High resolution X-ray photoelectron spectroscopic analysis of transformation of surface chromium species on Phillips CrO_x/SiO_2 catalysts isothermally calcined at various temperatures

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Abstract

Phillips CrO_x/SiO_2 catalyst is still producing several million tons of polyethylene each year. However, insufficient understanding of the surface chemistry of this important industrial catalyst hindered its further development. In this work, surface analytical approach on transformation of chromium(III) acetate into supported chromate species ($Cr(VI)O_{x,surf}$) of Phillips CrO_x/SiO_2 catalysts isothermally calcined at various temperatures was carried out by high resolution XPS method. High resolution XPS characterizations have elucidated the specific transformation process of chromium(III) acetate into bulky CrO_3 and subsequently into $Cr(VI)O_{x,surf}$ as a function of calcination temperature between 120 and 800 °C. The specific surface components in various catalyst samples versus calcination temperature were clarified. It was evident that chromium(III) acetate could be very easily oxidized and decomposed into bulky CrO_3 during 120 °C isothermal drying process. The bulky CrO_3 started to be transformed into supported chromate species at 200 °C and could be completely stabilized on silica gel surface as chromate species at 400 °C. Significant amount of bulky pentavalent Cr oxide (Cr_2O_5 or $(Cr_2O_7)^{4-}$) due to partial thermal decomposition of bulky CrO_3 was only observed on 200 °C-calcined sample due to the incomplete stabilization of bulky CrO_3 into chromate species at 200 °C. As the precursor of active site on calcined Phillips catalyst, the chromate species ($Cr(VI)O_{x,surf}$) was found to be gradually becoming more and more electron-deficient with increasing calcination temperature of the catalyst from 200 to 800 °C. Only a slight thermal-induced partial reduction of chromate species into $Cr(III)O_{x,surf}$ was observed at high temperature (600–800 °C).
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1. Introduction

Phillips CrO_x/SiO_2 catalyst is still extracting both academic and industrial interests due to its great importance in the field of industrial polyolefin production [1–10]. With its unique product properties, the catalyst is still quite competitive against Ziegler–Natta and metallocene catalysts in some application areas like blow molding HDPE products [11,12]. Further improvements of this catalyst are in high demand in the industrial field but still remained as a challenging work due to poor mechanistic understanding of it even after 50 years of great research efforts in this field [13–17]. A clearer understanding of the physico-chemical states of surface Cr

species on Phillips catalyst is expected to play an important role for further mechanistic exploration [15,17].

After impregnation of aqueous solution of Cr compounds (usually hexavalent: chromium(VI) trioxide) onto mesoporous and amorphous silica gel support (SiO_2), Phillips catalyst can be easily prepared through a very simple isothermal calcination process in dry air at temperature usually around 600–800 °C for several hours [15]. During the calcination process, the bulky chromium(VI) trioxide can be gradually grafted covalently onto silica gel surface through esterification reaction with surface hydroxyl groups [15]. A successive dehydration of residual surface hydroxyl groups will keep going on up to the end of calcination after a complete supporting of all the bulky CrO_3 [15]. At high temperature, those surface-stabilized chromate species ($Cr(VI)O_{x,surf}$) might partially be thermally reduced into surface-stabilized trivalent Cr species (defined as $Cr(III)O_{x,surf}$) or even the

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latter might be subsequently transferred into aggregated bulky Cr_2O_3 microcrystals by traces of moisture in the gas media of calcination [8]. In some circumstances, those trivalent Cr species might be re-oxidized and re-stabilized into chromate species ($Cr(VI)O_{x,surf}$) [18]. Usually, a highly dispersed state of surface-stabilized chromate species (i.e. monochromate and dichromate, sometimes even polychromate defined as $Cr(VI)O_{x,surf}$) can be achieved through many re-dispersing cycles of sublimation, volatilization, spreading, deposition and stabilization of bulk CrO_3 (mp 196 °C and bp 250 °C) on the silica support surface during calcination [16,17]. A pre-reduction of the hexavalent chromate species ($Cr(VI)O_{x,surf}$) either by monomer ethylene, CO or alkyl-Al cocatalyts will result in the formation of the final active site precursor, i.e. a surface-stabilized divalent Cr species ($Cr(II)O_{x,surf}$) before the start of ethylene polymerization [3,4,19]. Therefore, different nature of the hexavalent chromate species including its local surface environment will lead to different catalytic properties of the calcined catalyst. Thus the polymerization performance and properties of the resulting polymer from the final calcined catalyst drastically depend on the calcination conditions including the starting Cr compounds, additional Ti- or Al-promoter, temperature and calcination time, etc. [15]. A gradual increasing of polymerization activity associated with gradual decreasing of molecular weight of the polymer with increasing of calcination temperature or time for preparation of the catalyst was usually observed before catalyst sintering occurred at certain high temperature (in usual case around 900 °C), whereas, a good correlation of these polymerization behaviors and characteristics of the polymers with the physico-chemical states of surface Cr species on Phillips catalyst in terms of calcination conditions has not been established yet [15,17]. The difficulties mainly come from the fact that only small fraction of surface Cr species could be active for ethylene polymerization as well as insufficient knowledge concerning the physico-chemical states of surface Cr species on Phillips catalyst with respect to calcination conditions [15,17].

