO_x/SiO₂ catalyst

with 1 wt.% Cr under interaction with ethene at room temperature (RT) for 2 h. The great importance and informative characteristics of the induction period for possible further breakthrough in basic and mechanistic understanding of Phillips catalyst are substantiated.

2. Experimental

2.1. Catalyst and treatments

Nitrogen (B-grade, impurity <5 ppm) purchased from Uno Sanso Co. was used directly without further purification. An industrial Phillips $\text{CrO}_x/\text{SiO}_2$ catalyst (S-1) with 1 wt.% of Cr loading (i.e. 0.4 Cr/nm^2), which was donated by Japan Polyolefin Co., Ltd., is the same catalyst as we used in our previous study [43]. Another sample (S-2) was prepared from treatment of the catalyst (S-1) at RT for 2 h in ethene atmosphere in a glove box. A clean and dry agate mortar was used to mill the catalyst sample for promotion of the mixing and interaction between the catalyst and ethene gas. The glove box was preliminarily purged under nitrogen flow overnight before introduction of catalyst sample and ethene gas. Ethene of research grade, which was donated by Mitsubishi Chemical Co., was passed through a 4A molecular sieve (moisture scavenger) column, a Q-5 reactant catalyst (13 wt.% of copper(II) oxide on alumina, oxygen scavenger purchased from Aldrich) column and a 13X molecular sieve (moisture scavenger) column, successively, for further refining before entering the glove box.

2.2. Sample characterization

2.2.1. XPS and EPMA measurements

The specific procedures and instrumental conditions of XPS and EPMA measurements for Phillips catalyst samples were described in detail in our previous report [43]. Just a simplified introduction was given herein as following. XPS data were obtained on a Physical Electronics Perkin-Elmer Model Phi-5600 ESCA spectrometer with monochromated Al $K\alpha$ radiation (1486.6 eV) operated at 300 W. A vacuum transfer vessel (Phi Model 04-110, Perkin-Elmer Co., Ltd.) was used for sample transformation from catalyst storage vessel into the XPS instrument in N_2

atmosphere. Firstly, XPS survey scan was carried out on each sample within 2 min for surface elemental analysis. Then, XPS high resolution scan measurements for Si 2p, Cr 2p, C 1s regions of each sample were performed within 2 h with only negligible X-ray induced reduction to the surface Cr species [30]. All BEs were referenced to the Si 2p peak of silica gel at 103.3 eV to correct for the charging effect during acquisition [36,44]. To pursue precise multiplet fittings of the Cr 2p core level in a mixed oxidation states, some literature data for Phillips catalysts in single “pure” oxidation state were used as references for XPS data analysis [22,36,44]. Multiplet fittings of the Cr 2p XPS curves by the Gaussian–Lorentzian method were carried out to determine the mixed states of valences in all the samples. The fitting for each curve was repeated for several times to ensure a reproducible result. EPMA measurements were carried out on a JEOL JXA-8900L system operated under an accelerating voltage of 20 kV, a probe current of $2 \times 10^{-8} \text{ A}$ and a probe electron beam diameter of $1 \mu\text{m}$. Dispersive crystal of PETJ was used for wavelength dispersive X-ray analysis (WDX). Both map and line analyses of Cr were carried out for characterization of the distribution state of Cr species on the catalyst surface. For characterization of each catalyst sample, the distribution states of Cr on many different catalyst particles of the same sample were carefully observed to get the most typical and reproducible results.

2.2.2. TPD characterization

The TPD characterization of S-2 was carried out on a Multi-task TPD instrument produced by Bel Japan Inc. equipped with a quadrupole mass spectrometer. The experimental arrangements is described as following: open type of atmosphere under dynamic vacuum, fixed bed type of reactor with helium gas flowing through the sample and partial pressure monitoring of the whole desorption process by mass spectrometry. In a typical measuring procedure, helium gas was introduced into a quartz tube microreactor through the sample (ca. 100 mg) for 1 h at RT to remove the physically adsorbed species on the catalyst surface. Consequently, the helium gas flows through the thermal conductivity detector (TCD), MS systems (vacuum ca. $2.5 \times 10^{-8} \text{ Torr}$) and finally vent to the TPD glass vacuum line. Simultaneously, the computer system multicomplexed to the mass spectrometer and furnace

temperature controller-programmer was set-up for initializing all the controlling parameters including helium gas flow rate (50 ml/min), temperature controlling program, sampling time interval (15 s), bridge current (2 mA), number of Q-MS channels in use and corresponding mass numbers (restricted <100 for this MS instrument), etc. In this work, the temperature was ramped at a linear rate of 10 °C/min from RT to 800 °C. The gaseous component with mass number of 30 (formaldehyde) were continuously monitored using the MS. Sample S-1 was also characterized as a background experiment. Sample introduction into the quartz tube microreactor was carried out in a glove bag, which had been purged overnight with nitrogen gas in advance before the TPD characterization.