In the literature, numerous modern analytical methods including XRD [18–20], EPR [21], SIMS [22], Raman [23,24], UV-Vis DRS [25], EXAFS-XANES [26], PIXE [27], TPR [28], TPD [9,10], SEM/EDS [29], EPMA [8,9], FT-IR [7,30], XPS [1,8,9,31–45], AFM [46], and Solid State NMR [47], etc., had been utilized to characterize the surface physico-chemical states of various types of Phillips catalysts. In most cases of these previous studies, the highly toxic chromium(VI) trioxide was mainly used as starting raw material. In recent decades, trivalent Cr compound mostly chromium(III) acetate with much weaker toxicity was used as raw material instead of chromium(VI) trioxide for preparation of Phillips catalyst due to environmental and safety considerations [3,4,48–50]. In the case of using chromium(III) acetate as raw materials, it would be firstly transferred into chromium(VI) trioxide through oxidative decomposition before being supported on silica gel surface

[50]. Moreover, it has been reported that the polymerization behavior would be different if the starting Cr compound is changed from chromium(VI) trioxide to chromium(III) acetate [3,4]. However, a detailed understanding of the specific transformation process of the physico-chemical states of surface Cr species from chromium(III) acetate into hexavalent chromate species during isothermal calcination has not been reported yet.

The objective of this work is to get a much deeper understanding of the physico-chemical states of surface Cr species on various calcined Phillips CrO_x/SiO_2 catalyst starting from chromium(III) acetate as raw material prepared at different temperatures using high resolution XPS method. XPS is one of the most powerful and thus most frequently used surface analytic methods for both quantitative and qualitative measurement of the electronic states of surface Cr species on Phillips catalysts [1,8,9,31–45]. However, according to our knowledge, it has never been applied for study on the surface physico-chemical nature of chromium(III) Phillips catalyst precursors as well as its transformation during isothermal calcination process for preparation of the final catalysts for ethylene polymerization. As it has been demonstrated in our previous reports [8,9], the binding energy (BE) and the full width at half maximum (FWHM) value from the Cr 2p XPS spectra can be measured and used as criteria for identification of the oxidation state, distribution state and existing state (either bulky or covalently bonded to silica gel surface) of surface Cr species on catalyst surface. For XPS characterization of surface Cr species on calcined Phillips catalyst, photo-reduction of surface Cr species induced by the soft X-ray irradiation during high resolution XPS measurements should be eliminated through shortening the XPS acquisition time [32,33]. In general, the analytical approach in this work is based on high resolution XPS technique for a detailed investigation of the physico-chemical states of surface Cr species on industrial Phillips CrO_x/SiO_2 catalysts prepared from trivalent chromium(III) acetate at various temperatures. In particular, the isothermal transformation of surface Cr species from trivalent chromium(III) precursors into hexavalent chromate species ($Cr(VI)O_{x,surf}$) in the final catalysts calcined at various temperatures will be followed in detail by high resolution XPS characterization.

2. Experimental

2.1. Raw materials

Nitrogen of G3-grade (total impurity <5 ppm, in which $O_2 < 0.5$ ppm, $CO < 1$ ppm, $CO_2 < 1$ ppm, $CH_4 < 1$ ppm, dew point of $H_2O < -70$ °C) and pure air of G1-grade (total impurity <1 ppm, $CO < 0.1$ ppm, $CO_2 < 0.1$ ppm, THC < 0.1 ppm, $NO_X < 0.01$ ppm, $SO_2 < 0.01$ ppm, dew point of $H_2O < -80$ °C) were purchased from Uno Sanso Corp. Molecular sieves 4A and molecular sieves 13X, which were purchased from Wako Pure Chemical Industries

Ltd., were used as moisture scavenger for gas purification. Chromium(III) acetate was also purchased from Wako Pure Chemical Industries Ltd. Q-5 reactant catalyst (13 wt.% of copper(II) oxide on alumina), which was purchased from Aldrich, was used as oxygen scavenger for gas purification. A Phillips catalyst precursor (Crosfield ES370X donated from Asahi Kasei Corp.) with 1.0 wt.% of Cr loading, pore volume of 1.45 ml/g and surface area of 280–350 m^2/g was used for preparation of Phillips CrO_x/SiO_2 catalysts calcined at various temperatures. According to the company, the Phillips catalyst precursor ES370X (defined as PCP120) was prepared through impregnation of aqueous solution of chromium(III) acetate onto SiO_2 (Matthew Frosdyck ES70X) followed by drying in air at a certain temperature around 120 °C for a certain period of time. More specific information concerning the preparation conditions of the commercial Phillips catalyst precursors PCP120 could not be given due to confidential requirements. SiO_2, which is the same SiO_2 for preparation of PCP120 precursor and Phillips catalysts used in this work, was also donated from Asahi Kasei Corp.

2.2. Catalyst preparation

The preparation of Phillips CrO_x/SiO_2 catalysts calcined at various temperatures was performed using a spouted fluidized-bed quartz reactor under a procedure similar to our previous report [51]. The quartz reactor was set vertically into an electronic heater equipped with a temperature-program-controller. About 15 g of catalyst precursor PCP120 was added into the spouted fluidized-bed quartz reactor. Thereafter, an isothermal calcination process at 200, 300, 400, 600 and 800 °C, respectively, was carried out for 6 h to obtain five Phillips catalysts named as PC200, PC300, PC400, PC600 and PC800, respectively. During the first stage of the 6 h calcination process, pure air with a flow rate of 200 ml/min was used as gas media. It was switched to nitrogen (200 ml/min) during the natural cooling process. Pure air was further purified by passing through a 13X molecular sieve column before entering the catalyst preparation system. N_2 was further purified by passing through a Q-5 catalyst column and a 13X molecular sieve column before entering the catalyst preparation system. After preparation, each catalyst sample was distributed and sealed into several large glass tubes within N_2 for storage. Finally, each catalyst sample was further distributed and sealed in small glass ampoule bottles under nitrogen atmosphere. The amount of catalyst in each small glass ampoule bottle could be controlled at ca. 100 mg and precisely weighed. The chromium content for all catalyst samples was ca. 1 wt.%.

2.3. XPS characterization

The details concerning the XPS measurements for chromium(III) acetate, catalyst precursor PCP120 and five Phillips catalyst samples could be found in our previous

report [8,9]. A simple introduction of the instrumental procedure was described as follows. XPS data were obtained on a Physical Electronics Perkin-Elmer Model Phi-5600 ESCA spectrometer with monochromated Al Kα radiation (1486.6 eV) operated at 300 W. Each sample was embedded on a conductive copper tape to form a sample disc in a diameter of 5 mm and fixed on a XPS sample holder. The sample holder was then put into the vacuum transfer vessel (Phi Model 04–110, Perkin-Elmer Co. Ltd.), which can be connected to the sample introduction chamber on the XPS instrument for sample transfer without atmospheric exposure. The above procedures were carried out in a glove bag, which had been purged overnight with nitrogen gas in advance. The prepared sample was degassed in the introduction chamber to 10^{-7} Torr before entering the main chamber, in which the vacuum was kept above 3×10^{-9} Torr during XPS data acquisitions. Firstly, low resolution XPS survey scan was carried out on each sample disc within 2 min for surface elemental analysis. Then, high resolution XPS scan measurements for Si 2p, Cr 2p regions were performed for the sample disc within 10 min in order to neglect the photo-reduction of chromate species induced by soft X-ray irradiation during XPS measurement. For the bulk chromium(III) acetate sample, SiO_2 ES70X powder was used as an external reference through mixing into the sample discs on the XPS sample holder within nitrogen atmosphere. All binding energies were referenced to the Si 2p peak of silica gel at 103.3 eV to correct for the charging effect during acquisition. Precise multiplet fittings for deconvolution 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.

3. Results and discussion

The photo-reduction of surface Cr species induced by soft X-ray irradiation during XPS acquisition was reported to be significantly dependant on the preparation conditions of the catalyst [8,32–34]. For XPS characterization of surface Cr species on calcined Phillips catalyst, photo-reduction of surface Cr species induced by the soft X-ray irradiation during high resolution XPS measurements could be eliminated through shortening the XPS acquisition time [32,33]. According to the literature, X-ray induced photo-reduction of Cr species during high resolution XPS acquisition strongly depended on XPS measurement time and was negligible when the XPS measurement time is not more than 10 min for calcined Phillips catalyst [32,33]. Preliminary experimental results indicated that the signal to noise level of XPS spectra suddenly became rather poor when the acquisition time was less than 10 min for all high resolution XPS measurements. Therefore, high resolution XPS characterizations for all samples in this study were carried out for 10 min in order
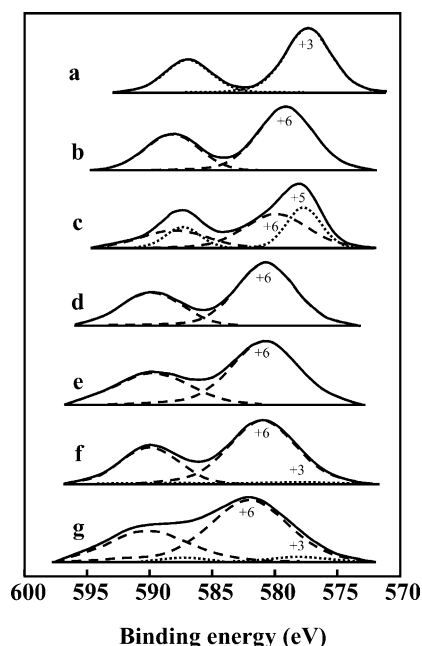
Fig. 1. Cr 2p XPS spectra of chromium(III) acetate, PCP120 and Phillips catalysts calcined at various temperatures (high resolution XPS acquisition time 10 min for all spectra): (a) chromium(III) acetate; (b) PCP120; (c) PC200; (d) PC300; (e) PC400; (f) PC600; (g) PC800.