3. Results and discussion

The main purpose of this study is focused on investigation of the physico-chemical states on the surface of the monomer-treated Phillips catalyst (S-2) engaged in an induction period through interaction with ethene atmosphere at RT within 2 h. The physico-chemical states including oxidation state and distribution state of surface Cr species on the original industrial Phillips $\text{CrO}_x/\text{SiO}_2$ catalyst (S-1) in calcined form had been

demonstrated in our recent report in detail [43] and will not be discussed specifically here again, whereas a comparison of the surface physico-chemical states between S-2 and S-1 will be necessary for facilitating the judgment on what's really going on within the induction period of Phillips catalyst on S-2: reduction, alkylation, initiation and/or propagation?

XPS survey scans were performed on the Phillips $\text{CrO}_x/\text{SiO}_2$ catalyst (S-1) and the ethene-treated catalyst sample (S-2) for the purpose of a preliminary surface elemental analysis [45]. The XPS survey scan measurement for each spectrum of each sample was carried out under survey acquisition mode between 0 and 1000 eV within 2 min. The survey spectra of S-1 and S-2 are shown in Fig. 1. The constituent atoms (Si, O, C, Cr) of S-1 and S-2 were observed to exist on XPS measurable surface, approximately 2 nm in sampling depth corresponding to the XPS surface sensitivity restricted by the typical mean photoelectron escape depth of ca. 2 nm [33,45]. The weak Cr 2p peaks in both spectra are reasonable due to the low Cr loading ca. 1 wt.% as well as the short time of XPS scanning at the low-resolution survey acquisition mode [44]. The most important information demonstrated in Fig. 1 is the evolution of a relatively strong C 1s peak on the ethene-treated catalyst sample S-2 compared with the original catalyst S-1. This is a clear

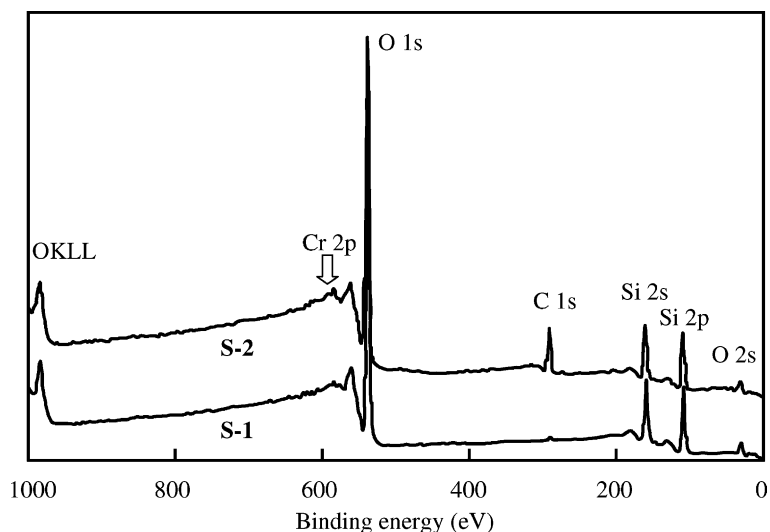


Fig. 1. XPS spectra of survey scan for the Phillips $\text{CrO}_x/\text{SiO}_2$ catalyst (S-1) and the ethene-treated catalyst sample (S-2); XPS measurements were carried out under survey acquisition mode within 2 min.

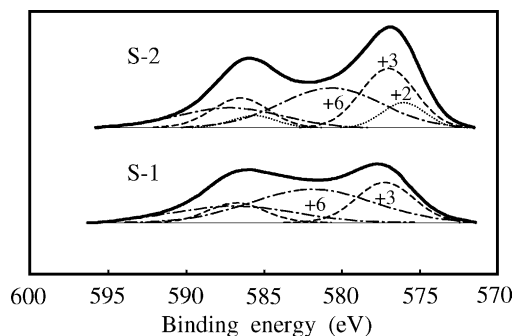


Fig. 2. XPS spectra of Cr 2p level for the Phillips $\text{CrO}_x/\text{SiO}_2$ catalyst (S-1) and the ethene-treated catalyst sample (S-2); XPS measurements were carried out under high resolution acquisition mode within 2 h.

indication of the formation of some surface carbon species on S-2 after the ethene treatment. The surface carbon species might be coordinatively-adsorbed ethene and/or newly-formed carbon species derived from some possible reactions between the catalyst and monomer within the induction period. Further analyses to the surface Cr and carbon species at high resolution XPS acquisition mode are needed for the elucidation of whether any surface reactions occurred resulting in the formation of some new surface carbon species or just ethene coordinatively-adsorbed on S-2 surface.