to neglect the photo-reduction of surface chromate species induced by soft X-ray irradiation during XPS measurement.

As the original raw material for preparation of the industrial catalyst precursor PCP120 and all Phillips catalysts isothermally calcined at various temperatures from PCP120, bulky chromium(III) acetate was also characterized by XPS method through mixing with SiO_2 powders. The XPS Cr 2p spectra for all samples obtained through 10 min high resolution XPS acquisition were shown in Fig. 1, which can be considered to reflect the real oxidation states of Cr species on all original samples with only negligible photo-reduction

induced by soft X-ray irradiation during XPS acquisition as mentioned above. Multiplet fitting for deconvolution was applied to all the spectra shown in Fig. 1 and corresponding BE, FWHM values of Cr 2p (3/2) level, assignment and atomic percentage of different oxidation states of Cr species for all samples were illustrated in Table 1. The rationalization for assignment of the oxidation state of surface Cr species for each sample was given in the forth-coming explanations.

According to Table 1, the BE and FWHM values from Cr 2p (3/2) core level of bulky chromium(III) acetate are 577.4 and 4.30 eV (corresponding to spectrum (a) in Fig. 1), respectively, with higher BE and larger FWHM compared with bulky Cr_2O_3 (BE = 576.59 eV, FWHM = 3.03 eV) [8]. The lower electron density of Cr atom in chromium(III) acetate than that of Cr in Cr_2O_3 indicates the electron-withdrawing effect from the acetate ligands. It is also reasonable for the much higher FWHM value corresponding to broader structural distribution for chromium(III) acetate thinking about its multiplicity and instability in molecular structure especially during XPS measurement under ultra-high vacuum [52].

The BE and FWHM values from Cr 2p (3/2) core level of the Phillips catalyst precursors PCP120 are 579.1 and 5.20 eV (Table 1, corresponding to spectrum (b) in Fig. 1), respectively. This BE value 579.1 eV, which is 1.7 eV higher than the BE of chromium(III) acetate raw material, is quite similar to our previous result of 579.24 eV (FWHM = 2.53 eV) [8] obtained for bulky hexavalent chromium trioxide and the same as that of 579.1 eV (FWHM = 2.9 eV) for CrO_3 reported by Merryfield et al. [35]. This experimental evidence clearly demonstrated that most of the raw material trivalent chromium(III) acetate impregnated onto silica gel surface had oxidatively decomposed into hexavalent bulky chromium(VI) trioxide during the 120 °C isothermal drying process for several hours in air. This interpretation is also supported by previous report of Augustine and Blitz concerning the mechanism of the activation of silica-supported basic chromium acetate [50]. They reported that the

Table 1
XPS data from multiplet fitting of Cr 2p spectra obtained with acquisition time of 10 min for Cr(III) acetate, PCP120 catalyst precursor and Phillips catalysts calcined at various temperatures

Samples	Cr 2p (3/2)		Oxidation state assignment[a]	Atomic percentage
	BE (eV)	FWHM (eV)		
Cr(III) acetate	577.4	4.30	Cr^{3+} (B)	100
CrO_3[b]	579.24	2.53	Cr^{6+} (B)	100
PCP120	579.1	5.20	Cr^{6+} (B)	100
PC200	579.8	5.80	Cr^{6+} (S+B)	62.0
	577.6	3.20	Cr^{5+} (B)	38.0
PC300	580.6	5.40	Cr^{6+} (S+B)	100
PC400	580.7	6.30	Cr^{6+} (S)	100
PC600	581.0	6.30	Cr^{6+} (S)	96.9
	577.6	6.49	Cr^{3+} (S)	3.1
PC800	581.9	7.28	Cr^{6+} (S)	95.0
	577.7	5.30	Cr^{3+} (S)	5.0

[a] B stands for bulky Cr species, S stands for supported Cr species covalently bonded on silica gel surface.
[b] XPS data for bulky CrO_3 were directly used from our previous report [8].