To investigate the states of the surface chromium and carbon species in detail, XPS narrow scans of the Cr 2p and C 1s regions were performed for 2 h under high-resolution acquisition mode for each sample. Fig. 2 shows the XPS spectra of Cr 2p core level for the Phillips $\text{CrO}_x/\text{SiO}_2$ catalyst S-1 and the ethene-treated sample S-2. The Cr 2p core level of

chromium species in a single oxidation state usually presents as a doublet with two peaks due to the 2p (3/2) and 2p (1/2) photoelectrons, respectively, from the Cr atoms existing on Phillips Cr-based catalysts [22,36,44]. A single doublet fitting for both spectra was found to be impossible for getting a perfect curve fitting indicating that a mixed oxidation states existed in both samples. Multiplet fittings were applied and the corresponding BE and FWHM values of Cr 2p(3/2) core level for S-1 and S-2 were tabulated in Table 1. According to the assignments in our previous report [43], 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 $\text{Cr(VI)O}_{x,\text{surf}}$ 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 $\text{Cr(III)O}_{x,\text{surf}}$ with an atomic concentration of ca. 29.6%) with a BE of 577.21 eV and a FWHM of 4.43 eV, respectively. The $\text{Cr(III)O}_{x,\text{surf}}$ species on S-1 has been supposed to be derived from thermal-induced partial reduction of some chromate species in the calcination process during catalyst preparation [43]. After S-1 was treated in ethene atmosphere at RT for 2 h, it can be seen in Fig. 2 that the shifting of Cr 2p peak to lower BE as well as the relatively increasing of peak intensity in the lower BE region of the Cr 2p core level for S-2 indicating the reduction of surface Cr species by ethene. Deconvolution of the spectrum of Cr 2p core level of S-2 by multiplet curve fitting revealed the coexistence of three oxidation states, namely, the first with a Cr 2p (3/2) BE of 580.64 eV and FWHM of 7.75 eV (atomic concentration 47.8%), the second with a Cr 2p (3/2) BE

Table 1
XPS data from multiplet fitting of Cr 2p spectra for the Phillips $\text{CrO}_x/\text{SiO}_2$ catalyst (S-1) and the ethene-treated catalyst sample (S-2)^a

Sample	Cr 2p (3/2)		Atomic percentage ^b (%)	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

^a XPS measurements were carried out under high resolution acquisition mode within 2 h.

^b Percentage of the fitted peak areas of each valence component vs. the whole area of the Cr 2p spectrum.

of 577.00 eV and FWHM of 4.18 eV (atomic concentration 39.3%) and the third with a Cr 2p (3/2) BE of 576.00 eV and FWHM of 3.29 eV (atomic concentration 12.9%) (shown in Table 1). The first Cr species with the highest Cr 2p (3/2) BE on S-2 can be ascribed to surface chromate $\text{Cr(VI)O}_{x,\text{surf}}$ species [22,36,43,44]. It means about one-third of chromate $\text{Cr(VI)O}_{x,\text{surf}}$ species (i.e. ca. 22.6% of the whole surface Cr) in S-1 was reduced to Cr species in lower oxidation states during the ethene treatment. The Cr 2p (3/2) BE of surface chromate $\text{Cr(VI)O}_{x,\text{surf}}$ species (including monochromate, dichromate and sometimes polychromate species chemically bonded on the support surface) has been reported to be possibly situated in a range between 580 and 582 eV depending on the support types, sample preparation and modification conditions, etc. [22,36,41,43,44]. The decreasing of the Cr 2p (3/2) BE value of $\text{Cr(VI)O}_{x,\text{surf}}$ species from 581.81 to 580.64 eV accompanied with decreasing of FWHM from 9.62 to 7.75 eV after ethene treatment (from S-1 to S-2) may be an indication of the preferential reduction of some specific $\text{Cr(VI)O}_{x,\text{surf}}$ species with the highest BE (corresponding to the lowest electron density and, thus, highest reduction-potential) on the silica surface during the ethene treatment, while the effect from the simultaneous variation of its neighborhood surrounding (e.g. the second and third surface Cr species with lower BE and, thus, lower oxidation states might contribute somewhat electronic effect) also can not be ruled out. Similar phenomenon in less extent has also been observed when the Phillips catalyst in calcined form suffered from thermal-induced reduction of surface chromate species during the calcination process [43]. The second Cr species with the second highest Cr 2p (3/2) BE (Cr 2p (3/2) BE = 577.00 eV and FWHM = 4.18 eV) on S-2 was assigned to be surface-stabilized trivalent $\text{Cr(III)O}_{x,\text{surf}}$ species (Cr(III) atomic concentration 39.3%) indicating an increase of 9.7% Cr in the whole as $\text{Cr(III)O}_{x,\text{surf}}$ species on S-2 after the ethene treatment to S-1. The decreasing of the Cr 2p (3/2) BE value of $\text{Cr(III)O}_{x,\text{surf}}$ species from 577.21 to 577.0 eV after ethene treatment (from S-1 to S-2) can be rationalized mainly by the following two points. The first one is that the by-product formaldehyde, which was usually generated from the redox reaction between surface chromate species and ethene as reported by Baker and

Carrick [49], might coordinate with the $\text{Cr(III)O}_{x,\text{surf}}$ species and create electron-donation effect. The second reason might be the slight aggregation of surface Cr species induced by the ethene treatment, which will be discussed in the latter section. The aggregation may also account for the slight decrease of FWHM value from 4.43 eV (for S-1) to 4.14 eV (for S-2) [43]. The third Cr species with the lowest Cr 2p (3/2) BE (Cr 2p (3/2) BE = 576.00 eV and FWHM = 3.29 eV) on S-2 was ascribed to surface-stabilized (chemically bonded to silica surface) divalent chromium species (expressed as $\text{Cr(II)O}_{x,\text{surf}}$ with atomic concentration of 12.9%). This assignment is supported by the report of McDaniel and coworkers [22], who prepared a standard surface-stabilized $\text{Cr(II)O}_x/\text{SiO}_2$ catalyst (using a $\text{Cr(VI)O}_x/\text{SiO}_2$ catalyst prepared by calcination in dry oxygen at 600–900 °C for 2–5 h and subsequently reduced by dry CO treatment at 350 °C for 30–60 min) with a BE value of 576.6 eV and a FWHM value of 5 eV for the Cr 2p (3/2) level. The possible coordinative adsorption of the redox by-product formaldehyde on the highly coordinatively-unsaturated $\text{Cr(II)O}_{x,\text{surf}}$ species might lead to electron donation and thus lower the BE value (576.0 eV) in our case. The lower FWHM value (3.29 eV) indicates the narrower distribution state of our $\text{Cr(II)O}_{x,\text{surf}}$ species compared with theirs (5 eV). Weckhuysen et al. reported the same Cr 2p (3/2) BE value at 576.0 eV for the divalent Cr species supported on inorganic oxides [10]. Gazzoli et al. identified a divalent Cr species with a BE of 576.0 ± 0.2 eV on a CO-reduced $\text{CrO}_x/\text{ZrO}_2$ catalyst [32]. So far, it seems evident that the redox reaction between the surface chromate $\text{Cr(VI)O}_{x,\text{surf}}$ species and ethene already occurred during the induction period on the Phillips catalyst under interaction with ethene at RT resulting in the formation of some $\text{Cr(III)O}_{x,\text{surf}}$ and $\text{Cr(II)O}_{x,\text{surf}}$ species. Baker and Carrick studied the redox reaction between bistrisphenylsilyl chromate and various olefins and also found the simultaneous formation of divalent and trivalent chromium esters [50]. They suggested a mechanism that chromate species was first reduced to divalent species and subsequently some divalent species reacted with unconverted chromate species to form some more stable trivalent species. A similar mechanism (as shown in Eqs. (1) and (2)) was postulated here to explain the simultaneous formation of $\text{Cr(III)O}_{x,\text{surf}}$ and $\text{Cr(II)O}_{x,\text{surf}}$ species through

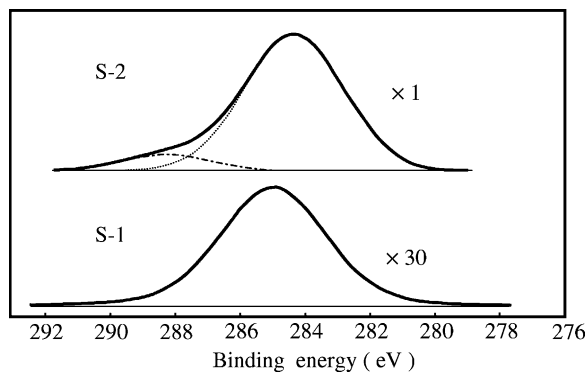


Fig. 3. XPS spectra of C 1s level for the Phillips $\text{CrO}_x/\text{SiO}_2$ Catalyst (S-1) and ethene-treated catalyst sample (S-2) (the relative intensity of spectrum of S-1 has been amplified ca. 30 times); XPS measurements were carried out under high resolution acquisition mode within 2 h.

reduction of chromate $\text{Cr(VI)O}_{x,\text{surf}}$ species by ethene.