oxidative decomposition of Cr(III) acetate into CO_2 and H_2O started from 90 °C in O_2/N_2 (21% O_2) followed by a main broad peak of CO_2 evolution between 250 and 350 °C accompanied with formation of Cr–O–Si and Cr=O bonds between 200 and 400 °C [50]. Moreover, they found that the main peak of CO_2 evolution between 250 and 350 °C gradually shifted to lower temperature with increasing of O_2 concentration [50]. According to Ruddick and Badal, Cr(III) acetate precursors can easily decompose either by thermal activation or even by O_2 plasma treatment at ambient condition [48,49]. Whereas, the latter showed only one sharp peak of CO_2 evolution at 290 °C for oxidative thermal decomposition of Cr(III) acetate precursors [48]. Their experimental conditions for oxidative thermal treatments might be different judging from the different decomposition products including not only CO_2, H_2O but also CH_4 and CO [48]. It is worthy to mention that the results of the former two groups mentioned-above were obtained through non-isothermal process within a fixed bed micro-reactor using TPD or TPR method. Taking into consideration of the experimental conditions in this work: spouted fluidized bed reactor (dynamically mixing state) and long time isothermal calcination in dry air, it would be reasonable to predict that the main temperature regions of the oxidative decomposition reaction, thermal desorption of carbon-contained species and esterification reaction between bulky CrO_3 and hydroxyl groups all should be shifted to lower temperature regions in this work. The much larger FWHM value of 5.20 eV for PCP120 precursors indicative of much broader compositional distribution compared with that of bulky chromium trioxide (usually less than 3 eV) [8] could be rationalized well by the following two factors. The first factor is its highly dispersing state on the heterogeneous surface of amorphous silica gel. The second is its possible multiplicity in surface chemical environment including mostly bulky CrO_3 and small amount of residual adsorbed decomposed gas species (CO_2 and H_2O). The existence of residual adsorbed decomposed gas carbon-contained species can be observed from the XPS spectra of survey scan as shown in Fig. 2. According to Fig. 2, bulky chromium(III) acetate blended with silica gel showed the strongest C 1s peak (spectrum (a) in Fig. 2), while, the Phillips catalyst precursor PCP120 still showed a relatively weak C 1s peak (spectrum (b) in Fig. 2). The C 1s peak further became weaker for PC200 (spectrum (c) in Fig. 2) and almost disappeared for PC300 (spectrum (d) in Fig. 2) as well as for other catalyst samples prepared at temperatures higher than 300 °C. The survey scan spectra for PC400, PC600 and PC800, which are not shown, are almost the same as PC300. All these above-mentioned experimental evidences and discussions suggested that the oxidative decomposition of chromium(III) acetate into bulky CrO_3 had been almost completely finished by 120 °C isothermal calcination and the residual adsorbed decomposed carbon-contained species could be almost completely desorbed through isothermal calcination at 300 °C or higher temperature.

The most unique Cr 2p spectrum in Fig. 1 was spectrum (c) of the PC200 catalyst sample, which was prepared
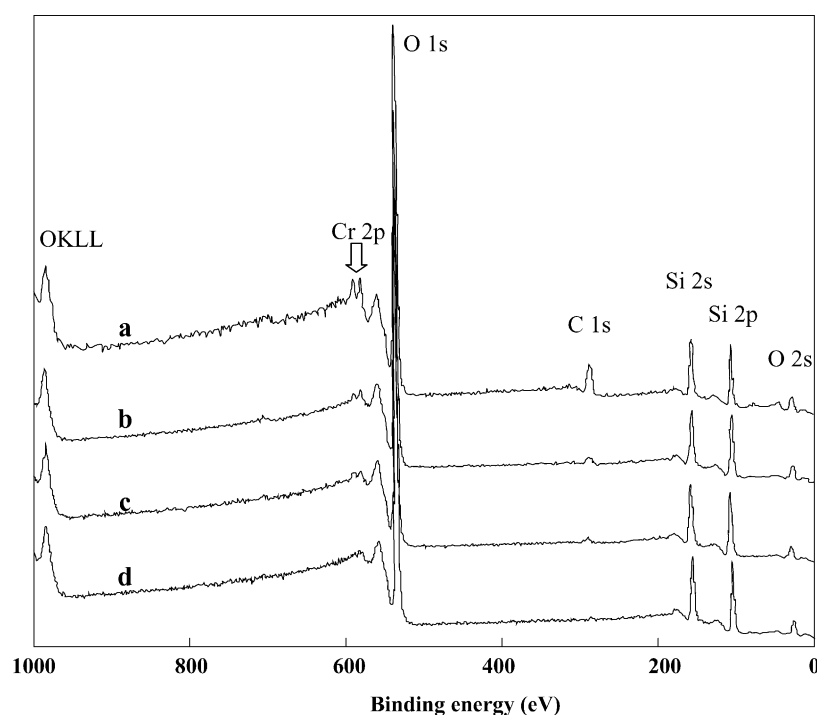

Fig. 2. XPS spectra of survey scan obtained with acquisition time of 2 min for: (a) chromium(III) acetate; (b) catalyst precursor PCP120; (c) PC200; (d) PC300.

through isothermal calcination of PCP120 precursors at 200 °C in dry air for 6 h. A perfect single doublet fitting for this spectrum was found impossible indicating the existence of a mixed oxidation states of surface Cr species in this catalyst. This is also an indication of possible calcination-induced reduction of supported hexavalent chromate species ($Cr(VI)O_{x,surf}$) and/or thermal decomposition of bulky CrO_3 during the isothermal treatment at 200 °C for 6 h leading to the formation of some surface Cr species in lower oxidation states. Multiplet fittings for deconvolution of spectrum (c) were applied and its corresponding BE and FWHM values of Cr 2p (3/2) level could be found in Table 1. Two oxidation states were found in this catalyst namely the first oxidation state with BE of 579.8 eV, FWHM of 5.80 eV and atomic concentration 62.0% and the second oxidation state with BE of 577.6 eV, FWHM of 3.20 eV and atomic concentration 38.0%. Thereafter, it is necessary to determine their real physico-chemical states of these two kinds of surface Cr species on PC200 catalyst surface: their valent states and chemically supported or unsupported on silica gel surface? The first Cr component (BE = 579.8 eV, FWHM = 5.80 eV) on PC200 can be assigned to hexavalent chromium species as a mixture of bulky CrO_3 and $Cr(VI)O_{x,surf}$. Up to now, it is still very difficult to distinguish $Cr(VI)O_{x,surf}$ from bulky CrO_3 in their mixture by XPS method especially at relatively low calcination temperature. The first evidence of the formation of $Cr(VI)O_{x,surf}$ is the 0.7 eV of increase of BE from PCP120 precursor (579.1 eV) to PC200 (579.8 eV). Another support for this interpretation comes from a previous report by Augustine and Blitz [50]. According to their report, the formation of Cr–O–Si bonding, i.e. the formation of $Cr(VI)O_{x,surf}$, lies mainly between 200 and 400 °C during a non-isothermal calcination process starting from chromium(III) acetate impregnated on silica gel [50]. Therefore, it is reasonable to consider that $Cr(VI)O_{x,surf}$ could be formed on PC200 under the isothermal calcination conditions in this study. Judging from the 0.7 eV of increase of BE compared with bulky CrO_3, the amount of $Cr(VI)O_{x,surf}$ formed in PC200 should not be a small fraction. The second Cr component (BE = 577.6 eV, FWHM = 3.20 eV) on PC200 was assigned to bulky pentavalent chromium oxide (e.g. Cr_2O_5 or $(Cr_2O_7)^{4-}$) derived from partial thermal decomposition of bulky CrO_3. This assignment was favored by previous reports of Guyot et al. [53] and Hogan [54]. The DTA results of Guyot et al. showed that bulky CrO_3 was first partially reduced into pentavalent chromium oxide $(Cr_2O_7)^{4-}$ around 330 °C and finally fully reduced into Cr_2O_3 from 470 °C during a non-isothermal calcination [53]. The TG results of Hogan indicated that there existed three regions for the thermal reduction of bulky CrO_3 as follows: partial reduction to Cr_2O_5 at 255–390 °C; partial reduction to CrO_2 at 390–460 °C and full reduction to Cr_2O_3 from 460 °C, during their non-isothermal calcination [54]. It is reasonable to consider that bulky CrO_3 was partially reduced into pentavalent chromium oxide in PC200 after an
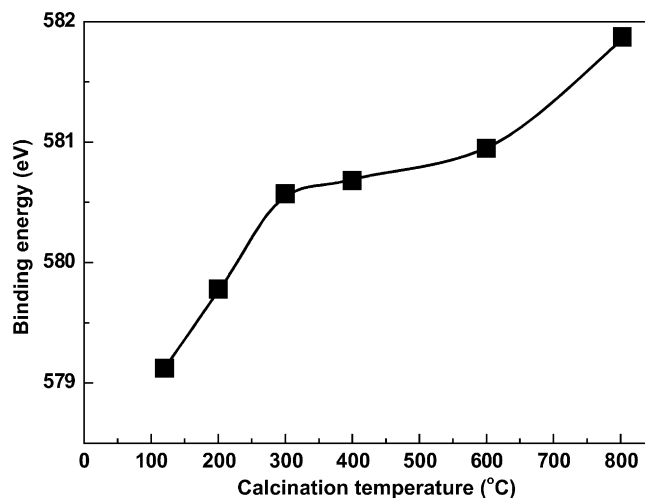

Fig. 3. Dependence of binding energy (Cr 2p (3/2)) of surface Cr^{6+} species of various Phillips catalysts on calcination temperature for preparation of the catalysts from PCP120 precursor.

isothermal calcination at 200 °C for 6 h because a complete stabilization of bulky CrO_3 into chromate species ($Cr(VI)O_{x,surf}$) on silica gel surface has not been achieved yet at this temperature. The BE value 577.6 eV for bulky pentavalent chromium oxide is consistent with those around 577.5–577.8 eV reported by Okamoto et al. [33]. The low FWHM value 3.2 eV also reflects its bulk characteristics corresponding to narrow distribution state.