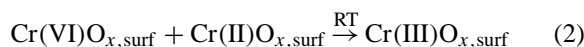
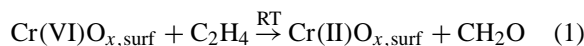


Fig. 3 shows the XPS spectra of C 1s core level (obtained under high-resolution acquisition mode for 2 h) for the Phillips $\text{CrO}_x/\text{SiO}_2$ catalyst S-1 and the ethene-treated sample S-2 (the relative intensity of C 1s spectrum of S-1 has been amplified ca. 30 times in Fig. 3, which can also be approximately judged from the C 1s peaks shown in Fig. 1). The corresponding XPS data from curve fitting of C 1s spectra were illustrated in Table 2. One carbon species with a BE of 284.98 eV, a FWHM of 3.80 eV and a relative peak intensity of 2.6 (referenced to Si 2p peak: intensity of Si 2p peak = 100) was identified on the original Phillips catalyst S-1, and it was known to be traces of carbon

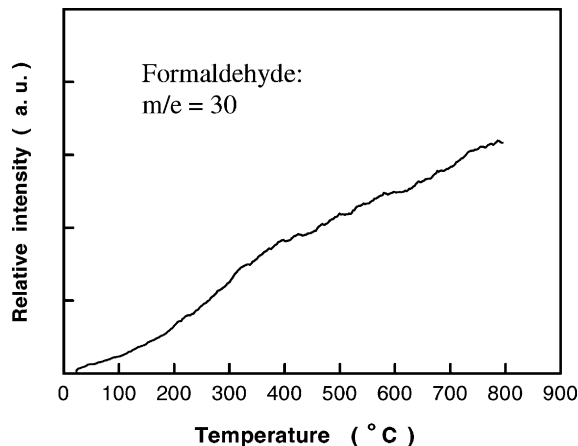


Fig. 4. TPD-MS formaldehyde ($m/e = 30$) evolution curve of the ethene-treated Phillips $\text{CrO}_x/\text{SiO}_2$ catalyst sample (S-2). TPD conditions: temperature elevation rate: $10^\circ\text{C}/\text{min}$, RT $\sim 800^\circ\text{C}$, helium gas flow rate: 50 ml/min.

contamination, which was frequently used as standard reference peak for charge correction during XPS characterization [28,29]. For the ethene-treated sample S-2, two surface carbon species were found with a total relative intensity of 78.5 (referenced to Si 2p peak: intensity of Si 2p peak = 100). The first carbon species on S-2 with a BE of 288.22 eV, a FWHM of 3.10 eV and a carbon atomic percentage of ca. 9% was supposed to be coordinatively-adsorbed formaldehyde i.e. the by-product originated from the redox reaction between the chromate species and ethene (as shown in Eq. (1)) [49,51]. This assignment was further confirmed by the evidence from the TPD characterization of S-2, i.e. the evolution of formaldehyde from S-2 as shown in Fig. 4. A significantly broad distribution state of surface Cr species on S-2 was reflected from the TPD evolution curve of formaldehyde.

Table 2

XPS data from curve fitting of C 1s spectra for the Phillips $\text{CrO}_x/\text{SiO}_2$ catalyst (S-1) and ethene-treated catalyst sample (S-2)^a

Sample	C 1s		Atomic percentage ^b	Carbon species assignment	Relative peak intensity ^c
	BE (eV)	EWHM (eV)			
S-1	284.98	3.80	100	Contamination	2.6
S-2	288.22	3.10	9.0	Formaldehyde	78.5
	284.34	3.61	91.0	Unsaturated hydrocarbons	

^a XPS measurements were carried out under high resolution acquisition mode within 2 h.

^b Percentage of the fitted peak areas of each valence component vs. the whole area of the Cr 2p spectrum.

^c Relative intensity referenced to Si 2p peak (intensity of Si 2p peak = 100).

The second carbon species on S-2 with a BE of 284.34 eV, a FWHM of 3.61 eV and a carbon atomic percentage of ca. 91% was envisioned to be coordinatively-adsorbed ethene and/or higher unsaturated hydrocarbons, which is compatible with BE values in the typical range of 284–285 eV observed for unsaturated hydrocarbons adsorbed on metal [52–54] and oxide [35,55] surfaces. The BE of C 1s of polyethene is usually >284.34 eV and situates at ca. 285–286 eV [51]. This demonstrated that the formation of long polymer chain on S-2 did not occur yet, whereas the presence of some short olefins possibly formed through ethene oligomerization can not be excluded. As it is generally accepted that chain transfer proceeds through β -hydrogen elimination on Phillips catalysts resulting in a double bond at one chain end of each polymer chain [3,56], short olefins would be expected when only ethene oligomerization occurs on Phillips catalyst. In order to confirm that whether the second surface carbon species (assigned as unsaturated hydrocarbons) is only coordinatively-adsorbed ethene or coordinatively-adsorbed ethene together with higher olefin species, an approximate and simple calculation was carried out as following. For simplification, firstly we supposed that the $\text{Cr(III)O}_{x,\text{surf}}$ species (with an atomic percentage of 39.3% corresponding to 0.16 Cr/nm^2) on S-2 owns the same number of coordination sites with $\text{Cr(II)O}_{x,\text{surf}}$ species (with an atomic percentage of 12.9% on S-2 corresponding to 0.052 Cr/nm^2) and all the coordination sites of these $\text{Cr(II)O}_{x,\text{surf}}$ and $\text{Cr(III)O}_{x,\text{surf}}$ species are available for monomer coordination (the carbon atoms from the adsorbed formaldehyde are also omitted). Under these assumptions, much more adsorbed monomer and thus much higher surface carbon concentration would be expected than the real case on S-2. One $\text{Cr(II)O}_{x,\text{surf}}$ site usually possesses maximum three coordination sites [3,18,56,57]. So a maximum surface concentration of carbon atoms through solely adsorbed ethene would be 1.272 C/nm^2 . Under the condition of 0.4 Cr/nm^2 contributing to a relative intensity of XPS Cr 2p spectrum of 3.8 [43], 1.272 C/nm^2 of surface concentration of carbon atoms through adsorbed ethene on S-2 might only be able to create a XPS C 1s peak with a relative intensity at ca. 13. This is by far less than the real relative intensity of XPS C 1s peak of 78.5 on S-2, which suggests that the second surface carbon species assigned as

unsaturated hydrocarbons should be composed of not only coordinatively-adsorbed ethene, but also newly-formed longer olefin species. Based on the above calculation, it was made clear that olefins longer than ethene monomer should have been formed possibly through ethene oligomerization (normal polymerization, i.e. the formation of polyethene has been excluded previously by the XPS evidence) and consequently adsorbed on S-2 accounting for the significantly high relative intensity of XPS C 1s spectrum. That is to say the alkylation of the potential active Cr species (corresponding to the formation of active sites after the reduction step) as well as the initiation of the insertion of the first ethene monomer had already occurred even during the induction period of Phillips catalyst under interaction with ethene atmosphere at RT. Most probably the coordinatively-adsorbed formaldehyde molecules on the active sites, which can not be desorbed under the mild conditions, hindered the formation of long polymer chains and solely permitted ethene oligomerization.

According to our previous report [43], the Cr species mostly dispersed uniformly on the surface of each catalyst particle of the original Phillips catalyst S-1 accompanied with the existence of a few local aggregates of Cr species in sizes of 200–300 nm on the surface of the catalyst, the latter were supposed to be aggregates of Cr_2O_3 formed through cleavage of $\text{Cr(III)O}_{x,\text{surf}}$ species during the calcination by traces of moisture from the simultaneous dehydroxylation of residual hydroxyl groups on silica surface [43]. As for the ethene-treated catalyst sample S-2, Fig. 5 shows its typical results of EPMA map and line curves of the Cr distribution. It is evident that the ethene-treatment induced somewhat small extent of surface chromium agglomeration to form a few larger aggregation areas in sizes of several microns on the catalyst surface which are corresponding to the red patches (marked in circles) in the map image and broad weak peak in the line curves in Fig. 5a and b, respectively (the sharp peak and small red dots in Fig. 5 are Cr aggregates formed during the calcination process from preparation of the original catalyst S-1). The EPMA results in this work implied that the reactions occurred during the induction period most probably induced the surface aggregation of chromium species in some extent. The surface Cr aggregation (usually indicating Cr_2O_3 in micro-crystallized form), which was thought