The BE and FWHM values from Cr 2p (3/2) core level of the Phillips catalyst PC300 are 580.6 and 5.40 eV (Table 1, corresponding to spectrum (d) in Fig. 1), respectively. The BE value of PC300 increased 1.5 eV compared with that of bulky CrO_3 in the PCP120 precursors. It is acceptable to think that most of the bulky CrO_3 has been transferred into chromate species ($Cr(VI)O_{x,surf}$) on silica gel surface at this condition. Nevertheless, the existence of small amount of bulky CrO_3 in PC300 can not be completely ruled out according to the report of Augustine and Blitz as mentioned-above [50]. Subsequently, the surface chromium species with a BE of 580.7 eV and FWHM of 6.30 eV on PC400 (see Table 1, corresponding to spectrum (e) in Fig. 1) can be assigned to 100% of chromate species ($Cr(VI)O_{x,surf}$). The BE values of the chromate species ($Cr(VI)O_{x,surf}$) on PC600 and PC800 (see Table 1, corresponding to spectra (f) and (g) in Fig. 1) were found to further increase to be 581.0 eV (FWHM = 6.30 eV) and 581.9 eV (FWHM = 7.28 eV), respectively. The successive increasing of BE values of hexavalent chromium species with increasing calcination temperature from PCP120 to PC800 was plotted in Fig. 3, which can be also observed from the gradual shifting of Cr 2p spectrum from low to high binding energy as shown in Fig. 1. Compared with the BE of bulky CrO_3 in PCP120, 2.8 eV of significant increase of BE value was observed for PC800. Similar tendency of such BE increase from bulky CrO_3 to chromate species of calcined Phillips catalysts has also been observed by Thüne

et al. [41] and Merryfield et al. [35], as well as in our previous report [8]. Such significant increase in binding energy of Cr species before and after grafting of chromium trioxide on silica gel surface is considered to originate mainly from the following three factors. Firstly, weak acidity of silica gel surface creates stronger electron extracting effect on the Cr atoms in chromate species of the catalyst than that from the CrO_3 lattice itself [8]. Secondly, successive dehydroxylation of catalyst surface is corresponding to removing 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 catalyst surface may indirectly induce the decrease of electron density of Cr atoms in chromate species of the catalyst [15]. The surface reactions of supporting of bulky CrO_3 on silica gel surface (reaction (1)) and successive dehydroxylating of catalyst surface (reaction (1) and (2)) are shown in Scheme 1. The dominant supporting of bulky CrO_3 on silica gel surface and simultaneous dehydroxylating silica gel surface at temperature between 120 and 300 °C account for the drastic increase of BE values of hexavalent chromate species in this temperature range for isothermal calcination (Fig. 3). The slowly increasing of BE values of chromate species from 300 to 600 °C is solely derived from dehydroxylating residual surface hydroxyl groups (Fig. 3). Another enhancement of increase of BE values of chromate species from 600 to 800 °C can be observed in Fig. 3. 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 [15]. 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. Another phenomenon induced by high temperature was partial thermal-reduction of chromate species ($Cr(VI)O_{x,surf}$) into surface stabilized trivalent Cr species ($Cr(III)O_{x,surf}$) as shown in Fig. 1 and Table 1. 3.1 and 5% of $Cr(III)O_{x,surf}$ were observed on PC600 and PC800, respectively, which was proposed to be formed through thermal-induced reduction at high temperature under even oxidizing atmosphere according to our previous report [8].