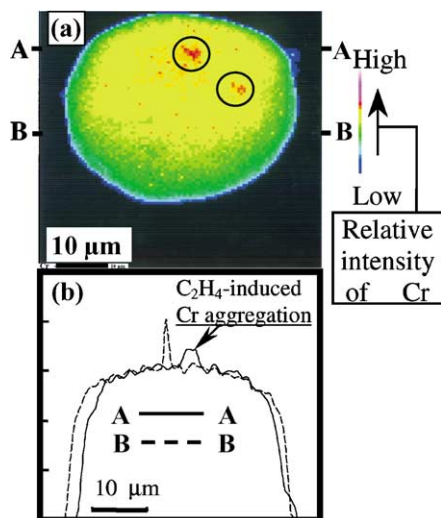
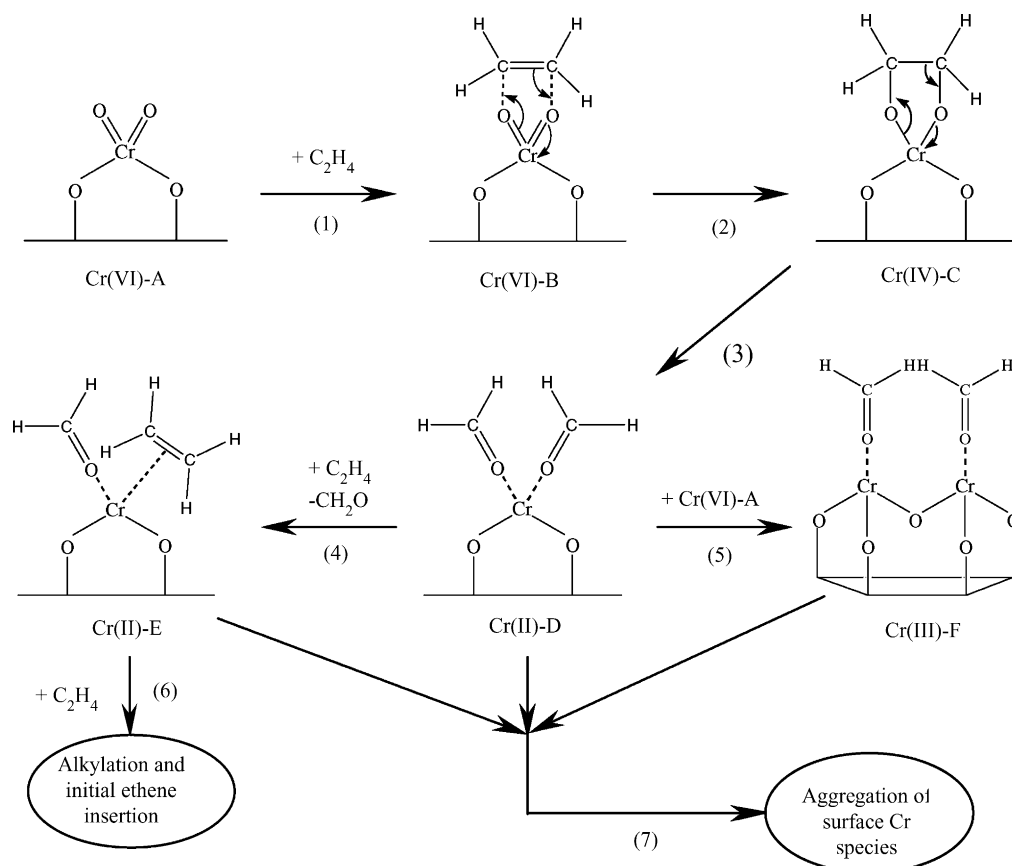


Fig. 5. EPMA map (a) and line curves (b) of the Cr distribution on the ethene-treated catalyst sample (S-2). The line curves of A—A and B---B in part (b) are corresponding to the Cr distribution at the straight-line positions of A—A and B—B in part (a), respectively.

to deactivate the catalyst for ethene polymerization, had been frequently reported to occur during the catalyst preparation (calcination) [3,28,30,43,56,58–61], CO- [16–18,20] and H₂-reduction [20,21], or even possibly during the catalytic polymerization process as suggested by Groeneveld et al. [20] and Józwiak and Lana [59]. Whereas the mechanism aspects were still not comprehensive. In this work, the aggregation of surface chromium species might be closely related to the redox process between the monomer and the surface chromate species. The by-product formaldehyde of this redox reaction strongly coordinated on the catalyst surface may play the most important role. The subsequent ethene alkylation and insertion reactions may also create some promotion effect to the interaction between the formaldehyde and surface Cr species. Further studies are necessary to establish a possible mechanism envision on the chromium aggregation phenomenon during the induction period on Phillips catalyst.

So far, a plausible reaction mechanism during the induction period of the Phillips CrO_x/SiO₂ catalyst under interaction with ethene at RT can be depicted as following (including seven reactions (1)–(7) as shown in Scheme 1). After contact with ethene, chromate species Cr(VI)-A was coordinated by ethene to

get an intermediate Cr(VI)-B species (reaction (1)), subsequently Cr(VI)-B species is reduced to another intermediate Cr(IV)-C species (reaction (2)), finally, Cr(IV)-C species is further reduced to Cr(II)-D species (reaction (3)) [49]. The Cr(II)-D species is one of the final reduction products Cr(II)O_{x,surf} species strongly coordinated with two formaldehyde molecules due to the high coordinative unsaturation of the Cr(II)O_{x,surf} species as well as the mild reaction conditions implemented in this study. The Cr(II)-D species is also possible to react with chromate species Cr(VI)-A in its neighborhood to give the trivalent Cr(III)-F species (reaction (5)) [50]. The latter is also one of the final reduction products Cr(III)O_{x,surf} species coordinated with formaldehyde molecules which have been identified by XPS characterization. The Cr(II)-D species is impossible to be an active site unless at least one of its adsorbed formaldehyde can be substituted by an ethene molecule forming Cr(II)-E species (reaction (4)). The Cr(II)-E species coordinated with one formaldehyde and one ethene still with one more vacancy available for the growing chain is supposed to be the active site precursor for the subsequent alkylation as well as initiation of the first ethene insertion (reaction (6)) [3–9,11,19,22]. The coordinatively-adsorbed formaldehyde molecule on the active site is the very reason for the possible ethene oligomerization (the formation of short olefin chains) rather than normal polymerization. Those surface Cr species coordinated with formaldehyde including Cr(II)-D, Cr(II)-E and Cr(III)-F are possibly subject to Cr aggregation most probably involved in the reactions during the induction period on Phillips catalyst under an ambiguous mechanism (reaction (7)) [20]. The formation of olefin chains longer than ethene during the induction period was further firmly confirmed by our recent systematic characterization of the hydrocarbon species formed on the Phillips catalyst engaged in induction period under interaction with ethene atmosphere at RT. The results supporting a unique mechanism concerning the alkylation and first ethene insertion during the induction period on Phillips-type catalyst will be reported in a forthcoming publication soon [62]. The ultimate objective is to elucidate the most complicated mechanisms concerning active sites formation and polymerization through directly and successfully catching the first hydrocarbon chains formed on the active sites, i.e. the most important fingerprint of the active sites



Scheme 1. Plausible mechanism of reactions occurred on the Phillips CrO_x/SiO_2 catalyst engaged in the induction period through interaction with ethene atmosphere at room temperature.

of Phillips catalyst [3,11] formed during the induction period, which had been preliminarily demonstrated from the new evidence disclosed in this study.

4. Conclusion

It was made clear that surface chromate $Cr(VI)-O_{x,surf}$ species on an industrial Phillips catalyst was partially reduced into $Cr(III)O_{x,surf}$ and $Cr(II)O_{x,surf}$ species during the induction period through interaction with ethene at RT for 2 h. The simultaneous formation of two kinds of carbon species namely formaldehyde and unsaturated hydrocarbon species was also observed. The unsaturated hydrocarbon species was supposed to be composed of not only coordinated

ethene, but also adsorbed longer olefin chains. TPD method confirmed the formation of formaldehyde during the induction period. EPMA characterization revealed that surface Cr aggregation occurred in a low extent during the induction period resulting in a few Cr islands in sizes of several microns on catalyst surface. In summary, the new evidence disclosed in this work demonstrated that not only reduction but also alkylation as well as initiation of the first ethene insertion probably through oligomerization had already occurred even in the induction period. A mechanism concerning the reactions occurred during the induction period on the Phillips catalyst at RT was proposed. The $Cr(II)O_{x,surf}$ species coordinated with one formaldehyde and one ethene is supposed to be the active site precursor for the alkylation as well as

subsequent initiation of the first ethene insertion. The coordinatively-adsorbed formaldehyde molecules on the active sites are considered to be the very reason for the possible hindered ethene oligomerization rather than normal polymerization. Those surface Cr species coordinated with formaldehyde including Cr(II)-D, Cr(II)-E and Cr(III)-F (in Scheme 1) are possibly subject to Cr aggregation which was most probably induced by the reactions related with formaldehyde during the induction period on the Phillips catalyst under an ambiguous mechanism.

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