In summary, the specific isothermal transformation process of chromium(III) acetate into supported chromate species ($Cr(VI)O_{x,surf}$) for preparation of calcined Phillips catalyst has been followed by high resolution XPS method with respect to different calcination temperatures. The specific surface physico-chemical states on Phillips catalysts isothermally calcined at different temperatures have been elucidated. The substantial dependence of surface components of Phillips catalyst on calcination temperature for isothermal preparation of the catalyst was summarized in Fig. 4. The general dependence of electronic nature of the surface chromate species for calcined Phillips catalysts on the calcination temperature has been clarified. Further investigation of photo-stability of surface chromate species on Phillips CrO_x/SiO_2 catalysts calcined at various temperatures is still in progress using high resolution XPS method, which will be available for a forthcoming publication soon.
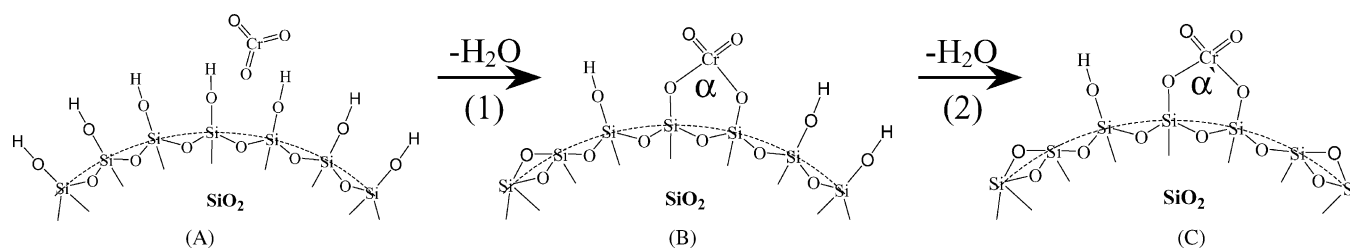
Scheme 1. Surface reaction diagram of the dehydration of residual hydroxyl groups, simultaneous formation of surface siloxane bridges and transformation of bulky CrO_3 into chromate species (using monochromate as an example) during calcination for preparation of Phillips catalyst from PCP120 precursor.
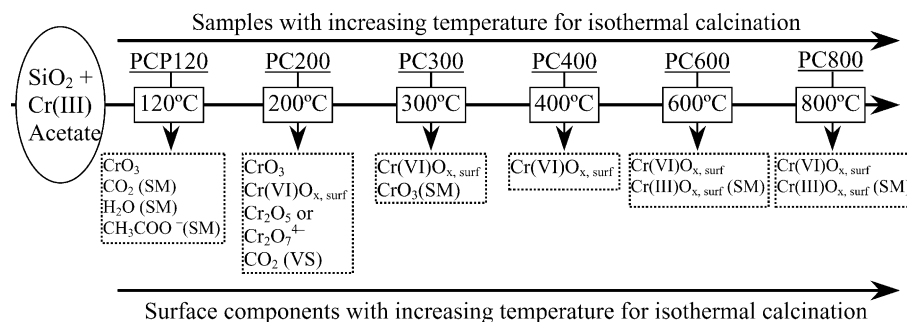

Fig. 4. Schematic diagram of the dependence of surface components of various Phillips catalyst samples on calcination temperature under isothermal condition: (SM) small amount; (VS) very small amount.

4. Conclusions

The industrial Phillips catalyst precursor PCP120 with 1.0 wt.% of Cr loading, which was prepared from chromium(III) acetate through isothermal drying at 120 °C after impregnation on silica gel, was used as starting material for preparation of Phillips catalysts isothermally calcined at various temperatures from 200 to 800 °C. High resolution XPS characterizations with acquisition time of 10 min, which can neglect the photo-reduction of surface chromate species induced by soft X-ray irradiation during XPS measurement, have elucidated the specific transformation of chromium(III) acetate into bulky CrO_3 and subsequently into chromate species ($Cr(VI)O_{x,surf}$) as a function of calcination temperature for preparation of Phillips catalyst. The specific surface components of various catalyst samples versus calcination temperature were clarified (see Fig. 4). It has been demonstrated that chromium(III) acetate could be very easily oxidized and decomposed into bulky CrO_3 under even 120 °C isothermal drying. The bulky CrO_3 started to be transformed into supported chromate species at 200 °C and could be completely stabilized on silica gel surface as chromate species at 400 °C. Obvious partial thermal decomposition of bulky CrO_3 into bulky pentavalent Cr oxide (e.g. Cr_2O_5 or $(Cr_2O_7)^{4-}$) was only observed on 200 °C-calcined catalyst sample due to the incomplete stabilization of bulky CrO_3 into chromate species at 200 °C. As the precursor of active site on calcined Phillips catalyst, the chromate species ($Cr(VI)O_{x,surf}$) on catalyst calcined at higher temperature was becoming more and more electron deficient with increase of calcination temperature from 200 to 800 °C. This might be correlated well with the typical polymerization behavior of Phillips catalyst in terms of increasing of polymerization activity and decreasing of molecular weight of the synthesized polymer versus increasing calcination temperature for preparation of the catalyst. Only a slight thermal-induced partial reduction of chromate species into $Cr(III)O_{x,surf}$ was observed at high temperature (600–800 °C). High resolution XPS method has been demonstrated to be very powerful for a better understanding of the physico-chemical nature of surface chromium species as well as its transformation on Phillips catalyst during isothermal calcination process.

Acknowledgements

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